GEOCHEMISTRY AND MINERALOGY OF CHALIYAR RIVER SEDIMENTS WITH SPECIAL REFERENCE TO THE OCCURRENCE OF PLACER GOLD

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CERTIFICATE

I certify that this thesis, **"Geochemistry and Mineralogy of Chaliyar river sediments with special reference to the occurrence of placer gold"** has been prepared by **G.N.Hariharan** under my supervision and guidance in partial fulfillment of the requirements for the degree of Doctor of Philosophy and no part thereof has been submitted for any other degree.

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Preface

This report deals essentially with the texture, mineralogy and geochemistry of bedload sediments of the Chaliyar river. The work also addresses the nature and distribution of gold in the sediments of the basin. For the sake of convenience, the thesis is divided into seven chapters.

The first chapter gives a general introduction to the topic in terms of geomorphology and regional geology of the study area, basin characteristics, general aspects and major objectives of the work. The methods of sample collection, processing and analytical procedures followed are presented in the second chapter.

The third chapter deals with the textural characteristics and statistical parameters of the bedload sediments and their interpretation.

Chapter IV describes the mineralogical and heavy mineral distribution of the river sediments and the control of source lithology.

The fifth chapter deals with the major element geochemistry of bedload sediments and its variation with distance as well as the mineralogical and textural controls in its over all chemistry.

The sixth chapter is mainly concerned with the REE geochemistry of sediments along with other selected trace elements and their importance in provenance studies.

The last chapter gives an account of the gold distribution in the basin, morphological and surface characteristics of gold particles and their possible effects on the transport and deposition in this dynamic fluvial system. It also includes grain chemistry.

At the end of each chapter the conclusions arrived at are furnished. A consolidated summary of the work is given at the end of the thesis which is followed by bibliography of cited references and appendices.

Contents

Chapter 1
INTRODUCTION

1.1 Introduction

Rivers constitute the lifeline for any country and some of the world's great civilizations (e.g. Indus Valley, Mesopotamian, and Egyptian) have all prospered on banks of river systems. People of ancient India considered rivers as sacred and have personified them as deities and sung their praises in their religious literature. In the broader perspective of geological evolution, disappearance or disintegration of rivers, shifting of their courses, capture of one river by another and steady decline of discharge resulting in drying up of their beds, are all normal responses to several geological processes singly or jointly acting on the Earth's crust. These include tectonism, resulting from both orogenic and epeirogenic causes, sea level changes, and even climatic factors such as rainfall. Human interaction with river systems may also bring about several perceptible changes. A few of the south Indian rivers like the east-flowing Pennar, Palar and Cauvery draining into the Bay of Bengal and west-flowing Swarna, Netravathi and Gurupur draining into the Arabian Sea are known to have changed their morphology due to several of these causes.

Erosion processes and fluvial transport of materials have become a focus of revived attention more recently owing to their significance in landuse and environmental aspects. Geological investigations of river basins and measurements of riverine transport of sediments and water can provide a reasonable estimate of several dynamic factors of a drainage basin. Most attempts to estimate denudation on a continental scale rely heavily on measurements of sediment yield from the rivers of the world. Considerable effort has been expended both to estimate sediment yield of the major rivers and to understand controls on sediment transfer within river systems. Studies on large rivers in transporting the denudation products of the continents to the sea have emphasized that topographical, lithological, and climatic factors play important roles in controlling the rate of weathering and continental denudation.

Assessing the impact of continental fluvial processes on the ocean require detailed studies of small and medium-size rivers in Asia. About 65% of fresh water and 80% of the sediment input to the oceans are from the tropics and a part of the subtropics (between 30°N and 30°S), where the major rivers are located (Eisma, 1988; Milliman, 1991). Rivers annually transport about 35 × 10^3 km^3 of fresh water (Milliman, 1991) and 4 × 10^9 tons of dissolved organic and inorganic matter (Emery and Milliman, 1978; Martin and Meybeck, 1979) to the world oceans. Small rivers (drainage basin <10,000 km^2) cover only 20% of the land area, but their large numbers result in their collectively contributing much more sediment than previously estimated. The estimates of contributions from small and large rivers to the total flux of particulate solids to the ocean has increased from *ca.* 16 × 10^9 ton/yr (large rivers alone) to *ca.* 20 × 10^9 ton/yr (Milliman and Syvitski, 1992). Of the total sediment yield to the world oceans, Indian sub-continent alone contributes about 35% (Milliman and Meade, 1983). Among the rivers of the Indian sub-continent, the sediment erosion is more significant than chemical erosion in the case of all the Himalayan rivers, whereas in the case of Peninsular rivers, chemical erosion is more significant. This is relatable to the active geodynamics of the Himalayas compared to the greater stability of the Peninsular shield, that make a marked difference to the eroding capacity of the rivers.

1.2 Sediment in stream channels

Alluvial stream channels are natural channels in which bed and bank materials have been deposited by the stream sufficiently recently and are still unconsolidated. These channels therefore are the product of processes produced by the interaction between flowing water and moving sediment. Furthermore, it is assumed that characteristic channel forms reflect the processes that produced them. Therefore, it is believed that an understanding of morphology, morphometry, and spatial relations of the characteristic forms in alluvial channels will facilitate deductions about the processes, which interact to produce the forms.

It is conceded that no two streams are exactly alike. The possible combinations and spatial arrangement of controlling variables such as climate, bed and bank material, and slope make each stream unique. Therefore, generalizations concerning fluvial processes are nebulous and the more general the statement the more exceptions may be found. However, when a certain type or group of streams such as gravel-bed or alluvial streams are considered, the number of exceptions to generalized statements may decrease.

1.3 Fluvial hydraulics

In many gravel-bed alluvial channels, pools, riffles and point bars appear to be produced at relatively high, channel - forming flows and are modified only at low flow. Under these conditions, conventional hydraulics apply at low flow, when the channel is essentially a rigid container for liquid phase. However, at high flow when appreciable sediment is being transported by the stream, the hydraulics becomes complex because many of the variables are not unique (cf. Maddock, 1969). Leliavsky (1966) distinguishes fluvial hydraulics from hydraulics in general as a necessity to understanding natural stream. Perhaps the most significant and early-recognised principle in fluvial hydraulics is de Leliavsky's (1894) convergence-divergence criterion: the processes by which bed forms like pools, riffles, and point bars are formed.

Excluding the fluid phase, the most obvious forms in an alluvial channel are bed forms. A bed form is any irregularity produced on the bed of an alluvial channel by the interaction between flowing water and moving sediment (Simons and Richardson, 1966). According to them there appears to be two main types of groups of bed forms: (a) pools, riffles, and point bars, which tend to give some gravel-bed channels their basic morphology; and (b) ripples, dunes, and antidunes, which are controlled by the fluid phase and are not generally a significant part of the basic channel morphology in gravel-bed channels. However, if sufficient sand is available, slowly migrating ripples and dunes at low flow may be superposed on and partly mask the more stable pools, riffles, and point bars.

Less than 5 percent of a stream's energy is available after overcoming friction. This is used for transporting sediment, which is carried in solution or suspension or dragged near the bed. The total amount of sediment transported is considered the load of the stream, differentiated according to the mode of transport. The total load of a stream therefore is the sum of dissolved load, suspended load, and bedload. Stallard, working in the basins of the Amazon and the Orinocco, has shown that in the humid tropics where chemical alteration of the bedrock is advanced, the amount of dissolved load in streams could vary extremely, depending on neotectonics, relief, and rock types (Stallard, 1985). Suspended load and bedload imply a two-way operation. The sediment grains first have to be picked up from their position of rest on banks, bars, channel bed, etc. Second, they have to be kept moving. Sand grains are eroded first as they are only 0.06 to 2 mm in diameter and lack adhesion. Finer grains (silt and clay) are eroded at higher velocity than sand because of their property of adhering to each other. Clasts coarser than sand (pebbles, cobbles, and boulders) are eroded also at higher velocity because of their size. The coarser they are, the bigger is the velocity of entrainment. Such coarse material moves only at very high velocities, i.e., floods. As the velocity drops, sediment of a given size cannot be carried any longer and is therefore deposited, this time in a regular fashion from the coarsest to the finest. The velocity at which the grains begin to be deposited, indicating the end of transportation, is known as fall velocity. Clay and silt therefore, once entrained, can be carried for a long distance. Pebbles, cobbles, and boulders are only carried in floods and even then probably not too far. Sand is carried shorter distance than clay and silt, but is carried frequently.

Sediment deposited during falling stage of the hydrograph is stored in the channel awaiting transportation in the next high flow. Such sediment may be stored (a) on the bed in the middle of the channel as bed material (b) on the side and middle of the channel forming bars (c) on banks or (d) on flat areas next to the river. Floodplain material away from the bank may stay in storage for at least hundreds of years. Material forming bank, bar and bed may be eroded and transported much more frequently, but there is no evidence to support a continuous transfer of a sediment grain along the entire length of the channel. That happens only in rivers with a length limited to tens of km in extremely high-magnitude floods (such as following rainfall from a tropical cyclone) which may flush the channel free of sediment. In general, sediment on channel bed tends to decrease in size relatively rapidly in the first few km, and rather slowly thereafter. Bed material also gets moderately sorted within a short distance of transport. Beyond this distance, sorting improves at a slow rate.

The discharge and sediment load of Indian rivers are measured routinely at various discharge/gauge stations set up by the State and Central government agencies. Most measurements of the sediment discharge carried by stream omit bedload which is estimated to be 10% or less of the annual total load for many rivers. In some rivers, such as the Brahmaputra or the Zaire (Congo), bedload is high and one does not enjoy this short cut in sediment estimation (Meade, 1996). Sediment load is taken as a measure of physical weathering in the drainage basin. The relative fractionation of the total load into suspension (TSM-total suspended matter) and bed depends on hydraulic conditions. Primary silicates produce clay minerals and also yield coarser size population due to physical weathering. Both these components are transported by rivers and interaction (re-suspension, deposition etc.) will be regulated by hydraulic parameters such as velocity, bed gradient, channel shape, depth and other factors.

1.4 Geochemical relationships between rocks and sediments

The chemical composition of stream sediments are better understood in comparison with the chemical composition of their probable source rocks. It is one of the important considerations in stream sediment geochemical studies (e.g. Cullers et al., 1988; Cullers, 1994) since stream sediments represent the rock materials derived from within a drainage basin. It is therefore necessary to study the behavior of these geochemical indicators in modern sediments with good provenance control (e.g. Cullers et al., 1988). Chemical weathering of rocks is involved in the consumption of atmospheric CO_2. Compared to carbonate weathering, the flux of atmospheric CO_2 consumed during the silicate weathering is high (Broecker and Peng, 1994; Macfarlane et al., 1994). The elemental composition of rock forming minerals and minerals formed during weathering make up a greater proportion of the elemental composition in stream sediments (Stendal and Theobald, 1994). In this respect, materials from present-day river systems are useful, because they integrate some of the lithological and chemical diversity of the local upper continental crust (Dupre et al., 1996)

Similarly, in order to understand the geochemical budget of individual elements, the chemical composition of river-borne sediments needs to be known. Several attempts have been made to estimate the average composition of modern river sediments, but the present understanding of sediment chemistry is limited to information available on the large sediment-carrying rivers of the world. On the other hand, our present knowledge of chemical composition of bedload sediments of small rivers is limited and scarce. In this background, the present work have studied various aspects of the chemical composition of a small river system on the basis of reconnaissance-scale sampling of bed sediments. An attempt is made in this study to understand some aspects of erosion, sediment transport mechanism, source area weathering conditions and provenance characteristics of the Chaliyar River Basin, which is one of the important and most intensively utilised basins in Kerala based on mineralogical and geochemical studies carried out on bedload sediments of the river system during the period 1996-99. The present doctoral work also incorporates a detailed study of bulk geochemistry in conjunction with the texture and mineralogy of bedload sediments in the Chaliyar main channel and its major headwater tributaries, and thereby to infer the provenance characteristics and the factors involved in the evolution of sediments as well as their changes in composition and petrography with degree of transport. In addition to this, an attempt is made to understand the distribution of gold in sediments, the variation in gold particle shape, chemistry and grain morphology in this dynamic fluvial system. The emphasis on gold arises from the fact that the source areas of Chaliyar are known for gold mineralization and extensive old workings.

1.5 Study area

The Chaliyar basin lies between Lat. (N) 11^{O} 08' & 11^{O} 38' and Long. (E) 75^{O} 45' & 76^{O} 35' and spreads over parts of Malapuram, Kozhikode and Wynad districts of Kerala and Niligiri district of Tamil Nadu. Chaliyar is the third largest river in Kerala with a catchment area of around 2900 km^2 and originates from the Niligiri hills at an elevation of 2100 m. The Chaliyar river joins the Arabian sea south of Calicut after flowing for a distance of ~140 km. The drainage area is dominated by rain forests of medium to high productivity and is submitted to a humid tropical climate. The major tributaries in the head water regions are Chali puzha, Punna puzha and Karim puzha. The name Punna puzha/Ponnu puzha (golden stream) points out that the river is known for its concentration of alluvial gold. During its course the river cuts through a number of lithologies like gneisses, charnockite, metapelites, schists and quartz reefs of Precambrian age. Laterites, older and younger gravels, sediments along river terraces, alluvium and soil represent Sub-Recent to Recent deposits seen in the basin. The Chaliyar is the major river which drains the Wynad Gold Fields (WGF). It is worth noting that the headwater tributaries flow exclusively above laterites developed over gneissic country rocks. However, the downstream tributaries that joins lower reaches of Chaliyar main stem is underlain essentially by charnockite. The present study essentially pertains to the main stem of the river which is around 80 km in length.

1.6 Geographic setting of Chaliyar basin

The basin includes parts of highly rugged Niligiri hills, the Nilambur valley with moderate relief and the more or less plain land between Nilambur and river valley. The basin covers parts of Mallapuram, Kozhikode and Wynad districts of Kerala. Nilambur valley is located in Malappuram district of Kerala bordering the Niligiri district of Tamil Nadu. Nilambur town lies about 40-60 m above sea level with some low hills rising to 180 m. The area is drained by Chaliyar river and its tributaries, where the main river is flowing from north to south. Punna puzha forms a major tributary in NE-SW direction. The lower reaches of the Chaliyar River is blessed with fertile alluvial soil and is densely populated and cultivated by the farming community. A good motorable road from Kozhikode to Mysore intersects the area. Nilambur lies 100 km to the north-east of Kozhikode.

1.7 Hydrological and sediment load characteristics of Chaliyar river basin

The chemical and sediment load carried by river depends on discharge and hence monthly variations in material transport is commonly observed for a number of rivers (Gibbs, 1967; Grove, 1972). Hydrological and sediment gauge data are available for the year 1993-94 from a single station of the Southern Water Resources Division (SWRD), Central Water Commission (CWC) at Kuniyil across the Chaliyar river. The total annual discharge from Chaliyar basin is around 45613 Cumec days, over 60% of it is in the monsoon months (July and August). The run off (in 1000 MC ft.) for Chaliyar river (Beypore) is 185. It is observed that the Chaliyar river is a truly monsoonal river, sediment discharge approaching to zero during non-monsoon months.

The dynamics of sediment transport complicates attempts to quantify both the influence of transport mode and intensity on channel form and the total denudational yield of sediments from the catchment. Suspended sediment and bedload transport are successively more discontinuous, responding variously to changes of stream discharge and sediment supply. It is well established that only bed material load has a definite relationship with water discharge whereas the wash load (the fine fraction of suspended material as defined by the Subcommittee on Sediment Terminology of the American Geophysical Union) carried by a river may not be related to discharge. While the amount of wash load is dependent upon the availablity of material in watershed and the processes of bank/sheet erosion, the transport of bed material load depends upon the hydraulic conditions and characteristics of bed material. As expected the maximum sediment load transport in the Chaliyar river (in Metric Tonnes) takes place between July and October (data source: Water Year Book 1993-94). However, the maximum sediment load transport takes place in the monsoon months (July and August) which also corresponds to the maximum water discharge. The sediment yield rate of catchment area during monsoon period is 0.1216 mm while during non-monsoon period is 0.0030 mm (data source: Water Year Book 1993-94).

1.8 Geomorphic and Geologic setting

1.8.1 Geomorphology of Chaliyar basin and drainage pattern

Geomorphologically the Chaliyar drainage basin includes parts of distinct provinces like the Wynad plateau and the Niligiri hills at higher altitudes, the Nilambur valley forming the slopes of the foot hills and low lands adjoining the main trunk of the Chaliyar river. Nilambur valley region has the characteristics of the gently undulating peneplain of semicircular shape, the area represents a low level tract bounded on the east and north by lofty hills of the Wynad and Nilgiris. The general elevation of the Nilambur valley is between 40-60 m above the sea level. Numerous mounds and ridges are enclosed in small flat land patches in between (mostly paddy fields). Susceptibility to weathering and denudational processes control the topography to a great extent. The low lying strips in the area is composed of schist and gneises, which are more susceptable to weathering; whereas banded magnetite quartzite, basic intrusives being less susceptable to weathering stand out as mounds and prominent hills. The flanks of these mounds and hills are highly lateritised.

The northern and eastern parts of the area are occupied by high hills of the Western Ghats, forming the southern slopes of the Wynad plateau and western flanks of Niligiri hills. The average elevation of the plateau is 966 m above M.S.L., the highest hill of the plateau falling in the area is the Elambaleri rising to a height of 2260 m. Deep gorges and mountain stream are characteristic of these ranges. The eastern and southern parts of the area falls in the Muriam and Nilambur Reserve Forests respectively and are infested with wild animals of varied types. Incidentally the Nilambur valley forms the western part of the area enclosed within two major shear zones viz., the Moyar shear trending E-W in the north and the Bhavani shear trending ENE-WSW in the south.

The relatively low relief of the Wynad plateau facilitated thick accumulation of residual soil concealing the bed rock. However, along the southern slopes of the plateau deforestation resulted in the exposure of the top soil to running water directly causing the removal of soil very rapidly.

Nilambur region is drained by Chaliyar river towards south. Punna puzha, Chali puzha and Karim puzha are the major tributaries draining the region. The perennial tributaries originates from Wynad plateau and hills surrounding the valley.

The lower reaches of the Chaliyar main channel shows a sudden change in the geomorphology beyond ~110 km from the source in the downstream direction. The channel takes a sharp bent at ~110 km and beyond this the river shows meanders at consistent intervals. Two major tributaries joins the right bank of the main stem beyond 110 km. The above change in the geomorphology and may be in the relief of the channel is reflected in the bi-modality of several parameters like texture, mineralogy and geochemistry of bedload sediments, undertaken in the present study which is discussed in the subsequent chapters.

The drainage network analysis by Cvetkovic (1980) of Nilambur region shows it to be dendritic combined with rectangular drainage (Fig. 1.1). The later is more characteristic for the area close to the confluence of Punna puzha with Chaliyar river. Dendritic pattern is typically developed on rocks with uniform resistance. The over print of rectangular drainage pattern over the dendritic pattern as seen to the north of

Nilambur, is due to the presence of right angle fault system. The drainage density of whole Nilambur valley is of medium texture (Cvetkovic, 1980).

The geomorphological studies of laterites by Sambandam and Krishnan Nair (1982) in parts of Nilambur valley has led to the identification of five sets of landforms formed during polycycles of erosion. The landforms consist of remnants of two older planation surfaces without laterite cover, two surfaces with laterite cover and the plains of contemporary cycle laterite. The vestiges of first two surfaces have been identified around 550 m and 350-400 m above sea level based on accordant summits, flat crests and smooth profile of ridge crests. The remnants of next two older surfaces occur around 150-230 m and 45-130 m above sea level forming summits of ridges, mesas and hillslope benches. The plains (planation surface-V) of contemporary cycle consist of pediments (1-1.5 km wide) and coastal plain (3-5 km wide) formed by the dissection of the above surfaces. All the five surfaces had been carved out in the charnockitic and migmatitic rocks and the last three surfaces are covered by primary laterite (5-8 m thick) derived from above rocks. The internal topography of the remnants of surfaces III and IV are subdued with central part of the summits subrounded. They collectively show regional basinward as well as seaward slope of about 1° and individual remnants show local slopes of about 1° - 2° towards the tributary valleys. The coastal plain and central parts of the pediments slope less than one degree while the slope of peripheral part of the pediment varies from 1° - 7°.

The operation of geomorphic processes on landscapes during periods of tectonic stability leads to the formation of planation surfaces having subdued topography. The geochemical weathering of the rocks on such plains leads to the formation of laterites. The polycyclic nature of the landforms of the region and the distribution of laterites at different level on the planation surfaces are due to repetitive regional uplifts (epeirogenic) with intermittent periods of quiescence or tectonic stablity. During the periods of quiescence, the planation surfaces were carved out and laterites were formed over them pari passu with planation.

1.8.2 Regional Geology

The area forms part of the Southern Indian Granulite terrain and is underlain by Precambrian metamorphic rocks (Fig. 1.2).

The geologic framework of southern India is broadly defined by granite-greenstone terrane in the north and a granulite facies terrane in the south. Gold deposits of economic significance occur in both terranes (cf. Ziauddin and Narayanaswami, 1974; Radhakrishna and Curtis, 1991 and 1999); the Kolar Gold Field is located in the Archean low-grade terrane, and the Wynad Gold Field in the Proterozoic high-grade terrane. The Wynad-Nilambur Gold Field consists of lowlands bounded on the east and north by the high hills of Wynad and Niligiris. The major rock types in this area comprise hornblende gneiss, granitic gneiss, pyroxene granulites inter-banded with magnetite quartzites, charnockites and granulite-grade metapelites.

In several places, at the margin of the quartz lodes with the host rocks, veins, and aggregates of carbonate minerals (principally calcite) have developed. Thin calcite veins, stringers, and pods also fill fractures within the quartz lodes and some times cut across and extend into the country rock. From the field relations, Santosh et al. (1995) inferred that the timing of carbonate precipitation was during the late, or post-emplacement stage of the quartz reefs.

Nilambur forms the eastern extension of Wynad gold belt. Gold is hosted by metamorphic rocks which consist mainly of biotite-hornblende gneiss, amphibolite, charnockite, pyroxene granulites and actinolite schist. Pegmatites, quartz veins, metagabroo, dolerites, norites represent the later intrusives. Laterite, older and younger gravels, recent river terraces, alluvium and soil represent the Sub-recent to recent deposits.

Banded-magnetite-quartzite (BMQ) forms elongated lenses and bands within the biotite-hornblende gneisses and stands out as hills and mounds due to its resistance to weathering. The strike of the BMQ varies from NW to EW in the southern parts to NS in the northern sector of the region. The general structure of the rocks in the southern sector of Nilambur conforms to the Dharwarian trend (Davay, 1975).

A few outcrops of pyroxene granulite are exposed west of Chaliyar puzha and along Karim puzha. Charnockite is observed south of Porur. Tremolite-actinolite-chlorite schists and talcose-carbonate rocks are exposed as lenticular bodies/isolated outcrops in Manali west of Edakkara. The rock types of Nilambur have resemblances to the occurrences in Wynad Gold Field and are presumed to be equivalents to those at Dharwars (Mahadevan, 1965). Dykes of norite, meta-dolerite and metagabroo are restricted to the southern part of the area.

The area is traversed by numerous quartz veins and quartz stringers. These quartz veins traverse almost all the rock types and are of two varities viz (i) milky white and massive type and (ii) small veins with ferruginous material and cavities typical of sulphides leaching. All the rock units of the area mentioned above are lateritised. Extensive laterite cover is seen as mounds, on the high grounds and on the flanks of the hills. Ferruginous and gravelly-pebbly laterites of secondary origin and insitu laterites have developed over the Pre-cambrian rocks. Soil forms a thin veneer over the laterite. Alluvium occupies the river valleys and depressions between mounds and ridges.

As described in the previous sections lateritization is wide spread in the region. Laterite profiles in the Nilambur valley generally consist of humus zone at the top followed by a pebbly layer. Further below is vermicular laterite. In some of the profiles, pallid zone consisting of kaolinitic clay is developed over granitic gneiss. This is followed by completely and partly weathered zones which merge with fresh parent rock below. Contacts between the various zones are gradational. All the weathering units are not exposed/present in a single profile. Maximum thickness of the weathering profile is 32 m over biotite-hornblende gneiss seen in the quarry cutting near Nilambur whereas bore holes in Maruda indicate a maximum thickness of 22 m (Narayanaswamy and Krishna Kumar, 1996). The laterites are compact and have brick red to purplish colour with cavities filled with kaolinitic clay. Laterites are also classified into two groups in terms of their genetic relation - (i) primary, the term used for insitu weathering product, (ii) secondary, for that formed by partial or complete consolidation of transported lateritic material.

1.8.3 Structure

The rocks of the Wynad - Nilambur Gold Field have been multiply deformed. The region falls within the Moyar-Bhavani lineament, a transcrustal shear system extending NW-SE from the western part of the craton and swinging to NE-SW in the east, dissecting major crustal blocks in southern India (Drury et al., 1984). Recent Nd-isotope data (Harris et al., 1994) indicate that this shear zone is of late Proterozoic age and is a major crustal divide between the Archean block in the north and the Proterozoic granulite blocks in the south.

Several mesoscopic shears and faults have developed within the major zone of shear, which are now occupied by quartz veins carrying gold and sulphide mineralization (Santosh et al., 1995). The veins comprise milky translucent quartz, fresh and unsheared. They occur as a series of sub-parallel, moderate to steeply dipping reefs, trending NNE-SSW to NE-SW, with widths varying from a few tens of centimeters up to few meters. Some veins extend in strike length up to 1600 m, as in the Richmond mine, and to an exposed depth of over 70 m as in the Solomon mine (cf. Ziauddin and Narayanaswami, 1974). All the reefs are emplaced within zones of faults/shears that cut across the regional metamorphic fabric of the country rocks. The quartz veins do not display any preference to particular lithology, but show a strong structural control.

The area is characterised by shear induced tension gashes and retrograded metamorphism as evident from the general observation of the contact zones between greenstone belt and granulite mobile belt. The regional trend of foliation is NNW-SSW with steep dips to SE. The foliation swerves to EW and NW-SE directions towards the foot of Wynad hills.

1.9 Economic geology

The geologic importance of the Wynad plateau and the Nilambur valley lies in their gold resources. The auriferous nature of some of the quartz veins of these areas has been established beyond doubt by earlier workers. Mineralization is confined to zones of intense shearing and dislocation which have acted as loci for emplacement of auriferous veins. The vein gold system of the Wynad - Nilambur Gold Field is associated with the Proterozoic granulite facies terrane of southern India. In the quartz veins, native gold occurs along fracture planes in quartz and as fine disseminations within sulphide minerals. Gold also occurs as subsequent grains, thin flakes, veins and as inclusions within pyrite, the principal sulphide mineral. Chalcopyrite, pyrrhotite and arsenopyrite are also identified as subordinate gangue minerals. The abundance of pyrite and gold are directly correlated, in that lodes rich in pyrite are usually found to contain more gold. Since the gold-bearing quartz veins are localized within this shear zone, it is inferred that the gold metallogeny in Wynad is post-Archean and most probably of late Proterozoic age, correlatable with late Proterozoic incipient charnockite formation and carbonate metasomatism found farther east and south of the terrain (cf. Farquhar and Chacko, 1991; Wickham et al., 1994). Stable isotopic evidences (Santosh et al., 1995) suggest a model involving derivation of CO_2 by degassing of underplated mantle-derived magmas and transfer of juvenile CO_2 to higher crustal levels through felsic magmatic conduits. They also envisage a common link between Proterozoic CO_2 influx and incipient charnockite formation, carbonate alteration, and gold mineralization in this terrain.

There are many abandoned gold workings in laterites near Nilambur town. Illegal mining activities are still prevalent in these areas. The main old workings are confined to the regions south of Nilambur town. A few occurrences are located to the north. Gold dust, grains and even nuggets are known to be present in the lateritic cover resting on the auriferous rocks of the Wynad belt in the Nilambur valley. Intensive panning is still going on even during the summer months in the Nilambur valley.

One of the principal modes of occurrence of gold in the area is as placers along the first order streams in the region. Nilambur is known for gold washing along the streams draining the area since previous century (Ainslie, 1826; Nicolson 1874; Smyth 1880). Gold occurrences have been reported in older gravels forming terraces and recent placers found in present day river channels draining the area (Sawarkar, 1965, 1980; Nair et al., 1987). First report on the primary gold mineralization from Wynad - Nilambur belt and auriferous gravel of Nilambur valley were from Geological Survey of India (Crookshank, 1940; Narayanaswami, 1963; Mahadevan, 1965; Sawarkar, 1980) and the exploration programme for primary/lateritic/placer gold recently carried out by KMED project (Cvetkovic, 1980; Anthrapar et al., 1985), CESS (Narayanaswamy, 1994; Narayanaswamy and Krishna Kumar, 1996) and GSI

(Nair and Suresh Chandran, 1996) have given a surge to the exploration activities in Wynad-Nilambur area. A number of quartz veins, most of them trending NE or NW were traced around Maruda (Vidyadharan and Sukumaran, 1978). They established the auriferous nature of some of these quartz veins by panning the soil nearby. Therefore the contention of earlier workers that the primary source for the alluvial gold in Nilambur valley lies only in the well known auriferous tract of Pandalur - Devala of Tamil Nadu is not valid. Certainly the Maruda source must be contributing a substsntial amount to the alluvial gold in the Nilambur valley - Chaliyar river. From the sediments of Chaliyar river and Punna puzha and their tributaries gold is even now being won by local panners (paniyars) using wooden pans (maravi).

Vidyadharan and Sukumaran (1978) reported an old working for gold right in the quartz vein south east of Maruda for a strike length of approximately one kilometer in a NE-SW direction. It is also reported to have produced lot of gold. It is gathered that panning the minewaste and the adjoining soil indicated specks of gold and during monsoon hundreds of people get engaged in panning here.

Thus, gold in the Chaliyar basin occurs in three geological set ups viz. (a) primary gold occuring in the quartz veins; (b) alluvial gold seen in the older gravels forming high and middle level terraces, which are invariably lateritised and (c) detrital gold seen in the present day river gravels/in the bed of the river channels. Recent offshore exploratory survey by the Geological Survey of India has also revealed interesting concentrations of gold in the marine sediments from the area adjacent to the place where Chaliyar meets the Arabian sea. More detailed discussions on different types and the occurrences of gold in the region is given in chapter 7.

A number of pegmatites are seen in the Wynad region. Although many of them are mica-bearing they may not be of economic significance owing to their small extent.

Some of the quartz veins in the Nilambur valley may be of optical quality. Magnetite quartzite bands are also numerous in the area, bu are of small dimensions.

Laterites as well as the crystalline rocks of the area are extensively used as building materials. Sand for construction purposes is mined from river channels and adjacent areas.

1.10 Environmental geology

In the plateau area of Wynad, deforestation and plantation of tea, coffee and spices like cardamom have resulted in environmental degradation and signifies increased human activity in the region. The uncontrolled use of pesticides, insecticides and herbicides in tea, coffee and cardamom estates may be polluting the surface and subsurface waters.

Coming down to the foot hills of Wynad to the Nilambur valley the problem is of a different type. Here, the illicit panning for gold by local people add lot of mercury to the river water. The panners use mercury for amalgamating the gold fines occuring associated with other heavies. For the past one decade or so the Chaliyar has become notorious for being a polluted river by industries like Mavoor Gwalior Rayons.

The strongly contrasting physiography of the hilly terrain and uncontrolled deforestation of the steep slopes by local settlers poses still another problem. This causes tremendous erosion of the top soil and frequent landslips during monsoons. Landslips, locally called "Urulpottal", resulting in loss of life and property are frequently reported at some parts in the Nilambur valley. Another side effect of deforestation is the heavy loss of water by evaporation from the streams so that many minor streams, which otherwise would be perennial go dry during summer.

Sand mining from the river channels too have attracted the concerns of environmentalists.

1.11 Accessibility

The area is easily accessible by road and rail. There are good net work of roads, Nilambur lies right on the Calicut - Ooty road is connected to Shornur. The railway broad gauge track which ends at Nilambur Road is connected to Shornur Junction of the Southern Railway.

1.12 Climate

The Chaliyar basin enjoys a humid tropical climate with alternative dry and wet season. The annual temperature ranges between 22° to 33°C. The area receives 300-400 cm/yr of rainfall, of which 75 per cent is received during southwest monsoon (June to August) and the rest during northeast monsoon (September to November).

Rainfall increases towards the hilly terrain. The dry weather is prevalent during January to May.

1.13 Objectives of the present work

The present research work is carried out with the following objectives :

1) to understand the elemental concentration and its distribution in the Chaliyar basin sediments in relation to mineralogy, texture and the degree of transport they have undergone;
2) to infer the provenance and weathering/transportation conditions utilizing major, trace and rare earth element analysis, by studying the bulk geochemistry of bedload sediments of Chaliyar river;
3) to estimate the concentration of gold in the Chaliyar river sediments and to establish geochemical affinity and differential migration of selected trace elements like Cu, Zn, Ni, Cr, Co and V in relation to gold in fluvial system;
4) to understand the various physical features like outline, shape, roundness, flatness index and rim characteristics of gold particles from different locations of Chaliyar river and their relationship with distance of transport from lode/lateritic source;
5) to study the chemical variation in gold grains and identify the factors causing it; and
6) to understand the mode of occurrence, genesis of gold associated with the Chaliyar river sediments and to have a preliminary estimate of placer gold in the main channel.

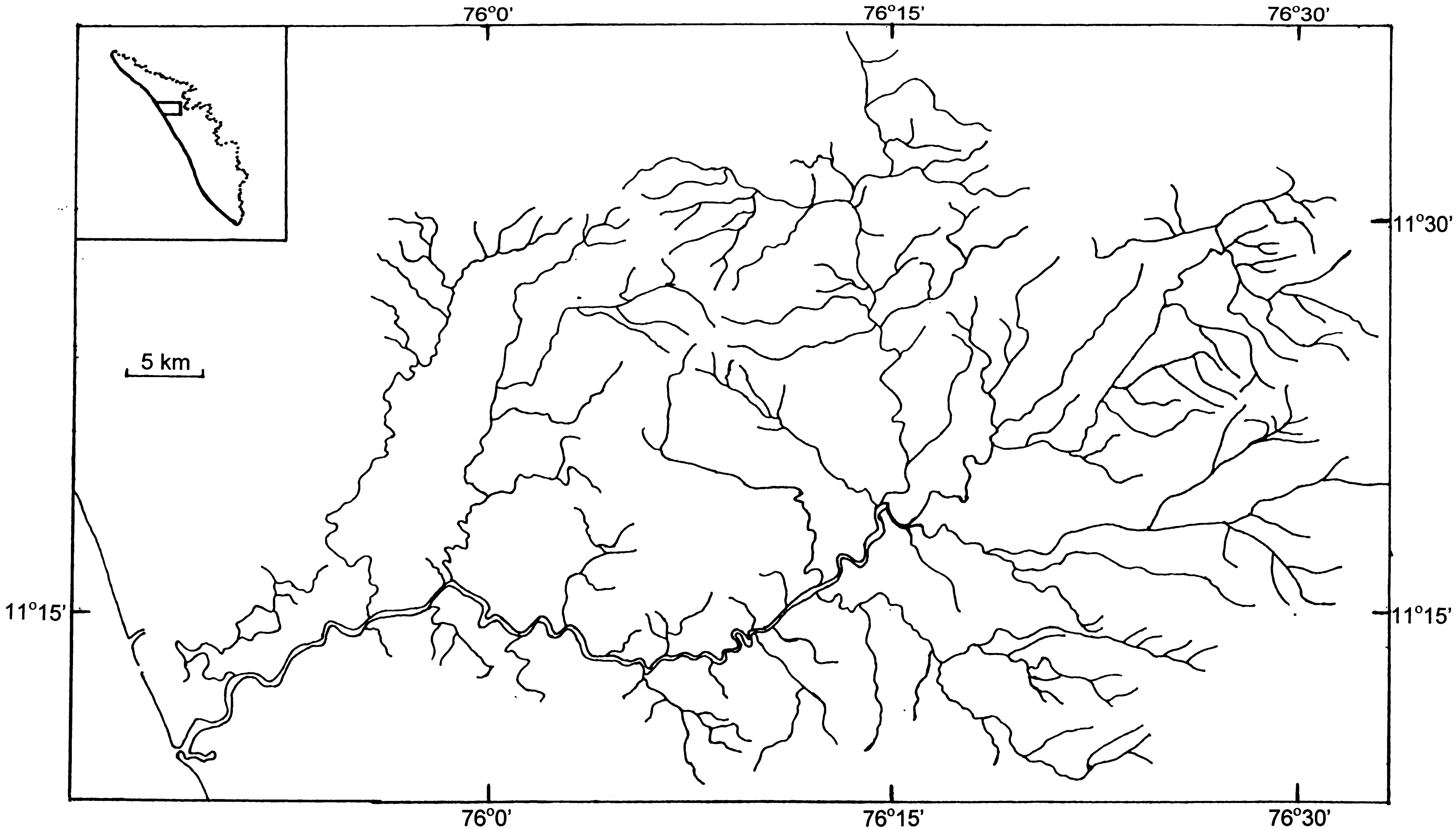


Fig. 1.1· Drainage pattern of Chaliyar basin. The inset is the key showing the map area in Kerala

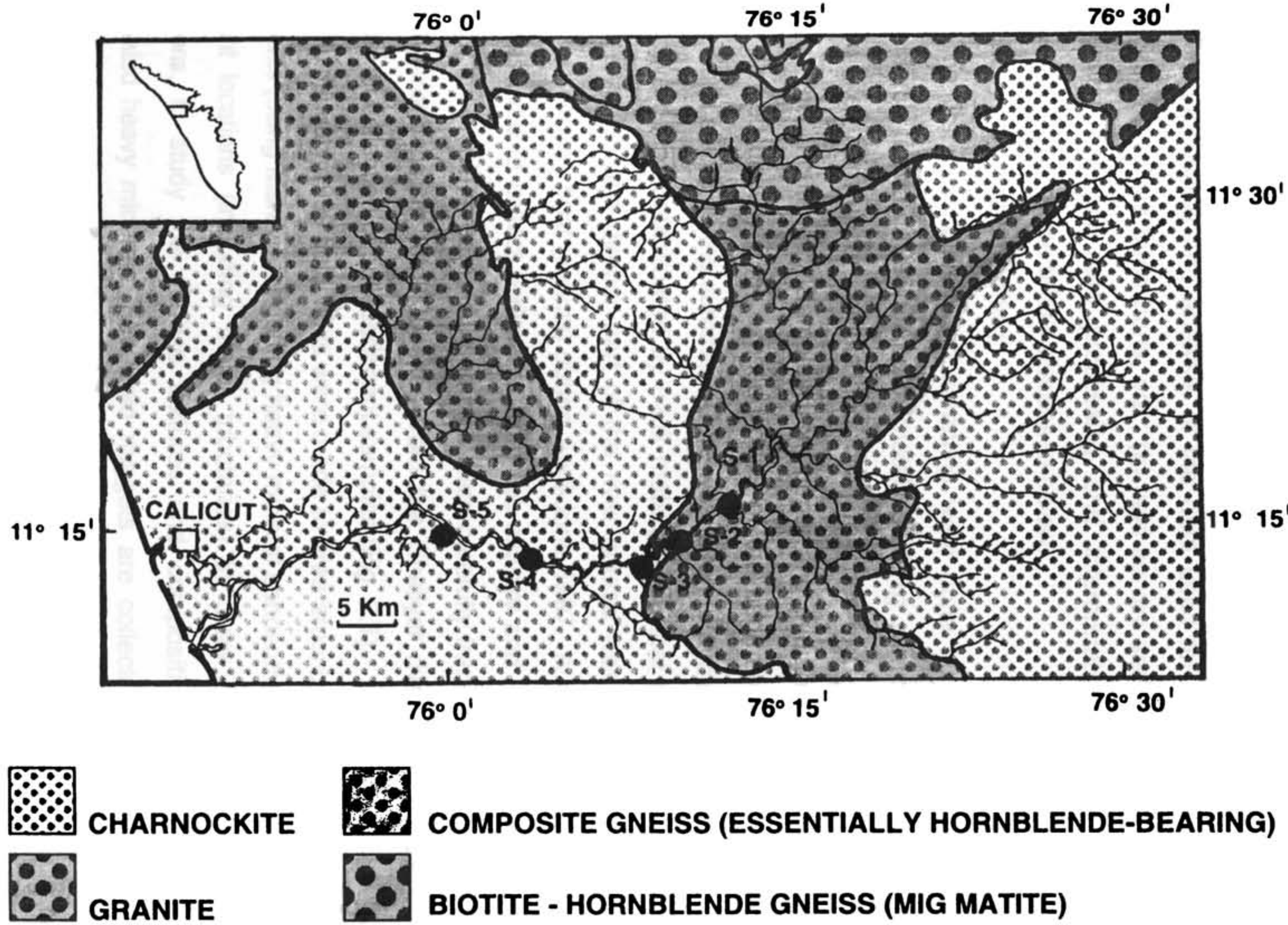


Fig. 1.2 Map showing the Chaliyar river, simplified lithology of the basin. The inset is the key showing the map area in Kerala. (MODIFIED AFTER GSI, 1995)

Chapter 2
MATERIALS AND METHODS

2.1 Introduction

This chapter deals with the various techniques and procedures adopted in the collection, processing and analysis of the data used for this work. The present investigation involves three parts, viz : (a) field survey and sampling, (b) laboratory investigation and (c) data processing and interpretation. Various procedures employed in the work are briefly discussed below.

2.2 Field survey and sampling

The first field survey and sampling were done in the pre-monsoon period during March to May 1996. Approximately 5-20 kg samples were collected from selected sites from upper, middle and lower reaches of Chaliyar river channel and from its major tributaries. Samples from upper and middle reaches of the channel were collected directly from exposed parts of the bed/major point bars which are exposed and stable during summer. Care was taken to avoid collecting samples that might have been contaminated by bank material. Further detailed sampling of the estuarine region and deeper part of the river course was done by undertaking a cruise in a country boat (vanchi) during April-June 1997. A stainless steel Van Veen grab was used to collect sediments from the estuary and also deeper parts of the Chaliyar river main stream. All samples were carefully transferred to neatly labeled polyethylene bags. In total 30 sites from the Chaliyar river drainage basin were selected for collection of bulk sediment samples (Fig. 2.1).

In January 1999 field visits were made to area around Nilambur for panning of sediments (using Maravi) for getting heavy mineral concentrates especially gold from different locations (including major tributaries) in order to understand the size variations, to study the surface textures and composition of gold grains and associated heavy minerals. Few gold nuggets are collected by panning the river sediments making use of the locally available wooden pans.

2.3 Laboratory investigation

2.3.1 Analytical methods

Sample preparation: Since wet chemical methods were essential and followed for the analysis, it is essential to bring the rock sample into solution. So, the samples were processed and were brought to solution by the procedures elaborated below:

Sample processing: About 20 kg of sediment sample from upper reaches and tributaries and 3-5 kg grab samples from lower reaches were dried in a hot air oven at 60^0C. The samples were then homogenised, coned and quartered, and a 'quartered-fraction' was taken for finer processing and each sample crushed by hardened steel mortar. The sample powder form was thoroughly homogenised. About 15-25 g of it was ground to –300 mesh size by the help of agate mortar and pestle. Care was taken to keep the contamination at the minimum level.

Sample dissolution: Sample dissolution was done by (i) acid digestion method (major and trace elements), (ii) aquaregia digestion method (platinum group elements) and (iii) sodium hydroxide-sodium peroxide fusion method (rare earth element). Because acid digestion method uses HF and HNO_3 and does not introduce any matrix element, through flux, the 'B-solution' gives low blank value, which, in turn, increases the sensitivity of the instrument. This solution is used for the analyses of all the major and trace elements except SiO_2 which is analysed by methods described later (see section 2.3.2). Because the latter method does not allow complete dissolution of Pt group elements the sample was decomposed with 10 ml of the 1:1 mixture of HF and HNO_3 and was treated with aqua regia (2 ml HNO3 + 4 ml HCl). This solution was used for Au determination. For the REE analysis of the samples of lower abundance, Na_2O_2-NaOH fusion method was followed. In this method, about 0.5 g of the sample was digested. The matrix of Na was scavenged by the precipitation with NH_4OH.

2.3.1.1 Preparation of 'B-solution' by acid digestion for major and trace element analysis

For the preparation of B-solution, the procedure formulated by Shapiro and Brannock (1962) modified by the geochemistry laboratory of School of Environmental Science, JNU, New Delhi was followed. 0.5 g of powdered sediment sample was digested with 10 ml conc. hydrofluoric and 5 ml conc. nitric and 1 ml conc. perchloric acid in a teflon crucible at a temperature range of 85^{0}C to 90^{0}C with lid on for 4 hours to ensure complete reaction. After 4 hours, the lid was removed and was heated till near dryness. In the second step, 5 ml conc. hydrofluoric and 10 ml conc. nitric acid were added and heated till dryness to 90^{0}C. In the third step, only 5 ml conc HNO_3 was added and heated till dryness. In the final step 30 ml of 1N HCl was added to the dry crucible and was heated to 100^{0}C to bring the digested sample into solution. After regular swirling, the solution was transferred to a 100 ml standard flask and was warmed in a hot plate to ensure complete dissolution of the crystalline salt. The teflon crucible was rinsed several times with 1N HCl and was allowed to cool and made up to volume with distilled water. This solution, with suitable dilution, was used for the analysis by ICP-AES and Flame Photometer. To check the reliability of the major element data duplicate analysis (XRF and ICP-AES) of few samples were also carried out (see Table 2.1).

2.3.1.2 Aqua regia digestion method

A known weight (≈ 1 g) of the well-ground sample was decomposed with 10 ml of a 1:1 mixture of hydrofluoric and nitric acids in teflon beaker. When the silica was expelled completely, the sample was treated with aqua regia (2 ml conc. HNO_3 + 4 ml conc. HCl) and evaporated to near dryness on water bath. When all the acid was expelled, 5 ml conc. HCl was added to drive off HNO_3. When dry, the residue was dissolved in 10 ml 2N HCl and made up to 25 ml. This solution was used for the Au separation.

2.3.1.3 Na_2O_2-NaOH fusion method

For REE determination, 0.5 g of powdered sample was fused with Na_2O_2 and NaOH pellets in a nickel crucible and then kept overnight in triple distilled water. The fused material was then dissolved in 6N HCl into a 500 ml beaker, and evaporated to near-dryness in a hot plate (90^{0}C-100^{0}C) till the silica precipitated in the form of a gel. The silica gel was filtered through whatman 42 and 41 filter papers and the residue of gelatinous silica was washed off several times with 6N HCl. The filtrate was completely dried and picked up in 30 ml of 1N HCl and transferred into a centrifuge bottle quantitatively. To this solution 10-12 drops of phenol red indicator was added. Then NH_4OH was added drop wise till the colour changes and trivalent cations precipitate. The solution was then ultra centrifuged for 10 minutes at 4000-

6000 rpm and the supernatant liquid discarded, leaving behind the precipitate in the centrifuge bottle. This precipitate contains all the REE's and was used for the REE separation.

2.3.1.4 REE separation and pre-concentration for ICP-AES analysis

The REE separation from matrix and pre-concentration were done by cation exchange chromatography. After decanting the supernatant liquid the precipitate in the centrifuge bottle (as prepared by the above said step) was then transferred into a Teflon beaker using 6N HCl and dried (Extract-1). This Extract-1 was picked up in 30 ml of 1N HNO_3 and was loaded through a whatman 42 filter paper in 2-3 steps, into the regenerated HNO_3 quartz columns (of length 26.5 cms and an inner diameter of 1.4 cm) packed with cation- exchange resin AG 50W-X8 (100-200 mesh in Hydrogen form) up to a height of 24.5 cms. The loaded solution was then washed with 50 ml of 1.8N HNO_3 for the removal of major and trace elements and discarded. The total REE rich fraction was eluted with 180 ml of 6N HNO_3 in a Teflon beaker. The above collected solution was dried (Extract-2) in a hot plate and re-dissolved in 30 ml of 1N HCl and loaded in 2-3 steps into the regenerated HCl columns (of length 24.5 cms and an inner diameter of 1 cm) packed with the same cation exchange resin up to a height of 22.5 cms. To get rid of iron fraction collected with 240 ml of 6N HCl and dried (Extract-3) in a hot plate. This dried final cut (Extract-3) was dissolved with 4 ml of 3N HNO_3 for analysis.

2.3.1.5 Au pre-concentration for the quantitative estimation by Instrumental Neutron Activation Analysis (INAA)

Concentration of gold was determined by following the method of determination of gold in low-grade ores and concentrates by anion exchange separation followed by Neutron Activation developed by Iyer and Krishnamoorthy (1976).

Of the aqua regia digested (see section 2.3.1.2) sample solution, 10 ml was added to a thoroughly washed anion exchange resin column (2 cm long; column dimension; 6 mm internal diameter × 10 cm long; Deacidite FF anion-exchange resin; 3-5% cross linking, 200-400 mesh) and the resin was washed using 15 ml of 1N HCl. Now more than 90% of interfering elements other than platinum group elements were eluted out from the sample. At the same time, the gold present in 1 g of the sample gets concentrated in 300 mg of resin.

The resin was then taken out of the column, dried under an infrared lamp and sealed in a polythene envelope (1.5 cm square). A standard containing ≈ 10 μg Au was prepared in a similar way.

2.3.2 Colorimetric determination of silica

Silica analysis for some of the samples were done by colorimetry using a spectrophotometer. The dissolution of the sample for this purpose was done by "A - solution" method as suggested by Shapiro and Brannock (1962).

2.3.2.1 Sample dissolution: Preparation of A-solution

A series of 75 ml nickel crucibles, cleaned with 1:1 HCl and washed with water, 10 ml portion of 15% NaOH was placed and evaporated to dryness under an infrared lamp. 0.05 g of -300 mesh samples were loaded to the crucibles and fused by Meker burner at red hot condition for 10 minutes. The crucibles were cooled and 2/3 of each was filled with H_2O and kept covered overnight. The contents of the crucible with the washings were transferred to 500 ml plastic beakers containing about 300 ml H_2O and 12N HCl. The contents in the beaker were quantitatively transferred to a series of 1000 ml flasks and were warmed up until the solution is clear. The volume was made up on cooling and 100 ml of each was further transferred to plastic bottles.

2.3.2.2 Determination of SiO_2

Reagents used were Ammonium Molybdate solution of 7.5% and Tartaric acid solution of 8%. Ammonium Molybdate solution of 7.5% was prepared by dissolving 7.5 g of reagent grade $(NH)_4Mo_7O_{24}.H_2O$ in 75 ml of water with gentle heating and subsequent addition of 10 ml of 1:1 H_2SO_4 on cooling. The solution was filtered and kept in a plastic bottle.

Tartaric acid of 8% was prepared by dissolving 40 g of reagent grade tartaric acid in water and stored in a plastic bottle.

Reducing solution was prepared by dissolving 0.5 g of reagent grade anhydrous sodium sulphite in 10 ml water with subsequent addition of 0.15 g of 1-amino-2-naphthol-4-sulphonic acid and stirring till complete dissolution. Solution of 9 g reagent grade sodium bisulphite in 90 ml water was added to the first solution and mixed thoroughly and was then stored in a plastic bottle in a dark place.

10 ml aliquot of each sample solution - A was pipetted out and transferred to a series of 100 ml volumetric flasks to which 1 ml of ammonium molybdate solution (7.5%) was added and stirred. This was allowed to stand for 10 minutes. To this solution, 5 ml of tartaric acid solution was added and thoroughly mixed. Further I ml of reducing solution was also added and stirred. The volume was made up to 100 ml and allowed to stand for 30 minutes.

The absorbance of each solution was measured at 650 nm with respect to "blank solution-A" used as a reference blank. This was compared with the absorbance of "solution-A" of in-house rock standards.

2.3.3 Estimation of Sodium and Potassium by flame photometer

Na and K analysis for some of the samples were done by flame photometer. The dissolution of the sample for this purpose was done by "B-solution" method (see section 2.3.1.1)

2.3.3.1 Determination of Na and K

Reagents used were NaCl (for sodium estimation) and KCl (for potassium estimation) for preparing primary stock solution. Primary stock solution of Na and K was prepared by dissolving 2.542 g of NaCl and 1.907 g of KCl respectively in distilled water and made upto 1000 ml.

Intermediate stock solution of Na and K was prepared by diluting 10 ml of the above stock solution to 100 ml with distilled water. By proper dilution of intermediate solution with distilled water different standards were prepared for Na and K.

Dilution principle:

(Required ppm × amount to be made up) / Parent ppm = Vol. to be pipetted

i.e., (10 ppm × 100 ml)/100 ppm = 10 ml of intermediate solution

The different standards of Na and K solution are aspirated to the flame photometer, fitted with Na and K filters respectively, under carefully controlled conditions and the photometer readings are noted down. A standard calibration curve was drawn for Na and K by plotting the concentration of the standard sodium and potassium solution respectively on the x-axes against their corresponding photometer reading on the y-axes.

5 ml of "B-solution" was diluted with distilled water and made up to 100 ml. Further, by proper dilution of the above samples they were also aspirated to the flame photometer and the corresponding photometer reading for Na and K was noted and plotted in the standard calibration curve. The concentration of Na and K was determined from the graph and computed for the whole sample. To check the accuracy of the analysis the solution of in-house rock standards was also run along with the sample solution and the analytical results are compared with the standard published values (see Table 2.2).

2.4 Analysis

2.4.1 Analysis of major, trace and REE by ICP-AES

Quantitative analysis of major and trace elements was done at SES, JNU, New Delhi and NIO, Goa by a Labtam 8440 ICP-AES and Perkin Elmer Plasma-400 ICP-AES respectively (few samples were analysed at NGRI, Hyderabad for its major elements by XRF, trace and REE's by ICP-MS). Rare earth elements were determined by a polychromator in the Labtam 8440 ICP-AES. The precision was found to be higher than ± 5% and ± 10% for major and trace elements respectively. It is found that the precision is better for samples with higher REE abundance. The accuracy of the major element analyses was better than 95%.

Standardisation for majority of the major and trace elements, (excluding REE) was based on in-house rock standards like 22-7, 22-22, VM-9 developed at JNU from the samples of the Kolar schist belt. However, due to shortage of proper rock standard and uncertainties in the internal rock standards, the accuracy for the trace elements could not be worked out.

Standardisation for REE's was done with metal standards obtained from Johnson Mathey Inc. and in-house rock standard 90-57, which was analysed several times by the isotope dilution method at SUNY, Stony Brook, USA. REE analysis by ICP-AES was done in the Geochemical laboratory under the supervision of Prof. V. Rajamani, SES, JNU, New Delhi. As a part of this the author has visited JNU from May-June 1998 and has undergone training in the analytical procedure. The data is quite consistent with the reported value (see Table 2.2). More details regarding precision and accuracy of analytical results of in-house rock standards and analytical conditions followed for ICP-AES analysis is discussed by Mohanta (1998).

Few samples were analysed for REE and trace elements using ICP-MS at the National Geophysical Research Institute (NGRI), Hyderabad, following the procedure outlined in Balaram et al. (1996).

2.4.2 Analysis of Au by Neutron Activation Analysis

The samples were analysed at BARC, Mumbai for their concentration of gold following the method of determination of gold in low-grade ores and concentrates by anion exchange separation followed by Neutron Activation developed by Iyer and Krishnamoorthy (1976). For this purpose the author has visited BARC and has undergone training in the analytical procedure during the year 1996.

The resin with pre-concentrated samples (see section 2.3.1.5) sealed in a polythene envelop and standards were irradiated for seven hours in the Apsara reactor at a neutron flux of 1×10^{12} n/cm^2/sec, cooled for 5 days and then activities were measured.

The γ activity of 412 KeV of ^{98}Au was measured using a HPGe detector {125 cc active volume, 25% efficiency w.r.t 3"× 3" NaI(Tl) having a FWHM of 2 KeV for the 1332 KeV of ^{60}Co} coupled to a PC based 4K multichannel analyser. The amount of Au adsorbed on the resin was thus computed, comparing the activities. From this, the concentration of Au in sample was calculated.

The sensitivity of the method depends on the weight of sample taken, length of irradiation, cooling and counting time (Iyer and Krishnamoorthy, 1976). In this work, it is found than an amount of 0.01 μg of gold in one gram of sample can easily be estimated.

2.4.3 Determination of Loss on Ignition (LOI)

Approximately 1 g of powdered sample was transferred to previously weighed silica crucible. The crucible with the sample was kept in a Muffle furnace and heated to pre set 500°C with open lids to drive off the adsorbed water. After this the silica crucible was closed with lid and heated to 1100°C to drive off the structurally held water. Then it was allowed to cool slowly. The crucible with the sample was carefully kept in a desiccator and accurately weighed. The loss of weight was computed by subtracting the weight of the heated sample from the initial weight.

2.5 Textural analysis

2.5.1 Statistical parameters

Samples (30 in numbers including major tributary samples) collected from upper (stable point bars), middle and lower reaches (grab samples) of Chaliyar mainstream were oven-dried and subjected to coning and quartering. A representative portion (100 g) was then subjected to mechanical analysis on a Ro-Tap sieve shaker using standard set of ASTM sieves at half phi (½ ∅) intervals. The fractions left over in each sieves were carefully transferred, weighed and cumulative weight percentages were calculated. Samples which contain significant amount of silt and clay fractions were subjected to combined sieving and pipette analysis as suggested by Lewis (1984).

The cumulative weight percentages of the above analyses were plotted against the respective grain sizes in phi units on a probability chart. The cumulative frequency curve is drawn and the phi values of 1, 5,16, 25, 50, 75, 84 and 95 were recorded. The grain size parameters such as mean size, median, standard deviation, skewness and kurtosis were calculated following Folk and Ward (1957).

2.5.2 Determination of sand:silt:clay ratios

Sand, silt and clay ratios were determined using standard techniques of wet sieving and pipette analysis (Lewis, 1984). Known quantities of silt and clay rich sediments were soaked in water for dispersion. The lumps were separated and were filled with water in a 1000 ml beaker. This was kept overnight for making it free of saline content. Excess water is removed using a decanting tube and 25 ml of 10% sodium hexametaphosphate was added to the sample. The sample containing $NaHPO_4$ was stirred at 20 minutes intervals up to 4 hours.

The total amount of samples were transferred to a 63 μ sieve (ASTM 230 mesh) and wet sieved. The washings were continued till clear water passes through the sieve. Care was taken to limit the total amount of aliquot to less than 1000 ml. The coarse fraction obtained in the sieve was dried, weighed to know the sand fraction in the sediment samples. The volume of aliquot in the cylinder was made up to 1000 ml.

Using a stirrer the contents in the cylinder was vigorously stirred for 45 seconds. Exactly after 1 hour 40 minutes 13 seconds using a 25 ml pipette connected to a tube was lowered to 10 cm down the water level and 25 ml of aliquots containing clay were pipetted out and transferred to a previously weighed 50 ml beaker. All the aliquots were oven dried to constant weight at 60±3^{0}C and weighed accurately after cooling at room temperature. The amount of $NaHPO_4$ was deducted from the weight of the sample.

Strength of $NaHPO_4$ = 10% (i.e., 100 g in 1000 ml)

In 25 ml amount of $NaHPO_4$ = 2.5 g

Amount of $NaHPO_4$ added to 1000 ml = 25 ml

Weight of $NaHPO_4$ in 25 ml of the aliquot = (2.5/1000) × 25 = 0.0625 g

Weight of clay fraction in 25 ml, W_1 = Weight of sample in 25 ml – 0.0625 g

∴Weight of clay fraction in 1000 ml, W_2 = W_1 × (1000/25) g

From the known weight of sand and clay fraction the weight of silt fraction present in the samples was computed. The relative proportion of sand, silt and clay in samples was also calculated.

2.6 Mineralogical analysis

Different methods were adopted to study the mineralogical constitution of riverine sediments. Heavy mineral separation (using bromoform) were carried out in the > 63 μ fraction of Chaliyar river sediments, which is dominantly sandy.

2.6.1 Bulk mineralogy

Representative bulk samples from selected site were mounted on glass slides using canadabalsm in order to understand modal composition of sediments. Percentage distribution of minerals (assessed by point counting of grain mounts) were presented in table 4.1.

2.6.2 Mineralogy of sieved fraction

A representative portion of sand fraction was washed thoroughly, oven dried and was subjected to sieve analysis at 1/2 ∅ intervals (see section 2.5). The coarse sand fraction 0.5 to 1.0 ∅ (ASTM mesh size +35), which represent mean size of 33% of the samples was selected for petrologic study to facilitate comparison of data from one location to other. A total of 300 - 400 grains of the above mesh size were mounted on a glass slide using araldiet. The sections were grinded and polished using carborandum and alumina powder respectively with a polishing machine. The individual minerals in each slide were studied under a petrological microscope and the percentage distribution of minerals (assessed by grain counting) were presented in table 4.2.

Photomicrographs of selected areas of grain mounts/polished grain mounts showing important textural and mineralogic features were taken using a Olympus polarizing microscope at the Department of Geology, University of Kerala, Kariavattom, Trivandrum.

2.6.3 Heavy media separation

In order to find out the percentage of heavy minerals in the sediments a few samples were subjected to heavy mineral separation. A representative portion of sand fraction (>63 μ in bulk sample) was washed thoroughly, oven dried and was subjected to heavy mineral separation. The bulk heavy and light minerals were separated using bromoform ($CH Br_3$; Sp.Gr. 2.89 g/cc) and separating funnel. The minerals thus separated were washed with acetone, dried and weighed to find out the total heavy and light minerals.

2.6.4 Mineralogy of clay fraction (<2 μ size)

Clays were separated from the bulk sediment by settling velocity employing Stoke's law. The clay mineral identification was carried out by X-ray diffraction technique.

After estimating percentage of sand, silt and clay fraction (see section 2.5.2) in the samples the contents in the cylinder was kept undisturbed. After 6 hour 41 minutes the whole aliquot upto 10 cm depth was pipetted out into a 500 ml beaker. Organic matter in the samples was removed by oxidising with 10 ml H_2O_2 and carbonate material removed with 5 ml of acetic acid. The sample was stirred well and kept overnight for settling. The top clear liquid was decanted and once again filled with distilled water and stirred well. The clay particles were allowed to settle and the water was removed. The clay-water suspensions were used to make slides of almost equal size and thickness by pipetting equal volume (~ 1ml) of sample and smearing on glass slides. The slides were dried at room temperature and placed in a desiccator to prevent rehydration before exposing to X-rays. These slides were subjected to X-ray analysis at NIO, Goa using Philips PW 1840 X-ray Diffractometer with Ni filtered CuKα as the target. Clay identification were carried out by following the scheme suggested by Biscaye (1965). The untreated clay slides were scanned through 3° to 33° (2θ) with a scan speed of 0.05°/sec. The analysis was carried out at 40 kV with a current of 20 mA.

2.7 SEM analysis of quartz grains

Approximately 10 g of selected samples were washed thoroughly with distilled water. The washed samples were soaked with H_2O_2 to remove organic debris. The sand fraction was separated using sieves. Quartz grains between -45 and +60 ASTM size (between 250 to 355 μ) were used for present study. According to Krinsley and McCoy (1977), the quartz grains in the size range 200 to 400 μm are generally considered to record all the depositional features in any given environment. Using an optical binocular microscope, samples of quartz grains were mounted on SEM stubs using double-stick tape, sputter coated with gold for 1 minute. The gold coated quartz grains were examined with JEOL Scanning Electron Microscope, Japan at IIT, Bombay. The SEM analysis was carried out at 18 kV acceleration voltage with a probe current of 6×10^{-9} AMPS. SEM photographs of few selected grains were taken to illustrate the shape and surface texture. Twenty quartz grains is thought to give a valid statistical representation of the sample and regarded as sufficient to represent the variability present in a single sample (Krinsley and Doornkamp, 1973; Baker, 1976) and accordingly twenty grains from each sample were selected for the present study.

2.8 SEM analysis of gold grains

From the panned heavy mineral concentrates gold grains were hand picked using hand lens in the field and also in the laboratory with the help of a Leica (WILD MZ8) binocular microscope, Switzerland. Gold grains from 10 different locations were studied for their size, shape etc. using a graduated eyepiece on a binocular microscope. Few gold particles from different locations were subjected to SEM and EDX analysis to understand the shape, surface texture and chemical composition. Around 50 gold particles were mounted on a stub using a double-stick tape and studied under JEOL JSM-5800LV Scanning Microscope (Japan), and few photographs were taken at NIO, Goa. Few gold grains were also mounted on a thin film of carbon coated stub and EDX analysis was carried out at NIO, Goa. All the analysis are carried out at 20 kV and 55 μA. For EDX analysis of gold grains, ME-XRS multi-element X-ray reference standard was used.

2.9 EPM analysis of gold grains

Representative samples of gold grains collected from different locations were subjected to electron probe micro analysis (EPMA). The analysis were carried out on polished sections at NGRI, Hyderabad and CSIRO, Australia to understand the chemical composition, zoning etc. Few backscattered electron images were also taken at CSIRO, Australia to study the process of rim formation and differential leaching of trace elements. The EPMA conditions and standards followed for platinum group and other trace element analysis at CSIRO, Australia is given in Appendix 7.4.

2.10 Data processing and computation

Data compilation and processing were done using a personal computer. The mathematical and statistical calculations and preparations of diagrams like scatter plots were done using available software.

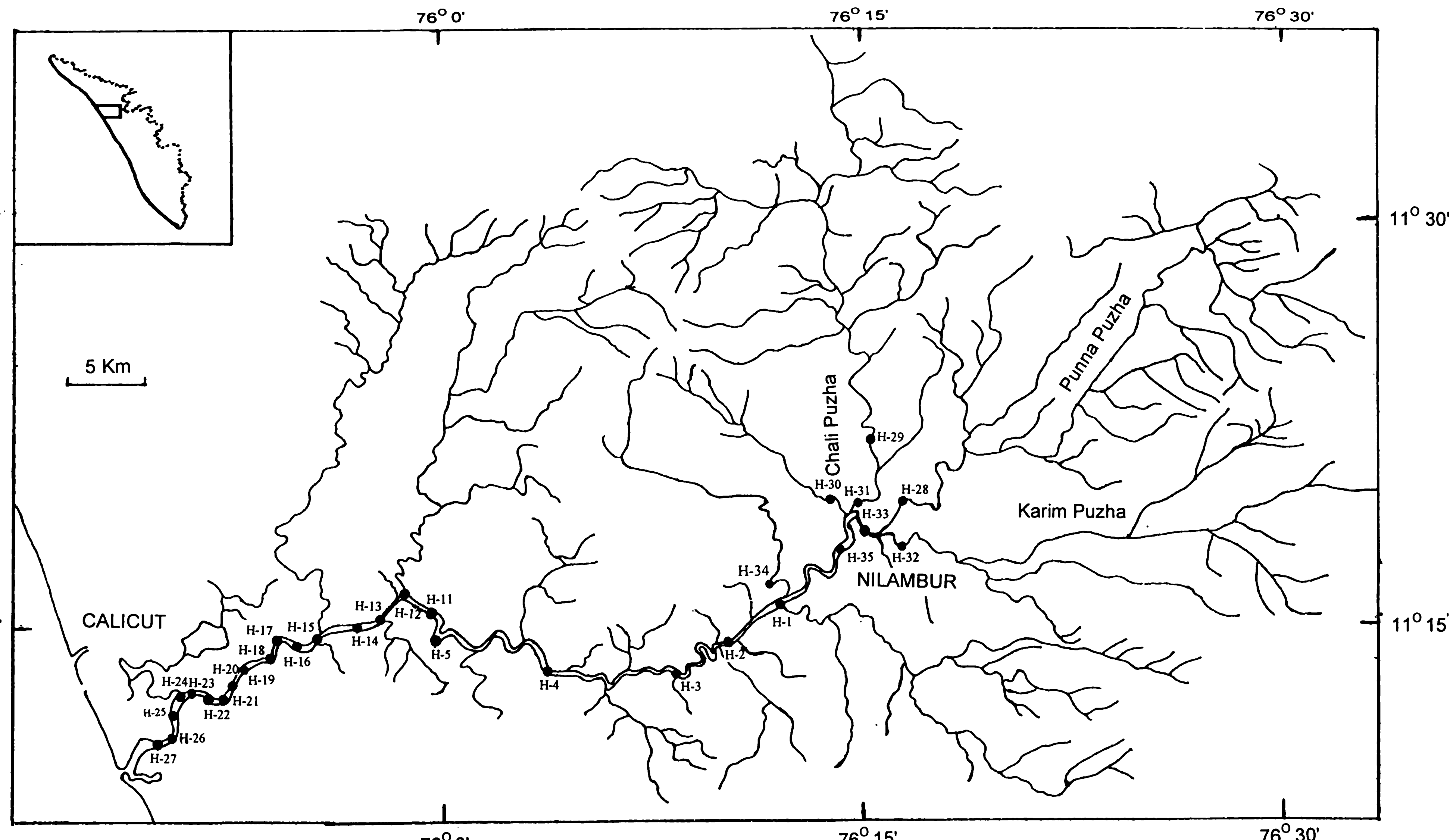


Fig. 2.1 Sketch Map Showing Showing Chaliyar River And The Location Of Samples Collected

Table 2.1 Duplicate analysis of major oxides (wt.%) present in Chaliyar river sediments using XRF and ICP-AES method

Sample No.	H-15		H-21		H-23		H-25		H-26		H-27	
Oxides	XRF	ICP-AES	XRF	ICP-AES	XRF	ICP-AES	XRF	ICP-AES	XRF	ICP-AES	XRF	ICP-AES
SiO_2	76.13	79.40	74.85	77.13	71.25	74.50	69.13	73.00	56.12	61.01	66.32	69.80
TiO_2	0.69	0.52	0.61	0.53	0.63	0.57	0.75	0.75	0.86	0.72	0.83	0.71
Al_2O_3	10.49	8.05	10.92	8.77	12.50	9.44	12.03	8.70	16.38	12.00	14.04	10.46
FeO(t)	5.00	4.42	4.44	4.03	4.94	4.26	5.59	4.99	7.02	5.77	5.71	4.87
MnO	0.06	0.05	0.06	0.05	0.05	0.05	0.06	0.06	0.06	0.05	0.06	0.05
MgO	1.08	1.15	1.23	1.32	1.24	1.32	1.44	1.43	2.32	1.91	1.72	1.61
CaO	2.19	1.91	2.39	2.24	2.25	2.04	2.12	1.89	2.49	2.03	2.48	2.12
Na_2O	1.57	1.35	1.85	1.70	1.96	1.97	1.71	1.56	3.48	2.32	1.96	1.97
K_2O	0.61	0.41	0.55	0.41	0.60	0.46	0.66	0.46	1.08	0.77	0.79	0.58
P_2O_5	0.07	0.10	0.08	0.08	0.11	0.10	0.14	0.11	0.30	0.18	0.17	0.14
LOI	1.66	1.66	2.04	2.04	3.49	3.49	5.56	5.56	9.34	9.34	4.92	4.92
Total	99.55	99.02	99.02	98.30	99.02	98.20	99.19	98.51	99.45	96.10	99.00	97.23

Table 2.2 Accuracy of the analyses measured by running several in-house rock standards as unknown sample. The analyte standard was not used for calibration during the analysis. All analyses are done by ICP-AES at JNU, New Delhi and NIO, Goa.

Major elements	Std. 22-7			Std. 22-22			Std. VM-9	
	NIO*	JNU1	JNU2	JNU*	JNU1	JNU2	JNU*	JNU2
	Analysis	Reported	Reported	Analysis	Reported	Reported	Analysis	Reported
TiO2	0.85	0.91	0.83	-	-	-	1.37	1.29
Al2O3	14.43	15.31	15.2	-	-	-	15.1	14.92
FeO (t)	11.31	11.36	10.87	9.71	9.86	9.72	-	-
MnO	0.17	0.17	0.18	0.23	0.24	0.22	-	-
MgO	9.42	10.26	9.87	5.77	5.51	5.72	-	-
CaO	11.16	11.34	11.01	-	-	-	4.24	4.55

* Present study

Analytical accuracy of SiO2, Na2O and K2O of in-house rock standards. All analysis carried out at CUSAT. Si is analysed by Spectrophotometer, Na and K by Flame Photometer.

Major elements	Std. 22-7			Std. VM-9		Std. 22-22		
	CUSAT*	JNU1	JNU2	CUSAT*	JNU2	CUSAT*	JNU1	JNU2
	Analysis	Reported	Reported	Analysis	Reported	Analysis	Reported	Reported
SiO2	-	-	-	-	-	56.78	53.84	53.94
Na2O	2.67	1.61	1.57	4.29	4.37	-	-	-
K2O	0.05	0.08	0.08	2.9	3.16	-	-	-

* Present study

Accuracy of REE data forin-house rock standard (90-57) analysed along with samples at JNU, New Delhi

Element	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb
Analysis	46.44	18.99	4.63	1.75	4.82	3.48	2.44	2.15
Reported	38.5	21.8	4.89	1.58	4.75	4.6	2.6	2.3

The data in column JNU1 and JNU2 in the above tables are as reported by Rajamani et al. (1985) and Mohanta (1998) respectively.

Chapter 3
TEXTURE

3.1 Introduction

The importance of large rivers in transporting the products of denudation of the continent to the sea has been known ever since Lyell (1873) described the flux of sediment into the Bay of Bengal from the Ganges and Brahmaputra Rivers. Since then, the estimates of contributions from large rivers have been updated and summarized in many studies (eg., Garrels and Mackenzie, 1971; Inman and Brush,1973; Milliman and Meade,1983; Meade,1996). Thus the estimated total flux of the particulate solids to the oceans is of ca. 16×10^{9} ton /yr. The contribution of small rivers (drainage basin < 10,000 km^2) to the global budget of sediment was documented by Milliman and Syvitski (1992) and later by Inman and Jenkins (1999). They showed that small rivers cover only 20% of the land area, but their large number results in their collectively contributing much more sediment than previously estimated, increasing the total flux of particulate solids by rivers to ca. 20×10^{9} ton/yr.

3.2 Significance of textural analysis of river sediments

In the past few decades, grain size, sorting, roundness and mineralogy in modern river sands have been studied extensively. Some notable studies of river sands include those of Burri (1929), who pioneered studies of the mineralogy of small rivers in Switzerland, the studies of the modern sands of the lower Mississippi River by Russell (1973), van Andel's (1950) and Koldewijn's (1955) study of heavy and light minerals along the Rhine River, Basu's (1976) study of Holocene river sands to evaluate the role of climate versus source rock, Potter's (1978) study of the mineralogy and chemical composition of many of the world's big rivers, Franzinelli and Potter's (1983) study on the petrology, chemistry and texture of modern river sand of Amazon River System, DeCelles and Hertel's (1989) study on the petrology of fluvial sands from the Amazonian foreland basin and Johnson, Stallard and Lundberg's (1991) study of tropical fluvial sands of the Orinoco River drainage basin. A comprehensive study of all aspects of river sands and alluvium is that of Kumar and Singh (1978). Krynine (1935,1936) was one of the first to come to the tropics to study modern sands to better understand their ancient equivalents. Further, a proper combination of statistical parameters can be used to discriminate various environments/ facies of deposition of ancient and modern sediments (Folk,1966; Friedman,1967 and Hails and Hoyt, 1969). Apart from this the particle size distribution can invariably influence the mineralogical (Mishra,1969; Patro et al.,1989) and chemical (Williams et al., 1978; Forstner and Wittmann, 1983) composition of sediments. Hence, an attempt has been made in this chapter to describe the grain size distribution of the sands of the Chaliyar river and its major tributaries so as to have a proper understanding of its influence on the mineralogy and geochemistry and further to examine the textural factors in relation to accumulation of placer gold.

3.3 Review of literature (Historical review)

History of fluvial sedimentology can be traced back to the times of ancient Greek philosophers like Thales of Militeus, Herodotus and Aristotle, who made some important observations on the depositional activity of river Nile. Similarly, in later centuries (14 - 17 centuries) Leonardo da vinci, Agricola, Bernard Verenius etc. tried to relate sedimentary rock with the river deposits.

Modern sedimentological concepts actually originated much later, beginning with Lyell, who published the book "Principles of Geology", in 1830, followed by Sorby, Walther, and Grabau.

In the last five decades, developments in fluvial sedimentology have been manifold, encompassing widely ranging areas of research such as application of hydraulics in the studies of bed forms, studies of modern environments and their application in understanding ancient deposits, concept of facies models and computer simulations, three dimensional alluvial stratigraphy, environmental management, mineral exploration etc.

A more concrete knowledge of processes and present day environments with applications to understanding the ancient and modern fluvial systems was established only in the early 1950's and 1960's. Perhaps the single most important advance which contributed to the development of modern fluvial sedimentology, in the early part of the century, is Fisk's (1944, 1947) work on Mississippi river. Other works of far reaching consequence were: statement of flow regime concept by Simons and Richardson (1961) and Bernad et al. (1962), and work on bedform and sedimentary structures culminating in a major structural classification by Allen (1963a). With an increasingly narrow focus of research in the 20th century, studies in fluvial sedimentology became more and more specialised, like studies on modern fluvial systems, fluvial facies and fluvial models, alluvial stratigraphy, sediment transport and bedforms, economic applications and environmental management.

3.4 A review of works on Indian rivers

The number of process-based case studies on Indian rivers is not very large. Even then it is apparent that the rivers of India have certain special characteristics. Indian rivers in general have to adjust to both the seasonal variation in discharge and the high - magnitude floods from episodic heavy rainfall. Equilibrium of river forms and sediment load carried by the rivers, therefore, have to be adjusted to multiscale discharges. Such a phenomenon occurs also in other parts of tropics and subtropics.

Interrelationship between grain-size frequency distribution and depositional environments and/or processes has been used successfully in many earlier studies (eg. Qidwai and Casshyap, 1978; Goldberg, 1980; Khan, 1984; Ramanamurthy, 1985; Mahendar and Banerji, 1989; Pandya, 1989; Joseph et al., 1997; Majumdar and Ganapathi, 1998) to identify the depositional environment and recognize operative processes of sedimentation of ancient terrigenous deposits. In India, textural characteristics of sediments from different environments have been attempted by many workers (Sahu, 1964; Mishra,1969; Seetharamaswamy, 1970; Veerayya and Varadachari, 1975; Rajamanickam and Gujar, 1985, 1997; Samsuddin, 1986; Seralathen, 1988; Jahan et al., 1990; Seralathen and Padmalal, 1994). Subba Rao (1967) has made a detailed investigation on the composition and texture of the shelf sediments of the east coast of India. Grain size characteristics of sediment deposited at mouth of Hoogly river were carried out by Mallik (1975). Rajamanickam (1983), Rajamanickam and Gujar (1985) have investigated the grain size distribution of surficial sediments of west coast of India. Gupta and Dutt (1989) have studied the Auranga river, a seasonal river which carries sand predominantly, to understand the physiography, sedimentary texture and structure and its transportational behaviour. The Narmada (Rajaguru et al., 1995) is a much larger river which alternates between rocky gorges and rapids and alluvial reaches and carries coarser materials, its sediment load predominantly sandy, is studied to know the channel physiography, morphology and sediment transport of the river. But studies on the textural characteristics of short flowing rivers are meager. Naidu (1968) has studied the textural variations of Godavari river sediments. Sediment texture of Krishna and Mahanadi drainage systems has been covered by Seetharamaswamy (1970) and Satyanarayana (1973) respectively. Dora (1978) has investigated the textural characteristics of Vasistha - Godavari drainage system. A detailed granulometric investigation of the sediments of the major and subenvironments of the modern deltaic sediments of Cauvery river has been carried out by Seralathan (1979). Mohan (1990) has studied grain size parameters and its significance of Vellar river and its estuary. Seralathan and Padmalal (1994) have carried out textural studies on the surfacial sediments of Muvattupuzha river and Central Vembanad Estuary. From the above studies Indian rivers tend to display a wide variety of characteristic forms, depositional features and sediment transportational patterns. It is necessary to study the processes and sedimentological characteristics of these rivers especially the small rivers. Apart from satisfying geomorphological curiosity, our understanding of these rivers may lead to better sedimentological and environmental planning and better appreciation of processes of mineral concentrations (gold).

3.5 Results and Discussion

The importance of grain size analysis of clastic sediments arises from the fact that (i) the grain size is a basic descriptive measure of the sediments; (ii) the grain size distributions may be characteristic of sediments deposited in specific environments like river, beach, dune etc.; (iii) the grain size analysis may yield information regarding the physical transport the sediment has undergone before deposition; (iv) the grain size may be related to other properties such as permeability, mineralogy, geochemistry etc. and (v) grain size may constrain localisation of alluvial placers in relation to texture of associated sediments. The characteristics of grain size distribution of sediments may be related to the physiography of the channel, source materials, process of weathering, abrasion and corrosion of the grains and sorting processes during transport and deposition.

Present study: Seven samples from major tributaries in the head water region and 23 samples from different locations along the main stem of the Chaliyar river have been analysed, the locations of which are given in figure 2.1. The percentage variation in different grain size along the Chaliyar and the percentage of different fractions present in the major tributaries are given in table 3.1 and figure 3.1a & b respectively.

3.5.1 Size variation

Gravel: The major tributaries like Punna puzha, Karim puzha and Chali puzha are characterised by large amounts of gravels, which gradually decrease in the downstream direction. Highest percentage of gravel (42%) is present in a comparatively smaller tributary known as Kanjira puzha followed by the sample H-33 (40%; just below the confluence zone of Punna puzha and Karim puzha) and they are the main sources of gravels in the Chaliyar main channel. Apart from this there are minor inputs from the tributaries in the downstream direction and notable among these are sample H-14, H-18, H-20, H-22 and H-24. It is interesting to see that, these sample sites are slightly downstream, except sample site H-24, from the tributary confluences indicating that the gravel rich bedload from these tributaries are carried by the main channel and gets deposited further down and along the meanders or bends. However, sample H-24 which is approximately 10 km from the coast is having high percentage of gravels (31.57%) contributed by a tributary which almost flows parallel to the main channel. From the physiography of the above tributary we can say that it does not have the strength/energy to cut its own channel which is also the vicinity where the gravel percentage is high. Generally speaking the gravel percentage fluctuates between high and low and gradually decreases downstream probably indicating inputs from tributaries along the main channel.

Coarse sand: Variation of very coarse sand follows that of gravels especially in the lower reaches of the main channel. That is, wherever the gravel percentage is high a corresponding high for very coarse sand is also seen and similarity for low percentage of gravel also. In general corresponding locations of gravel highs are the sites of very coarse sand enrichment. The significant similarities in the percent variation of gravels and very coarse sand in the middle and lower reaches is an indication of close range of its sizes. Most strikingly, though the locations of gravel high are the sites of also very coarse sand enrichment, the actual percentages of very coarse sand is high when compared to gravels in the main channel. But this is not true in the case of tributaries. Though there are similarities between the gravel and very coarse sand percentage in the tributaries the actual percentage of gravel is higher than the very coarse sand which is just opposite to what we have seen in the lower reaches of main channel. This could be attributed to wide range in the sizes between the gravels and very coarse sand. In other words the decrease in the content of very coarse sand in the tributaries is compensated by an increase in the gravel content, while the decrease in the gravel content in the main channel is compensated by an increase in the content of very coarse sand. It is also due to progressive sorting from gravel rich tributary to sand rich main channel. In addition to this change in the flow pattern in the upper reaches and lower reaches imparts considerable effect on the grain size distribution.

From the table and figure it is clear that the content of coarse sand is much less in the tributaries when compared to the Chaliyar main channel. A notable feature of the Chaliyar main stream is the gradual decrease in the coarse sand content along the downstream direction especially between 63-85 km. This decrease in the coarse sand content could be attributed to the progressive sorting in the downstream direction. The coarse sand content, however, is not less than 17.9% (sample H-3) which is almost same as that of the average coarse sand content in the tributaries (17.82%). Beyond this distance (85 km) there is a gradual increase in the coarse sand downstream probably due to inputs from the tributaries and also due to the transport and deposition of this fraction from the upper reaches. Hence we are seeing a decreasing trend in the coarse sand fraction in the region between 63-85 km from the source.

Medium sand: Variation of medium sand clearly indicates deviation from coarser entities by showing an increase towards the downstream direction. Variation of medium sand is complimentary to that of the coarse sand. This is well reflected through out the main channel. Most strikingly, in general, the subsequent locations of coarse sand highs are the sites of medium sand enrichments. It is probably due to the progressive decrease in the competency of the river water downstream. The decrease in the content of coarse sand in the upper reaches (63-105 km) of the

Chaliyar main stem is compensated by a drastic increase in the medium sand content, while in the downstream section (beyond 105 km) the small decrease in the medium sand content is compensated by the small increase in the coarse sand. In general high content of medium sand in the upper reaches could be attributed to progressive sorting while in the lower reaches the higher content of coarse sand and a small increase in the content of medium sand could be attributed to minor inputs from the adjacent tributaries having predominantly coarser material. Thus it can be seen that the coarse sand marks the transition phase of the spectral changes in the sub-populations of size distribution.

Fine sand: Variation of fine sand shows a sudden increase in its content beyond 110 km. This is probably due to a drastic change in the energy conditions prevailing in the channel above and below this point. It is noted that at this point the river takes a huge turn which probably causes a change in flow pattern thus reducing the stream power and deposition of the finer fractions. The low content of fine sand in the upper reaches could be attributed to the high energy conditions prevailing in this region which is partly effected by the steeper gradient of the terrain. Though there are minor inputs of coarser material in the lower reaches by the tributaries, they have not masked the content of fine sand in main channel. No significant increase in the very fine sand content is seen in the lower reaches beyond 107 km, and it remains very low (maximum in H-17: 4.92% in the main channel; in the tributary H-29: 6.07%). But as can be seen from the spectral pattern of fine sand and very fine sand that as the river reaches the coast the river loses its energy thus allowing the above fractions also to get deposited in the channel. However, the content of very fine sand is comparatively low in this river probably due to the following reasons: (a) though the source area is highly weathered, the detritals which survived the weathering are mainly of coarser material due to the coarse-grained nature of provenance rocks; (b) these coarser materials have undergone lesser abrasion even though they are carried by traction and saltation probably indicating that the river bed is not rough enough to reduce the size of the particles; and finally (c) the energy conditions prevailing in the river is high which carries the fine particles beyond the fluvial system. The latter reason (c) can be ruled out since as it can be seen that the lower reaches of the Chaliyar main channel has significant amount of mud (silt + clay) when compared to fine sand. However, the contents of very fine sand and mud are negligible, except sample H-26 which is having the highest percentage of mud 42.58%, and do not characterise significant variation as the flow conditions do not facilitate its deposition. To have fine sand in sediments there should be (a) fine grained rocks at source and or (b) high degree of physical weathering during transport. Since both the factors are absent or negligible in the Chaliyar basin the fine sand mode is almost absent in the bedload sediments.

Spectral analysis: Spectral analysis of various size fractions with distance of transport shows marked variations in the Chaliyar basin. (a) The high content of gravels, and very coarse sand in the tributaries indicate the existence of high energy conditions owing to the high gradient of the tributaries and (b) Chaliyar river main channel mainly consists of sand with a downstream increase in medium and to a lesser extent in fine sand due to progressive sorting which is partly controlled by the physiography of the channel and partly by the energy regime as evident in the variation in the gradient in different channels of the basin (see Fig. 3.1c). From this it is evident that the sediment transport pattern of bedload in the tributaries is characterised by rolling processes while that of the main channel include both rolling as well as saltation.

3.5.2 Statistical Relationships

Textural studies of clastic sediments have revealed the existence of statistical relationships between the different size parameters such as mean size, standard deviation (sorting), skewness and kurtosis. Studies have shown that the best sorted sediments are those with mean size in the fine sand grade (Pettijohn, 1957; Griffiths, 1967 and Allen, 1970). Several attempts have been made to differentiate various environments from size spectral analysis as particle distribution is highly sensitive to the environment of deposition (Mason and Folk, 1958, Friedman, 1961, 1967; Griffiths, 1962; Moiola et al., 1974; Stapor and Tanner, 1975; Nordstrom, 1977; Goldberg, 1980; Sly et al., 1982; Seralathan, 1988; Selvaraj and Ramaswamy, 1988; Seralathan and Padmalal, 1994 and Majumdar and Ganapathi, 1998). Friedman (1961, 1967) has studied fine grained sands taken from various environments such as dunes, beaches and river, from different locations around the world. He noted that the most characteristic distinction of sands from these three environments is shown by a scatter diagram of moment standard deviation versus moment skewness. Visher (1969), based on the log normal distribution of grain size, has identified three types of populations such as rolling, saltation and suspension, which indicate distinct modes of transportational and depositional processes. According to Passega (1957, 1964) a clastic deposit is formed by sediments transported in different ways. In particular, the finest fraction may be transported independently of the coarser particles. Swift sedimentary agents are characterised best by parameters, which give more information on the coarsest than on the finest fractions of their sediments. Since the Chaliyar river sediments consist predominantly of coarser material, the logarithmic relationship between the first percentile (C) and median (M) of the sediments is highly significant in understanding the transportational regimes in this river (see section 3.7 for a detailed discussion).

Mean size: The mean size of clastic sediments is the statistical average of grain size population expressed in phi (∅) units. The spatial variation of phi mean in the Chaliyar main channel is shown in figure 3.2. The phi mean ranges between –0.50 to 1.8 (very coarse sand to medium sand) in the tributaries whereas it varies between –0.27 to 2.24 (very coarse sand to fine sand) in the main channel (Table 3.2). Grain size spectra reveal that gravels, very coarse sand and coarse sand dominate in the upper reaches, coarse sand and medium sand in the mid lands with an increase in coarse, medium and fine sand towards the river mouth. The presence of coarse sand in the downstream direction is due to inputs from tributaries. Allen (1970) stated that the downstream decrease in phi mean and the progressive enrichment of finer fractions could be attributed to two processes; (a) abrasion and (b) progressive sorting. Thiel (1940) and Berthois and Portier (1957) has noted that abrasion plays a significant role in the transformation of textural classes downstream. But later Kuenen (1959, 1960) opined that abrasion is not so significant in a fluvial system having sandy sediments. Instead, progressive sorting will be prominent in causing the textural diversities. Since the upper reaches of the Chaliyar river basin show significant amount of gravels and very coarse sand, abrasion plays a significant role in their size reduction and gradual disappearance downstream. However, in the bed sediments of Chaliyar main channel, in the downstream section (mainly of sand grade) progressive sorting seems to be more important in the size segregation of sediments than abrasion.

As the river water loses its velocity, the coarser fractions will be deposited where as the finer will be transported further downstream. From the figure 3.2 it is evident that the capacity and competency of the river fluctuates at many locations especially beyond 110 km due to natural factors. From the physiography of upper reaches of the main channel, it is evident that the river almost flows straight with small meanders appearing intermittently, which does not influence the velocity of river water. But when it reaches 110 km from its source the river course takes a huge turn, which facilitates the deposition of finer fractions. Hence we see a sudden increase in the phi mean size beyond 110 km in the down stream direction. In addition to this the river shows more meanders at almost equal intervals beyond 110 km from the source, which causes the fluctuations in the river water velocity at many locations thus facilitating the deposition of finer sediments. The abrupt decrease in phi mean (increase in grain size) at stations H-14, H-18 and H-24 (see Table 3.2 and Fig. 3.2) is resulted from input from the tributaries having predominantly coarser material. The downstream fluctuations in phi-mean is thus partly controlled by the natural turbulences brought about by the human influence like sand mining. It is important to note that the sample H-3 located at 85 km (upper reaches of main channel) is having a mean size 1.42 even though it mainly consists of coarse (17.9%) and medium sand (71.88%). This comparatively high mean size in this location is mainly due to progressive sorting downstream and the narrow difference in sizes between the coarse and medium sand. Even though the source area is highly weathered (lateritized) the average mean size in the Chaliyar main channel is (1.06 ∅) which clearly indicates that the finer fractions are selectively removed from the fluvial system and carried further downstream due to high-to-low energy conditions. In general mean size frequency percentage shows 50% of sediment samples are coarse sand (0-1∅) and 33% are in medium sand fraction (1-2 ∅).

Again it is significant to note that the phi-mean fluctuates less between the 63-110 km (0.45 ∅ to 1.42 ∅) where as it fluctuates significantly beyond 110 km (see Fig. 3.2) (Mean: -0.27∅ to 2.24∅). This kind of smaller fluctuations in mean size in the region 63-110 km could be attributed to progressive sorting mechanism in a relatively straight flowing fluvial environment. The larger fluctuations in mean size beyond 110 km could be : (i) minor inputs from adjacent tributaries which consists of coarser materials and (ii) probably due to the presence of more meanders at consistent intervals beyond this point which facilitates the deposition of bedload carried by the main channel. The presence of such meanders at regular intervals causes differential flow patterns where the coarser materials from the nearby tributaries will be deposited in the adjacent meander. With time these coarser materials may again be carried by the river water and redeposited in the next meander especially during successive monsoon seasons when the velocity of the medium is high. This kind of flow pattern carries the sediment load in pulses and hence we are getting such a spectral pattern for mean size. It could be for the same reason, due to selective removal of finer fractions especially during non-monsoon season, that we are not getting finer sediments in the lower reaches even though river meanders are important sites of sediment deposition in a fluvial system.

Sand waves: Sand transport along the bed is slow compared with that of water; sand may indeed remain stored for periods with no movement at all. The bed of the Chaliyar river characteristically is marked by large sand waves especially in the lower reaches. The composition of a sand sample taken from the bed represents a time-averaged quantity owing to sediment storage and slow material transport, whereas that of a water sample largely does not. The presence of discreet bodies of coarser materials at lower reaches of the Chaliyar main channel suggests that sand is moving downriver in pulses that do not disperse over long distances of transport. Large-scale pulses of sediment might travel downriver following accelerated erosion or mobilization of stored sediments in tributaries. Such wave-like movement of bedload sediments has been documented in numerous rivers (Gilbert, 1917; Kelley, 1959; Mosley, 1978; Griffiths, 1979; Hayward, 1979; Pickup et al., 1983; Meade, 1985; Johnsson et al., 1991).

Standard deviation: Standard deviation or sediment sorting is the particle spread on either side of the mean/average. The sediment sorting is good if the spread sizes are relatively narrow. Studies have proved that mean size and sorting show strong correlation in sand grade sediments and it worsens as the grain size increases. Similarly silt and clay show improved sorting to a certain extent as size increases.

In the major tributaries of the Chaliyar basin, the standard deviation varies between 0.98 ∅ and 1.99 ∅ whereas in the main channel it ranges between 0.46 ∅ and 2.00 ∅ (Table 3.2). The spatial variation of standard deviation in the Chaliyar main channel is presented in figure 3.2. In the river environment as the particle size decreases downstream, the sorting improves. In the main channel the sample H-3 located at 85 km show well sorted character (standard deviation 0.46 ∅). This observed increase in sorting is presumably due to the differential transport of sediments downstream and also due to the close range in sizes, i.e., the spread on either side of the phi mean size is narrow (medium sand). Inman (1949) pointed out that once sediment attains maximum sorting value, any further fall in the competency of the transporting medium results in the increase of the finer fractions in the sediments which will again impart immaturity to the sediments. However such a phenomenon does not exist in the Chaliyar main channel even though there is an increase in finer entities towards the river mouth probably due to minor input from the nearby tributaries. It is interesting to note that least sorted sediment (S.D. 2 ∅) is seen approximately 10 km upstream from the river mouth, (sample no. H-24) nearby which a tributary joins which predominantly consists of gravels and coarse sand. A comparative study of the sediment sorting in the Muvattupuzha river and Central Vembanad Estuary, Kerala has revealed that the best sorting occurs in medium and fine sand grades (Padmalal, 1992). It is found to be true in the Chaliyar river also because the best sorted sediment sample H-3 is having a mean size 1.42 ∅ (i.e., medium sand). Such relationship has also been reported by earlier workers like Inman (1949), Griffiths (1951), Pettijohn (1957), Folk and Ward (1957) and Dyer (1987).

It is interesting to see that the sorting in the Chaliyar main channel between 63 to 110 km exhibits minimum fluctuations (S.D. 0.46 ∅ to 1.04 ∅) and it fluctuates more beyond 110 km (S.D. 0.6 ∅ to 2.0 ∅) as seen in figure 3.2. This wide fluctuation in the sorting beyond 110 km is primarily caused by the inputs from the adjacent tributaries to the main channel.

In general 83% of Chaliyar river sediments are moderately to poorly sorted, 13 % are moderately well sorted. The abundance of coarser particles like gravels and coarse sand in sample H-24 imparts broad particle dispersion which in turn causes poor sorting (S.D. 2.0 ∅) of sediments.

Skewness: Skewness of sediments reflects the environment of deposition and is a measure of the asymmetry of grain size population. In textural analysis skewness is considered as an important parameter because of its extreme sensitivity in subpopulation mixing. Well-sorted unimodal sediments are usually symmetrical with zero skewness. In a fine-skewed (positively skewed) sediment population, the distribution of grains will be coarser to finer and the frequency curve show a peak at the coarser end and a tail at the finer. It is exactly opposite condition for coarse-skewed sediments (negatively skewed). According to Martin (1965) the coarse-skewness in sediments could be attributed to two possible reasons:

i) Addition of materials to the coarser terminal or

ii) Selective removal of finer particles from a normal population by the action of moving water.

The skewness varies from –0.48 to 0.18 (very coarse-skewed to fine-skewed) in the major tributaries of the Chaliyar river basin while it varies from –0.34 to 0.23 (very coarse- skewed to fine-skewed) in the main channel (Table 3.2). Majority of the tributary samples are coarse-skewed due to the presence of coarser materials like gravels and coarse sand. The variation of skewness with distance in the riverine environment is given in figure 3.2, which shows that the skewness does not vary much from the 63 to 107 km mark in main channel and they show coarse-skewed nature all along. Beyond this in the down stream direction the skewness varies more, mainly due to the addition of coarser materials by the tributaries and partly due to the removal of fine particles from a normal population by the flow of water. Samples nearer to the river mouth yield coarse-skewness because they consists mainly of finer fraction possibly because sub silt or clays are not counted here. This could be attributed to the wide variation in sizes within the finer ones (H-26 & H-27).

As mentioned earlier well sorted unimodal sediments are usually symmetrical with zero skewness. It is interesting to note that sample H-3 is well sorted and show coarse-skewness while moderately and poorly sorted samples (H-35, H-12, H-24, H-

25, H-33) are near symmetrical. This may be due to the polymodal nature of sample H-3. Similarly, from the occurrence of the coarse-skewness seen in the samples H-26 & H-27 towards the river mouth it may be presumed that the suspended load contribution of the tributary adjacent to the sample location H-24 to the Chaliyar main channel could be quite significant and may be an important factor in the silting of the Chaliyar in its lower reaches. Alternatively, it may be due to the addition of sand modes to the silt and clay modes seen in the lower reaches. The latter one is more likely, because the samples H-24 and H-25 (samples from locations just upstream of samples H-26 and H-27) consists mainly of gravels and coarse sand and hence they might be contributing sand fractions to the silt and clay fractions already present in the estuarine environment. The presence of nearly symmetrical-skewed samples in the Chaliyar main channel suggests an equal proportion of different modes (H-12, H-24, H-25, and H-35). The presence of fine-skewed sediments (samples H-15, H-19, H-20) in the main channel may be attributed to the addition of medium sand, fine sand, silt and clay to the coarser fractions. In general, 70% of the sediment samples in the Chaliyar basin show very coarse-skewed to coarse-skewed nature, 16.67% are near symmetrical and 13.3% are fine-skewed.

Kurtosis: Kurtosis or the peakedness of the frequency curve, is a measure of the contrast between sorting (S.D.) at he central part of the size distribution curve and that of the tails. The kurtosis value varies between 0.82 to 1.37 ∅ (platykurtic to leptokurtic) in the tributaries while it varies between 0.78 to 1.61 ∅ (platykurtic to very leptokurtic) in the Chaliyar main channel (Table 3.2). The spatial variation of kurtosis along the profile of the river is shown in figure 3.2. In natural environments, the kurtosis values reflect the fluctuations in the velocity of the depositing medium. A value greater than unity suggests greater fluctuations (Verma and Prasad, 1981). It is evident from the spatial variation diagram that kurtosis does not fluctuate much between 63 to 108 km probably due to the morphology nature of the main channel (almost straight) while it fluctuates severely beyond 108 km reflecting the meandering nature of the channel which causes the fluctuations of the velocity of the depositing medium and hence wide fluctuations in the kurtosis values. But it is important to note that the kurtosis value gradually reduces to less than unity towards the mouth of the river (sample H-26 & H-27) due to the decrease in the velocity of the depositing medium in the estuarine environment. Even though kurtosis values are ≥ 1.0 ∅ for the samples between the 63 and 108 km, the velocity of the depositing medium does not change very much probably due to the gentle gradient of the main channel along the sector. At the same time the tributary samples show wider fluctuation in kurtosis values (0.82-1.37 ∅) when compared to the 63 to 108 km stretch main channel. The platy to leptokurtic nature of the samples in the tributaries is probably due to the fluctuations in the velocity of the depositing medium brought about partly by the gradient of the river and partly by the channel morphology.

3.6 Bivariate plots

Interrelationship between grain-size frequency distribution and depositional environments and/or processes has been used successfully by several investigators (Folk and Ward, 1957; Qidwai and Casshyap, 1978; Goldberg, 1980; Abed, 1982; Khan, 1984; Pandya, 1989; Ramanamurthy, 1985; Mahender and Banerji, 1989; Joseph et al., 1997; Majumdar and Ganapthi, 1998 and Selvaraj and Ramaswamy, 1998) to identify the depositional environments and recognize operative processes of sedimentaion of ancient terrigenous deposits. The conclusions arrived at in most of these works were primarily based on comparison with standard grain-size frequency curves (Visher, 1969), linear discriminant equations (LDE) and multi group discriminatory plots (MDP) (Sahu, 1964 and 1983) or with various standardized bivariant discriminatory plots proposed by Passega (1957), Stewart (1958), Friedman (1967), Moiola and Weiser (1968) and others. According to Amaral and Pryor (1977) and Moshrif (1980), the reliability of these linear discriminant functions and bivariant size parameter diagrams in interpretation of ancient rock records are inherently subjective and empirical. Though the sediment samples in the present investigation belongs to a fluvial environment, the results of the above study can throw more light on the operative processes taking place in a fluvial system and the outcome of it can be used to understand the ancient sediments and their depositional environment in the light of readily available and easily applicable techniques of environmental analysis based on grain size frequency distribution.

Scatter plots of various statistical parameters of the riverine sediments are depicted in figure 3.3. The phi mean versus standard deviation plot shows a linear relationship between the two parameters. As the phi mean size decreases the sorting worsens. This is true in the case of gravel-rich tributary sediments and also in stations just below the confluences of tributaries or adjacent to the tributary in the downstream direction of the Chaliyar main channel. The medium and fine sand (1 - 2 ∅) show moderate to moderately well-sorted nature except sample H-3 whose mean size falls in the medium sand category (1 - 2 ∅) and show well-sorted nature. Such a phenomenon seen in the above sample (H-3) is an indication of close range in size of medium sand. This is true also because H-3 contains 71.9% medium sand with 17.9%, 8.9% coarse and fine sand respectively. The sediment samples show an increase in the sorting with an increase in mean size from poorly sorted samples in the tributaries to moderate to moderately well sorted in the downstream direction of the Chaliyar main channel. However, the intermittent appearance of poorly sorted samples with corresponding decrease in phi mean size beyond 110 km is mainly due to the addition of coarser materials from the nearby tributaries which are carried in pulses and deposited in the channel.

As mentioned in the above paragraph for the sample H-3, consider the cases of samples H-16, H-17, H-21 and H-23 all of them showing moderately well sorted nature with phi mean ranging from medium (H-16, H-21 and H-23) to fine sand (H-17) categories. Though they are having phi mean in the medium and fine sand categories their sorting is less when compared to sample H-3 which is mainly due to the wide range in sizes of different fractions which is given below:

Sample No.	**Coarse sand (%)**	**Medium sand (%)**	**Fine sand (%)**	**Very fine sand (%)**	**Mud (%)**
H-16	8.00	40.8	28.2	0.5	19.8
H-17	4.53	18.6	60.4	4.9	10.14
H-21	15.36	37.7	39.5	1.25	5.60
H-23	13.6	43.7	26.0	1.63	13.68
H-3	17.9	71.9	8.9	0.46	-

Thus the appearance of coarser grains (very coarse to coarse sand) during various stages especially between 109 to 131.5 km of the Chaliyar main channel is contributed by the adjacent tributaries and are believed to be responsible for imparting a poorer sorting of sediments in this region.

The plots of mean size versus skewness depict curves which are convex upwards and downwards. Roughly from the figure 3.3, samples with skewness value between –0.15 to 1.23 ∅ and mean size between –0.5 to 1.04 ∅, the curve is convex downward. Similarly, samples with skewness value below –0.15 Ø and mean size above 0.5 Ø, the curve is convex upward. Though we cannot delineate the curve facing upwards and curve facing downwards are due to the deposition of samples in a riverine and estuarine environments and their mixing by tributary influx. But combining these two, yields a perfect sinusoidal curve. Thus the sediment distributional behaviour of the Chaliyar basin agrees with the classic work of Folk and Ward (1957) and Friedman (1961). The scatter plot between phi mean size and kurtosis show a linear relationship, i.e., as the phi mean increases the kurtosis value also increases. From the above bivariate plot majority of the samples are having kurtosis value greater than unity reflecting the fluctuations in the velocity of the depositing medium but these fluctuations are mainly seen beyond 110 km in the downstream direction of the Chaliyar main channel (see Fig. 3.2). Similarly consider the samples having kurtosis value greater than unity. From the figure it is evident that an increase in the phi mean size corresponds to an increase in kurtosis value signifying that coarser fractions are transported by lesser fluctuations in the velocity of the depositing medium while medium and finer fractions are transported by greater fluctuations in the velocity of the depositing medium. In other words coarse sand falls closer to the kurtosis value unity while medium and fine sand fall slightly away from unity. This is true because most of the tributary and upper reach samples are coarse sand while samples below the 110 km mark in the downstream direction is an admixture of coarse, medium and fine particles. Hence the sediments of the Chaliyar river in the upper reaches including tributaries are transported by smaller fluctuations in the velocity of the depositing medium which is primarily controlled by the higher gradient of the river while the sediments downstream in the main channel beyond 110 km is transported by greater fluctuations in the velocity of the depositing medium. This is further controlled by (i) lower gradient of the river, (ii) physiography of channel and (iii) inputs of coarser materials by adjacent tributaries. The scatter plot of standard deviation versus kurtosis shows almost a linear relationship. The sorting worsens as the kurtosis value decreases which implies that moderate to moderately well-sorted samples are transported mainly by greater velocity fluctuations (samples beyond 110 km) and partly by lesser fluctuations (samples beyond 110 km especially at stations H-19, H-21, H-26 and H-27 towards the mouth of the river) in the velocity of the depositing medium. Samples H-1, H-3, H-4, H-5, H-11, H-13 and H-35 from the upper reaches of the Chaliyar main channel also show characteristics of sediments transported by fluctuating velocity in the transporting medium, but actually they are not. The kurtosis value greater than unity does not signify fluctuations in the velocity of the depositing medium in this region which is controlled by river gradient. It results between sorting at the central part of the size distribution curve and that of the tails. Similarly moderately and well-sorted nature of the above samples is due to progressive sorting in the downstream direction. Poor sorting and kurtosis values greater than unity are seen for samples beyond 110 km in downstream directions and they are seen mainly just below the confluences of tributaries (stations H-14, H-15, H-18, H-20 and H-22) and also adjacent to the tributary confluence (station H-24) which reflect the fluctuations in the velocity of the depositing medium. Samples with poor sorting and kurtosis value less than unity are seen in the major tributaries in the headwater region and they reflect less fluctuations in the velocity of the depositing medium which is strictly controlled by the steep gradient and physiography of the tributaries.

The interrelationships between standard deviation versus skewness, and skewness versus kurtosis do not provide much information as they do not vary systematically. Moreover, the sediment samples from different sub-environments in the Chaliyar basin does not show clustering or grouping in the above bivariate plots.

In general, the fields defined by Friedman (1961, 1967, 1979) and Moiola and Weiser (1968) as characteristic of river sands on bivariate plots of mean, standard deviation, skewness, and kurtosis are grossly consistent with the above parameters calculated for the Chaliyar river sands.

Bivariant plots of Andrews and van der Lingern (1969) for selected Folk and Ward (1957) statistical parameters (standard deviation versus mean size) are presented in figure 3.4. They show that all the tributary samples are polymodal in nature and they fall farthest from the upper limit of the sinusoidal field. In the upper reaches (63 to 109 km) the samples are predominantly unimodal in nature except sample H-2 and H-3 which are falling in the poly modal field, but very close to the sinusoidal curve. It is interesting to note that of all the samples, there is only one sample (H-3) that is falling below the lower limit of the sinusoidal curve. In the region below the 109 km in downstream direction the samples show alternatively unimodal and polymodal nature. The polymodal samples in this region fall slightly away from the upper limit of the sinusoidal curve but they fall in between the polymodal fields of tributary and upper reach samples. The appearance of alternatively unimodal and polymodal samples beyond 109 km is probably due to the fluctuations in the velocity of the depositing medium and also due to the minor contributions of coarser materials by the adjacent tributaries which results in an admixture of coarse and finer particles. Towards the river mouth the samples show unimodal nature (H-25, H-26 and H-27).

3.7 CM pattern

The CM pattern of the sediment samples of Chaliyar river basin is shown in figure 3.5 and the values of first percentile (C) and medium (M) of size distribution (in microns) used in the plot are presented in table 3.3. The figure CM pattern represents a complete model of tractive current (depositional process) as shown by Passega (1964) which consists of several segments such as NO, OP, PQ, QR and RS indicating different modes of sediment transport. Majority of the samples in the tributaries, upper and lower reaches, especially sediments having <5% clay, of the Chaliyar main channel show marked deviation from the standard segments in the CM pattern. CM pattern of Chaliyar river sediments was worked out following Passega (1964).

When plotted in the CM pattern diagram of Passega (1964), the Chaliyar river sediments in the main channel, except the lower reach clay bearing sediments, fall either close to NO or further high `C' areas indicating that the sediments have been transported largely by the mechanism of rolling. Majority of the clay bearing samples fall in the lower most part of OP segment. The tributary samples plotted, mostly fall right above the NO segment. The segment NO represents the coarsest bedload materials which are larger than 2000 microns of C. These particles are transported by rolling and are enriched in the tributaries, upper and lower reaches of main stem (main channel sediments having <5% clay). The rolling mode of transportation is intensively taking place in the gravel rich tributaries and upper reaches in which the competency of the stream is enormously high probably due to their high gradient. The segment OP consists of particles having diameter roughly between 1000 and 2000 microns of C which are moved mainly by rolling and bottom suspension. Majority of the lower reach clay bearing samples in the main stem are carried by this mode of transport. The segment PQ represents particles ranging from 400 to 1000 microns of C and indicates that the particles are moved predominantly by suspension and partly by rolling, which is not represented in the Chaliyar river. The segment QR is parallel to C-M lines and this also is not represented by the present samples, which suggests that graded suspension is absent in Chaliyar river. In general, majority of the sediment samples in the tributaries, upper reaches and to a certain extent samples in the lower reach segments of the main channel are carried by rolling while some of the samples in the lower reaches of the main channel are carried either by rolling and bottom suspension. Since Chaliyar river sediments are predominantly gravelly and sandy in nature, the segment RS (uniform suspension of sediment) which is characteristic of low energy transport, is totally missing in the river environment.

3.8 Textural classification of sediments

The interrelationships that exist between textural parameters have been worked out to understand the hydrodynamic conditions of the depositing medium. In addition to this, the relative percentage of gravel (> 2 mm), sand (0.063 – 2 mm), silt (0.063 - 0.004 mm) and clay (< 0.004 mm) of Chaliyar river sediments were also plotted on a triangular diagram of Folk et al. (1970) to determine the sediment types. Nomenclature of sediment types is based on the scheme described by Folk et al. (1970).

Ternary plots of gravel:sand:mud and sand:silt:clay were used to classify the sediments of Chaliyar river and its major tributaries. The weight percentages of gravel, sand and mud (Table 3.1) and sand, silt and clay (Table 3.4) in the sediments of Chaliyar river show downward variations. Since majority of the river sediments contain substantial amount of gravel and sand, the textural classification of Folk et al. (1970) for gravel bearing sand and gravel-free sand is followed to decipher the sediment types of the river basin. From the triangular plot of gravel, sand and mud (Fig. 3.6a) it is clear that the river sediments show wide range of sediment texture. Gravelly sand (43.33%), slightly gravelly sand (23.33%), slightly gravelly muddy sand (23.33%) and sandy gravel (10%) are the dominant sediment types of the Chaliyar basin. Similarly the triangular plot of sand, silt and clay (Fig. 3.6b) show less variation in the sediment texture. Sand (76.67%) and muddy sand (16.67%) are the dominant sediment types of the Chaliyar river bed. Clayey sand (3.33%) and silty sand (3.33%) are less dominant. Sand predominates throughout the length of the river except at the estuarine region where muddy sand dominates which reflect the prevalence and low energy conditions.

When analysed with the help of the gravel:sand:mud triangular plot, gravelly sand predominates in the tributaries and upper reaches whereas slightly gravelly sand and slightly gravelly muddy sand are seen intermittently in the lower reaches of the main channel. Slightly gravelly muddy sand is progressively enriched in the lower reaches (estuarine). Sandy gravel types are found in tributary/tributary confluences (station H-24, H-30 and H-33).

Pipette analysis of clay-bearing samples indicates that the sediments in the Chaliyar river are sandy in nature with about < 20% mud (silt + clay) except sample H-13 and H-26. Sample H-13 is collected at a depth of 8 m below the water level (the deepest among all sample locations) which acts as a sink for the finer particles while sample H-26 is collected from an estuarine/deltaic environment. This indicates that the silt and clay sized fractions are preferentially removed from the channel downstream which either get accumulated at local sinks or beyond estuary.

3.9 Microtextures on quartz grains

Scanning electron microscopy (SEM) has been employed extensively since the 1970s in the study of surface textures on detrital quartz sand grains in order to understand the transport history of the sediment (Margolis and Kennett, 1971; Margolis and Krinsley, 1971; Krinsley and Smalley, 1972; Krinsley and Doornkamp, 1973; Margolis and Krinsley, 1974; Whalley and Krinsley, 1974; Krinsley and McCoy, 1977; Bull, 1981; Mahaney et al., 1996). Various mechanical and chemical processes leave their marks on the surface of the grains, and the distribution and combinations of these subsequent microtextures, together with an understanding of hydrologic, climatologic, and other aspects of the depositional environment, should prove useful in unraveling the depositional history of an area (Krinsley and Doornkamp, 1973; Whalley and Krinsley, 1974; Krinsley et al., 1976; Higgs, 1979; Hodel et al., 1988; Mahaney et al., 1996).

Surface textures of clastic particles give information about the physical and chemical processes to which the particles have been subjected. The best tool used for understanding of the provenance, processes of transport, and diagenetic changes that the detrital sediments have undergone is by studying under Scanning Electron Microscopy (SEM). In the present study SEM data is used to examine transport and depositional processes as they are reflected in quartz grain textures. Examination of over 200 sand-sized quartz grains from ten different locations (sample no. H-1, H-2, H-3, H-4, H-5, H-11, H-13, H-17, H-21 and H-26) in the Chaliyar main stem revealed the presence of mechanically produced breakage features (such as conchoidal fractures) indicative of fluvial transport and modification by chemical weathering processes, such as dissolution pits/etch pits.

Shape analysis of quartz grains from the upper reaches of Chaliyar main stem shows that they are extremely angular to sub-angular characterised with medium to large conchoidal fractures (Plate 3.1 A, B and C) and some of them show smoothening of outline depending upon distance of transport (Plate 3.1 D and E). In addition to this a few grains show solution crevasses/pits formed by dissolution of mineralization and or lateritization processes (Plate 3.1 F). In the middle reaches (midstream) of the main channel the quartz grains are sub-angular to subrounded, reveals fractures with meandering ridges (Plate 3.1 G and H) and some of them show adhering particles/secondary infillings in pits (Plate 3.1 I); relatively fresh, less abraded, sub-angular grains show arcuate steps (Plate 3.1 J), medium to small conchoidal fractures (Plate 3.1 K) and they may be from a nearby source which is brought by the downstream tributaries to the main stem. The above shape and surface textural features are believed to mask the characteristics of sediments which have relatively undergone greater degree of riverine transport. Increasing abrasion occurs with increasing river transport distance, but this pattern does not extend along the Chaliyar river especially in the lower reaches of the main stem. Sub-rounded quartz grains from middle to lower reaches of main stem also shows surface textures like v's, straight and curved scratches (Plate 3.1 L & M) depending upon the fluvial and wave induced transport mechanism. The surface textures in quartz grains from the lower reaches of Chaliyar main stem show numerous etch pits of varying sizes indicating chemical dissolution in estuarine environment (Plate 3.1 N). Furthermore, mechanically produced (fluvial transport) breakage features in some of the sub-rounded to rounded, subhedral quartz grains (see Plate 3.1 H & O) in the lower reaches suggest that the grain shape is produced by collision-induced comminution of the particles.

To a certain extent, progressive decrease in mechanically produced breakage features from upper to lower reaches of Chaliyar main stem indicates that fluvial transport has significantly altered the pre-transport, inherited shapes and surface textures. In general, formation of chemical surface features on Chaliyar river sediments suggests conditions favourable for chemical weathering in hot, humid environments. In other words, the grains exhibit provenance-indicative shapes and surface textures suggesting that primary and multicyclic particles have been introduced into transport system as discrete entities.

Previous studies have reported irregular projections, breakage blocks and similar characteristic shape and surface textures as seen in upper reach sand grains of Chaliyar river, from crystalline rock weathering environments. Krinsley and Margolis (1969), Krinsley and Doornkamp (1973), Margolis and Krinsley (1974) have attributed these morphologies to the formation of first-cycle detrital particles by breakage. The breakage presumably occurs during the initial mechanical disintegration of crystalline rocks in the source area by thermal expansion and contraction. The grain morphologies represent pretransport, source-inherited shape and surface texture features.

In contrast, the lower reach fluvial sand-sized quartz grains display a greater degree of roundness and sphericity and chemically produced surficial features indicative of a multicyclic origin and derivation from weathering/pedogenic environments where chemical processes dominate. Thus the shapes and surface features of sand-sized quartz grains from Chaliyar main stem are highly variable and complex, but can be directly related to the transport and sedimentary history of the particles.

Conclusions

- The river sediment samples as a whole are gravelly sand (43%), slightly gravelly sand (23%), slightly gravelly muddy sand (23%) and sandy gravels (10%). In terms of Sand : Silt : Clay they are essentially sand (76%) with subordinate amount of muddy sand (16%).
- They are moderately to poorly sorted. The mean size of the sediments in the main stem ranges from –0.27 Ø to 2.24 Ø (very coarse sand to fine sand) while in the tributaries from the headwater region it ranges from –0.5 Ø to 1.86 Ø (very coarse sand to medium sand). The phi mean shows moderate fluctuations along the upper reaches of the Chaliyar main stem, between 63 – 110 km (0.45 Ø – 1.42 Ø) whereas it fluctuates significantly beyond 107 km from the source (-0.27 Ø – 2.24 Ø). Most of the tributaries have significant amounts of gravel while the lower reaches of the main channel are characterised by the presence of clay. The upper reach sediments are unimodal in nature while those in the lower reaches show alternatively unimodal and polymodal nature along the length of the river.
- Though many of the sands from the Chaliyar river drainage basin show negatively-skewed grain size distribution the other statistical parameters are similar to those of most other fluvial sands reported in literature.
- Their position in CM pattern indicates that the coarser Chaliyar river sediments are transported by rolling, while the clay bearing sediments are transported by rolling and suspension.

- The highly variable and complex shape and surface textures of sand-sized quartz grains from the main stem can be directly related to the transport and sedimentary history of the particles. They reveal pre-transport, source-inherited shape and surface features, mechanically produced breakage features (such as conchoidal fractures) indicative of fluvial transport and modification by chemical weathering processes, such as dissolution pits/etch pits. The above features are indicative of a multi cyclic origin and derivation from mechanical breakdown of crystalline rocks as well as from the weathering/pedogenic environments where chemical processes dominate.
- The observed complexity in sediment distribution/ granulometric variation and highly complex statistical and textural parameters, especially in the lower reach bedload sediment samples (beyond 107 km in the downstream direction) indicate the effects such factors as :
  (1) the temporal heterogeneity of source area,
  (2) more than one cycle of sediment genesis,
  (3) down stream transport in pulses, and
  (4) acceleration of erosion and mobilization of stored sediments mainly in tributaries and in the stable point bars on the main stem.
- Tributary influx constitutes the major cause of natural turbulence in sedimentation.

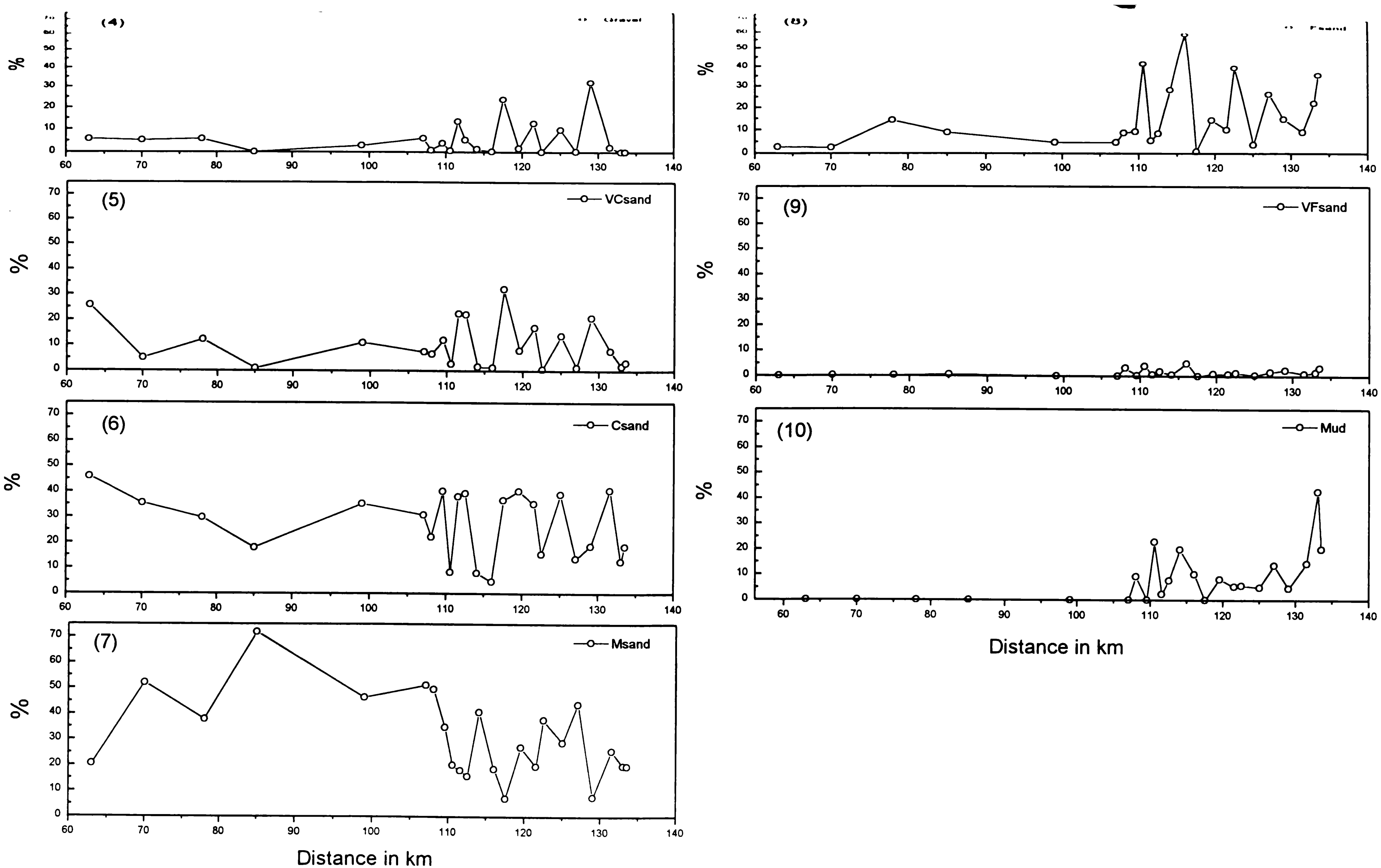


Fig. 3.1a Variations of grain size fractions with distance in the sediments of the Chaliyar river main stem.

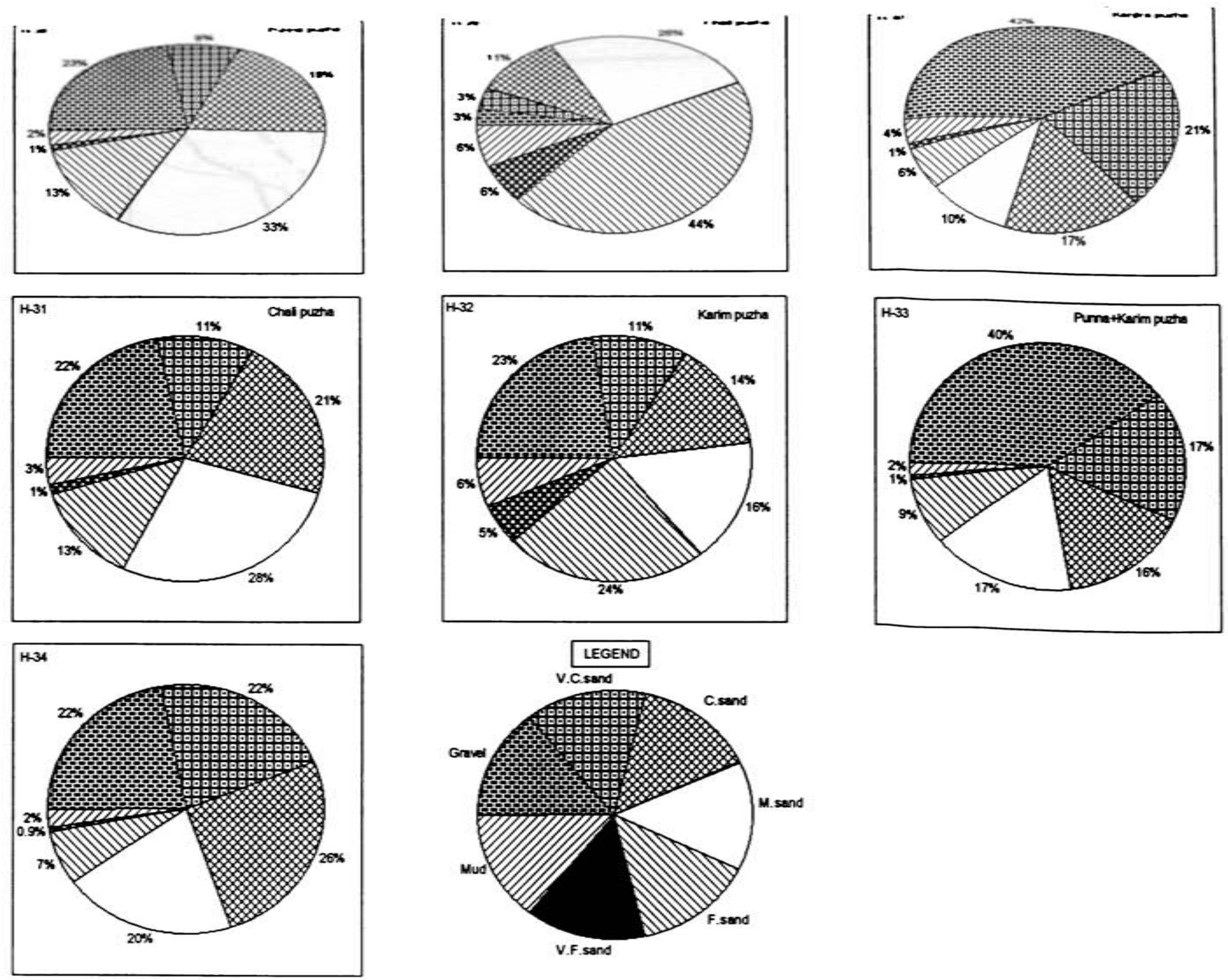


Fig. 3.1b Pie diagrams showing wt.% of various size fractions seen in major tributaries of Chaliyar river basin

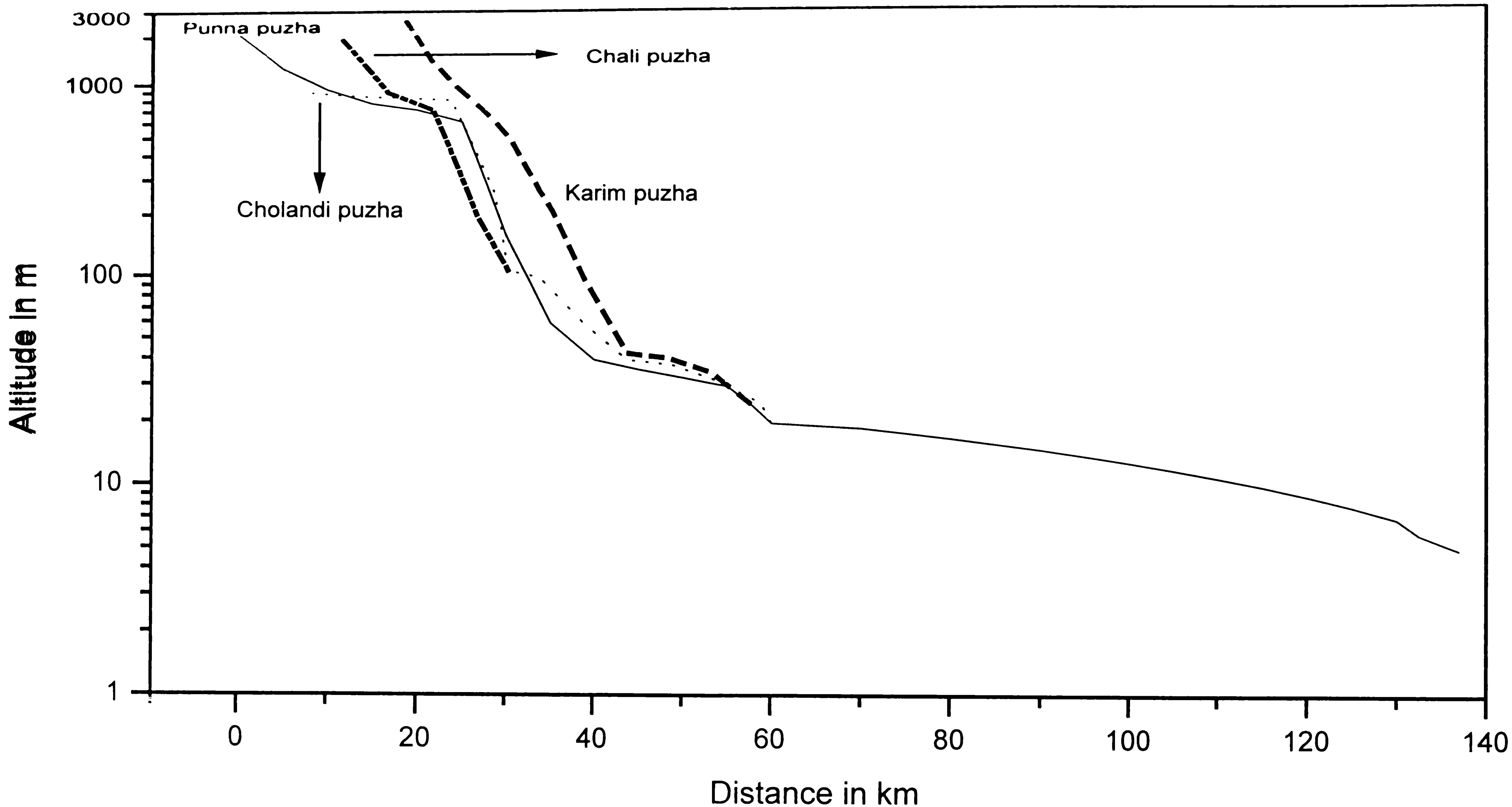


Fig. 3.1c Longitudinal profile of the Chaliyar river basin

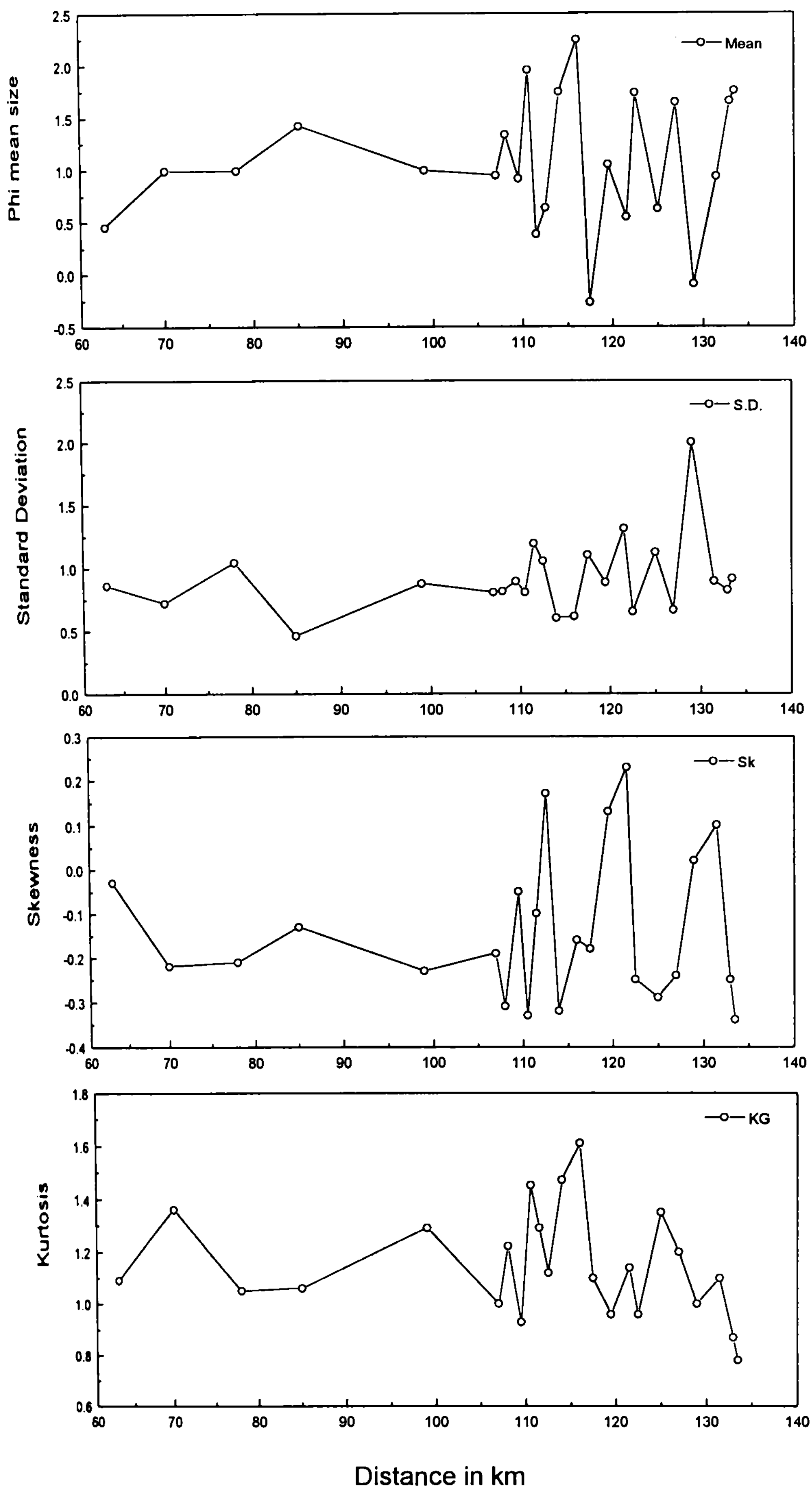


Fig.3.2 Variation of textural parameters along the profile of the Chaliyar main channel

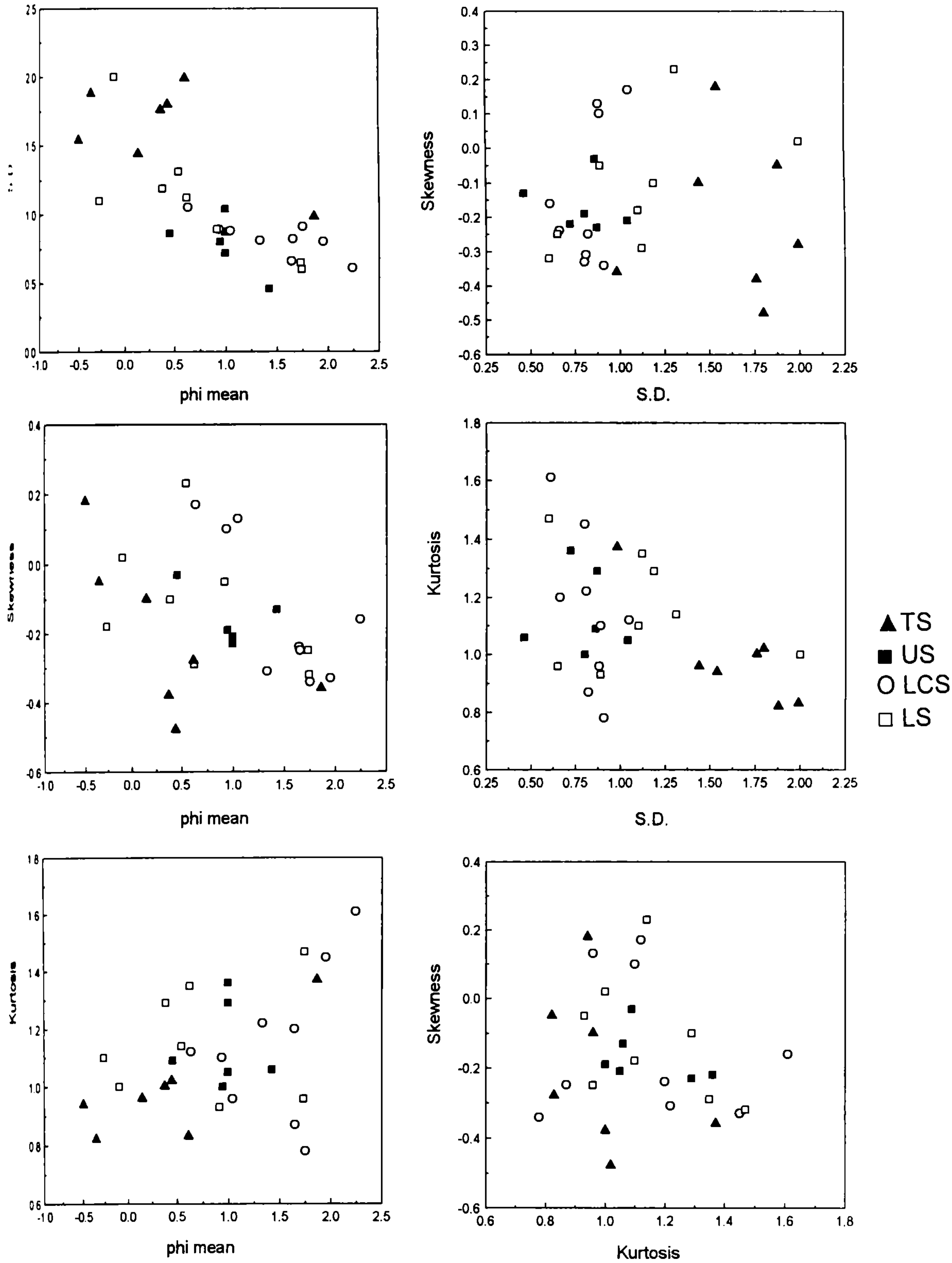


Fig.3.3 Scatter plots of various Folk and Ward (1957) statistical parameters and their interelationship in the sediments of Chaliyar river

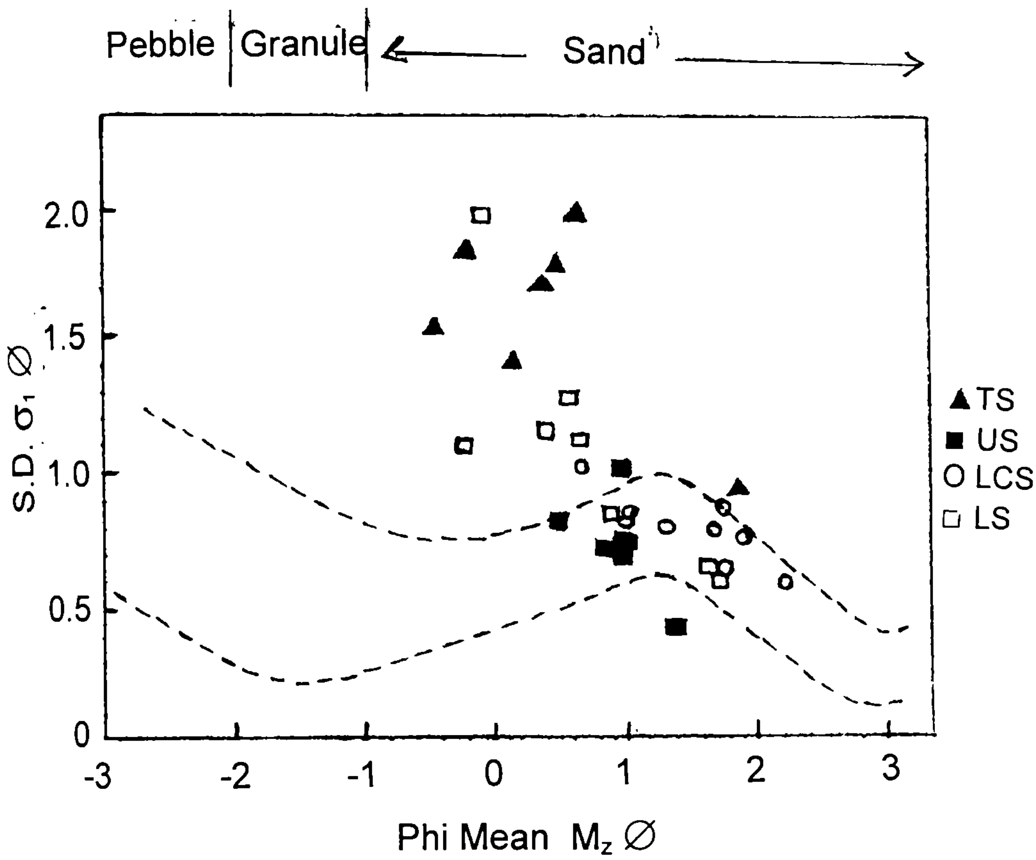


Fig. 3.4 Scatter plot of selected Folk and Ward statistical parameters. Sinusoidal field represent samples having unimodal distribution (after Andrews and Van der Lingen, 1969). Symbol legends as in Fig. 3.5.

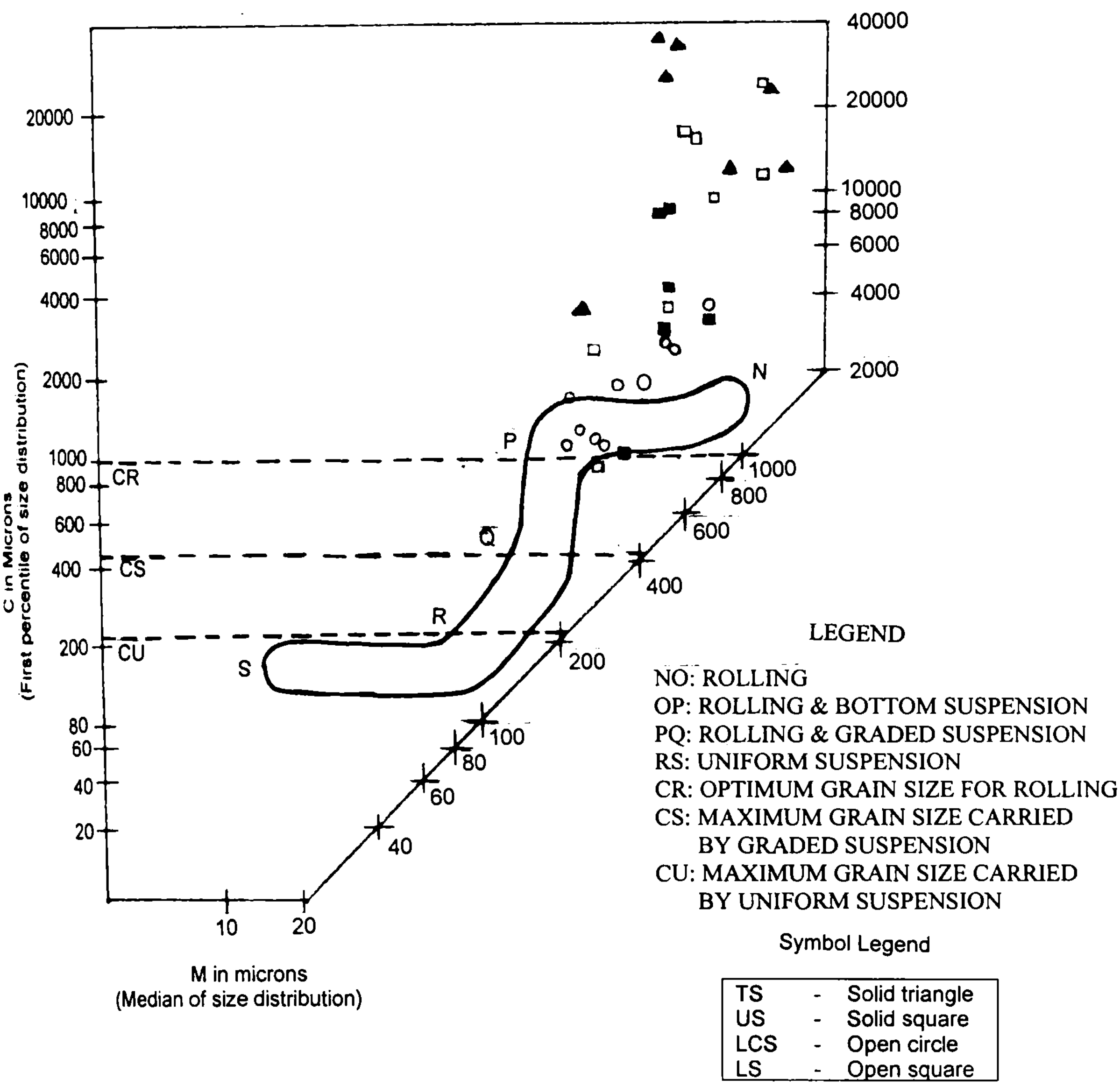
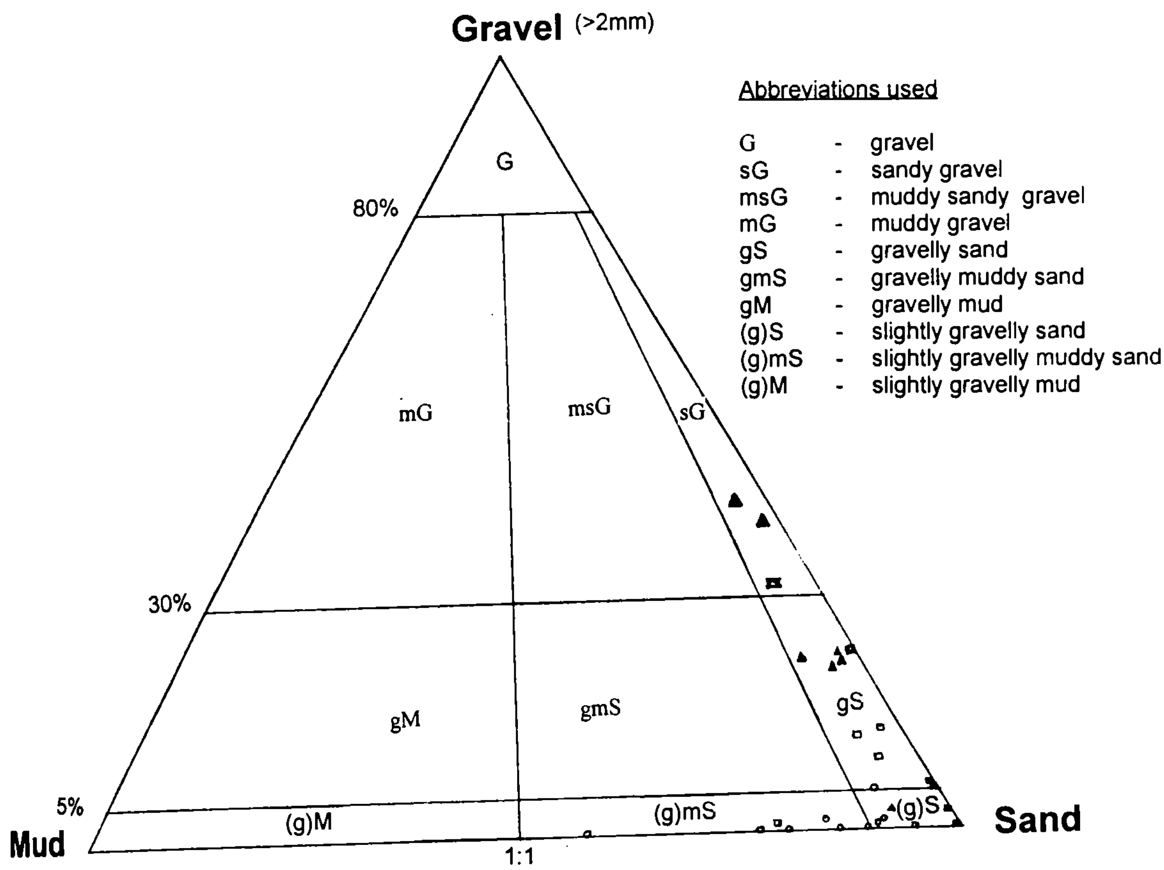


Fig. 3.5 C-M Pattern of Chaliyar river sediments (after Passega, 1964)



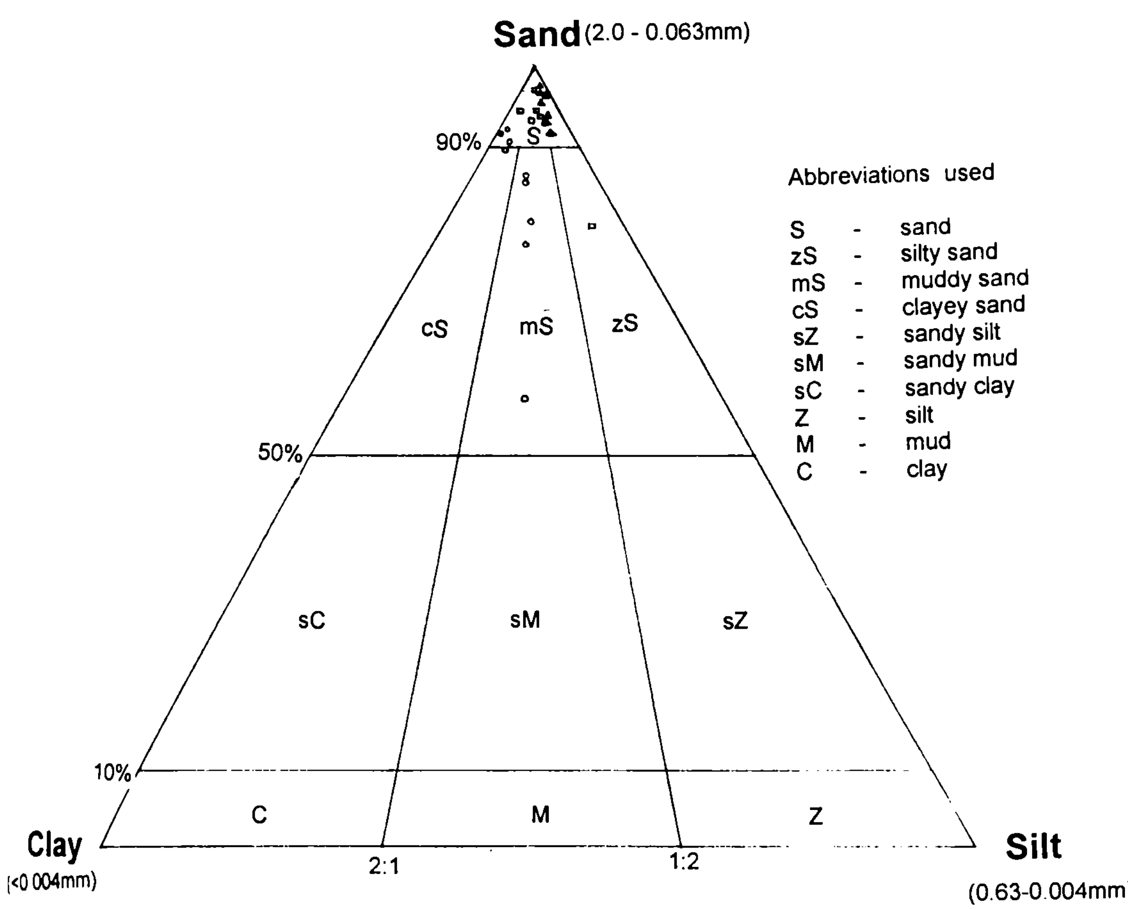


Fig. 3.6a&b Ternary diagram illustrating the nature of sediments in the Chaliyar basin
Symbol legend as in Fig.3.5

Table 3.1 Percentage of various size fractions in the sediments of Chaliyar river (T/TC represent samples from tributary or tributary confluence)

Sample No.	Distance (km)	Depth (m)	Gravel (a)	Very Coarse Sand (b)	Coarse Sand (c)	Medium Sand (d)	Fine Sand (e)	Very Fine Sand (f)	Mud (Silt + Clay)	Sand (b+c+d+e+f)	Gravel (a)	Textural terminology (Folk et al., 1970)
									100%			
1	2	3	4	5	6	7	8	9	10	11	12	13
H-35	63.0	-	5.64	25.59	45.73	20.54	2.63	0.07	0.00	94.56	5.64	Gravelly sand
H-1	70.0	-	5.11	5.02	35.42	51.94	2.39	0.13	0.00	94.90	5.11	Gravelly sand
H-2	78.0	-	5.63	12.29	29.65	37.84	14.34	0.26	0.00	94.38	5.63	Gravelly sand
H-3	85.0	-	0.07	0.85	17.90	71.88	8.87	0.46	0.00	99.96	0.07	Slightly gravelly sand
H-4	99.0	-	2.91	11.02	35.22	46.30	4.54	0.03	0.00	97.11	2.91	Slightly gravelly sand
H-5	107.0	-	5.92	7.38	30.84	51.16	4.65	0.06	0.00	94.09	5.92	Gravelly sand
H-11	108.0	5.00	0.74	6.53	22.17	49.60	8.58	3.15	9.24	90.02	0.74	Slightly gravelly sand
H-12	109.5	1.00	3.80	11.96	40.11	34.76	9.27	0.10	0.00	96.20	3.80	Slightly gravelly sand
H-13	110.5	8.00	0.48	2.68	8.40	20.09	41.55	3.96	22.83	76.68	0.48	Slightly gravelly muddy sand
H-14	111.5	1.00	13.25	22.49	38.07	18.06	5.34	0.48	2.31	84.44	13.25	Gravelly sand
H-15	112.5	2.00	5.19	22.12	39.31	15.79	8.25	1.78	7.57	87.24	5.19	Gravelly sand
H-16	114.0	1.50	1.24	1.59	7.95	40.77	28.16	0.50	19.80	78.96	1.24	Slightly gravelly muddy sand
H-17	116.0	1.00	0.19	1.27	4.53	18.56	60.40	4.92	10.14	89.67	0.19	Slightly gravelly muddy sand
H-18	117.5	2.00	23.36	32.25	36.63	7.01	0.68	0.08	0.00	76.65	23.36	Gravelly sand
H-19	119.5	2.00	1.66	7.99	40.23	26.99	14.12	0.95	8.07	90.28	1.66	Slightly gravelly sand
H-20	121.5	2.00	12.38	16.97	35.13	19.58	9.96	0.65	5.33	82.29	12.38	Gravelly sand
H-21	122.5	3.00	0.00	0.61	15.36	37.71	39.47	1.25	5.60	94.40	-	Slightly gravelly sand
H-22	125.0	2.75	9.63	13.73	38.93	28.92	3.46	0.37	4.96	85.41	9.63	Gravelly sand
H-23	127.0	2.75	0.10	1.30	13.58	43.69	26.02	1.63	13.68	86.21	0.10	Slightly gravelly muddy sand
H-24	129.0	2.75	31.57	20.96	18.52	7.61	14.50	2.22	4.62	63.81	31.57	Sandy gravel
H-25	131.5	3.00	1.86	7.84	40.45	25.67	8.85	0.97	14.37	83.77	1.86	Slightly gravelly muddy sand
H-26	133.0	3.00	0.00	1.78	12.64	19.80	21.72	1.50	42.58	57.43	-	Slightly gravelly muddy sand
H-27	133.5	3.00	0.00	3.18	18.36	19.68	35.72	3.11	19.95	80.05	-	Slightly gravelly muddy sand
H-28 T		-	22.54	8.55	19.37	33.01	13.08	1.04	2.41	75.05	22.54	Gravelly sand
H-29 T		-	2.82	3.39	11.16	25.64	44.50	6.07	6.43	90.76	2.82	Slightly gravelly sand
H-30 T		-	42.05	20.99	16.57	9.61	6.08	0.92	3.78	54.18	42.05	Sandy gravel
H-31 T		-	21.75	11.31	21.40	27.90	12.86	1.38	3.41	74.84	21.75	Gravelly sand
H-32 T		-	22.52	11.33	14.18	16.13	24.05	5.41	6.30	71.19	22.52	Gravelly sand
H-33 TC		-	39.72	17.13	15.71	16.72	8.53	0.67	1.53	58.75	39.72	Sandy gravel
H-34 T		-	22.04	21.55	26.34	20.15	7.02	0.50	2.41	75.55	22.04	Gravelly sand

Table 3.2 Folk and Ward (1957) grain size statistical parameters of the Chaliyar river

Sample No.	Phi Mean	Standard Deviation	Skewness	Kurtosis	Distance (km)	Depth (m)
H-28 T	0.44	1.80	-0.48	1.02		-
H-29 T	1.86	0.98	-0.36	1.37		-
H-30 T	-0.50	1.54	0.18	0.94		-
H-31 T	0.37	1.76	-0.38	1.00		-
H-32 T	0.61	1.99	-0.28	0.83		-
H-33 TC	-0.35	1.88	-0.05	0.82		-
H-34 T	0.14	1.44	-0.10	0.96		-
H-35	0.45	0.86	-0.03	1.09	63.0	-
H-1	0.99	0.72	-0.22	1.36	70.0	-
H-2	0.99	1.04	-0.21	1.05	78.0	-
H-3	1.42	0.46	-0.13	1.06	85.0	-
H-4	0.99	0.87	-0.23	1.29	99.0	-
H-5	0.94	0.80	-0.19	1.00	107.0	-
H-11	1.33	0.81	-0.31	1.22	108.0	5.00
H-12	0.91	0.89	-0.05	0.93	109.5	1.00
H-13	1.95	0.80	-0.33	1.45	110.5	8.00
H-14	0.38	1.19	-0.10	1.29	111.5	1.00
H-15	0.63	1.05	0.17	1.12	112.5	2.00
H-16	1.74	0.60	-0.32	1.47	114.0	1.50
H-17	2.24	0.61	-0.16	1.61	116.0	1.00
H-18	-0.27	1.10	-0.18	1.10	117.5	2.00
H-19	1.04	0.88	0.13	0.96	119.5	2.00
H-20	0.54	1.31	0.23	1.14	121.5	2.00
H-21	1.73	0.65	-0.25	0.96	122.5	3.00
H-22	0.62	1.12	-0.29	1.35	125.0	2.75
H-23	1.64	0.66	-0.24	1.20	127.0	2.75
H-24	-0.10	2.00	0.02	1.00	129.0	2.75
H-25	0.93	0.89	0.10	1.10	131.5	3.00
H-26	1.65	0.82	-0.25	0.87	133.0	3.00
H-27	1.75	0.91	-0.34	0.78	133.5	3.00

Table 3.3 First percentile (C) and Median (M) of size distribution of Chaliyar river sediments

Sample No.	C (in microns)	M (in microns)
H-35	3500	740
H-1	8600	500
H-2	4150	485
H-3	1000	367
H-4	2950	500
H-5	8000	470
H-11	1870	342
H-12	3600	540
H-13	1700	235
H-14	9800	765
H-15	3250	710
H-16	2580	280
H-17	1190	212
H-18	12200	1100
H-19	2580	530
H-20	17300	670
H-21	920	270
H-22	17900	600
H-23	1140	300
H-24	26000	1170
H-25	2560	570
H-26	1180	288
H-27	1370	255
H-28 T	37000	500
H-29 T	3380	240
H-30 T	12000	1630
H-31 T	36000	580
H-32 T	28000	520
H-33 TC	26800	1280
H-34 T	12000	880

Table 3.4 Percentage of Sand : Silt : Clay in the Chaliyar river sediments

Sample No.	Sand	Silt	Clay	Textural terminology (Folk et al., 1970)
H-35	100.00	-	-	Sand
H-1	100.00	-	-	Sand
H-2	100.00	-	-	Sand
H-3	100.00	-	-	Sand
H-4	100.00	-	-	Sand
H-5	100.00	-	-	Sand
H-11	90.69	1.97	7.34	Sand
H-12	100.00	-	-	Sand
H-13	77.06	10.33	12.61	Muddy sand
H-14	97.34	1.37	1.29	Sand
H-15	92.02	0.61	7.37	Sand
H-16	79.95	16.48	3.56	Silty sand
H-17	89.84	1.22	8.94	Clayey sand
H-18	100.00	-	-	Sand
H-19	91.80	0.07	8.13	Sand
H-20	93.92	3.82	2.26	Sand
H-21	94.40	0.92	4.68	Sand
H-22	94.51	2.79	2.70	Sand
H-23	86.31	5.94	7.76	Muddy sand
H-24	93.25	3.19	3.57	Sand
H-25	85.36	6.30	8.35	Muddy sand
H-26	57.43	20.33	22.25	Muddy sand
H-27	80.05	9.86	10.09	Muddy sand
H-28 T	96.89	2.41	0.70	Sand
H-29 T	93.38	4.53	2.09	Sand
H-30 T	93.48	4.50	2.02	Sand
H-31 T	95.64	2.99	1.37	Sand
H-32 T	91.87	5.70	2.43	Sand
H-33 TC	97.46	1.68	0.86	Sand
H-34 T	96.91	2.28	0.81	Sand

SEM images of quartz grains

Plate.3.1 (A, B & C) Extremely angular quartz grain from upper reaches of Chaliyar river with medium to large conchoidal fractures.
Sample. no. H -1 (A & B) & H-3 (C).

Plate.3.1 (D & E) Sub-angular quartz grains showing smoothening of outline with large V's (D)
Sample. no. H-13 (D) & H-3 (E).

Plate.3.1 (F) Surface of the Quartz grain reveals the solution crevasses/pits formed by dissolution of mineralization and or lateritization on processes.
Sample. no. H-4

Plate.3.1 (G & H) Sub-angular and sub-rounded quartz grains reveal fractures with meandering ridges and fresh breakage surfaces. [G – polycrystalline (?) quartz]
Sample. no. H-21 (G) & H-3 (H)

Plate. 3.1 (I) Adhering particles on the Quartz grains from middle reaches of Chaliyar river.
Sample. no. H-11

Plate. 3.1 (J) Quartz grain from mid stem showing numerous steep arcuate steps as well as adhering particles.
Sample. no. H-3.

Plate.3.1 (K) Sub-angular quartz grains with medium to small concoidal fractures and slightly meandering ridges in the lower reaches of Chaliyar river.
Sample. no. H-17.

Plate.3.1(L) Quartz grain from lower reaches of Chaliyar river show small V's and
Sample. no. H-11.

Plate.3.1 (M) Sub-rounded Quartz grain showing straight scratches (see left side of the grain)
Sample. no. H-5.

Plate.3.1 (N) Surface of Quartz grains from estuarine environment show solution pits/ holes
Sample. no. H-26.

Plate.3.1 (O) Subhedral quartz grains show relatively fresh breakage features on one side from lower reaches of Chaliyar river main stem.
Sample. no. H-17.

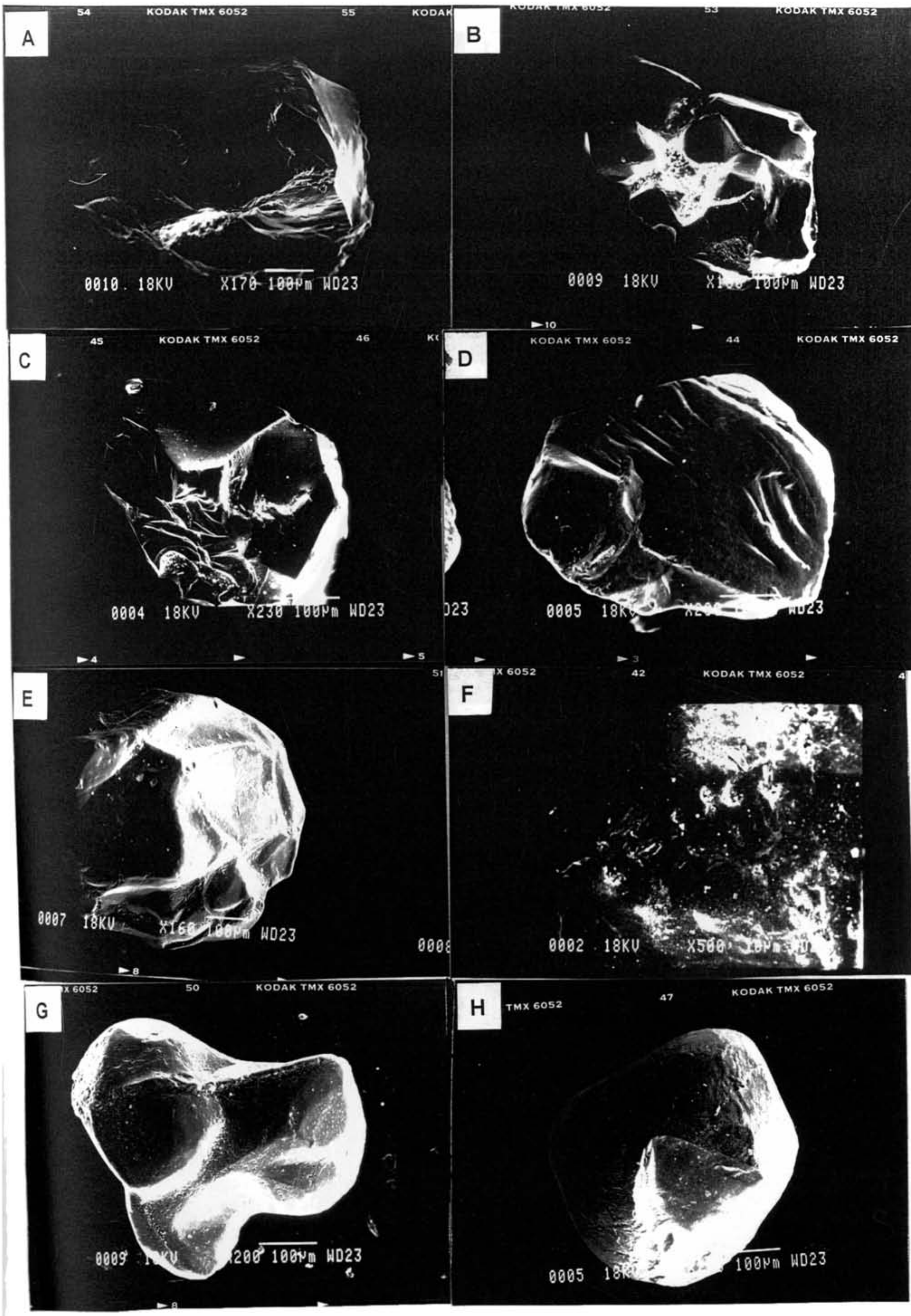

A
KODAK TMX 6052
0010 18KV X170 100µm WD23
B
KODAK TMX 6052
C
KODAK TMX 6052
0004 18KV X230 100µm WD23
D
KODAK TMX 6052
E
0007 18KV
F
KODAK TMX 6052
0002 18KV X500
G
KODAK TMX 6052
100µm WD23
H
TMX 6052
KODAK TMX 6052
0005
100µm WD23

Plate 3.1

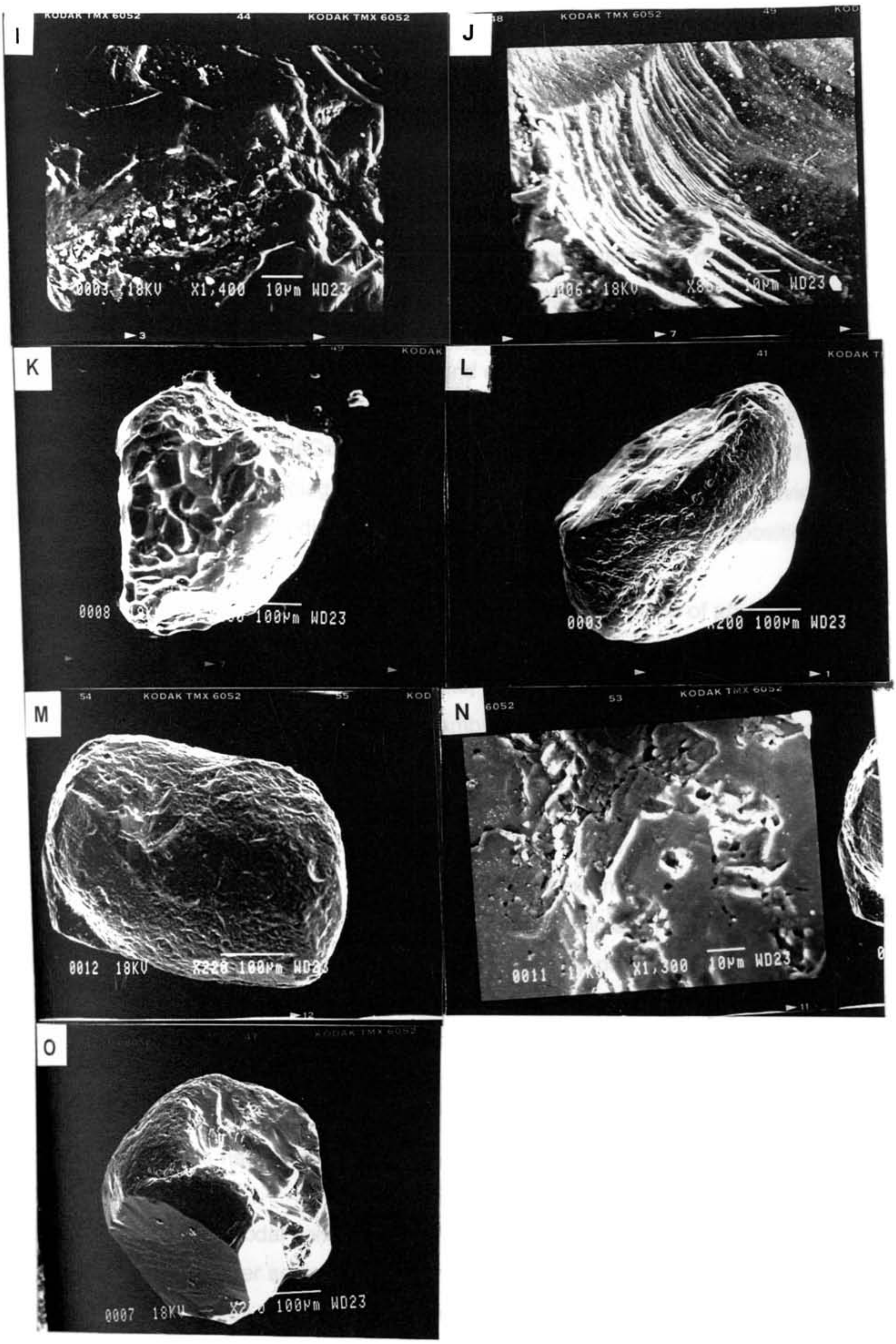


Plate 3.1

Chapter 4

MINERALOGY

4.1 Introduction

Source-rock composition, climate, relief, slope, vegetation and dynamics of the fluvial environment all play important roles in controlling the composition of fluvial sand (see for example, Blatt, 1967; Ruxton, 1970; Cameron and Blatt, 1971; Suttner, 1974; Basu, 1976, 1985; Potter, 1978; James and others, 1981; Suttner and others, 1981; Mack, 1984; Velbel, 1985; Dutta and Suttner, 1986; Suttner and Dutta, 1986; Grantham and Velbel, 1988; DeCelles and Hertel, 1989; Johnsson et al., 1991). Although most sand in the geologic record at one time passed through a fluvial system, little research has been directed at evaluating controls on sand composition in river systems.

Study of modern river sand can elucidate the relative importance of processes controlling the composition of sand in the geologic record. An advantage of studying modern sand is that sands, their source rocks, and physiographic and climatic characteristics of the source regions can be unambiguously correlated. For example, in the absence of distinctive dense-mineral suites, can the "lineage" of a fluvial sand be traced via a specific river to a particular source area? If so, can we use petrologic and textural data of sand for determining the fluvial dynamics, deposition of sediments and its composition in the river basin? To what extent are composition of fluvial sand influenced by source-terrain composition, climate, fluvial mixing, downstream transport, and intra-basinal reworking of slightly older, unconsolidated sediments? Unequivocal answers to these questions can be obtained only by studying the petrography of fluvial sands. Relatively little light, however, has been shed on the detailed processes and responses within a fluvial system which ultimately govern the framework composition of river sand, and some of the answers for the above questions has been addressed in this chapter using the data for the Chaliyar river.

The knowledge of modal composition, relative abundance of heavy, light and clay mineral fractions in river sediments renders valuable information on the nature of contribution and energy conditions of the depositing medium. Study of the mineralogical make up of sediments should always accompany the study on textural characteristics, as the texture has a direct bearing on the mineralogical constitution of sediments. In many published works, one size fraction have only been examined to represent the entire mineralogical assemblage of sediments. Since heavy minerals are deposited according to the difference in size, shape and density, a single size fraction seldom represents the entire mineralogical composition of sediments (Rubey, 1933; Rittenhouse, 1943; Friedman, 1961; Mishra, 1969; Blatt et al., 1972 and Patro et al., 1989). On the other hand, study of light minerals and their ratios can give information regarding source rock characteristics and the maturity of sediments. The principal interests related to the study of clay minerals are its sensitivity to source area fluctuations and diagenetic changes of sediments.

4.2 Review of literature

Several investigators have made systematic approach to study the mineralogical diversities observed along the course of rivers. The concentrations and settling velocity relationships of light and heavy minerals as placers and in sedimentary deposits generally, have been studied by Rittenhouse (1943), Van Andel (1950), Sundborg (1956), McIntyre (1959), Hand (1967), Briggs (1965), White and Williams (1967) Grigg and Rathbun (1969), Lowright et al. (1972), Stapor (1973), Slingerland (1977, 1980, 1984) and Sallenger (1979). Briggs et al. (1962) have pointed out that both density and shape of minerals are important factors which control the sorting mechanism of minerals downstream. The role of progressive sorting based on size and specific gravity differences has also been studied by investigators like Allen (1970), Carver (1971), Blatt et al. (1972), Komar and Wang (1984) and Komar et al. (1989).

The effects of physical and chemical weathering on minerals are often difficult to distinguish (Edelman and Doeglas, 1931; Dryden and Dryden, 1946 and Raeside, 1959). Pettijohn (1941) suggested that the diversities in heavy mineral assemblages are more in the youngest sediments than ancient ones, and further, the number of heavy mineral species may gradually decrease as the age of the sediment increases. Such a decrease in the heavy mineral species could be due to the action of intrastratal solution (Pettijohn, 1941). But contrary to this, Krynine (1942) emphasised provenance as the key factor for the above said mineralogical diversities. Blatt and Sutherland (1969) have shown that the rate of chemical alteration is greater in coarse grained sediments than in less permeable fine grained sediments due to the availability of enough intrastratal solution in the former. The work of Rittenhouse (1943) stressed the complex interrelationship between source rock characteristics and transport processes that determine the heavy mineral distribution in fluvial set up.

The composition of light minerals of clastic sediments has been studied for a better understanding of the mineralogical maturity and fluvial processes. In 1957, Pettijohn has pointed out that the mineralogical maturity of sediments can be expressed by quartz/feldspar ratio. Though there is not much difference in the specific gravities between quartz (2.65) and feldspar (2.70), there exists considerable difference in the stability index between the two, because feldspars especially plagioclase feldspar is comparatively less stable than quartz. Many workers found that the increase of quartz/feldspar ratio downstream is the result of selective abrasion of easily weatherable feldspars (Russel, 1937; Pettijohn, 1957; Pollock, 1961; Seibold, 1963; Seetharamaswamy, 1970; Potter, 1977; Seralathan, 1979; Franzinelli and Potter, 1983 and Johnsson et al., 1991). The relative proportions of these minerals in sediments have also been extensively used for reconstructing climatic as well as tectonic history of ancient sedimentary deposits (Blatt et al., 1972; Hashmi and Nair, 1986).

In India, detailed studies on heavy mineral variations have been restricted to some major river systems which include Godavari (Naidu, 1968), Krishna (Seetharamaswamy, 1970), Mahanadi (Sathyanarayana, 1973), Vasishta-Godavari (Dora, 1978) and Cauvery (Seralathan, 1979). Unlike river systems, considerable amount of information exists on the heavy mineral occurrences of the beach environments. Mohan and Victor Rajamanickam (2000) carried out a comprehensive study on the buried placer mineral deposits along east coast between Chennai and Pondicherry.

Clay minerals are important constituent of sediments. Investigations regarding the distributional patterns and origin of clay minerals have proved to be important tool for elucidating pathways of fine grained sediments (Weaver, 1959; Biscaye, 1965; Scafe and Kunze, 1971; Shaw, 1973; Kolla et al; 1981 and Nair et al., 1982).

Tagaart and Keiser (1960), Subba Rao (1963), Seetharamaswamy (1970), Seralathan (1979), Mohan (1990), Seralathan and Padmalal (1994) and Pandarinath et al. (1999) has pointed out that nature of source rock, source area weathering conditions, climate, relief and hydrodynamic conditions have tremendous influence on the quality and quantity of clay minerals. The effect of diagenesis on the dispersal pattern of clay minerals has been emphasised by Grim et al. (1949), Grim and Johns (1954), Nelson (1959) and Caroll (1969). In recent years clay mineral studies are being carried out to understand the dispersal pattern of major and trace elements in the sediments of rivers, estuaries and near shore environments (Reinson, 1975; Prithviraj and Praksh, 1990; Pandarinath and Narayana, 1998; and Sing, 1999).

4.3 Results and discussion

4.3.1 Mineralogy of bulk sand

The percentage distribution of detrital minerals present in the sediments of the upper reaches of the Chaliyar main channel (sample no. : H-1, H-2, H-3, H-4 and H-5) has been assessed by point counting of grain mounts. The results are presented in table 4.1 (see Fig. 2.1 for sample locations). The detrital minerals mainly consist of quartz and feldspar, with subordinate amounts of heavy minerals like opaques, garnet, zircon, monazite, sillimanite. From the table, it is seen that there is a progressive downstream increase in the percentage of quartz and a corresponding decrease in feldspar content. This probably indicate progressive sorting and maturity of sediments. Other accessory minerals do not slow any specific trend in the downstream direction.

4.3.2 Modal composition of +35 ASTM size fraction (0.5 to 1.0 ∅)

In order to normalize for composition-grain-size dependency, all modal analyses were performed on a single size fraction. Mean size versus frequency percentage show 50% of the sediment samples are coarse sand (0-1 ∅) and 33% of sample are in the medium sand fraction (1-2 ∅) (see Fig. 4.1). Of the 50% coarse sand samples 16.67% are in the phi range 0 to 0.5 ∅ and 33.33% are 0.5 to 1.0 ∅ range while 10% of the 33% medium sand samples are in the 1.0 – 1.5 ∅ range and 23% are in the 1.5 – 2.0 ∅ range. The coarse sand fraction (0.5 – 1.0 ∅) was selected to facilitate comparison of data between the samples in the Chaliyar basin.

This size fraction also represents the mode of the sand carried in the Chaliyar river main stem.

Grain mounts were prepared for the above sand fraction and modal abundances of detrital grains in 30 samples (7 tributary samples and 23 channel samples; see Fig. 2.1 for sample locations) were determined by grain counting method with sample numbers covered. 300 t0 400 grains were counted in each sample. The results are presented in table 4.2.

4.3.3 Grain type and mineral assemblage

These detrital mineral types were identified with their diagnostic optical properties and are briefly described below :

Quartz: The monomineralic grains of sands sampled in the Chaliyar basin is dominated by quartz and it averages 75.9% (Table 4.2). Most of the quartz grains are angular in the tributary samples while they are sub-angular to sub-rounded in samples in the upper, middle and lower reaches of the Chaliyar mainstem. They show undulatory extinction. Some amount of angular to sub-angular quartz grains are seen in the sample sites adjacent to the tributary confluences beyond 110 km in the down stream direction of the main channel. These grains include polygonised grains, grains with elongated and sutured or crenulated boundaries, and grains with two or more crystals joined along smooth faces. Some of the mono and polycrystalline quartz also show brown stains of iron oxide along the fractures and grain boundaries respectively. Mono and polycrystalline quartz grains in the sand samples analysed exhibit characteristic of quartz derived respectively from plutonic and metamorphic source terraces. Other sources include lateritized rocks and terrace sediments (Plate 4.1A).

Amphibole: Hornblende is the next abundant mineral seen in the sediment samples of the Chaliyar river and it averages about 7.5% (Table 4.2). The average content of hornblende is seven fold higher than the average pyroxenes (1.1%) in the samples. It shows characteristic pale green to dark green or bluish green pleochroism. These grains generally are prismatic in nature, angular to moderately rounded, single crystals. They probably were derived principally from composite hornblende bearing gneisses.

Feldspar: The content of feldspar in the samples averages 6.9 % (Table 4.2) and they are mainly K-feldspar. Most potassium feldspar in the samples counted is orthoclase, but minor amounts of microcline is also present. Orthoclase and microcline generally are sub-hedral, angular to sub-angular, single grains and they show characteristic simple twinning and cross hatched appearance respectively. Smaller quantities of plagioclase feldspar occur in the fluvial sands of the Chaliyar basin and they show polysynthetic twinning. Feldspar grains probably were derived from plutonic (granite) and metamorphosed rocks, or their weathered equivalents.

Opaques: The opaques averages about 5.9% in the samples of the Chaliyar basin (Table 4.2). The most common opaque minerals are ilmenite, magnetite, hematite and trace amount of leucoxene. The leucoxene present in the fluvial sands may be derived by the alteration of ilmenite, in the highly lateritized source rocks in the region.

Garnet: The garnet content in the samples averages about 2.2% in the fluvial sediments of Chaliyar river (Table 4.2). Even though the garnet in the sample counted averages only 2.2%, it has a wide range and goes up to 10% in some of the samples (Table 4.2; sample no. H-12 & H-24). Most of the garnet is pinkish to reddish in colour and often with conchoidal fracture. These grains generally are subrounded, occur as single crystals and few of them contain inclusions. Garnet in the sedimemts is derived from metamorphic source rocks.

Pyroxene: Grains of hypersthene are present in small amounts (average: 1.1%) in sand samples from the Chaliyar basin (Table 4.2). It is the principal pyroxene mineral identified in the fluvial system and its content goes up to ≅ 6% in some of the samples (see Table 4.2; sample no. H-24 and H-33). It occurs as irregular grains and exhibits marked pleochroism, pale green to pale pink. These grains probably were derived from charnockites, which constitute one of the major rocks in the basin.

Biotite: Biotite grains are present in small amounts and it averages 0.4% in the sand samples of Chaliyar basin (Table 4.2). In some of the samples it is found missing. They commonly occur as flaky and appears light or dark brown under plane polarized light. Majority of them do not show pleochroism due to alterat[illegible] mineral probably is derived from migmatite and granite.

Rutite: Rutite averages about 0.2% in the sand samples of the Chaliyar basin. In majority of the samples it is found as inclusions in quartz. But single crystals of the mineral rutile is sub-angular to subrounded in shape and shows blood-red colour under plane polarized light.

Zircon, Sillimanite, Monazite, Sphene and Apatite: These dense minerals constitute < 1% in total in the fluvial sand of the Chaliyar basin and they are mainly seen as inclusions in quartz grains. Since they are present only in trace amounts these dense minerals were ignored in this quantitative provenance analysis (Table 4.2). Among them zircon is the most dominant and is seen in almost all samples except in H-4, H-13, H-15, H-21 and H-24. It is seen as inclusions in quartz grains. The zircon grains are elongate or near spherical (Plate 4.1B). Next abundant dense mineral is sillimanite even though it is absent in some samples. It is also seen as inclusions in quartz and occur as slender prismatic grains (Plate 4.1C). Sphene, monazite and apatite are seen in almost equal proportions but in minor amounts in the samples. Sphene is identified by its characteristic wedge shape, very high refractive index and very strong birefringence (Plate 4.1D). Monazite grains are subrounded to rounded with honey-yellow colour. Apatite is seen as small prismatic needle shaped crystals in quartz (Plate 4.1E). These dense mineral suites indicate a high grade metamorphic provenance.

Altered minerals, ferricrete and biogenic debris (organic matter or skeletal debris) : Majority of the altered minerals are hypersthene, feldspar, hornblende and biotite. Ferricrete or laterite fragments are derived from lateritic rocks and Tertiary and Quaternary alluvial terraces. Biogenic or skeletal debri are also present in a few samples.

4.4 Down stream changes in mineral assemblage

4.4.1 Tributary/tributary confluences

The percentage variation in the detrital mineral assemblage seen in the sediment samples of the major tributaries like Punna puzha, Karim puzha, Chali puzha, Kanjira puzha and Kuruman puzha (sample no. H-28, H-32, H-29 and H-31, H-30, H-34 respectively) and its confluences (H-33) are presented in figure 4.2 (see Table 4.2). The quartz percentage varies between 64.3 to 86.4% (averages about 74%) in these tributaries. A decrease in the quartz content in this tributary samples

(Chali puzha sample no. H-29 and H-31) is compensated by a corresponding increase in dense minerals like hornblende (14 and 19.7 % respectively) and opques (6.7 and 3.4% respectively). As will be seen in the later half of this chapter (see section 4.6; Table 4.3) that these samples contain highest amount of bulk heavy minerals, 22.8 and 27.57 wt.% respectively. However, in the case of other tributary samples like H-28 (Punna puzha) and H-32 (Karim puzha), even though the quartz percentages are higher (74.2% and 70.8 % respectively) when compared to the Chali puzha, they have lesser and almost equal proportions of dense minerals like hornblende and opaques (see Table 4.2 and Fig. 4.2). This may probably due to following reasons :

(i) the source rocks in this region contain lesser amount of dense mineral suites,

(ii) the stream gradient and velocity of the medium is less allowing the deposition of light minerals like quartz and feldspar and

(iii) the rocks along which these rivers drain are less weathered when compared to the rocks along which the Chali puzha drains.

The former two reasons (i) and (ii) may be ruled out because the samples H-28 and H-32 contains substantial amount of heavy minerals (14.07 and 21.03 wt.% respectively; see Table 4.3) and these tributaries are having a steep gradient which does not facilitate deposition of materials especially lighter ones like quartz and feldspar. From this it can be concluded that the Chali puzha flowing almost perpendicular to the main stem of Chaliyar river is draining along comparatively more weathered rocks than the rivers Punna puzha and Karim puzha, which almost flow parallel or sub parallel to the main stem.

Of the detrital minerals in these major tributaries, hornblende, varies between 1.4 to 19.7% (average: 8.7%), feldspar varies between 2 to 12% (average: 7.7%), opaques varies between 3.1 to 8.9% (average: 5.8%), garnet varies between 0.4 to 4.7% (average: 2.5%), hypersthene varies between 0 to 6.4% (average: 1.4%), and biotite varies between 0 to 1% (average: 0.4%) (see Table 4.2).

4.4.2 Chaliyar main stem

The spatial variation and the percentage of individual minerals like along the Chaliyar main channel is shown in figure 4.3 and table 4.2 respectively. Systematic downstream changes in the percentage of individual minerals are more clear in the upper reaches (63 to 108 km) while the mixing patterns are more obvious in the downstream (beyond 108 km). The general lack of systematic trends, from the head water regions towards the mouth of the river, results from the influx from tributaries of sand with highly variable composition.

Quartz: The quartz percentage ranges between 64.2 to 84.7% (average: 76.4%) in the sediment samples of Chaliyar main stem (Table 4.2). The spatial variation diagram (Fig. 4.3a) of quartz percentage show a broad variation trend in the upper reaches i.e., between 63-108 km, which may not be significant enough to draw any conclusions regarding sorting mechanism. Beyond this in the downstream direction the quartz content fluctuates more severely probably indicating a shift in the mixing pattern as a result from the influx from tributaries of sands with highly variable composition (quartz poor). To a certain extent the change in the velocity of the medium brought about by the channel physiography (meandering) in this stretch might have also contributed the above mixing pattern. A slight decline in the quartz percentage in sample stations H-19, H-21 and H-25 and a corresponding increase in feldspar content in those stations in the lower parts of the river are particularly notable and may result from contributions by tributaries carrying sands of highly variable composition and texture that enter the Chaliyar main stem, and even possibly by less tropical weathering of country rock (charnockites) in transit. Whatever its causes the near absence of rock fragments and the downstream increase especially towards the mouth of the river in the progressive maturity of main stem sands are consistent with the idea of Krsheninnkov (1968), Franzinelli and Potter (1983) that river sands nearer the sea are more mature than their upstream counter parts even though data towards the mouth of the river in this study (nearer to the sea) are not large.

In comparison with the spectral variation of quartz content the various grain-size statistical parameters like mean size, standard deviation, skewness and kurtosis show subtle changes in the 63-110 km sector. Beyond this in the downstream direction the quartz content as well as the statistical parameters vary drastically probably indicating mineralogical control over them (see figure 3.2 and 4.3). The lowest percentage of quartz in the sand sample is seen closer to the river mouth (H-24: 64.2%) whose mean size falls in the very coarse sand category, poorly sorted (this sample has the highest standard deviation 2∅) but symmetrically skewed and mesokurtic in nature. However, there is a drastic increase in the quartz content further downstream (samples H-26 & H-27), suggestive of sorting and enrichment. Maximum quartz content is seen in upper reaches (H-4: 84.7%) of the Chaliyar main stem and its mean size falls in the coarse sand category, moderately sorted, coarse skewed and leptokurtic in nature.

Feldspar: The content of feldspar in the samples varies between 1.8 to 16.4% (average: 6.6%) and is less than average hornblende content (7.1%) in the main stem (Table 4.2). The downstream variation in the feldspar content is shown figure 4.3b. In general the spectral diagram of quartz and feldspar content show a contrasting downstream trends (Fig. 4.3a and b). In other words, stations in which there is an increase in feldspar content, with respect to adjacent locations, show a corresponding decrease in quartz content throughout the main stem. From the spectra (Fig. 4.3b) it is clear that the feldspar percentage shows a slight decreasing trend between 63 to 108 km while it shows an increasing trend in the downstream direction beyond 108 km. The down stream decrease in feldspar content between 63-108 km signifies progressive sorting while the increase in feldspar percentage beyond 108 km is mainly due to the mixing of the sand from adjacent tributaries carrying slightly different mineralogical and textural characteristics with the sediments of the main channel. Among all the samples in the main stem including tributaries the highest and lowest contents of feldspar are seen beyond 120 km downstream from the source (H-21 and H-24 respectively). Sample H-21 has the highest percentage of feldspar (16.4%) with equal or lesser amount of quartz in them (74.7%) when compared to the adjacent sites (sample no. H-20: 74.7% and H-22: 79.1%). Similarly, consider the sample H-24 which is approximately 10 km upstream from the river mouth. As mentioned earlier, this sample should have greater amount of quartz when compared to the adjacent locations. But it is seen that this station (H-24) also corresponds to lowest amount of quartz (64.2%) among the samples. As noticed, from the feldspar spectra the station next to sample number H-24 (H-25) has the second highest percentage of feldspar (15.6%) which is consistent with the lighter minerals like quartz and feldspar having been carried from station H-24 and deposited in the next station H-25 by the river water in the main channel. It is already mentioned in this chapter that at station H-24 a tributary carrying predominantly coarser material joins the Chaliyar main channel. The decrease in quartz and feldspar content at station H-24 is compensated by a corresponding increase in other minerals like garnet, hornblende and hypersthene (explained in the later part of this section) which also supports that lighter minerals are carried downstream from this site to the adjacent site (H-25) while the more dense minerals are deposited there itself. The opaques are present in least amount (2.3%) in this sample since the tributary might have contributed less. Because of the high specific gravity of opaques (Sp. Gr. of ilmenite is 4.7) they might have settled down in the tributary itself. The spectral variation of feldspar when compared with spectral variation of textural parameters (Fig. 4.3b and 3.2) indicates that, a slight decreasing trend in feldspar content between 63-108 km corresponds to a slight increasing trend in mean size and sorting while majority of the samples in this sector are coarse skewed and lepto to mesokurtic in nature. The feldspar content and also the textural parameters fluctuate severely beyond 108 km in the down stream direction. It is seen that where ever there is an increase in feldspar content when compared with adjacent sites there is a corresponding increase in the phi mean size between 63-107 km, then it reverses its pattern between 107-114 km and finally it again returns to the initial pattern beyond 114 km and finally even though the pattern is opposite in sample H-26 and H-27. Similarly feldspar content and standard deviation follows opposite trend between 63-107 km, it becomes almost parallel between 107-116 km and there after it again reverts to the initial pattern. From this we may conclude that in the upper reaches, the quartz content and other minerals like opaque, garnet, hornblende and hypersthene have more control on the textural characteristics of sediment samples than feldspar while in the lower reaches to a certain extent the feldspar content has some bearing on the textural variations. As mentioned earlier sample H-24 has the lowest feldspar content and it also shows second lowest mean size (-0.1∅ - coarse sand), maximum standard deviation (2∅ - poorly sorted) but symmetrically skewed and mesokurtic in nature which may probably due to the differences in the sizes of quartz and opaques with other minerals like garnet, hornblende and hypersthene. Though sample station at H-25 has second highest amount of feldspar the statistical parameters like mean size increases (0.93 ∅ -

coarse sand) and standard deviation decreases (0.89 ∅ - moderately sorted) when compared to H-24 but it is symmetrically skewed and mesokurtic in nature. This probably may indicate that there is better size comparison between quartz and feldspar grains because other minerals like garnet, hornblende and hypersthene are present in lesser amounts in the sample H-25 when compared to sample number H-24. In general the feldspar content also has an important role in controlling the textural characteristics of the bedload sediments in the Chaliyar main channel.

Opaques: The content of opaques in the samples of Chaliyar main stem varies between 2.3-11.9% (average: 6.0%) (Table 4.2) and downstream variation is given in figure 4.3c. The spectral variation diagram does not show any specific trend but it fluctuates more in the lower reaches (beyond 108 km) than in the upper reaches (63-108 km) of the main channel. Even though it fluctuates it is not that much erratic as seen in the feldspar spectrum. Among all the samples including major tributaries the maximum and minimum content of opaques is seen in the lower reaches beyond 114 km of the Chaliyar main stem (H-17: 11,9% and H-24: 2.3%). The spectral pattern of opaques when compared with the spectral pattern of mean size show a strong correspondence i.e., where ever there is an increase in mean size of the sediment samples in the Chaliyar main stem with respect to the adjacent sites there is a concomitant increase in the percentage of opaque minerals. This means that the opaques which are denser and relatively smaller in size might have contributed for such a relationship. Similarly in comparison with spectral pattern of the standard deviation the opaques show opposite relationship which means that wherever there is a high content of opaques there is a corresponding decrease in the standard deviation values and vice versa. In other words the samples in which the contents of opaques are higher when compared to adjacent sites, the sorting also increases. Since opaques are dense minerals and are comparatively smaller in sizes, they might have played an important role in controlling the above phenomenon. Thus it seems likely that the opaques have played an important role in controlling the textural characteristics of sediments in the Chaliyar main stem, even though they are present in lesser amounts when compared to feldspar and hornblende.

Garnet: The percentage of garnet in the sediment samples ranges between 0-10.4% with an average 2.1% (Table 4.2). The variation of garnet content along the Chaliyar main stem is given in figure 4.3d. The samples between 63-107 km remain almost steady and becomes zero at the site H-5 in the downstream direction. Beyond this point the garnet content increases at sites H-12 (10.4%), H-19 (4.5%), H-24 (10%) and H-25 (4.9%) which is 2 to 5 times more than the average garnet percentage in samples. This is probably due to the local inputs from the tributaries that is draining the charnockitic terrain. The above samples H-12, H-14, H-19 and H-24 in the main stem when compared with statistical parameters show complementary pattern with mean size and almost parallels the peaks of the standard deviation spectra except sample H-19. In the lower reaches, therefore, the textural parameters and mineralogical variations are controlled mainly by the influx of sands of variable composition from nearby tributaries.

Amphibole: Hornblende is the second dominant mineral present in the sediment samples of the Chaliyar main stem. It varies between 0.4 to 15.6% (average: 7.1%) in the main channel (Table 4.2). The downstream variation of hornblende content in samples is depicted in figure 4.3e. It almost shows a steady decrease in the hornblende content between 63-107 km probably indicating progressive sorting downstream. Beyond this point in the downstream direction it fluctuates erratically and show slight increasing trend which might be due to the accumulation of hornblende in sites adjacent to the sites where there is a depletion in this mineral. From the spectral pattern it is clear that there is no noticeable peaks above the average hornblende content (7.5%) except in sample number H-24, but there are noticeable sharp decline in this mineral content especially in sample H-21 probably indicating that the flow pattern characteristics of the medium is more important rather than the influx of sand bearing low percentages of hornblende from local tributaries for the above pattern because these tributaries drain mainly through the charnockitic terrain. All the major tributaries of the Chaliyar basin in the headwater region drain mainly through the hornblende bearing composite gneiss. With the steep gradient and high velocity of the medium in these tributaries, the minerals from the weathered horizon especially hornblende which is having comparatively a lower specific gravity (Sp. Gr. = 3.21), might have carried further downstream and almost evenly distributed through out the main channel. The difference in the flow pattern beyond 107 km in the downstream direction might be the real cause for the accumulation of hornblende in certain sites. A corresponding depletion of the mineral in the downstream direction is primarily caused by the channel physiography and to a certain extent the influx of sediments from local tributaries to the main stem. The sorting processes downstream that lead to the decrease in the content of hornblende between 63-107 km might have played important part in controlling also the textural characteristics. Beyond the 107 km mark, the hornblende percentage fluctuates severely and wide fluctuations in the texture of the sediments are consistently noticed.

Pyroxene: The content of hypersthene varies between 0-6% (average 1%) in the Chaliyar main stem (Table 4.2). The variation in the hypersthene content from 63 km to the river mouth is given in the figure 4.3f. After an initial increase (H-1: 2.1%) there is a steady decline in the content of hypersthene and it is totally absent in H-4 sample. Beyond the 99 km mark in the down stream direction its percentage increases but fluctuates erratically. This sudden increase in the hypersthene content in some of the sites in this sector of the main channel is mainly contributed by the sediments from the tributaries which drains the charnockitic terrain. At the same time the fluctuating nature of the mineral content is mainly due to the energy conditions prevailing in the channel caused by the meandering nature of the main stem. The highest content of hypersthene is seen in the sample H-24 (6.1%) and at this site a tributary joins the Chaliyar main channel. Due to its dense nature (Sp. Gr. = 3.43) it is found right at the area of confluence while the less dense minerals are carried further downstream. Comparatively lesser amount of light minerals like quartz and feldspar in this sample is compensated by the corresponding increase in the dense minerals like garnet, hornblende and hypersthene. The very coarse nature and poor sorting of this sample may be due to the addition of coarser materials of quartz and feldspar rather than the coarser nature of the dense minerals because as mentioned earlier (see feldspar section) this area experiences less tropical weathering. The downstream decrease in the content of hypersthene might have contributed for the progressive sorting mechanism and more uniform textural characteristics in the 63-107 km stretch while the inputs of small amounts of hypersthene by the downstream tributaries below 107 km might have also contributed for the wide variations in the textural parameters and its non-uniform nature.

Biotite and rutile are present in small amounts (average: 0.5 and 0.2% respectively) in the samples of the Chaliyar main channel. They are found missing in some of the samples and in some they are present either as inclusions in quartz or as attached grains with quartz/feldspar. Hence they are not included in this quantitative provenance analysis even though in some samples they are seen as single crystal big enough to be counted and so they are expressed in percentages. The biotite is mainly seen in the upper reaches (H-1, H-2, H-3, H-4 and H-11) and in lower reaches it is present in trace quantities or absent in majority of the samples (Table 4.2). Similarly rutile varies between 0 to 1.1% but in majority of the samples they are present in trace amounts in the Chaliyar main channel or are absent as in samples H-11, H-15, H-20 and H-27 they are found missing (Table 4.2). Dense minerals like sphene, zircon, sillimanite, monazite and apatite were ignored in this quantitative provence analysis for reasons outlined earlier in this chapter but their presence or absence is indicated in the table 4.2.

4.4.3 Possible factors for mineralogical diversities observed in the Chaliyar main stem

The mineralogical diversities and variation observed along the profile of the Chaliyar river sands (+35 ASTM size) could be explained mainly by progressive sorting based on densities of the minerals in the upper reaches (63-107 km) while in the lower reaches beyond 107 km it is mainly due to mixing of sands from tributaries having different compositions. During deposition, denser minerals such as opaques (Sp. Gr. of ilmenite = 4.7) and garnet (Sp.Gr. = 4.3) settle quickly at the point of current impingements owing to its greater settling velocities; while the less dense hornblende (Sp. Gr. = 3.2%) and hypersthene (Sp. Gr. = 3.42) are transported still further down stream. Moreover, the high competency of the river water does not allow the free settling of amphiboles and pyroxenes in the upper reaches, and as a result these minerals will be flushed further downstream and deposited. Therefore opaques and garnet remain upstream owing to there higher specific gravities. This again supplements the role of progressive sorting based on density in the segregation of minerals in the Chaliyar river main stem. Slingerland (1984) has pointed out that denser minerals like ilmenite once deposited will not be entrained as easily as the lighter minerals like quartz. Similarly Seralathan (1979), Lewis (1984), Kundras (1987) and Padmalal (1992) found that denser minerals once deposited will not be entrained as easily as the lighter heavy minerals like hornblende and hypersthene. This may explain the low fluctuations in the concentrations of opaques and almost even amounts of garnet in the upper reaches (63-107km), while there is a steady decline in the less dense minerals like hornblende and hypersthene could be explained. The cause of decrease in the content of hornblende and hypersthene in the upper reaches is that, once they get deposited, in the next generation of flood/bankfull discharge these minerals get entrained, carried further downstream and redeposited. This has also contributed for the increases in these mineral contents in the lower reaches (beyond 107 km) in addition to the tributary influx.

It is evident from the figures 4.3a,c,e & f that locations showing positive anomalies of denser minerals (opaques) coincide with negative anomalies of light (quartz) and lighter heavy minerals (hornblende and hypersthene) in the lower reaches (stations H-12, H-17 and H-23) having a prominent positive anomalies of opaques. But in quartz-opaques plot (Fig. 4.3a & c) this behaviour is seen throughout the main channel. Further, the maximal values of feldspar, amphiboles and pyroxenes are found to be shifted slightly downstream with respect to that of the opaques and garnet. All these clearly indicate the role of progressive sorting based on density in differentiating the minerals downstream. The anomalous increase of feldspar and dense minerals in the lower reaches is mainly due to following reasons:

i) local hydraulic conditions owing to the presence of almost equally spaced meanders/bents

ii) natural turbulences resulted from the tributary influx.

iii) influx of bedload sediments (quartz poor) containing variable sand composition from tributaries which drains less weathered rocks and

iv) the main channel sediments are less diluted by the lighter quartz grains of sand size from the tributaries.

Investigators like Pollock (1961), Briggs et al. (1962), Shideler (1975) and Flores and Shideler (1978) have opined that progressive sorting based on shape of heavy minerals also plays a significant role in the distribution of heavy minerals. Assuming that all factors including the size of the grains are constant, the settling rates of different heavy minerals would depend not only on their densities but also on their shapes. When particles of the same volume and densities having different shapes are allowed to settle through a column of liquid, the particles with greatest sphericity will have the highest settling velocity (Pettijohn, 1957 and Blatt et al., 1972). This may also attribute some role in the observed diversity of heavy mineral assemblage in the Chaliyar river main stem. Since opaques are more spherical than amphiboles and pyroxenes, the former would have settled considerably first (i.e. in the tributary channels) than the latter, consequently the amphiboles and pyroxenes suite would be depositing farther downstream. In general the distributions of dense minerals like opaques, garnet, amphiboles and pyroxenes in the Chaliyar main stem are the combined effect of the shape and sizes of the minerals in the source terrain, and the sorting processes during transport and deposition.

4.4.4 Mixing patterns

The sand samples from the Chaliyar main stem and its major tributaries are enriched in quartz and deficient in feldspar grains (average % QF=92,8). As mentioned earlier in this chapter (see section on grain type and mineral assemblage) rock fragments content was not evaluated quantitatively in this study. The ranges and averages of QF compositions of the 30 sections that were grain counted are presented in table 4.2. Majority of the samples have more than 90% quartz grains. In the tributaries the average % QF=91,9 while in the main stem the average % QF=92,8. From this we can infer that sand of the Chaliyar river basin is mineralogically mature, with high content of quartz and minor amount of feldspar.

When samples from upper reaches (63-107 km) are grouped and compared with the lower reach samples (beyond 107 km), some systematic downstream mixing patterns become apparent. It may be noticed that a few tributaries which are comparatively smaller flow into the upper part of the Chaliyar main stem, ar [illegible] comparatively larger tributaries joins the main channel along its lower rea[illegible] Fig 2.1). The composition of sands from the farthest upper reach

QF=91,6. Beyond 107 km in the downstream direction these sands are mixed with sands contributed by the downstream tributaries, and they have an average composition of % QF=91,9; which is almost similar to that of the mean sand composition of the Chaliyar basin. A rough theoretical or expected average composition of sand for the entire main channel can be calculated by taking the average QF composition of the upper and lower reaches of the Chaliyar main stem samples, which is % QF=92,8. The actual average composition for the Chaliyar main stem (% QF=92,8) is remarkably same as that of the above theoretical/expected average compositions. Thus, data from the Chaliyar main stem suggests that fluvial sands from major rivers in the basin may indeed retain a traceable signature of their compositional "lineage". Such a consistency of mixing patterns and compositional "lineage" is earlier reported by DeCelles and Hertel (1989) for the fluvial sands from the Amazonian foreland basin.

4.5 Influence of source composition, weathering and climate in the minerological diversities observed in the Chaliyar river

The influence of source-terrain composition upon sand composition in the Chaliyar river basin can be assessed by comparing bedrock compositions in source terrains (Fig. 1.2) with compositions of sand from upper parts of the main stem (63-107 km) and major tributaries. In the lower reaches, the rivers are draining areas of the basin that are underlain almost exclusively by charnockites, and the degree to which the composition of the rock have been altered by weathering is unknown. The samples from the upper reaches of the main channel are by far the most quartz-rich of all sands in the Chaliyar basin (Table 4.2). The mafic population of the upper reach sands is dominated by hornblende, which probably was derived from hornblende gneiss that underlies vast portion of the major tributaries in the Chaliyar drainage basin. In the lower reaches the tributaries in the Chaliyar basin is underlain essentially by charnockitic rocks, and sands from the main channel in this area are correspondingly rich in hypersthene, garnet and slightly poorer in quartz. In general, sand carried by rivers that drain basins underlain by large areas of hornblende gneiss and charnockite are enriched in quartz (Table 4.2).

The progressive downstream decrease in maturity of Chaliyar main stem sands is apparent on a QF longitudinal profile (Fig 4.3a and b). This is also apparent from average % QF in the upper reaches (63-107 km) and lower reaches (beyond 107 km) of the Chaliyar main stem sand samples (Table 4.2). Increase in feldspar content is particularly notable beyond 107 km and may result from the influx from tributaries of sand with variable composition and even possibly by less tropical weathering in transit. But the downstream trends in mineralogical maturity of sand in the Chaliyar main stem is, in general, only weakly systematic. For example, the downstream trend in the content of quartz fluctuates erratically, especially beyond 107 km, in response to influx of quartz-rich or quartz-poor sand from tributaries which is underlain by charnockites. Thus, spatial trends in mineralogic maturity in fluvial sands of Chaliyar main stem should be interpreted with caution. Potter (1978) has recognized that sampling any large river system (modern/ancient) for its grains size and sorting is much more difficult than sampling its sands for petrological and chemical study, and hence comparisons should be made with caution. In this study, however, it is found that sampling of small river system like Chaliyar not only for its grain size, sorting but also for the petrological study is difficult. The principal control on sand composition in the Chaliyar main stem is source lithology and to a certain extent the intensity of weathering.

Although anthropogenic perturbation of erosion processes on the Chaliyar drainage basin were largely unaffected, human activity should not be totally ignored. Widespread deforestation, agricultural expansion, illegal placer gold mining by local panners, extensive laterite and sand mining are becoming increasingly important in the basin. Human activity probably has been most disruptive to natural erosion processes in the source terrains and river banks where bulk of the population is concentrated. Of the major Chaliyar tributaries draining the Wynad Gold Field, Karim puzha and Punna puzha carry the least mature sands, perhaps human activities have accelerated natural erosion processes, resulting in erosion of deep comparatively less weathered soil horizons. Nevertheless, much of the Chaliyar river drainage basin has remained almost untouched by human activity.

The climate in Kerala is hot and humid, with mean annual temperature of 28.5^{0}C and mean annual rainfall of 300 cm, precipitated mainly during southwest and northeast monsoons (Soman, 1997). Several studies have demonstrated that hot, humid climate can cause accelerated mineralogical and textural maturation of fluvial sand (for example, Basu, 1976; Mack, 1981; James et al., 1981; Suttner et al, 1981 and Johnsson et al, 1988). The data of modal sand composition from Chaliyar main stem is reflective of the intense weathering regime by the near absence of rock fragments in the sand and wide spread occurrence of laterite in the Chaliyar basin. The Chaliyar upper reach sands including major tributaries are compositionally indistinguishable from most lower reach sand samples. This may owe in part to the fact that the Chaliyar basin contains relatively minor proportions of feldspar to begin with, intense tropical weathering and insitu destruction of feldspar does not significantly alter their over-all composition. This is given in table 4.2, which indicates that sands derived directly from headwater regions in three major tributaries (namely Punna puzha, Karim puzha and Chali puzha), and sands in the Chaliyar main channel (upper and lower reaches) derived by mixing and influx from tributaries of sands with variable composition contain approximately identical proportions of feldspar.

4.6 Heavy mineral percentage in sand samples of Chaliyar basin and its downstream variation

The heavy mineral weight percent in the sand samples of major tributaries of the Chaliyar river ranges between 4.8 to 27.57 while it varies between 8.99 to 22.09 in the main stem (Table 4.3) (Fig. 4.4). The mean heavy mineral in sand is 13.59 wt. % for the Chaliyar basin. The spectral pattern shows that after an initial increase between 63-78 km there is a steady, decrease between 78-107 km of the main channel. Beyond this (107 km) in the down stream direction, even though there are few positive anomalies, they generally show a decreasing trend. Towards the mouth of the river the samples show slightly increasing trend which may be due to the action of wave. The positive anomalies and more fluctuating nature of the heavy mineral weight percent in this sector is probably due to the influx of tributary sediments and the hydrodynamic variations respectively. The absence of any similarity in the spectral pattern between heavy mineral weight percent in sand and dense minerals like opaques, garnet, hornblende and hypersthene in the +35 ASTM size (compare Fig 4.3c, d, e, f and Fig. 4.4) suggests that these dense minerals and its contribution of total heavy mineral content in Chaliyar main stem samples is not clear. This also points that the heavy minerals are mainly seen in medium sand and below fractions. Even though as mentioned earlier the spectral variation pattern of heavy mineral and light heavy mineral especially between 63-107 km show some similarities (decreasing trend) probably indicating that hornblende is having some control over the heavy mineral content in samples. This has been supported by the fact that hornblende is the second highest mineral present in the modal sand composition in the Chaliyar basin after quartz. It is interesting to note that among the upper reach samples in the main stem (63-107 km), H-2 sample has the highest heavy mineral content (18.49 wt.%), low mean size (0.99 ∅ - coarse sand), poor sorting, second lowest gold value (0.09 ppm) and is 7 km upstream from H-3 having high mean size (1.42 ∅), well sorted nature and highest gold concentration (0.53 ppm) even though its heavy mineral content is only 14.26 wt %. The factors controlling the Au concentration are discussed in chapter 7.

The light mineral content in the sand samples of the Chaliyar basin averages 86.65 wt.% and the heavy to light mineral ratio averages 0.16 (Table 4.3). The heavy mineral to sand ratio averages 0.15 (Table 4.3) in the samples of the Chaliyar basin and it is almost same as that of average heavy to light mineral ratio. This signifies that the entire heavy mineral is seen in the sand fraction (1 to 4 ∅ - very coarse sand to very fine sand) of the Chaliyar basin sediments.

4.6.1 Bivariate plots

Figures 4.5a & b depict scatter plots of phi-mean size standard deviation versus heavy mineral percentage respectively in the sediment samples of Chaliyar basin. Phi mean size versus heavy mineral percentage (Fig. 4.5a) show linear, though weak, relationship. As the phi mean size increases the weight percent of heavy mineral also increases which implies that coarser fraction has low heavy mineral content while the finer will have higher even though majority of the samples in the Chaliyar basin have a phi mean size in the coarse sand category followed by medium sand. The standard deviation versus heavy minerals (Fig. 4.5b) also shows that the heavy mineral percentage decreases as the sorting worsens. This relationship is shown especially by the samples in the Chaliyar main stem. Downstream variation of sand and heavy mineral/sand ratio in the sediments of Chaliyar river is depicted in figure 4.6. It shows that in the upper reaches (63-107 km), after an initial increase there is a steady decrease in the ratio even though the samples are cent percent sand. Beyond the 107 km mark in the downstream direction curves show almost an opposite trend. In other words wherever there is a decrease in the sand content there is a corresponding increase in heavy mineral/sand ratio implying that samples having low content of sand are enriched in heavies; conversely samples having comparatively low percentage of sand are depleted in light minerals.

4.7 Correlation and mineralogical maturity of basin sediments

The concept of textural and mineralogic maturity for sand and sandstones stems from the broader concept of sedimentary differentiation. The progressive elimination and segregation by weathering and transport of minerals unstable at the earth's surface so that the end product of the weathering and transport of granitic colluvium is a well rounded and well sorted sand of unitary quartz that lacks clay matrix and mostly consists of heavy minerals.

A correlation matrix between individual minerals in different samples with respect to total heavies in sand, gold concentration and mean size is worked out to delineate the relationships (Table 4.4) existing between them. Table 4.4 shows significant positive and negative loadings especially between major heavy mineral components. Total content of heavy minerals in sand is positively correlated with hypersthene, biotite and rutile although only weakly so, 0.09, 0.17 and 0.48 respectively (see Table 4.4). It is moderately well correlated with light heavy mineral hornblende, 0.59. On the other hand, negative correlation occurs between total heavy mineral in sand on the one hand and opaques, between total heavy minerals in sand and garnet and between total heavy minerals in sand and quartz and between total heavy minerals in sands and feldspar. The increase in the content of the lighter heavy minerals with the increase of total heavies in sand illustrates a high energy regime required for the selective sorting of these minerals. The depletion of opaques and garnet with the increase of total heavies in sand manifests that these dense heavy minerals are not transported along with the light heavy minerals in the sediments (mainly hornblende and hypersthene) which implies that the river flow is not competent to transport denser heavy minerals. At the same time the negative correlationship between light heavy minerals and light minerals (mainly quartz and feldspar) suggest that the river flow is not only incompetent to transport denser heavy minerals but also light heavy minerals. This is further evidenced from negative correlation of quartz and feldspar with almost all the heavy minerals except between quartz and biotite, between feldspar and opaques between feldspar and rutile it is positive. The positive correlation of hornblende and hypersthene (r=0.24) and negative relationship between hornblende and opaques (r=-0.34), and between hypersthene and opaques (r=-0.34) re-affirms the above view. As expected, total heavy mineral content in sands is positively correlated with phi mean size. It is interesting to note that gold concentration in the Chaliyar river sediments is negatively correlated with total heavies in sand (r=-0.01), positively correlated (weakly) with quartz (r=0.15) and phi mean size (r=0.19). The highest positive correlation however, is between garnet and rutile, 0.73. Opaques exhibits a positive relation with phi mean size implying its rich availability in the coarser fractions while garnet exhibits a negative relationship with mean size implying its poorer availability in the coarser fractions.

Figure 4.7a & b illustrates the percentage variation of normative quartz and feldspar in the quartz + feldspar (+35 ASTM size) fraction respectively in the Chaliyar main stem samples. It is seen that between 63-107 km there is a slight increase in the quartz content in the downstream direction. Beyond this (107 km) in the lower reaches the percentage of quartz show a slight declining trend with high fluctuations in normative quartz percentage probably indicating the influx of quartz rich or quartz poor sediments from the downstream tributaries. In addition to this the average modal %QF=94,6 for the upper reach samples (63-107 km) and average %QF=91,9 for the samples below 107 km. This also indicates a slight decrease in the maturity of sediments samples in the lower reaches even though the average %QF=92,8 which almost similar to the %QF=91,9 in the lower reaches. This decrease in maturity is attributed to the mixing of comparatively more mature upper reach samples (63-107 km) with that of the less mature downstream samples (beyond 107 km). But the near absence of rock fragments in main stem samples is particularly notable and this may result from abrasion, dilution by streams that enter the Chaliyar main stem. Such a decrease is probably most apparent in the sands of tropical, low relief rivers where opportunities for weathering on the flood plain are maximal (Potter, 1978). Researchers have postulated intrastratal weathering in alluvium; which Bradley (1970) suggest it for modern gravels in Central Texas and Qalker et al. (1978) document it in alluvium of adjacent parts of Mexico and the United States. Even though Chaliyar basin experience tropical climate the extent to which the weathering of alluvium on the floodplains and intrastratal weathering has contributed to the mineralogical maturity of sand in the main stem may not be significant because majority of the west flowing rivers especially in Kerala are short flowing, having high gradient/slope and experiences heavy rainfall.

In sum, the near absence of rock fragments, negative correlation between quartz and feldspar and weak positive correlation between phi mean size and total heavy minerals in sand gives an idea about the textural and mineralogical maturity of modern small river sands. Thus total quartz (unitary + poly), total heavy minerals in sand and phi mean size form a tightly correlated array of maturity variables which show that the sands of modern small river systems reflect the process of sedimentary differentiation whose end product is a mature, essentially quartzose sand. The grains may not be well rounded because of shorter distance of transport. Because these sediment samples from Chaliyar river and its major tributaries sample some 40-45 % of the whole drainage basin, the correlations of table 4.4 are probably a reasonable estimate for the whole basin.

4.8 Clay mineralogy

As detailed in the previous chapter (section 3.8) in the sediment samples from locations close to the Chaliyar estuary considerable amounts of clays are noticed. Mineralogically they contain the clay group minerals as well as oxide and hydroxide minerals derived from weathering zone.

Physical techniques are of limited application to study the oxide phases. X-ray diffractometry (XRD) is not sensitive to phases present in amounts smaller than 3-5%, and the particle size of most natural oxides (< 100 nm) is smaller than the spatial resolution of electron microprobe analysis (Eggleton, 1988). In lateritic environments, iron oxides, i.e., gibbsite, goethite, hematite, and maghemite, typically contain a larger proportion of metal than any other mineral constituents. With the above limitations in the analytical techniques in identifying the oxides, an attempt is made to study the clay mineralogy of selected sediment samples (see chapter 2 section 2.6.4 for clay separation technique, analytical conditions and clay identification) from Chaliyar river and the nature of possible source rocks from which they are derived. The relative importance of clay minerals in controlling the chemistry of Chaliyar bedload sediments is also discussed in the subsequent chapters.

The XRD analysis of clay sized fractions from selected samples indicates that the minerals present in them are mainly kaolinite, chlorite, gibbsite, goethite, quartz and trace amounts of illite (Fig. 4.8 for XRD pattern and sample number). This clearly indicates that the source area is highly weathered and possibly of feldspar rich parent rock. Presence of iron rich clay minerals like gibbsite and goethite is due to lateritization processes and trace amounts of illite in some of the samples may be due to transformation or replacement of kaolinite in the saline environment. Chlorite is formed by the alteration of hornblende which is abundant in the metamorphic rock, gneiss.

Conclusions

- The Chaliyar basin sands are quartzose. The quartz and feldspar contents in the sediment samples of 0.5 to 1.0 Ø size fraction (coarse sand) of the Chaliyar basin range from 64 to 86% and 2 to 16% respectively. The quartz percentage in the Chaliyar main stem averages 76.4%. In the tributaries also it is almost similar and averages 74%. The Q/F ratio ranges from 4 to 38 with a slight decrease in the lower reaches. In the lower reaches the quartz percentage show a declining trend with high fluctuations in [(Q/Q+F)*100]. Other minerals present include hornblende (average: 7.5%), pyroxene (average: 1.1%) and heavy minerals like opaques (average: 5.9%), garnet (average: 2.2%), rutile (average: 0.2%) and biotite (average: 0.4%). Sphene, silliminite, zircon, apatite and monazite are mainly seen as inclusions in quartz. The above mineral suites indicate a high grade metamorphic provenance. The coarse sands are almost devoid of rock fragments and the sediments have a sub-arkose affinity.

- The mineralogical diversities and variation along the profile of the Chaliyar river could be explained mainly by progressive sorting based on densities and shapes of the individual minerals in the upper reaches (63-107 km) while in the lower reaches beyond 107 km it is mainly due to mixing of sands from tributaries having different compositions.
- The remarkable consistency of mixing patterns as evidenced from rough theoretical or expected average composition of sand (%QF=92,8) for the whole river basin, with that of the actual average composition for the main channel (%QF=92,8) suggests that fluvial sands from major rivers in the basin may indeed retain a traceable signature of their compositional "lineage".
- The headwater tributaries drain through areas underlain by gneisses and charnockites while the downstream tributaries in the lower reaches drain areas almost exclusively underlain by charnockites. Hence the principal control on sand composition in the Chaliyar main stem is from source lithology.
- The heavy mineral weight percent in the bulk sediments of the main stem varies from 8.9 to 22.0 and from 4.8 to 27.5 in major headwater tributaries. The mean heavy mineral content in sand is 13.5 wt.% for the whole basin. Plot of sand content against heavy mineral/sand ratio in the lower reaches of the Chaliyar river indicates that samples having low content of sand are enriched in heavies and depleted in light minerals.
- The near absence of rock fragments, negative correlation between quartz and feldspar and weak positive correlation between phi mean size and total heavy minerals in sand suggest that they form tightly correlated array of textural and mineralogical variables and in turn indicate high degree of sedimentary differentiation in the Chaliyar basin.
- The clay minerals like kaolinite, gibbsite, goethite and iron-oxides in sediments suggest weathering of feldspar-rich parent rocks and lateritization processes in the Chaliyar basin.

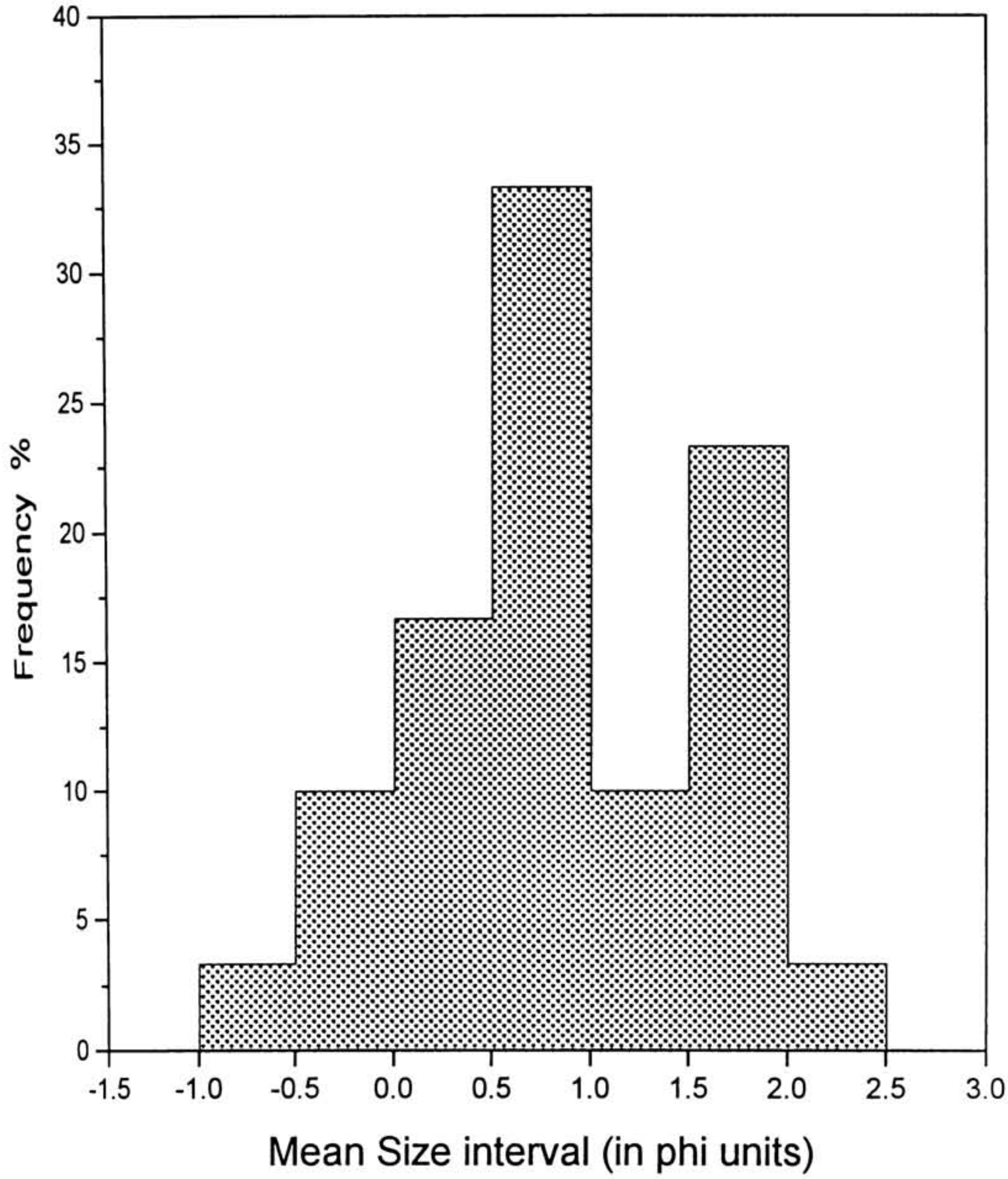


Fig.4.1 Frequency distribution of mean size in the Chaliyar river sediments

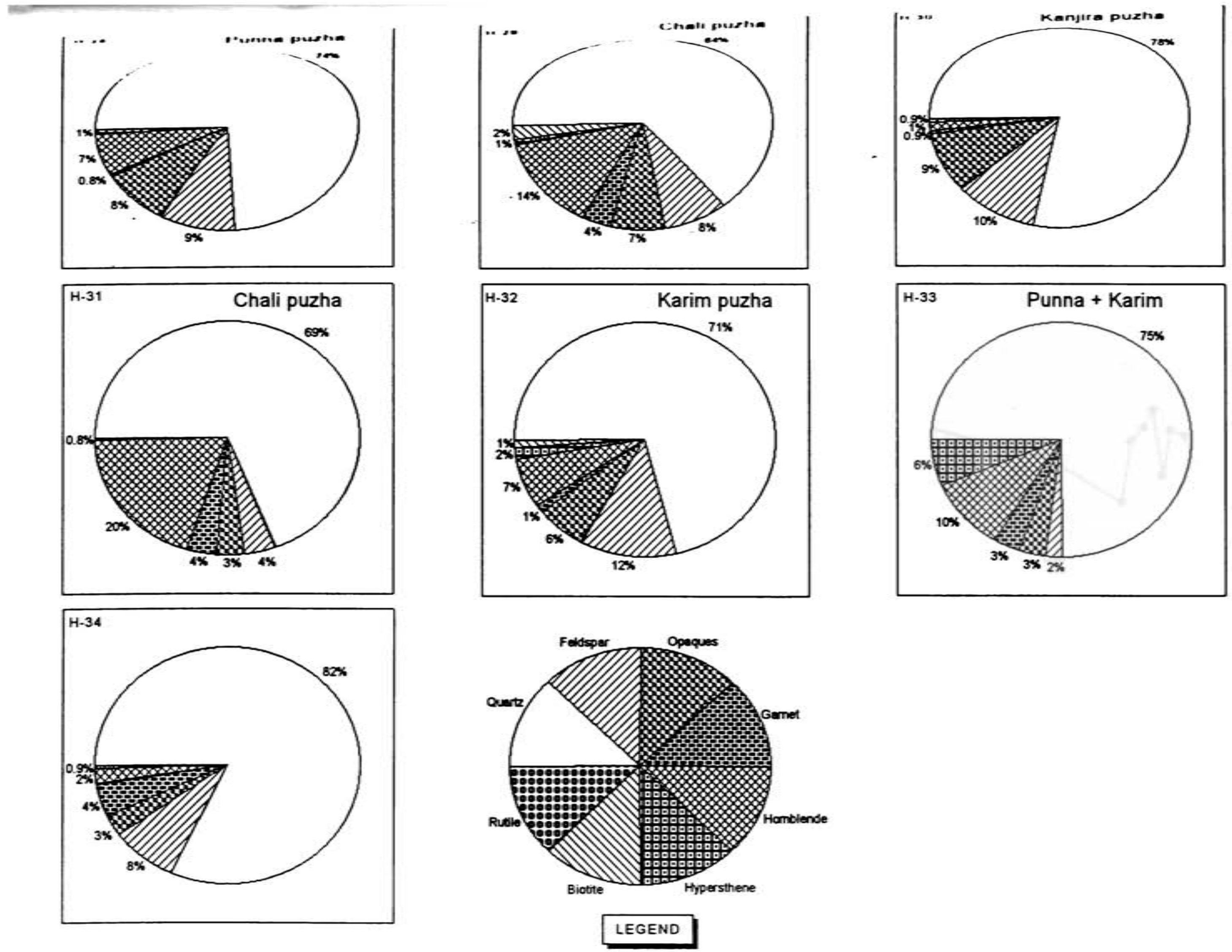


Fig. 4.2 Pie diagrams showing percentage variation in mineral contents in the sediment samples (+35 ASTM) of the major tributaries of Chaliyar river

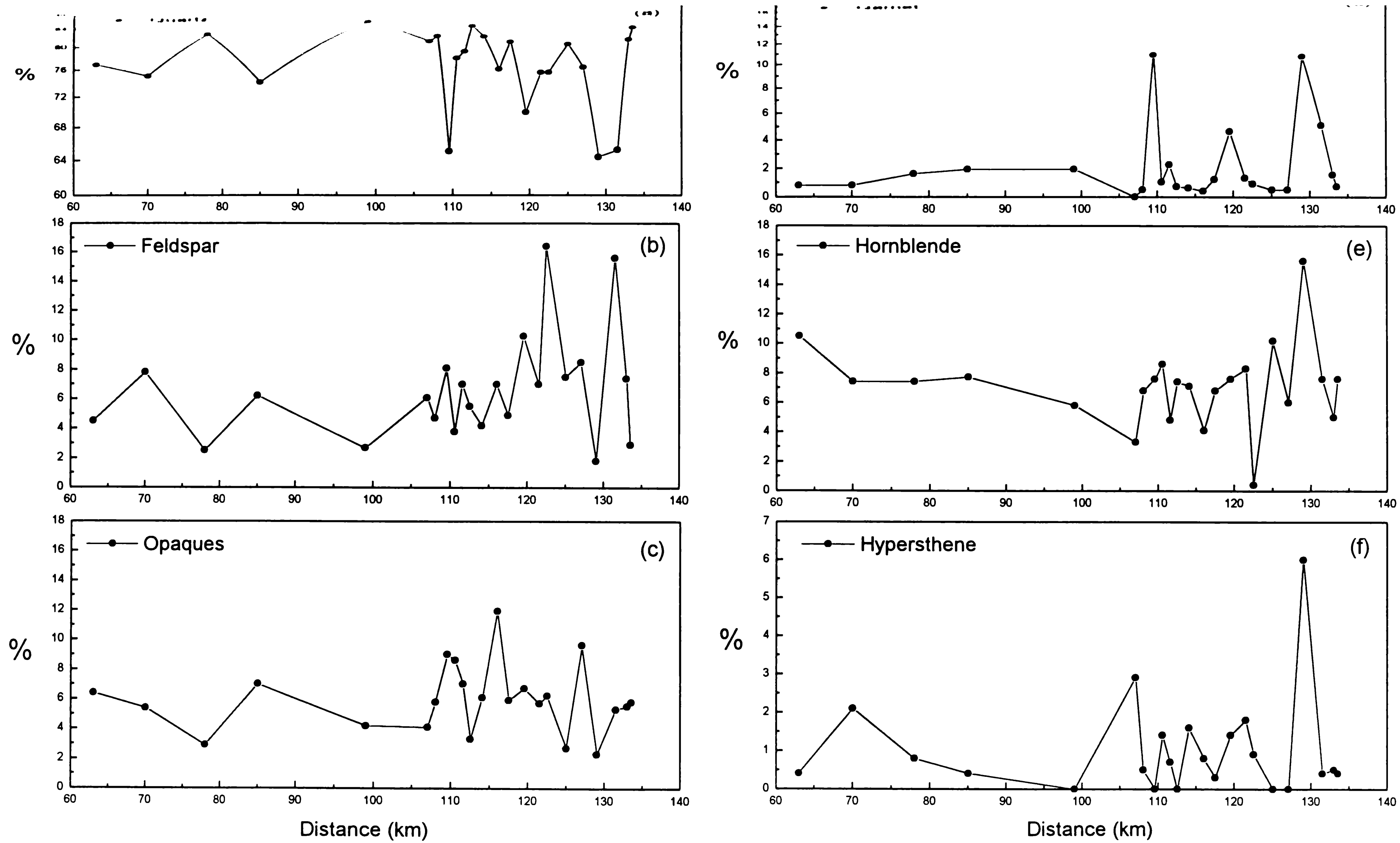


Fig.4.3 Down stream variation of various mineral contents (+35 ASTM size) seen in the sediment samples of Chaliyar main stem

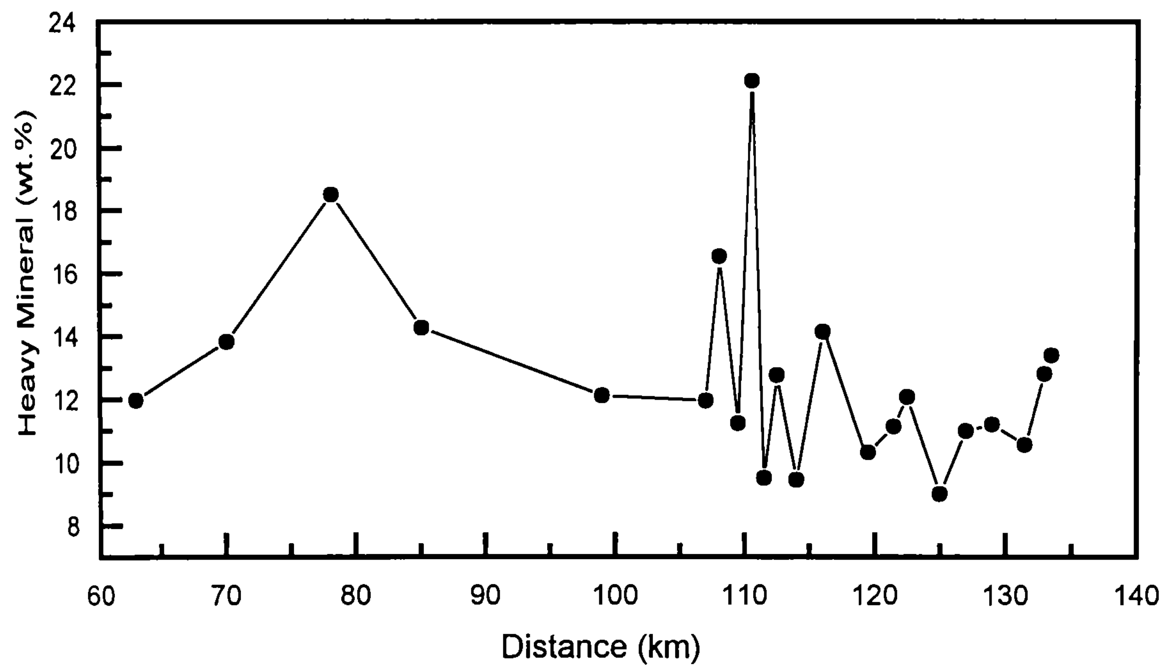


Fig.4.4 Down stream variation of heavy mineral percentage in sand in the Chaliyar main channel

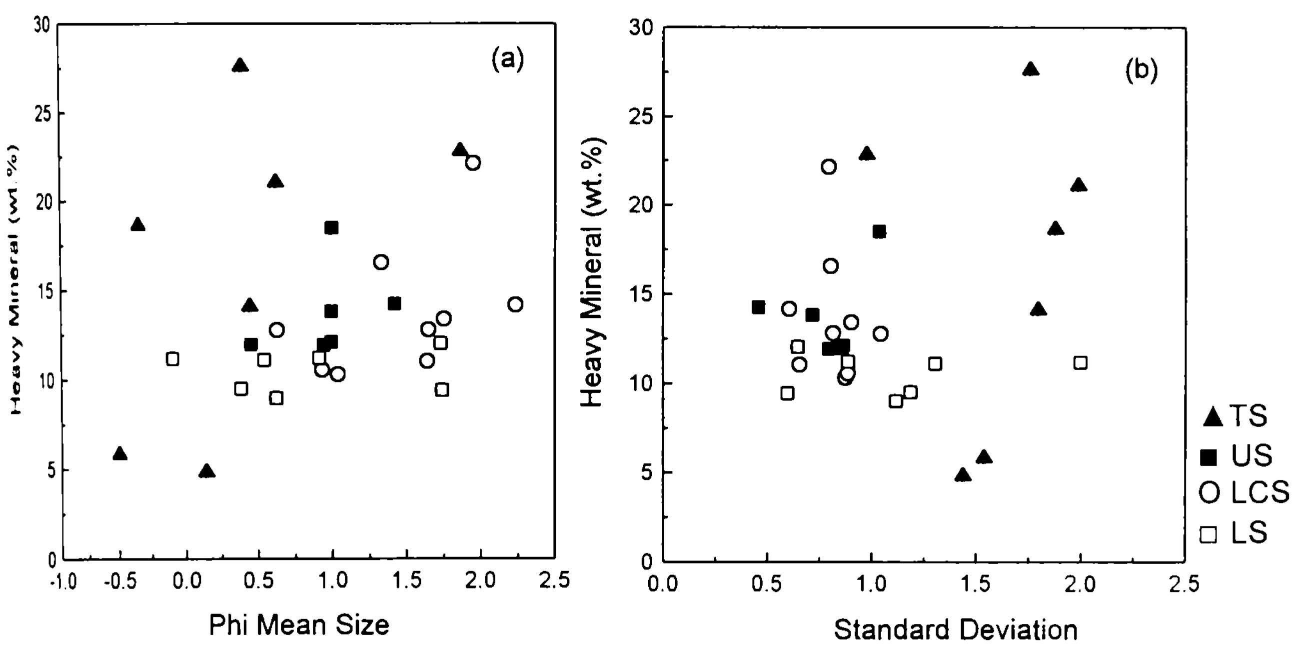


Fig.4.5 Bivariet plot showing relationship between heavy mineral percentage and textural parameters (phi mean size and standard deviation)

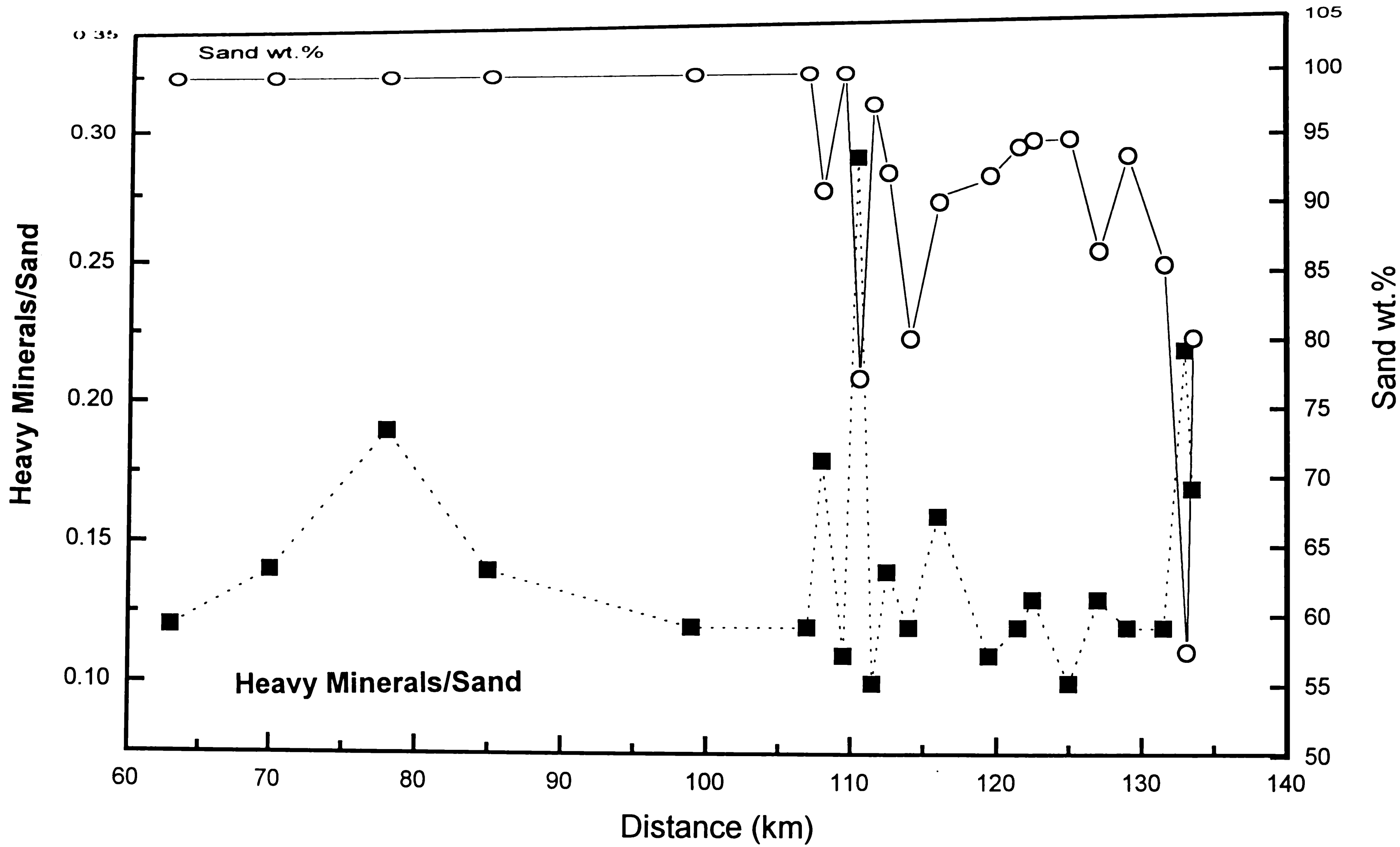


Fig.4.6 Down stream variation of sand and heavy mineral/sand ratio in the sediments of Chaliyar river

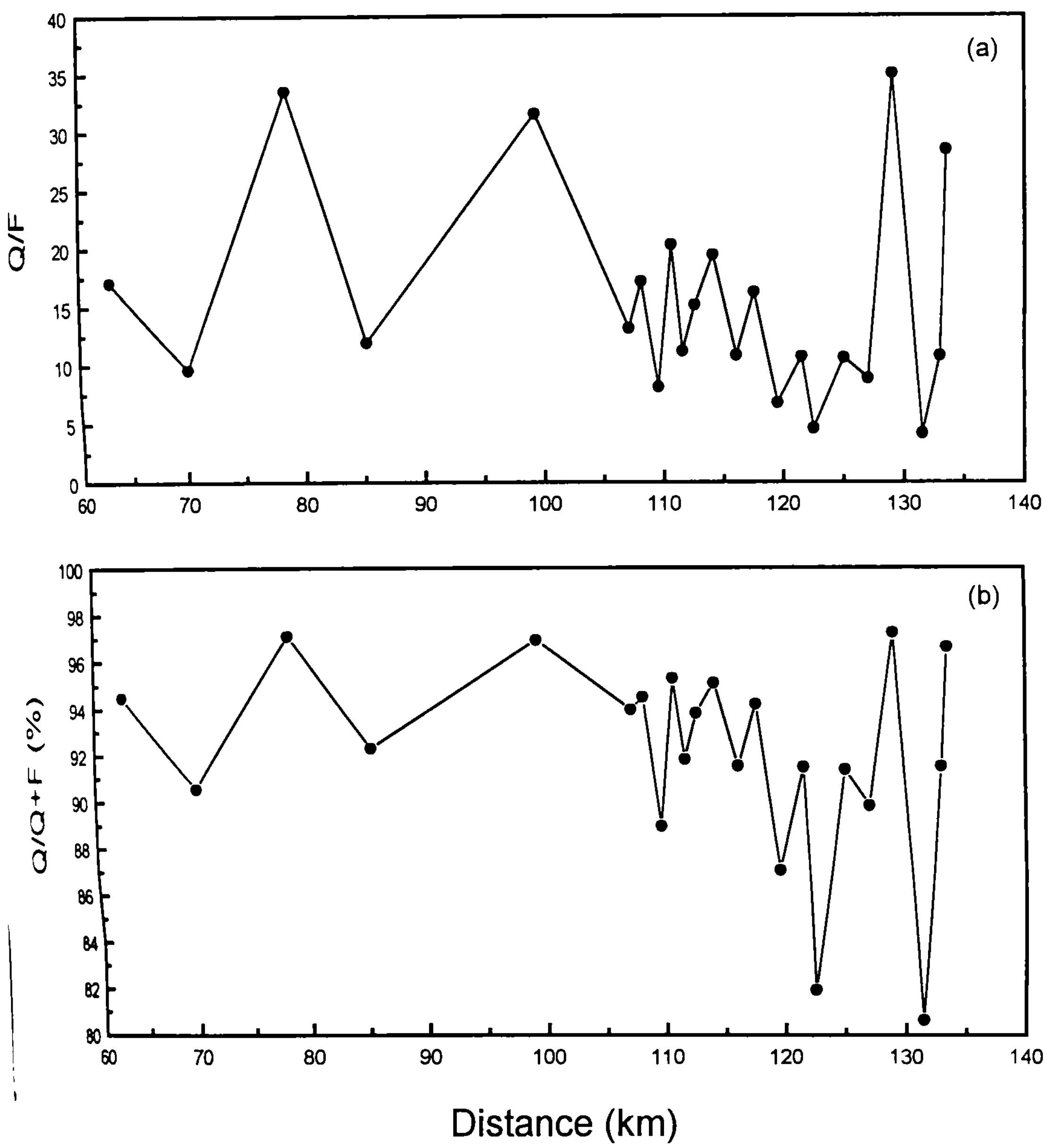


Fig.4.7 (a) Q/F ratio and (b) percentage of normative quartz in the quartz+feldspar (+35 ASTM size fraction) of Chaliyar river main stem samples

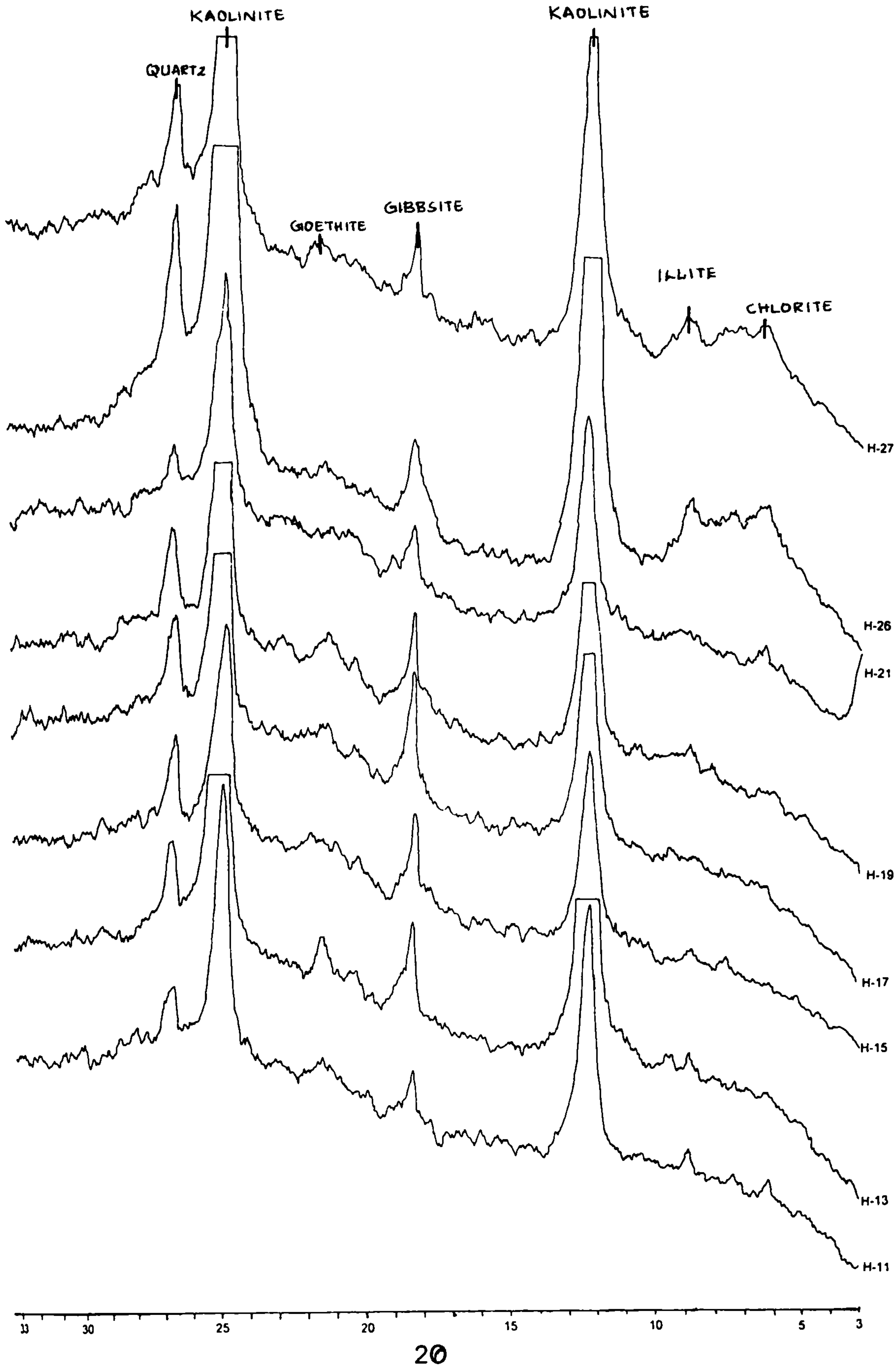


Fig. 4.8 XRD patterns of clay minerals

Table 4.1. % distribution of minerals (assessed by point counting of grain mounts) in the five samples (bulk sand)

Sample No.	H-1	H-2	H-3	H-4	H-5
Quartz	53	57	66	64	71
Feldspar	35	30	26	24	17
Opaques	8	8	5	6	9
Garnet	2	2	1	3	1
Rutile	1	1	1	2	3
Ferromagnesium minerals	1	2	1	1	1
Zircon	✓	✓	✓	✓	✓
Monazite	–	✓	–	✓	✓
Sillimanite	✓	✓	–	–	✓

(✓ mark indicates the presence in trace amounts)

Table 4.2 Modal composition of +35 ASTM size fraction of Chaliyar river sediments expressed in % (assessed by grain counting method)

Sample No.	Distance (km)	Quartz	Feldspar	Opaques	Garnet	Hornblende	Hypersthene	Biotite	Rutile	Sphene	Sillimanite	Monazite	Zircon	Apatite	%QFR
		Mineral %								(✓ indicates presence in trace amounts)					
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
H-35	63.0	76.8	4.5	6.4	0.8	10.5	0.4	0.8	✓	✓	✓	–	✓	–	95,5,0
H-1	70.0	74.9	7.8	5.4	0.8	7.4	2.1	1.7	✓	–	✓	✓	✓	–	91,9,0
H-2	78.0	82.4	2.5	2.9	1.6	7.4	0.8	2.1	0.4	–	–	✓	✓	–	97,3,0
H-3	85.0	73.8	6.2	7.0	1.9	7.7	0.4	2.7	0.4	–	✓	✓	✓	–	92,8,0
H-4	99.0	84.7	2.7	4.2	1.9	5.8	-	0.8	✓	✓	✓	–	–	–	97,3,0
H-5	107.0	80.1	6.1	4.1	-	3.3	2.9	-	✓	–	✓	–	✓	–	93,7,0
H-11	108.0	81.1	4.7	5.8	0.5	6.8	0.5	0.5	-	–	✓	–	✓	✓	95,5,0
H-12	109.5	64.9	8.1	9.0	10.4	7.6	-	✓	✓	✓	✓	–	✓	✓	89,11,0
H-13	110.5	77.1	3.8	8.6	1.0	8.6	1.4	-	✓	–	✓	–	–	–	95,5,0
H-14	111.5	78.2	7.0	7.0	2.2	4.8	0.7	✓	✓	–	✓	✓	✓	✓	92,8,0
H-15	112.5	83.1	5.5	3.3	0.7	7.4	-	-	-	–	✓	–	–	–	94,6,0
H-16	114.0	80.8	4.2	6.1	0.6	7.1	1.6	-	✓	–	✓	✓	✓	✓	95,5,0
H-17	116.0	75.3	7.0	11.9	0.4	4.1	0.8	-	0.4	–	✓	✓	✓	–	91,9,0
H-18	117.5	79.7	4.9	5.9	1.2	6.8	0.3	0.3	0.9	–	✓	–	✓	✓	94,6,0
H-19	119.5	69.5	10.3	6.7	4.5	7.6	1.4	-	✓	–	✓	✓	✓	✓	87,13,0
H-20	121.5	74.7	7.0	5.7	1.3	8.3	1.8	1.3	-	–	✓	✓	✓	–	91,9,0
H-21	122.5	74.7	16.4	6.2	0.9	0.4	0.9	-	0.4	–	✓	–	–	–	82,18,0
H-22	125.0	79.1	7.5	2.7	0.5	10.2	-	-	✓	–	✓	–	✓	–	91,9,0
H-23	127.0	75.4	8.5	9.6	0.5	6.0	-	✓	✓	✓	–	–	✓	–	90,10,0
H-24	129.0	64.2	1.8	2.3	10.1	15.6	6.0	-	✓	–	✓	–	–	–	97,3,0
H-25	131.5	65.0	15.6	5.3	4.9	7.6	0.4	-	1.1	–	–	✓	✓	✓	81,19,0
H-26	133.0	79.7	7.4	5.5	1.5	5.0	0.5	-	0.5	–	✓	✓	✓	–	92,8,0
H-27	133.5	82.0	2.9	5.8	0.7	7.6	0.4	0.7	-	✓	✓	✓	✓	✓	97,3,0
H-28 T		74.2	9.3	8.5	0.4	6.9	0.8	-	✓	–	✓	✓	✓	✓	89,11,0
H-29 T		64.3	8.0	6.7	3.7	14.0	-	1.0	2.3	–	–	–	✓	–	89,11,0
H-30 T		78.5	10.3	8.9	0.5	1.4	-	-	0.5	✓	✓	✓	✓	–	88,12,0
H-31 T		69.1	3.9	3.4	3.6	19.7	0.3	-	✓	✓	✓	✓	✓	✓	95,5,0
H-32 T		70.8	12.0	6.3	1.0	6.8	1.6	1.0	✓	–	✓	–	✓	–	86,14,0
H-33 TC		75.0	2.0	3.4	3.4	9.8	6.4	-	✓	–	✓	–	✓	–	97,3,0
H-34 T		86.4	8.4	3.1	4.7	2.1	0.5	✓	✓	✓	✓	✓	✓	–	91,9,0
Mean		75.9	6.9	5.9	2.3	7.5	1.4	1.2	0.8						92,8,0

Table 4.3 Heavy mineral weight persent in sand and Q:F ratios in the Chaliyar river sediments

Sample No.	Distance (km)	Heavy Mineral (wt.%)	Light Mineral (wt.%)	Q/F	Q/Q+F (%)	Mean Size	S.D.	H.M./L.M. (3/4)	H.M./Sand
1	2	3	4	5	6	7	8	9	10
H-35	63.0	11.95	88.05	17.08	94.47	0.45	0.86	0.14	0.12
H-1	70.0	13.82	86.18	9.58	90.55	0.99	0.72	0.16	0.14
H-2	78.0	18.49	81.51	33.50	97.10	0.99	1.04	0.23	0.19
H-3	85.0	14.26	85.74	11.94	92.27	1.42	0.46	0.17	0.14
H-4	99.0	12.11	87.89	31.57	96.93	0.99	0.87	0.14	0.12
H-5	107.0	11.93	88.07	13.13	93.93	0.94	0.80	0.14	0.12
H-11	108.0	16.53	83.47	17.11	94.48	1.33	0.81	0.20	0.18
H-12	109.5	11.23	88.77	8.06	88.96	0.91	0.89	0.13	0.11
H-13	110.5	22.09	77.91	20.25	95.29	1.95	0.80	0.28	0.29
H-14	111.5	9.49	90.51	11.16	91.78	0.38	1.19	0.11	0.10
H-15	112.5	12.74	87.26	15.07	93.78	0.63	1.05	0.15	0.14
H-16	114.0	9.42	90.58	19.39	95.09	1.74	0.60	0.10	0.12
H-17	116.0	14.15	85.85	10.77	91.50	2.24	0.61	0.17	0.16
H-18	117.5	N.D.	N.D.	16.19	94.18	-0.27	1.10	N.D.	N.D.
H-19	119.5	10.29	89.71	6.74	87.08	1.04	0.88	0.12	0.11
H-20	121.5	11.12	88.88	10.69	91.44	0.54	1.31	0.13	0.12
H-21	122.5	12.05	87.95	4.54	81.95	1.73	0.65	0.14	0.13
H-22	125.0	8.99	91.01	10.57	91.36	0.62	1.12	0.10	0.10
H-23	127.0	10.99	89.01	8.82	89.82	1.64	0.66	0.12	0.13
H-24	129.0	11.18	88.82	35.00	97.22	-0.10	2.00	0.13	0.12
H-25	131.5	10.54	89.46	4.17	80.66	0.93	0.89	0.12	0.12
H-26	133.0	12.80	87.20	10.73	91.48	1.65	0.82	0.15	0.22
H-27	133.5	13.40	86.60	28.38	96.60	1.75	0.91	0.16	0.17
H-28 T		14.07	85.93	8.00	88.89	0.44	1.80	0.16	0.15
H-29 T		22.80	77.20	8.04	88.94	1.86	0.98	0.30	0.24
H-30 T		5.79	94.21	7.64	88.42	-0.50	1.54	0.06	0.06
H-31 T		27.57	72.43	17.73	94.66	0.37	1.76	0.38	0.29
H-32 T		21.03	78.97	5.91	85.54	0.61	1.99	0.27	0.23
H-33 TC		18.60	81.40	38.25	97.45	-0.35	1.88	0.23	0.19
H-34 T		4.80	95.20	10.31	91.16	0.14	1.44	0.05	0.05
Mean		13.59	86.41	15.01	91.77	0.90	1.08	0.16	0.15

Table 4.4 Correlation between key petrographic variables, total heavy minerals in sand, gold concentration and mean size in the Chaliyar river basin

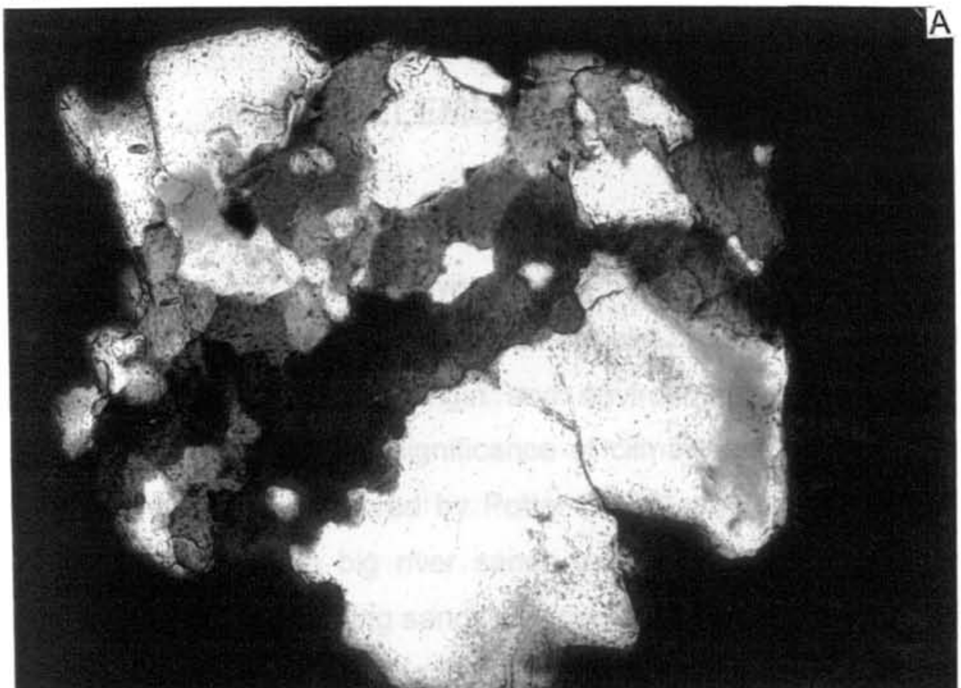
	HMs	Qtz	Feld	Op	Ga	Horn	Hy	Bi	Ru	Au	Mz
HMs	1.00										
Qtz	-0.30	1.00									
Feld	-0.27	-0.33	1.00								
Op	-0.05	-0.20	0.32	1.00							
Ga	-0.06	-0.62	-0.03	-0.18	1.00						
Horn	0.59	-0.52	-0.44	-0.34	0.39	1.00					
Hy	0.09	-0.23	-0.31	-0.34	0.31	0.24	1.00				
Bi	0.17	0.05	-0.15	-0.05	-0.11	0.04	-0.15	1.00			
Ru	0.48	-0.75	0.29	0.12	0.73	0.50	-0.40	-0.01	1.00		
Au	-0.01	0.15	-0.16	-0.09	-0.12	-0.12	-0.03	0.63	-0.10	1.00	
Mz	0.22	0.00	0.11	0.41	-0.25	-0.14	-0.32	0.13	0.10	0.19	1

HMs - Heavy mineral wt.% Qtz -Quartz Feld - Feldspar Op - Opaques Ga - Garnet

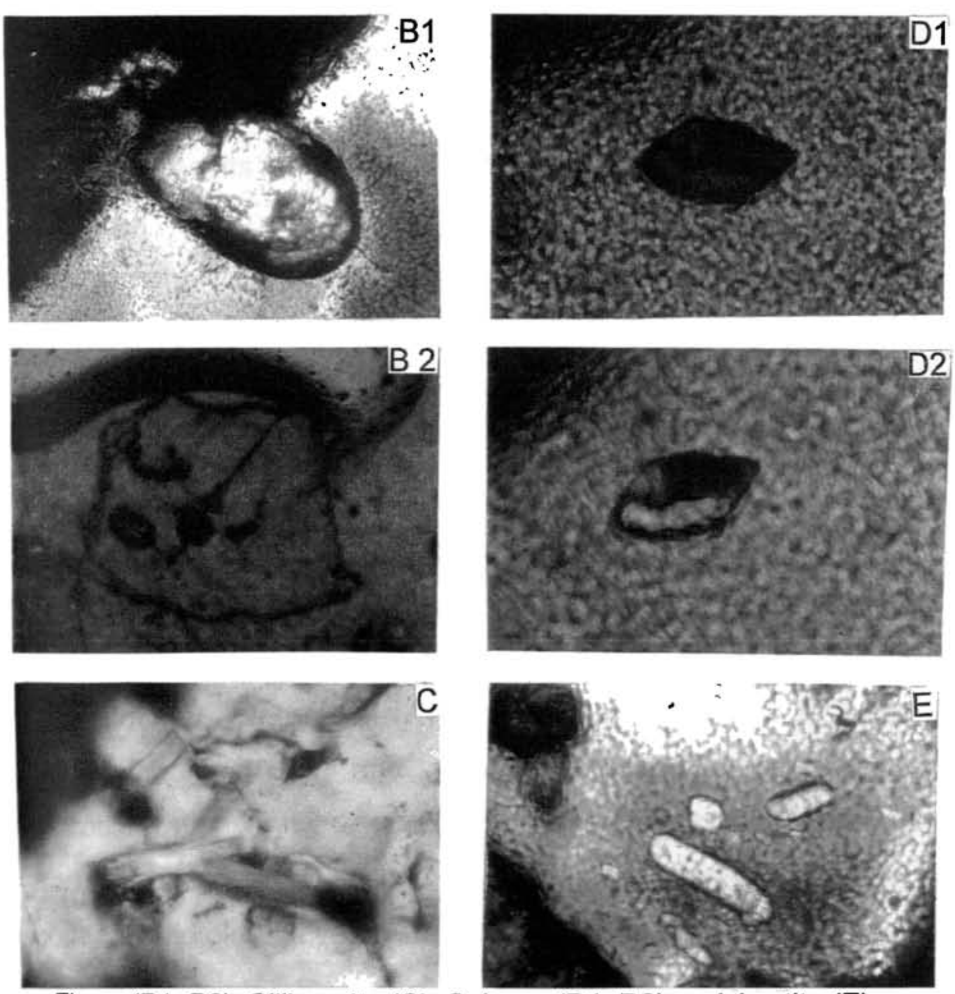
Horn - Hornblende Hy - Hypersthene Bi - Biotite Ru - Rutile

Au - Gold Mz - Mean size

Plate 4.1



(A) Polycrystalline Quartz (X125)



Zircon (B1, B2), Sillimanite (C), Sphene (D1, D2) and Apatite (E) inclusions within Quartz.A, B 1, C, D 2 and E under crossed nicols; B2 and D1 under open nicols. (B1, D1, D2 & E : X 250; B2:50; C: X125)

Chapter 5
MAJOR ELEMENT GEOCHEMISTRY

5.1 Introduction

Composition of modern river sands, has been studied by sedimentary petrologists to relate composition to, source rocks, relief, climate and tectonics and sometimes to understand the origin and environment of deposition of ancient sandstones. For example, the significance of climate and geologic controls on big river systems has been explored by Potter (1978) who examined the petrography and chemistry of modern big river sands to evaluate some current problems in sedimentary petrology including sandstone composition. Albarede and Semhi (1995) carried out geochemical investigation of on three sand size fractions from the Meurthe river and its tributaries and brought out the tight control of the bedrock geology on the geochemistry of the bedload. Dupre et al. (1996) studied the chemical composition of different phases carried in the Congo river. Vital et al. (1999) successfully utilized clay as well as heavy mineral fractions to deduce provenance. Based on the results of the study on geochemistry of sediments of lowermost Amazon river, Vital and Stattegger (2000) opined that chemical weathering processes strongly modify original sediment composition and can be recognized on the basis of their geochemical signature. Chandrajith et al. (2000) carried out regional geochemical and mineralogical study on different size fractions of stream sediments in order to understand the mineralization and provenance in the Walawe Ganga river basin in Sri Lanka.

Geochemical data collected in the surficial environment may reflect the influence of several sources and factors. Chemical elements in stream sediments may be found as constituents of primary rock-forming minerals, of minerals formed during weathering, of minerals typical of mineralization, of ions adsorbed onto colloidal particles and clays and in combination with organic matter (Rose, 1975). The characterization of these sources is dependent on the materials collected and analysed. These chemical elements can be removed from continental crust and transported by the global river system to the ocean in essentially three ways:

1) Reaction of groundwater with crustal rocks and soils (weathered material).
2) Small particles and flocs predominantly of clay minerals and oxyhydroxides, typically smaller than a few μm and are buoyant enough to be transported continuously to the sea.
3) Larger particles like silts, sands and gravels of the bottom river sediments (bedload), that have much more irregular patterns of downstream motion controlled by the local energy of the flow, inputs from tributaries and their variation in time (floods).

The above three modes of transport namely dissolved load, suspended load and bedload, grade into one another and the transitions depend upon the hydrological conditions of each river. Chemical compositions of suspended and bedloads are distinct enough (Stallard and Edmond, 1983) that they should not be considered as hydrodynamically distinct samples of the same material. How the contributions of each transport mode to the ocean compare to each other is only partially understood. Bedload sediment discharge is deemed to represent not more than 10% of the suspended load (Meade, 1981) but the data substantiating this estimate are still fragmentary (Milliman and Meade, 1983; Albarede and Semhi, 1995). Geochemists have extensively studied the major rivers of the world in order to estimate fluxes of continental material supplied to the oceans (Potter, 1978; Martin and Whitfield, 1983; Milliman and Meade, 1983; Meybeck, 1988).

Studies by Blatt (1967), Ruxton (1970), Cameron and Blatt (1971), Suttner (1974), Basu (1976, 1985), Potter (1978), James et al. (1981), Suttner et al. (1981), Franzinelli and Potter (1983), Mack (1984), Velbel (1985), Dutta and Suttner (1986), Suttner and Dutta (1986), Grantham and Velbel (1988), Johnsson et al. (1991) have found that source-rock composition, climate, relief, slope, vegetation and dynamics of the fluvial environment all play important roles in controlling the composition of fluvial sand. Study of modern river sand can elucidate the relative importance of processes controlling the composition of sand in the geologic record. An advantage of studying modern sand is that their source rocks and physiographic and climatic characteristics of the source regions can be unambiguously correlated.

Data from smaller river basins are simpler and more useful in studying the above discussed factors. The headwaters of the major tributaries of the Chaliyar river lie in a single physiographic province and are underlain by limited ranges of rock types. Similarly the low degree of variability in geology and to certain extent geomorphology of the drainage basin allows the examination of processes occurring in different environments viz., tributaries, upper and lower reaches of the Chaliyar main channel and their relative importance in controlling the bedload chemistry.

5.2 Previous work

The classic studies by Russell (1937) on sands of the Mississippi River system, by Friberg (1970) of sands in the Ohio River drainage, or DeCelles and Hertel (1989) on the petrology of sands derived from a fold-and-thrust belt in the Madre de Dios River drainage basin in Peru and Bolivia, and of Johnsson et al. (1991) on sands of the Orinoco River drainage basin, Venezuela and Colombia are some of the important works on fluvial sand. Nevertheless, it is only through Franzinelli and Potter's studies of sands in the Amazon River system (Franzinelli and Potter, 1983, 1985; Potter and Franzinelli, 1985) that we have gained a basin-wide perspective on sand composition throughout a large, varied drainage system. Potter (1978) also studied sands of many of the world's modern big rivers to provide a world wide baseline of their petrology and chemistry.

The geochemistry of sediments of the Indian rivers has received wide attention in the recent past (e.g. Borole et al., 1982; Subramanian et al., 1985; Seralathan, 1987; Ramesh et al., 1990; Biksham et al., 1991; Jha et al., 1997; Konhauser et al., 1997; Singh, 1999) to understand the elemental composition of the sediments, the influence of anthropogenic activities on riverine chemistry and the transport of metals from rivers to the coastal oceans. A comprehensive review of environmental geochemistry of Indian river basins is that of Subramanian (1987). Mass transfer studies of geochemical constituents in Indian rivers have been activated by researchers like Subrâmanian (1980), Sarin and Krishnaswami (1984), Sitasawad (1984), Seralathan and Seetharamaswamy (1987) and Chakrapani and Subramanian (1990). The geochemical transfer of metals through Cauvery river has been carried out intensively by Seralathan (1979), Subramanian et al. (1985 b) and Seralathan (1987). Seetharamaswamy (1970), Rao et al. (1988) and Ramesh et al.

(1989, 1990) made a through study on the mineralogical and geochemical association of metals in the Krishna river sediments.

Very little previous work has been directed at sand composition in small drainage basins. Geochemical work especially major element chemistry has not been carried out in the short flowing rivers of Kerala particularly in relation to the texture and mineralogy of the sediments. Murthy and Veerayya (1972 a, b and 1981) made a preliminary investigation on organic carbon, phosphorous and trace element contents in the bulk sediments of Vembanad lake. Mallik and Suchindan (1984) have analysed a few major and trace elements in the bulk sediments of the Vembanad estuary. Padmalal (1992) has studied a few major and heavy metal contents in the sediments of Muvattupuzha river and Central Vembanad estuary in relation to the granulometry of the sediments.

By discussing the major element chemistry in the light of their textural and mineralogical data, in this chapter a systematic attempt is made to provide a proper understanding of the processes operating in the Chaliyar basin and how they interact to control sand composition in this small tropical river system. The details regarding sampling, sample processing, dissolution, analysis and analysis are given in chapter 2. The results of the study are discussed below.

5.3 Results and Discussion

The major element composition of 28 bedload sediment samples collected from major headwater tributaries and the Chaliyar main stem is given in table 5.1. The locations of samples are shown in figure 2.1. To have a better understanding of the major element transport along the Chaliyar river, the samples are broadly classified as follows:

1) **Tributary sediments (TS)** : - Samples H-28, H-29, H-30, H-31, H-32 and H-33 are from the major tributaries of Chaliyar river namely Punna puzha (H-28), Chali puzha (H-29 and H-31), Kanjira puzha (H-30), Karim puzha (H-32) and a sample taken just below the confluence of Punna puzha and Karim puzha (H-33) *(Notations used in figures: solid triangle);*
2) **Upper reach sediments (US)** :- Samples H-1, H-2, H-3, H-4 and H-5 are from the upper reaches of the Chaliyar main stem between 70-107 km from source *(Notations used in figures: solid square);*

3) **Lower reach clay-bearing sediments with>5% clay (LCS)** :- Samples H-11, H-13, H-15, H-17, H-19, H-23, H-25, H-26 and H-27 are sediment samples beyond 107 km from the source in the downstream direction of Chaliyar main stem *(Notations used in figures: open circle);* and

4) **Lower reach sediments with <5% clay (LS)** :- Samples H-12, H-14, H-16, H-18, H-20, H-21, H-22 and H-24 are sediment samples beyond 107 km the downstream of Chaliyar main stem *(Notations used in figures: open square).*

Strong relationships can be found for the major element concentrations with the texture and mineralogy of the sediment samples which together are further controlled by the degree of transport or the location of the samples along the Chaliyar river main stem as well as in the basin. The major element composition of TS samples are quite distinct with that of the main stem samples. The most striking and almost smooth pattern of US samples (63-107 km) in their textural and mineralogical characteristics is consistent with their chemistry in terms of major elements. The fluctuating nature of the downstream samples is also consistent with their changing textural and mineralogical attributes.

5.3.1 Tributary sediments

SiO_2 is the most dominant major element present in the bedload sediments of the major tributaries of the Chaliyar river and is reflected in the high content of quartz. It varies between 67.77 to 76.10 wt.% (Table 5.1) with an average of 70.93 wt.%.

TiO_2 varies between 0.43-1.37 wt.% (Table 5.1) with an average of 1.02 wt.%. The highest content of TiO_2 is seen in the Punna puzha tributary which also corresponds to lowest FeO(t)+MgO content (see Table 5.1). Thus the high content of TiO_2 in the Punna puzha tributary may be explained mineralogically as due to high percentage of opaques (8%). This may essentially due to ilmenite present in Punna puzha rather than the rutile content since the latter is present only in trace amounts (see Table 4.2). The lowest content of TiO_2, MgO, CaO and Na_2O in the Kanjira puzha tributary (H-30) signifies that they are poorer in minerals like amphibole, garnet, hypersthene and ilmenite. But as mentioned earlier, the high content of FeO(t) in this tributary is mainly due to the presence of magnetite/hematite. Even though this tributary has the lowest content of CaO and Na_2O, it has a high content of feldspar among the tributaries (10%) which means that the entire CaO and Na_2O present in this is due to plagioclase rather than mafics because it also has very low MgO. Thus Kanjira puzha is another tributary contributing significant proportion of feldspar and opaques in addition to quartz. The low content of K_2O in the tributaries indicates that the source rock is poorer in K-feldspar. K_2O varies between 0.22-0.68 wt.% (Table 5.1) and averages 0.38 wt.% in the tributaries. The highest content of K_2O is seen in Karim puzha (H-32: 0.68 wt.%) which also has highest amount of feldspar (12%). As mentioned earlier this tributary also has highest content of Na_2O which again gives an indication that Karim puzha tributary is the major contributor of not only plagioclase but also K-feldspar. Similarly, among the tributary samples the lowest content of K_2O is seen in Punna puzha (H-28: 0.22 wt.%) which also corresponds to low amount of Na_2O and CaO.

The Al_2O_3 content varies between 7.25 and 10.60 wt.% and is the second dominant major oxide present (Table 5.1). Al_2O_3 averages about 9.08 wt.% in the tributaries and the variation from this average value in some samples can be attributed to the role of clay and feldspars. The maximum Al_2O_3 content is seen in Karim puzha (H-32: 10.60 wt.%) which also has maximum amount of feldspar (12%) and comparatively high proportion of silt and clay, 5.7 and 2.43 respectively. The high contents of feldspar content and finer sediments may explain the high Al_2O_3 in the Karim puzha sample.

FeO(t) is the third dominant major oxide and it varies between 6.32-7.83 wt.% (Table 5.1) with an average of 7.04 wt.%. The maximum content of FeO(t) is seen in the Chali puzha sample (H-31: 7.83 wt.%) which is upstream and very near to the confluence point of the Chaliyar main stem. Mineralogically this sample has the highest content of amphibole (20%) which may account for the high FeO(t). Sample having lowest amount of Al_2O_3 and FeO(t) among the tributaries (H-28) has maximum SiO_2. Kanjira puzha tributary has the second highest FeO(t). The high content of FeO(t) in this tributary can be mineralogically attributed to the highest percentage of opaques probably magnetite/hematite in it. The high content of FeO(t)+MgO (>8 wt.%) in the tributaries Chali puzha, Karim puzha and also the sample taken just below the confluence of Punna puzha and Karim puzha (H-29 and

H-31, H-32, H-33 respectively) is mainly due to the presence of mafic minerals like hornblende, garnet, small amounts of hypersthene and opaques.

Other dominant oxides are CaO, Na_2O and MgO. CaO varies between 1.94-3.21 wt.%, Na_2O between 1.43-2.32 wt.%, MgO between 0.61-2.25 wt.% and averages 2.69, 1.73, 1.68 wt.% respectively (Table 5.1). The high content of CaO and Na_2O in the TS samples reflect the significant proportion of plagioclase which in turn points to a source area mainly consisting of plagioclase rich rocks. The highest content (3.21 wt.%) of CaO among the tributary samples is seen in Chali puzha (H-29) which corresponds to lowest in SiO_2 and second highest in Al_2O_3 content. The highest content of CaO in sample H-29 and H-31 (Chali puzha) could be attributed to the high percentage of amphibole, 14 and 20% respectively. The lowest content of CaO, 1.94 wt.% is seen in Kanjira puzha tributary (H-30) which corresponds to the lowest percentage of amphibole. It is seen that Na_2O varies less compared to CaO in the tributary samples and MgO varies more compared to the above two. The maximum content of Na_2O, 2.32 wt.%, is in the Karim puzha bedload sediment. Together with its high Al_2O_3, it signifies that it is the major tributary which is contributing feldspathic sediments to the Chaliyar main stem. The striking variation observed in the MgO content in the tributaries can be attributed to the varying amounts of amphibole present in the sediments. The lowest content of MgO is seen in Kanjira puzha which also corresponds to the lowest content of CaO.

MnO does not vary much and it ranges from 0.05 to 0.10 wt.% in the tributaries. LOI varies between 2.18-4.97 and averages 3.36 in the major tributaries of the Chaliyar basin. Among the tributary samples the highest LOI of 4.97 and 4.88 (H-29 and H-30) is seen in Chali puzha and Kanjira puzha tributaries respectively.

In general SiO_2 with Al_2O_3, FeO(t) and CaO constitutes >85 wt.% of the the bedload sediments of the tributaries.. Being mainly gravel bearing sand, mineralogical effects seem to be more dominant than texture and the high contents of Al_2O_3, Na_2O, CaO, FeO(t) and MgO indicate feldspathic, mafic and soil components have strongly influenced the bedload chemistry.

5.3.2 Downstream variation in chemistry in the Chaliyar main stem

Some chemical variables change downstream which can be illustrated with the 22 samples of the Chaliyar main stem plotted against their distance of transport (Fig.5.1). These samples are distinguished on the table 5.1 as US, LCS and LS.

SiO_2: The SiO_2 content remains almost steady in the upper reaches (between 70-107 km) while it shows a slightly decreasing trend and fluctuates more in the lower reaches, beyond 107 km in the downstream direction (Fig. 5.1a). This down stream decrease in silica content corresponds to a slight decrease in the quartz present in them (see Fig. 4.7). The fluctuating nature of SiO_2 content in the lower reaches is mainly due to the varying presence of clay in the sediments.

TiO_2: The TiO_2 content shows a slight increase in the upper reaches upto sample H-2 and beyond this up to 99 km there is a steady fall (Fig.5.1b). Beyond the 99 km mark the TiO_2 fluctuates and towards the mouth of the river it shows a slight increasing trend. Among the US samples the high content of TiO_2 in sample H-2 but a corresponding low in the percentage of opaques like ilmenite in coarse sand (see Fig. 4.3c) indicate that the minerals like ilmenite are seen mainly in the medium to fine sand fraction. Because of the hydrodynamic equivalence ilmenite is usually found in finer fractions. This is consistent with the content of ~15% fine sand (see Table 3.1). On the other hand, beyond the 99 km mark, the downstream spectral variation of TiO_2 has some close similarities with that of the spectral pattern of percentage opaque minerals which strongly suggests that ilmenite in the coarse fraction has played an important role in controlling the TiO_2 contents in the bedload sediments.

Al_2O_3: As seen in the case of SiO_2 the Al_2O_3 content remains steady between 70-107 km as expected, but there is an opposite and fluctuating nature of Al_2O_3 spectral pattern with that of SiO_2 in the lower reaches (Fig. 5.1c). It is interesting to note that even though the spectral pattern of quartz and feldspar percentages in the upper reaches fluctuates (but less when compared to lower reach samples) the SiO_2 and Al_2O_3 contents in this sector do remain steady. This probably indicates that there is only a minor variation in contents of major minerals like quartz (± 10%) and feldspar (± 6%) and this has little effect on the SiO_2 and Al_2O_3 contents. It can be said that the entire Al_2O_3 content in these samples is due to feldspar rather than clay because they are texturally made up essentially of sand. The highly fluctuating and slightly increasing trend in the Al_2O_3 content beyond 107 km in the downstream direction can be due to either one or both of the following reasons:

a) the fluctuating nature of clay content which is one of the chief factors in controlling the Al_2O_3 content and

b) the increased and variable amount of feldspar percentage probably indicating small inputs of feldspar minerals from downstream tributaries.

The maximum content of Al_2O_3 in the sample H-26 (16.38%) is seen towards the river mouth (estuary) is mainly due to high content (~40%) in it.

FeO(t): The spectral variation of FeO(t) content in the main stem shows significant similarity with that of TiO_2 (compare Fig. 5.1d & b). This invariably points that ilmenite has an important bearing on the FeO(t) content in the sediments of Chaliyar main stem. In general the FeO(t) content in the upper reaches (70-107 km) shows a decreasing trend similar to the pattern seen for TiO_2 except in sample H-5 at location 107 km from source. As mentioned earlier that sharp increase in that TiO_2 content in sample H-2 among the US samples is mainly due to ilmenite because there is slight increase in FeO(t) content in that sample when compared to H-1. Similarly the increase in content of both FeO(t) and TiO_2 in sample H-5 when compared to H-4 points that ilmenite as well as magnetite/hematite has influenced the slight increase. Beyond the 107 km mark in the downstream direction FeO(t) content fluctuates but the positive anomalies of TiO_2 except in samples H-19 and H-24. When one considers the TiO_2 spectra the negative anomaly in sample H-18 becomes positive in the sample H-19. But the FeO(t) spectra the FeO(t) content show decreasing trend at H-18 and H-19 probably indicating that there is small input of ilmenite by tributary sediments to the main channel in the above stations which has resulted in a increase in the TiO_2 content in H-19 while there is no corresponding increase in FeO(t). Again when the TiO_2 spectra is considered the sample H-24 which is having a negative anomaly but in the FeO(t) spectral pattern it corresponds to the positive anomaly indicating that the tributary inputs from this region mainly consists of mafics and opaques. Beyond 127 km towards the river mouth the more increasing trend in FeO(t) content (not much in the case of TiO_2) points a significant abundance of iron rich minerals like magnetite/hematite probably effected by the sorting mechanism and concentration of opaques for causing an increase in FeO(t).

MnO: The content of MnO in the Chaliyar main channel (Fig.5.1e) shows a steady decrease in the upper reaches, between 70-107 km except in the location at 107 km (sample H-5) where it is slightly higher than the sample from the previous location H-4 (99 km). The spectral pattern of upper reaches almost resembles the spectral pattern of the TiO_2 and FeO(t) in this stretch. Beyond the 107 km mark, that is in the lower reach samples the MnO content fluctuates but the positive anomalies corresponds to the positive anomalies seen in TiO_2 and MgO spectra except in sample H-26. Similarly the positive anomalies in the MnO spectra in the lower reach samples corresponds to the positive anomalies in the FeO(t) spectra except in stations at H-19, H-24 and H-26. This is mainly due to inputs of sediments from downstream tributaries having slightly different mineralogy to the main channel at locations H-19 and H-24. In the MnO spectra the negative anomaly in sample H-26 towards the river mouth with a corresponding prominent positive anomalies in FeO(t), MgO and to a small extent in TiO_2 in this mud rich (~40%) sample points that Mn is preferentially leached out from finer fractions.

MgO:. The content of MgO remains more or less constant in the upper reach between 70-107 km but shows a slightly decreasing trend (Fig.5.1f). This is mainly due to the almost uniform nature of distribution of amphibole, garnet and to a less extent pyroxene in the sediments. Beyond the 107 km in the downstream direction the spectral pattern of MgO fluctuates and positive anomalies corresponds to the positive anomaly of FeO(t) except at H-19 and H-24 locations. The fluctuating nature of MgO content is mainly due to the influx of tributary sediments, having pyroxene and garnet, to the main stem as reflected in the mineralogy of these lower reach sediment samples (Fig. 4.3d & f). As explained earlier (chapter 4) the downstream tributaries drain mainly through charnockitic terrain. There is no significant positive anomaly of MgO which corresponds to the positive anomaly of the mineralogic spectra of garnet, hypersthene and hornblende except in some locations like H-11 and H-19. Nevertheless, a more similar spectral pattern of MgO with that of the opaques can be seen especially beyond 107 km in the downstream direction (compare figure 5.1f & 4.3c). The significant similarities between the spectral pattern of FeO(t) and MgO essentially point that the relative abundance of mafic minerals like hypersthene, hornblende and garnet have strong bearing on the bedload chemistry of the Chaliyar main stem.

CaO:. There is a strong similarity between the spectral pattern of CaO and FeO(t) in the upper reaches (70-107 km) indicating that hornblende has an important role in controlling the chemistry of sediments in this stretch (Fig. 5.1g). This is reflected to a certain extent in the spectral pattern of the percentage variation in hornblende content in the upper reach samples (70-107 km; see Fig.4.3e) except in sample H-5 where the CaO is having a positive anomaly while the percentage of hornblende decreases still further when compared to sample at H-4 location. The decreasing trend in the CaO content in the upper reach samples is also partly due to the slight decrease in the feldspar content (see Fig. 4.3b). In the lower reaches the CaO content fluctuates severely depending upon the contents of clay, plagioclase feldspar and mafic minerals like hornblende and garnet in the samples. The positive anomalies in the lower reaches (beyond 107 km in the downstream direction) of CaO spectra corresponds to the positive anomalies in the MgO spectra except in sample H-13 where the negative anomaly in CaO spectra corresponds to positive anomalies in MgO, FeO(t) and also positive anomaly in hypersthene spectra while positive anomaly of CaO in H-24 corresponds to positive anomaly in FeO(t) and negative anomaly in MgO spectra. Thus the maximum content of CaO in the sample H-24 is mainly due to hornblende and garnet because it has maximum percentage of the above minerals (Fig. 4.3 d & e) and they contain <5% clay and <2% feldspar (see Table 4.2). Similarly the maximum content of CaO in sample H-26 corresponds to maximum content of FeO(t) and MgO but negative anomaly in the spectral patterns of garnet and hornblende pointing that they are adsorbed in clay minerals like kaolinite as this sample which is seen towards the estuary has the maximum amount of clay among the sediment samples collected from the basin. The maximum content of garnet and hornblende in the sample H-24 has contributed to the high CaO rather than the feldspars because among the channel sediments it has the lowest content of feldspar (see Fig. 4.3b). Similarly the maximum content of CaO in the sample H-26 (positive anomaly) even though corresponds to the negative anomaly in the feldspar spectra (see Fig. 4.3b), the CaO maximum in this sample is also partly due to feldspar because the feldspar content is more or less same as that of some of the upper reach samples H-1, H-3 and H-5 (see Fig. 4.3b). As mentioned earlier the negative anomaly of CaO in the sample H-13 corresponds to positive anomaly in FeO(t), MgO and hypersthene spectra while in feldspar spectra this sample has the third lowest content (negative anomaly) among the lower reach samples (see Fig. 4.3b) even though it has the 2^{nd} highest amount of clay among the main stem sediments. Another significant point to be noted is that the positive anomalies in the CaO spectra at stations H-17, H-19, H-21 and H-23 also corresponds to positive anomalies in the feldspar spectra even though these samples have >5% clay which again suggests that downstream tributaries have contributed small amounts of feldspar to the bedload sediments of the Chaliyar main stem. In comparison the spectral pattern of CaO with Al_2O_3 in the downstream samples (beyond 107 km), the positive anomaly of CaO spectra corresponds to the positive anomaly of Al_2O_3 spectra except in samples H-13 and H-24. The negative anomaly of CaO in H-13 corresponds to positive anomaly of Al_2O_3 which suggests that the clay percentage has (this sample has the 2^{nd} highest amount of clay) little influence on the CaO content rather amphibole percentage has influenced the CaO content while clay has influenced the Al_2O_3 content. Similarly positive anomaly at location H-24 corresponds to negative anomaly for Al_2O_3 suggesting that low clay and feldspar percentages (<5% and ~2% respectively) have influenced the Al_2O_3 content in the sample at the same time garnet and hornblende (~10 and 15% respectively) have more to do with the maximum content of CaO.

Na_2O:. In the upper reach samples the Na_2O content almost remains constant between 70-107 km (Fig.5.1h). Such a pattern is mainly consistent with SiO_2, Al_2O_3, MgO, K_2O and P_2O_5 spectra. In the lower reaches, beyond 107 km in the downstream direction, even though the Na_2O content fluctuates but not severely as seen in most of the other major oxides except in sample H-26. This may be due to the uniform content of sodic plagioclase in the bedload sediments. The positive anomalies in the Na_2O spectra especially beyond 114 km in the downstream direction, corresponds to the positive anomalies in the CaO spectra except in sample H-24 which probably suggests that in addition to clay content in these samples (>5%) the influx of feldspar by the downstream tributaries has to a small extent influenced the Na_2O content also. The negative anomaly of Na_2O in sample H-24 suggest there is decrease in feldspar content because this sample also contains minimum amount of feldspar among the main stem sediments and also that it has <5% clay. As explained earlier the positive anomaly of CaO for sample H-24 is mainly due to the high content of garnet and amphibole rather than feldspar/clay percentage because it contains minimum feldspar and very little clay. The maximum content of Na_2O is seen in H-26 and this corresponds to negative anomaly of feldspar spectra which strongly suggests that a major proportion of Na_2O is adsorbed in this clay rich sample. Another possible reason for the high content of Na_2O in H-26 is the adsorption of sodium in clays from the saline water of estuarine environment.

K_2O: The spectral variation of K_2O content in the main stem sediments remains constant in upper reaches (70-107 km) while it fluctuates and shows a slightly increasing trend in the lower reaches (beyond 107 km) especially towards the river mouth (Fig. 5.1i). The constant nature of K_2O content in the upper reach sandy sediments suggest uniform distribution of K-feldspar which is reflected in the less fluctuating nature of feldspar spectra (see Fig. 4.3b) in this stretch of the main stem. Beyond 107 km in the downstream direction the K_2O spectra fluctuates similar to the Na_2O spectra but the K_2O content shows an increasing trend towards the river mouth indicating small amount of influx of tributary sediments in the lower reaches containing K-feldspar to the main stem. The positive anomalies in the K_2O spectra in the lower reaches (beyond 107 km) corresponds to positive anomalies in the CaO spectra except at locations H-12, H-14 and H-18 which may be probably due to an increase in K-feldspar content rather than clay because these samples has low clay percentage (<5%) and moreover the illite content is negligible in clay fraction. This is reflected in the feldspar spectra also where in the above stations except H-18 it is having a positive anomaly. The strong resemblance of K_2O spectra with that of CaO especially beyond 119.5 km (station no. H-19) in the down-reaches suggest that in addition to plagioclase, K-feldspar is also being contributed by downstream tributaries to the main stem sediments. This is reflected in the positive anomalies in the feldspar spectra (samples H-19, H-21 and H-23) except in sample H-24. The positive anomaly in the feldspar spectra (see Fig. 4.3b) which suggests that the positive anomaly of K_2O is entirely due to the K-feldspar content even though it is having the minimum amount of feldspar among the main stem samples and also the clay content is <5%. Another possible reason for the increase in the K_2O content in lower reach samples is due to progressive enrichment of K-feldspar with distance from the source with a decrease in plagioclase content due to preferential weathering. But such a kind of increase in K-feldspar has to be carefully interpreted because the CaO as well as the total feldspar content in the lower reach samples show increasing trends. In comparison the positive anomaly in the K_2O spectra in the lower reaches (beyond 107 km) corresponds to positive anomaly of Na_2O except in stations H-18 and H-24. Similarly the negative anomaly in K_2O at stations H-11 and H-16 corresponds to positive anomaly in the Na_2O spectra. The positive anomaly of K_2O in stations H-18 and H-24 and a corresponding negative anomaly of Na_2O again suggests that K-feldspar is the important mineral among the total feldspar even though these sites corresponds to the negative anomaly in the feldspar spectra. The contribution of clay for the positive anomaly of K_2O in the above stations can be negligible since these stations contain <5% clay. The maximum content of K_2O in the sample H-26 is partly due to feldspar content (7.4% total feldspar) and partly due to the high percentage of clays (~22%) like kaolinite as they have the property of adsorbing highly mobile elements like Ca, Na and K. The consistent negative anomaly of all the alkali elements (Ca, Na and K) along with total feldspar in the sample H-13 which is having the 2nd highest content of clay among the sediment samples suggests that the above elements are less adsorbed in clays. At the same time the significant positive anomaly in sample H-26 for the alkali elements and a corresponding negative anomaly in total feldspar content (but higher than H-13) suggests that significant proportion of the above elements are adsorbed in clays along with negative anomaly in feldspar spectra has contributed for the persistent positive anomaly in alkali elements and hence this sample show less chemical maturity even though it has the maximum content of clay (~22%) when compared to H-13 (~12%). When the K_2O spectra, beyond the 107 km distance in the downstream direction, is compared with Al_2O_3 spectra the positive anomalies in K_2O corresponds to positive anomalies in Al_2O_3 except in H-13 and H-24. The positive anomaly of K_2O in H-13 corresponds to positive anomaly in Al_2O_3 suggesting that in the clays potassium is less adsorbed and also the K-feldspar is less in the sample . Similarly the positive anomaly of K_2O in H-24 corresponds to negative anomaly in Al_2O_3 which suggests that K-feldspar is high in the sample because the adsorbed K_2O will be negligible as it has <5% clay. Thus it can be concluded that the downstream tributaries have contributed small amounts of additional plagioclase and K-feldspar to the main stem sediments thus giving a slightly immature character to it when compared to the upper reach sediment samples (between 70-107 km).

P_2O_5: In the upper reaches between 70 – 107 km the P_2O_5 remains constant but beyond 107 km in the downstream direction it fluctuates less (because P_2O_5 is determined mostly for samples having >5% clay) and shows a slightly increasing trend (Fig. 5.1j). The positive anomaly of P_2O_5 corresponds to samples having >5% clay except in sample H-15 which is having negative anomaly. A steady increase in P_2O_5 content is seen in samples beyond 119.5 km similar to clay content (for samples H-20, H-22, H-24 the P_2O_5 is not determined and they have <5% clay). The samples H-26 and H-13 have high content of total P_2O_5 and they contain maximum clay among the main stem sediments (~22 and 12% respectively). The positive anomalies in the lower reaches (beyond 107 km) of the P_2O_5 spectra corresponds to positive anomalies in the Al_2O_3 spectra except in H-15. The increasing trend in P_2O_5 content in samples H-19, H-21, H-23, H-25, H-26 and H-27 also corresponds to an increase in Al_2O_3 content.

Al_2O_3/SiO_2: The ratio of Al_2O_3 to SiO_2 is a good chemical measure of sandstone maturity, the downstream variation of which in the Chaliyar main stem sediments is given in figure 5.1k. In the upper reach between 70-107 km the Al_2O_3/SiO_2 ratio remains constant while it fluctuates beyond 107 km in the downstream direction and shows an increasing trend especially towards the river mouth. This increase of the Al_2O_3/SiO_2 ratio together with that of K_2O and to a small extent in Na_2O content reflect higher feldspar content in the lower reaches than in the upper reaches (between 70-107 km) which again points that significant amount of feldspar is being added by downstream tributaries to the main stem. This behaviour is just the opposite of the downstream increase of the SiO_2 content observed elsewhere like, in South Carolina, USA (Cleary and Conolly, 1971), Amazon sands, South America (Franzinelli and Potter, 1982) and bedload of Meurthe River, NE France (Albarede and Semhi, 1995). This increase in the Al_2O_3/SiO_2 ratio in the main stem sediments is also reflected in the average increase in %QF (modal % of Quartz+Feldspar) in the lower reaches when compared to the average %QF in the upper reach sediment samples (average %QF=94,6 in upper reach sediment samples while average %QF=91,9 in the lower reaches) of the Chaliyar river.

Na_2O/K_2O: The ratio Na_2O/K_2O is a measure of change in the albite/orthoclase ratio in the sediment samples. The Na_2O/K_2O ratio in the bedload sediments of Chaliyar river shows a decreasing trend even though it fluctuates less in the upper reaches (between 70-107 km) while it fluctuates severely beyond 107 km in the downstream direction.(Fig.5.1l) The high Na_2O/K_2O ratio in the upper reach samples points to the relatively more albitic nature of feldspars in them. This may be true because the headwater tributaries in the upper reaches mainly drains through gneisses. It is important to note that the positive anomalies of Na_2O/K_2O ratio corresponds to the positive anomalies of the total feldspar spectra (compare Fig. 4.3b and Fig. 5.1l). The fall in the Na_2O/K_2O ratio seen beyond 107 km in the downstream direction points that the orthoclase content increases, which may be due to following reasons:

a) progressive downstream preferential weathering of plagioclase which results in the relative enrichment of orthoclase and
b) influx of sediments containing significant proportions of orthoclase by the lower reach tributaries to the main channel sediments.

The former reason should be applied with caution because the K_2O content is very less through out the main stem samples even though it shows a slight increase towards the river mouth. In addition to this for the differential elimination of albite in the sediments it has to undergo weathering along flood plain which is unlikely because there is no flood plain developed in this kind of rivers which is having high relief in its head water regions, heavy rainfall and they are short flowing tropical river systems even though Nilambur valley consists of small terraces especially at valley slopes. Hence the latter explanation is preferred because the sediments carried by the downstream tributaries drains through different rock type (charnockitic terrain).

5.4 Variation with silica

Variations in the major element geochemistry of bedload sediments of Chaliyar river and its major tributaries are shown on SiO_2 vs other oxide diagrams (Fig. 5.2) The most obvious relationship is the negative correlation of virtually any oxide with SiO_2 due to variable dilution of other minerals abundances especially by quartz and clay content. There is a strong negative correlation between SiO_2 and Al_2O_3 (correlation coefficient, r=-0.84), SiO_2 and FeO(t) (r=-0.72), SiO_2 and MgO (r=-0.75), SiO_2 and Na_2O (r=-0.65), SiO_2 and P_2O_5 (r=-0.95). TiO_2 (r=-0.53), MnO (r=-0.36), CaO (r=-0.48) and K_2O (r=-0.48) have moderate negative correlation with SiO_2. Though in general, SiO_2 is negatively correlated with most of the other oxides, TiO_2 and K_2O show different relationship in tributary samples. In the TS samples TiO_2 and K_2O are positively correlated with SiO_2 while it is negatively correlated with main stem samples. Linear trends from TS to main stem sediments especially from US samples containing almost cent percent sand to lower reach sediment samples containing >5% clay and <5% clay can be observed, with variations mainly due to grain-size effects and partly due to mineralogical maturity. This mineralogical maturity is characterised by an increase in quartzose content and a decrease in unstable detrital grains (e.g., feldspar). However, as mentioned earlier the mineralogical maturity slightly decreases in lower reaches due to influx of sediments from downstream tributaries to the main stem. This is to a certain extent reflected in the CaO, Na_2O and K_2O diagram (see Fig. 5.2) The CaO content decreases from tributaries, upper reach to lower reach samples containing <5% clay in the main channel. This is an indication of progressive decrease in plagioclase content with increase in quartz. Similarly the K_2O content decreases less with increase in SiO_2 in the upper and lower reach sediment samples containing <5% clay in the main stem even though the TS samples show positive correlation with SiO_2. This can be understood because K-feldspar are more stable than Ca-plagioclase and also the absolute abundance of K_2O is very less in the Chaliyar river sediments. It is considered that Ca and Na behave similarly even though Ca is typically lost more rapidly than Na during weathering. So in the case of Na_2O even though there is an increase in SiO_2 content from tributaries to main stem sediments of US and LS samples, the decrease in Na_2O content is considerably less when compared to CaO. Not only that the tributaries as well as main stem sediments has similar Na_2O content even though it shows negative correlation with SiO_2 (r=-0.65). The US and LS samples are more homogeneous and overlapping occurs (see Fig. 5.2), indicating that the differences between sandy sediments are not very high. The LCS samples

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are inhomogeneous and are discriminated from the above group but less when compared to TS samples. Some of the samples in this group also have slight overlapping with the above group (see Fig. 5.2). The highly inhomogeneous nature of the above samples is mainly due to the percentage clay content and also due to the adsorptive capacity of clay minerals like kaolinite, chlorite, gibbsite, goethite and illite. The TS are well discriminated from other groups in almost all diagrams, showing that mineralogy has played an important role in distinguishing this from other groups rather than the sand or clay content. Even though the TS show strong contrast with other groups, they do not overlap/cluster indicating slightly inhomogeneous nature (see Fig. 5.2). This is mainly due to varying amount of minerals present especially mafics and opaques and to a small extent the weathering conditions prevailing in the source area drained by major tributaries of Chaliyar river. The above reasons emphasize that the differences between tributary sediments and other groups are very high. It is interesting to note that the oxide content in the TS samples are all on the higher side of the main stem sediments except in Al_2O_3, K_2O and to a certain extent Na_2O. The Al_2O_3, K_2O and Na_2O fall on the lower side of the main stem sediments (see Fig. 5.2). The low content of Al_2O_3 is mainly due to the very low content of clay (averages around 1.5%) even though silt content is comparatively higher than clay (averages around 3.6%). Similarly the low content of K_2O in most of the TS samples is mainly due to the low availability of K-feldspar in the source rocks even though it shows a positive correlation with SiO_2.

5.5 Variation with Al_2O_3

As seen in the case of SiO_2 variation diagram the US and LS samples of the main stem are more homogeneous than the LCS and TS even though there is no overlapping between individual samples. But at the same time overlapping of fields between the US and LS samples of the main channel occurs. But among the sand groups (US and LS) the Al_2O_3 content of the US samples varies least. The more homogeneous nature of sands in the above groups indicates that the differences between the sandy sediments are not very high and the LS samples of the Chaliyar main stem are mature similar to the US (see Fig. 5.3). From this it may be concluded that the more inhomogeneous nature of the LCS of Chaliyar main stem is mainly due to the mud content along with sand. The above behaviour of LCS samples of the

Chaliyar main stem is just opposite to what is seen in muds from the lowermost Amazon (Vital and Stattegger, 2000). This behaviour of Chaliyar main stem LCS samples is mainly due to high proportion of sand with mud. However there is a strong discrimination between sandy sediments (US and LS) and clay bearing sediments of the Chaliyar main stem which is consistent with the sand and mud of the lower most Amazon. In other words the sand group (US and LS) of the main stem has lower Al_2O_3 even though it varies (Al_2O_3 varies less in US and more in LS) and almost all other oxides while the majority of the LCS samples have higher Al_2O_3 and other oxides.

In the case of Na_2O there is a significant overlap between the TS and US, LS of main stem, while to a lesser extent in the case of K_2O. The strong discrimination of TS with (except in the case of Na_2O and K_2O) all the oxides fall in the higher side of the main stem sediments which again points that the mineralogy of the detritals has played an important role in controlling their chemistry. The most contrasting discrimination is seen in FeO(t) and MgO which points that mafics has important bearing in the sediment chemistry of major tributaries. Among the groups the US and LS of the Chaliyar main stem are more homogeneous, TS are less homogeneous and LCS of the main stem are the least homogeneous in nature.

5.6 Variation with Fe_2O_3(t)+MgO

Compositional indices such as Fe_2O_3(t)+MgO content, along with parameters that are sensitive to the presence of continental detritus like TiO_2 and ratios such as Al_2O_3/SiO_2, K_2O/Na_2O, $Al_2O_3/(CaO+Na_2O)$, have empirically been shown as useful discriminants of the various tectonic settings of sedimentation (Bhatia, 1983). Along with these other major oxides are also employed in order to understand the variation and to classify/discriminate among different groups – in the Chaliyar river sediments. Fe and Ti are useful because they are relatively immobile. Bhatia (1983) has shown that the ratio Al_2O_3/SiO_2 gives an indication of quartz enrichment in sandstones, the K_2O/Na_2O ratio is a measure of the K-feldspar and mica versus plagioclase content in the rock, while the $Al_2O_3/(CaO+Na_2O)$ parameter is a ratio of the most immobile to the most mobile elements. In order to have a more meaningful comparison major oxides of all the samples were recalculated to 100% on a volatile-free basis. As expected, similar to Al_2O_3 and SiO_2 variation diagram, all the major oxides in Chaliyar river sediments show linear trends with Fe_2O_3(t)+MgO wt.% (Fig. 5.4).

Among the Chaliyar main stem sediments the fine fraction i.e., LCS samples are usually poor in SiO_2, and rich in all other major oxides. In this group the Fe_2O_3(t)+MgO% varies maximum (~ 5-11%) due to which considerable overlapping of fields is seen between sediments of upper and lower reaches of the main stem than between Al_2O_3 and SiO_2. This probably indicates that Fe_2O_3(t)+MgO is more or less uniform in different groups of the main stem sediments. However, overlapping among different groups is almost nil except in the case of Fe_2O_3(t) where there is significant overlap especially within the sandy sediments indicating that iron is homogeneously distributed in the main stem sands. The least amount of overlapping among samples occur in MnO (Fig. 5.4). As expected the most mature sands of the Chaliyar main stem have least amount of Fe_2O_3(t)+MgO % which is consistent with that of Al_2O_3 variation diagrams. Even though the fields of sand and muddy sand group overlap there is a significant discrimination existing especially between the above groups in SiO_2, Al_2O_3, MgO and to a certain extent in the case of CaO diagrams (see Fig. 5.4). The least amount of variation in the content of Fe_2O_3(t)+MgO % among the Chaliyar main stem sediments and tributary sediments are shown by sandy sediments of the upstream and lower reaches of the main stem (~ 5 to 7.5 wt%) (see Fig. 5.4). Among the sandy sediments of the main stem the variation in Fe_2O_3(t)+MgO% for US and LS are almost similar but in their absolute abundance they slightly differ. The absolute content of Fe_2O_3(t)+MgO for US samples of the main stem varies from ~ 5.25 to 7.5% (see Fig. 5.4). Hence main stem sands of the lower reaches are mature than the upper reach samples (US). At the same time the immature and highly variable nature of the LCS of the main stem is mainly due to the varying amounts of mud present. Due to less variation of Fe_2O_3(t)+MgO% in the sands of the main stem the samples cluster together but with little overlapping among samples except in the case of Fe_2O_3(t). As already mentioned earlier this indicate more homogeneous nature of the sand composition. The high content of CaO and to a certain extent Na_2O, very low K_2O, especially in the most mature sands of the lower reaches of the Chaliyar main stem probably indicate that the sediments are derived from Archean terrain. Though the granulite blocks of Northern Kerala (Wynad gold field) has been assigned Proterozoic age (i.e., the age of granulite facies metamorphism) by many workers geochemically the rocks retain their Archean identity. McLennan (1984) has found that K_2O was not as abundant in the Archean sediments and upper continental crust as in the Proterozoic and Phanerozoic eras, instead, K_2O/Na_2O was apparently lower in Archean continental rocks. In contrast the relatively immobile elements Fe and Mg in the matured sands of the main stem almost have close similarities with that of the present upper crust. Furthermore, major uncertainties exist in extrapolating Phanerozoic tectonic settings to the Archean (McLennan, 1984; Feng and Kerrich, 1990). Hence it may be concluded that the Chaliyar river sediments were derived from continental crust showing affinities towards Archean terrain.

The strongest discrimination of TS samples from other groups is well depicted in all the diagrams (except in the case P_2O_5 where not determined in TS) showing their more intense weathering conditions (Fig. 5.4). Such behaviour is consistent with that of Al_2O_3 and SiO_2 variation diagrams. But the most discriminating diagrams are those of SiO_2, Al_2O_3, Na_2O and K_2O (see Fig. 5.4). In others the tributary sediments (TS) slightly overlaps with the field of LCS group of the Chaliyar main stem. As seen in other groups the TS samples show positive correlation with Fe_2O_3(t)+MgO% except in SiO_2 and to a certain extent in TiO_2. The SiO_2 and TiO_2 in the TS samples are negatively correlated with Fe_2O_3(t)+MgO% which is consistent with the Al_2O_3 and SiO_2 variation diagrams (see Fig. 5.2 & 5.3). The highest content (~ 11.5%) and the second highest variation (~ 8.5 to 11.5%) in Fe_2O_3(t)+MgO% among all the groups is shown by TS. Due to the above nature the individual samples do not overlap which makes the TS samples a less homogeneous group among the Chaliyar river sediments.

A significant positive correlation exists between Al_2O_3/SiO_2 with Fe_2O_3(t)+ MgO% of different groups in the Chaliyar river sediments (Fig. 5.5). The lowest ratio of Al_2O_3/SiO_2 among the different groups is seen in the sandy sediments of the lower reaches (LS) of the Chaliyar main stem, which gives an indication of quartzose enrichment. Among all the ratios the most discriminating one between different groups is shown by Al_2O_3/SiO_2 ratio. There is a strong discrimination between sandy sediments (US and LS), LCS and TS in this diagram. The Al_2O_3/SiO_2 ratio varies between 0.075-0.15, in LCS it varies between 0.1-0.30 and in TS it varies between ~0.1-0.16 while the Fe_2O_3(t)+MgO in sands varies between ~ 5-7%, in LCS between ~ 5-11.5 %, and in TS between ~ 8.5-11.5 %.

The Fe_2O_3(t)+MgO and K_2O/Na_2O does not vary systematically with Fe_2O_3 (t)+MgO % except in TS the K_2O/Na_2O ratio show a slight positive correlation (Fig. 5.5). However the K_2O/Na_2O ratio is slightly higher in the sandy sediments when compared to tributaries. Not only that in sandy sediments of the main stem (US and LS) the K_2O/Na_2O ratio varies less (~ 0.25-0.37) when compared to LCS of the main stem (~ 0.2 to 0.4). Because of less content of Fe_2O_3(t)+MgO% and minimum variation of K_2O/Na_2O ratio in the sandy sediments of the Chaliyar main stem, the samples cluster and hence they are more homogenous in nature than the LCS of the main stem and the TS. The slightly high K_2O/Na_2O ratio in the LS samples of the main stem when compared to TS indicates that there is a slight increase in K-feldspar rather than mica which is also reflected in the increase in total feldspar content in the lower reaches. This as mentioned in earlier chapters could be due to minor inputs of K-feldspar from the down stream tributaries into the main channel. But as you will see later in this chapter, the weathering indices (CIA, CIW, PIA) for these sandy, most mature sediments of the lower reaches of the main stem are slightly lesser than the other groups suggesting that this group is chemically immature even though it is having high SiO_2 and low Al_2O_3 contents. This provides a strong evidence that some amount of feldspar especially plagioclase is carried by down stream tributaries to the Chaliyar main stem which resulted in the slight chemical immaturity for this group.

The Fe_2O_3 (t) + MgO ratio almost remain the same in all the group except one sample in the tributary. Because of this there is less discrimination among groups. The ratio varies between ~ 3 and 6 in all the groups except one tributary sample, (H-30: ~13) and also the US samples of Chaliyar main stem. Among all groups the US samples in the main stem the ratio varies least (~ 3.5-4.75).

It is interesting to note that in the $Al_2O_3/(CaO+Na_2O)$ vs Fe_2O_3(t)+MgO diagram the $Al_2O_3/(CaO+Na_2O)$ ratio show positive correlation in the Chaliyar mains stem sediments (US, LS and LCS) while it is negatively correlated with TS (Fig. 5.5).

As seen in the case of Al_2O_3/SiO_2 ratio the $Al_2O_3/(CaO+Na_2O)$ also show strong discrimination between different groups. Among the different groups the ratio most immobile to most mobile elements varies maximum in the LCS of the main stem followed by TS (~ 2.25-3.75 & ~ 1.75-2.75 respectively). The US and LS of main stem, the ratio varies least (~ 2.0-2.6) indicating their more homogenous nature. Among the sandy sediments of the main stem, in the US the ratio varies least (~ 2.2-2.5) while the ratio varies approximately between 2 - 2.6. The slight decrease in the $Al_2O_3/(CaO+Na_2O)$ ratio in the LS of the main stem when compared to the US again emphasize that there is inputs of less weathered material consisting of plagioclase feldspar or probably a slight increase in Na_2O due to the albitisation of Ca-plagioclase in the aqueous/estuarine environment. But as it is already seen that there is a decreasing trend in the Na_2O/K_2O spectral pattern in the main stem especially towards the river mouth and also slightly higher ratio of K_2O/Na_2O in the Fe_2O_3 (t) + MgO diagram for the sandy sediments especially of the lower reaches (LS) of the main stem in comparison with that of the US, the latter reason (albitisation of Ca-plagioclase) may be less significant. It is very clear from the diagram that there is strong discrimination between different groups in comparison with other ratios. In addition to this the distinction between sands of upper and lower reaches of the main stem is more clearer in the $Al_2O_3/(CaO+Na_2O)$ vs Fe_2O_3 (t) + MgO diagram and to a certain extent in the Al_2O_3/SiO_2 vs Fe_2O_3(t)+MgO diagram.

5.7 Chemical classification, maturity, climate, tectonic setting

The geochemistry of sedimentary rocks reflects the tectonic setting of the basin and also provides insights into the chemical environment of deposition (Garrels and MacKenzie, 1974; Maynard et al, 1982; Bhatia, 1983; Bhatia and Crook, 1986; Roser and Korsh, 1986, 1988; McLennan et al, 1990; Erickson et al, 1992).

5.7.1 Chemical classification

Numerous sandstone classification schemes exist, most of them based on the work of Krynine (1948). Pettijohn et al. (1972) reviewed twenty of the more notable schemes and many of the difficulties and shortcomings involved in sandstone classification. In most schemes, the fundamental classification of sands and sandstones involved four principal components: quartz, feldspar, rock or lithic fragments and matrix. Blatt et al. (1980) have presented a triangular plot (Fig. 5.6a) using major elements data to express the tectonic classification of sandstone sedimentation suggested by Krynine (1942). As most of the plotted samples represent field no. 1, it may be inferred that the Chaliyar bed load sediments are dominantly graywacke (sodic sandstone subtriangle) with strong affinity towards Fe_2O_3(t)+MgO apex. However, Potter (1978) used same variables for the modern big river sands of the world and failed to show any comparable groupings and suggested that the three variables useful to a study of ancient sandstones may have been strongly influenced by the chemistry of diagenesis.

The chemical classification of sedimentary rocks differentiates between mature and immature sediments. Similarly chemical concentrations of terrigenous sands and shales can be related to common sandstone classification. The most commonly used parameters are (1) the SiO_2/Al_2O_3 ratio (Potter, 1978) reflecting the abundance of quartz as well as clay and feldspar content; (2) the Na_2O/K_2O ratio (Pettijohn et al., 1972) an index of chemical maturity; and (3) the Fe_2O_3 (t) + K_2O ratio (Herron, 1988), which allows arkoses to be more successfully classified and is also a measure of mineral stability.

These parameters have been applied to Chaliyar bedload sediments using the diagram scheme from Pettijohn et al. (1972) and Herron (1988) (Fig. 5.6b & f). The samples are plotted as TS (solid triangles), US and LS (solid and open square), LCS (open circle) of the Chaliyar main stem. Pettijohn's diagram identified US and LS of the main stem as lithic arenite while the LCS of the main stem and TS as graywacke except two muddy sand samples falls in the lithic arenite. Even though the sands of the Chaliyar river can be compared with some of the Amazon sands they significantly vary in the log (Na_2O/K_2O) values. In the Chaliyar sands the log (Na_2O/K_2O) values are positive (~ 0.4-0.6) while the values are negative (average around : –0.2) for Amazon sands (Vital and Statteger, 2000, cf. Fig. 4A). This probably indicates that Chaliyar sands are sodic rich while the Amazon sands are K-rich. Pettijohn's classification does clearly distinguishes LCS as graywacke. But at the same time it does not clearly distinguish TS from either graywacke or lithic arenite. These samples shift towards matrix-rich sandstones, because of the lower SiO_2/Al_2O_3 ratio in sediments. The data indicates that the sands from lower reaches of the Chaliyar main stem are more mature than in the upper reaches and both of them are more homogenous, while the LCS and TS are comparatively less homogeneous in nature. However Herron's diagram is not effective in distinguishing various groups as majority of sediment samples of main stem falls in the Fe-sand field. Thus, based on Herron's diagram the Chaliyar river sediments can be classified as Fe-rich sands with little discrimination among groups and significant overlapping of sample from different groups, except in TS. It may be noted that the Chaliyar river sediments contain more mafic minerals even though they are completely devoid of rock fragments due to lateritization processes which is a characteristic feature of intense chemical weathering of source rocks in a tropical drainage basin. However, in comparison with other major tropical river systems like Amazon River and Orinoco River the Chaliyar river sediments are highly immature. This is mainly due to the slightly low content of SiO_2 (mainly quartz), high Fe_2O_3(t), MgO, CaO, Na_2O and very low K_2O in the sediments of Chaliyar river. According to Herron (1988) at low temperatures and pressures characteristics of sedimentary environments the most stable rock-forming minerals are K-feldspar, muscovite mica, and quartz, the first two of which are rich in potassium and all three of which are low in iron content. However, the less stable rock-forming minerals, commonly occurring in lithic fragments, tend to be richer in Fe and Mg. Therefore, as a general rule: stable mineral assemblages have low Fe_2O_3(t)/K_2O ratios; less stable mineral assemblages containing abundant lithic fragments, have high Fe_2O_3(t)/K_2O ratios. In contrast to the above rule, in terms of the %QFR data the sediments of the Chaliyar river are feldspathic with little rock fragments, ranging in composition from sub-arkose (%QFR=81,19,0) to quartz arenite (%QFR=97,3,0). Thus it is difficult to measure the maturity and also to classify the sediments using framework components, chemical concentrations especially of Fe, Mg rich sands.

Pettijohn's (1972) sandstone classification diagram does clearly distinguish argillaceous sediments from either graywacke or litharenite. But Herron's (1988) sandstone classification diagram does not discriminate the above groups. Even though Vital and Stattegger (2000) found that Herron's diagram can distinguish iron rich sands it cannot distinguish the graywacke and litharenite which are Fe-rich. Thus the Na_2O/K_2O ratio discriminates more clearly the Fe-rich graywacke and litharenite than does the Fe_2O_3(t)/K_2O ratio, and Pettijohn's classification can be more satisfactorily applied to modern unconsolidated coarse and fine grained sediments. As it will be seen later in this chapter that even though the Chaliyar river sediments chemically behave to a certain extent as active continental margin type in the Roser and Korsch (1986) diagram they are mineralogically mature (framework composition) (quartz-rich, varies 81-93% and averages 92%) mainly because of the near absence of rock fragments (petrologically evolved) signifying intense chemical weathering in the source area.

5.7.2 Maturity- Climate

Pettijohn (1984) on the study of feldspar opined that the survival of feldspars appears to be a function of both intensity of the decay processes and duration of weathering action. Suttner and Dutta (1986) while dealing with sandstone composition and palaeoclimate have observed that the compositional maturity plays an important role in predicting climatic conditions. A bivariate plot of SiO_2 against Al_2O_3+K_2O+Na_2O (Fig. 5.6c) best represents the chemical maturity trends which is a function of climate. This plot distinctly reveals the existence of the humid climate in the source area. Maturity of the TS and LS of Chaliyar main stem, all of US fall on the humid climate field with high degree of chemical maturity while the majority of LCS and few TS fall in the arid field with less degree of chemical maturity. The above characteristics for LCS is mainly due to the presence of varying amount of clay while for TS it may be due to rapid erosion rate because of which they undergo less intensity of chemical weathering that is also reflected in their mineralogy (slightly higher content of feldspar). However, in the above plot few LS samples of the main stem plot in the arid region or closer to the dividing line. This may be due to the existence of semi-arid climate in the source areas drained by downstream tributaries. This interpretation reinforces the idea of slight influx of less weathered material to the main stem by the downstream tributaries. The above reason is substantiated by slight increase in total feldspar content and high proportion of silt content at some stations (H-13 and H-16) in the lower reaches of the Chaliyar main stem. Moreover, since the downstream tributaries are closer to the coast the country rocks (charnockite and gneisses) undergo less intense chemical weathering thus contributing less weathered material to the main stem sediments.

5.7.3 Tectonic setting

Roser and Korsch (1986) proposed a tectonic discrimination diagram for sandstone - mudstone suites using SiO_2 content and K_2O/Na_2O ratio. Crook (1974) divided graywackes into three classes and assigned each to a major plate tectonic environment. The three groups are :

a) Quartz-poor graywackes : with <15% framework quartz, volatile free SiO_2 averages 58%, and $K_2O/Na_2O<<1$. They are basic volcanic provenance in magmatic island arcs.

b) Quartz-intermediate : Quartz varies between 15-65%, SiO_2 averages 68-74%, and $K_2O/Na_2O<1$. Provenance, is mixed and rocks of this class are typical of evolved active continental margins.

c) Quartz-rich : Quartz is >65%, SiO_2 averages 89% and $K_2O/Na_2O>1$. They are deposited at passive continental margin and in plate interiors.

The above classification was based on apparent breaks in the frequency distribution of QFR framework compositions of Phanerozoic graywackes. However, Korsch (1978) and Valloni and Maynard (1981) have shown that these breaks may not be real or may occur elsewhere in ancient as well as modern sediments, but in principle the division remains a useful starting point for chemical discrimination.

Roser and Korsch (1986) found that the chemical composition of sediments is influenced by grain size, hence they plotted sand - mud couplets from single sites. The Chaliyar bedload sediments plot in the active continental margin field (Fig. 5.6d) except one LCS sample in main stem (H-26) which fall in the oceanic island arc margin field. TS, US, LCS and LS samples all fall in the active continental margin field but the sands especially from the lower reaches (LS) of the main stem fall nearer to the passive margin field while the LCS and TS samples fall further away from the passive margin field. This reflects the effect of grain-size as well as the influence of mafic content (TS). The above behaviour with respect to grain-size is also seen in Amazon sediments (Vital and Stattegger, 2000) where the muds plot more closer to the active continental margin field while the sands plot further away from the active continental margin field even though the Amazon sediments plot in the passive margin field. This signifies that the Amazon sediments are enriched in

SiO_2, K_2O and depleted in Na_2O suggesting their highly recycled and mature nature while the Chaliyar sandy sediments have intermediate SiO_2, slightly high Na_2O and very low K_2O indicating their mixed provenance even though they show evolved as well as matured characteristics (average %QFR=92,8,0). Again, as seen in earlier cases the TS are almost well differentiated from US and LS samples, to a certain extent from the LCS of the Chaliyar main stem, reflecting the importance of intense chemical weathering in the source terrain. The TS are Fe_2O_3(t), MgO rich (proximal to the lateritic source) and slightly SiO_2, K_2O/Na_2O poor. In general, the immature characteristics even to the LS of the Chaliyar main stem in comparison to the highly mature sands of Amazon river is mainly due to high Fe_2O_3(t), MgO, CaO, Na_2O, intermediate SiO_2 and very low K_2O. According to Bhatia (1983) the active continental margin type sandstones are characterised by low Fe_2O_3(t)+MgO (2-5%), TiO_2 (0.25-0.45%) and K_2O/Na_2O ratio $\cong$ 1. In comparison to the above sandstone the LS of Chaliyar main stem are characterised by high Fe_2O_3(t)+MgO (range: 5.06-6.86%; average: 5.81%), TiO_2 (range: 0.23-0.66%; average: 0.45%) and very high K_2O/Na_2O ratio (range: 2.54-3.95%; average: 3.28%). The above differences as already mentioned earlier in the chapter does not distinguish the Chaliyar river sands (LS - open square) from either active or passive margin type.

Roser and Korsch (1986) have proposed another tectonic discrimination diagram (Fig. 5.6e) using major element ratios SiO_2/Al_2O_3 and K_2O/Na_2O for sandstone - mudstone suites. Considering that SiO_2 and Al_2O_3 vary antipathetically in sediments, grain-size effects will also be apparent on plots using SiO_2/Al_2O_3 in conjunction with K_2O/Na_2O. It is seen that the majority of the LS samples of the Chaliyar main stem plots in the passive margin field. All US samples in the main stem and majority of the TS samples plot in the active continental margin field while majority of the LCS plot in the A_2 field indicating the transitional nature. This clearly emphasize the effect of grain-size as well as influence of intense chemical weathering in the source area of the Chaliyar basin. Thus the above diagram discriminates more clearly the different groups of Chaliyar river sediments than the former one (Fig. 5.6d) and moreover the most mature sands of the lower reaches of main stem (LS) is classified in the passive margin field. Vital and Stattegger (2000) found similar kind of behaviour for lower most Amazon sediments and also strong discrimination between groups, with sands falling away from the active continental margin field while the muds falling more closer to the active continental margin field. However, the TS, US and LCS samples of Chaliyar river, which are classified as active continental margin and A_2 category of Maynard et al. (1982) respectively, they preserve the signature of the most mature sand of the main stem, LS. Hence, the latter tectonic discrimination diagram (SiO_2/Al_2O_3 vs K_2O/Na_2O) of Roser and Korsch can be more convincingly applied to modern fine as well as coarse grained sediments.

According to Roser and Korsch (1986), the success of chemical approach suggests that chemistry alone could be used for tectonic discrimination in place of petrographic analysis, but they emphasized that the two methods are complementary and should be combined if possible. The provenance information from petrography is unique, particularly with respect to the nature and amount of detrital lithics. Thus in this study also the above said technique proved to be more successful as some interpretations which is obscured in chemistry can be explained using petrography. The most important difference noted is that the Chaliyar basin sediments is from a known tectonic setting, namely passive margin, but when plotted in the tectonic discrimination diagram of Roser and Krosch (1986) they are classified in active margin field (in the first diagram Fig. 5.6d all the samples while in the second Fig. 5.6e except LS samples of main stem all others either falls in the active continental margin field/A_2 boundary. LS samples of the main stem fall in the passive margin field) and hence becomes indistinct. But petrographically (framework composition) the Chaliyar basin sediments are almost completely devoid of rock fragments and enriched in quartz (average: 92%) which is quite similar to the Crook's quartz-rich passive continental margin sediments. The chemical immaturity shown by majority of the sediments of the lower reaches of the main stem of Chaliyar river and TS is mainly due to presence of varying amounts of clay, small increase in feldspar content and high proportion of mafic mineral respectively. Even though they are petrologically quartz-rich their SiO_2 content and K_2O/Na_2O ratio resemble more of the Crook's active continental margin sediments. This is mainly due to mixed provenance character (differentially lateritized Archean and Proterozoic terrane) and very low K_2O content in sediments indicating as if they are mainly derived from Archean rocks. Another reason for low K_2O/Na_2O ratio for Chaliyar river sediments is that these rivers are characterised by high relief in its head water regions, erosion is faster due to heavy rain fall causing floods (bank-full discharge) thus not allowing flood plains to develop in order to undergo plagioclase weathering and most importantly they are short flowing. The above factor has an important bearing on the increase in the K_2O/Na_2O ratio in sands in most of the big rivers like Amazon and Orinoco show an increasing trend towards the river mouth indicating complete weathering of plagioclase feldspar and enrichment of K-feldspar suggesting their highly recycled and mature nature. The above reasons are the causes for the mis-match of tectonically known passive margin type Chaliyar river sediments in active continental margin field. Therefore, in the major element tectonic discriminant plot of Roser and Korsch (1986), this study supports the idea that the Chaliyar basin sediments are associated with passive margins but with dual characteristics of passive/active margin type. The low K_2O/Na_2O ratio inherited from the source rocks and the intense weathering in the basin have made the Chaliyar river sediments to show a pseudo signature of 'active margin' in some of the discrimination diagrams. Chaliyar is along a passive margin. So the effectiveness of the discriminant functions should be evaluated against this fact. If any active margin characteristics are seen it should be interpreted with caution.

5.8 Weathering Indices

5.8.1 Chemical Index of Alteration (CIA)

Chemical weathering may have important effects on the composition of siliciclastic rocks, where larger cations (e.g., Rb, Ba), remain fixed in the weathered residue, in preference to smaller cations (Ca, Na, Sr), which are preferentially leached (Nesbitt et al., 1980). These chemical trends may be transferred to the sedimentary record (Nesbitt and Young, 1982; Wronkiewicz and Condie, 1987), and thus provide useful tool for monitoring source-area weathering conditions (Eriksson et al., 1992; Fedo et al., 1995; Fedo et al., 1996).

Chemical weathering strongly effects not only the major-element geochemistry but also mineralogy of siliciclastic sediments (Nesbitt and Young, 1982; Johnsson et al., 1988; McLennan, 1983). Chemical Index of Alteration (CIA), a quantitative measure proposed by Nesbitt and Young (1982) is therefore potentially useful to evaluate the degree of chemical weathering. High CIA values reflects the removal of mobile or unstable cations (Ca, Na, K) relative to highly immobile or stable residual constituents (Al, Ti) during weathering (Nesbitt and Young, 1982). Conversely, low CIA values indicate the near absence of chemical alteration, and consequently might reflect cool and /or aerid conditions.

Nesbitt and Young (1982) defined a CIA to quantitatively measure the degree of weathering (in molecular proportions), where CaO* represents the Ca in the silicate fraction only.

$CIA = [Al_2O_3/(Al_2O_3+CaO^*+Na_2O+K_2O)]\ 100$

where all oxides are in molecular proportions except CaO*

$CaO^* = \text{mol } CaO - \text{mol } CO_2\ (cc) - (0.5\times\text{mol } CO_2)\ (dol) - [(10/3) \times P_2O_5]\ (ap)$

(cc = calcite; dol = dolomite; ap = apatite)

In the above formula and in other indices like Chemical Index of Weathering (CIW; Harnois, 1988), Plagioclase Index of Alteration (PIA; Fedo et al; 1995), triangular diagrams like ACF, A-CN-K which would be discussed later, it is necessary to make a correction to the measured CaO content for the presence of Ca in carbonates (calcite, dolomite) and phosphates (apatite). This is normally accomplished by calculating corrections from measured CO_2 and P_2O_5 contents. Where such data are not available (generally the case for CO_2), approximate corrections can be made by assuming reasonable Ca/Na ratios in silicate material. For this study, CaO was corrected for phosphate using P_2O_5, where data is available. In the absence of CO_2 data correction for CaO in carbonate mineral is difficult. Therefore, after applying correction for apatite in the samples if the remaining number of CaO moles less than that of Na_2O, this CaO value was adopted. If the number of CaO moles is greater than Na_2O, CaO* was considered to be equivalent to Na_2O assuming a Na_2O/CaO ratio of unity. Since Ca is typically lost more rapidly than Na during weathering, this is likely to yield minimum CIA values, by upto 3 units (McLennan, 1993). Donnelly (1980) and McLennan et al. (1990) have found that the discrepancies are likely to be greatest for intermediate CIA (60-80), since at low CIA this approach is generally valid, and at high CIA both Na and Ca concentrations are low and uncertainties have little effect on CIA.

CIA values for average shales range from 70-75, which reflects the compositions of muscovites, illites, and smectites. Intensely weathered rock yields mineral compositions of kaolinite or gibbsite or chlorite and a corresponding CIA that approaches 100. Maynard et al. (1991) found chemical, as distinct from physical, reworking of the sediments can be estimated by using the Chemical Index of Alteration (CIA).

CIA values for Chaliyar river sediments range from (including major tributaries) 55.9-73.1 with an average of 60.5 (Table 5.2). The minimum CIA value of 55.9 is seen in one of the TS sample, Karim puzha (H-32) and also in the LS sample of Chaliyar main stem (H-22). The minimum value of CIA for the Karim puzha tributary is mainly due to high content of total feldspar among tributary samples (12%). However the minimum CIA value for the sample H-22 could be due to feldspar content in the coarser fraction because this sample has ~ 62% coarse sand and above material which is not reflected in the modal mineralogy. This is because the modal analysis is carried out only in a single size fraction (+35; coarse sand). The maximum CIA value of 73.1 is seen in the sample H-13 which has the second highest proportion of mud (~ 22%) among all the samples. The close similarity of CIA value of this sample with that of the average shale indicates that they are highly weathered nature consisting of kaolinite, chlorite and gibbsite. Modal analysis also shows that they have low content of feldspar (3.8%). The high CIA value for this sample points that the clays are highly matured with least amount of adsorbed mobile elements like Ca, Na and K. This again is reflected in the CaO, Na_2O and K_2O spectral patterns, all of them showing negative anomalies. Among all the samples in the Chaliyar river this sample has the lowest Na_2O and K_2O content. In contrast, the sample H-26, which is very near to the river mouth (estuarine), has the highest content of mud (~ 42%) but the CIA value is only 60.5 which is same as that of average Chaliyar river sediments. This indicates that the clays in this sample show less maturity due to adsorption of mobile cations like Ca, Na and K. Clays have very good adsorptive or ion exchange property especially in the saline environment. Hence it is seen that these elements are enriched in the sample H-26. Similarly in the Chaliyar main stem sample H-16 and H-27 consists of equal amount of mud (~20%) but in sample H-16 the silt proportion is very high (~ 16%; second highest among all the samples) when compared to clay (~4%) and in sample H-27 the silt and clay proportion are almost same (~ 10% each). Following the textural classification of Folk et al. (1970), H-16 and H-27 are named as silty sand and muddy sand respectively. The CIA of the above two samples also show contrasting values, 57.2 and 65.8 respectively. This clearly indicates that the silt fraction in the sample H-16 is less weathered probably containing some amount of unweathered feldspars while the sample H-27 has more weathered finer material even though their chemistry indicate the presence of adsorbed cations like Ca, Na and K as expected because they are nearer to the river mouth and in the estuarine environment. Similarly, samples H-26 and H-27 are from locations close to the Chaliyar estuary. Their CIA values 60.5 and 65.8 respectively differ by approximately five units, which again emphasize the idea that the higher proportion of silt and clay (mud) has the more adsorptive capacity of mobile cations because of which the intensity of chemical alteration is masked or tend to show lower values similar to the effect of K-metasomatism seen in some of the mud stones and siltstones (Eriksson et al., 1992), and shales (Fedo et al., 1996). However the two processes differ, the former being a surficial one and the latter is associated with diagenesis.

In the TS the CIA value ranges between 55.9-64.8 with an average of 60, in the US it varies between 59.2-61.4 with an average of 60.5, in LCS it ranges between 56.8-73.1 with an average of 63.4 and in the LS the CIA value ranges between 55.9-62.1 with an average of 57.8 (see Table 5.2 for variation and for averages 5.4a). This clearly indicates that the highly weathered material and less weathered material are seen in the lower reaches of the Chaliyar main stem. The lower average CIA values for the LS in comparison to the TS and US emphasize that the downstream tributaries, which drains mainly through charnockitic terrain, carries less weathered material to the Chaliyar main stem. This view is supported by a slight increase in the feldspar content in lower reaches and high content of silt at some stations. However, the average quartzo-feldspathic content (%QF) in the LS and LCS looks identical (%QF=91,9) and almost similar to the average Chaliyar river sediments including tributaries - but relatively higher than the US (%QF=94,6). Among the groups the US show least variation in CIA values varies least and hence they show striking similarity to that of average Chaliyar CIA value. Interestingly the average CIA value of 60 for TS is also same as that of average Chaliyar even though they contain significant percentage of gravels (see Table 3.1). Thus in comparison with LS, other areas or groups yielded higher average CIA values for the Chaliyar river sediments, reflecting the incorporation of slightly more weathered materials (particularly LCS samples).

Several workers have used the CIA values to infer degree of weathering in Precambrian pelitic rocks (Wronkiewicz and Condie, 1989, 1990). However, Maynard et al. (1991) applied this technique to sand -sized clastic rocks. According to them as long as Al_2O_3 is greater then 1%, they believe that the procedure provides useful information if comparative data from modern sands are used.

Tables 5.3a, b & c show the chemical composition of modern sands (sands from selected major rivers of the world as well as from known tectonic settings), suspended or fine-grained delta muds from the various rivers and estimates of the average composition of fine-grained erosional products from some of the major denudation regions of the world respectively. Chaliyar river sediments yielded average CIA value of 60.5, same as or close to the value obtained from sediments from the 33 modern river sands, Average Brazil-Peru Border main stem sands of Amazon river (headwater regions), Irrawaddy river and slightly lower than those of Average Amazon river, Niger (Table 5.4a) (see Fig. 5.7a). This support the view that not only big rivers like Amazon are important in revealing the information concerning the average major element chemical characteristics of the continental crust but also small rivers can also provide important information. Other rivers yield CIA values either higher (e.g. Orinoco, Brahmaputra, Ganges) or lower (e.g. Modern leading and trailing edge sand, Columbia river sand, Mekong, Indus and F2, F3, F4 fractions of Meurthe River main stem, France) than those of the Chaliyar river sediments, reflecting the incorporation of slightly more weathered materials in higher CIA values while slightly less weathered/unweathered materials in lower CIA values respectively. Sediments from Orinoco and Brahmaputra show high values (78 & 73 respectively). According to Nesbitt and Young (1982), such a high degree of chemical alteration is caused by weathering under humid tropical conditions. In contrast, the Indus river contains sand with CIA values close to those of unweathered crystalline rocks (46). According to Maynard et al. (1991), the very low CIA values for Indus sands is due to virtual absence of chemical weathering in its source region. (note that for Orinoco river after applying phosphate correction alone using P_2O_5 for CaO, the remaining number of moles is found to be negative. Hence the CaO* for this river is assumed as zero. Also note that for the Average Brazil-Peru border main stem sands of Amazon river and Average Amazon river both P_2O_5 as well as CO_2 correction is made).

CIA values of suspended sediments from selected major rivers of the world are compared to Chaliyar river sediments in table 5.3b (see also Fig. 5.7c). Among this the closest in comparison in CIA values are that of the suspended sediments of the Columbia river and Mississippi river. It is interesting to note that (comparison is made only for rivers having CIA values of both sand and suspended load) the CIA values are very high for suspended load (Amazon, Indus and Niger) than sand while it is almost same for both suspended sediment and sand (Columbia, Ganges and Orinoco) though in Ganges and Orinoco the CIA values for sand is slightly higher (compare table 5.4a & 5.3b) As explained earlier the CIA values of Indus river sand resemble close to those of unweathered crystalline rock (46; granodiorite would be about 45) but the CIA value of suspended sediments is high (66) which indicates that the finer suspended matter carried by the rivers will be highly weathered products in almost all the rivers (except in Ganges and Orinoco river the suspended sediments show slightly lower values of CIA when compared to sand) and also that the suspended load is not an analog to the bedload material even though the suspended load gives information about the intensity of weathering in the source region. However in the case of Indus river this is not true because as already mentioned earlier there is virtual absence of chemical weathering in its source region. But physical break down of especially plagioclase feldspar during transport and weathering in flood plains may be the major cause for the high CIA value for the suspended sediments of Indus river. The generally high CIA values for the suspended load implies that they are highly leached out in unstable cations like Ca, Na and K and enriched in Al. Study of Dupre at al. (1996) on the Congo basin proved that the river-borne suspended sediments are depleted in most soluble elements (U, Rb, Ba, K, Na, Sr and Ca) while the above elements are enriched in dissolved phase. Moreover the CIA values of suspended sediment does not always show source area weathering conditions but as already shown by McLennan (1993) they are very useful phase among the three, namely dissolved, suspended and bedloads.

CIA value of Chaliyar river sediments show striking similarity with the erosional products from some of the major denudation regions of the world (Table 5.3c) (Fig. 5.7d). CIA values of Central America (61) and New Zealand (S.Island) (61) have similar value to that of average Chaliyar river sediments (60.5). Other areas like Alpine Europe (CIA=64), Northwest South America (CIA=63) show slightly higher CIA values while Western Europe (CIA=76) and U.S. Atlantic Coast (CIA=67) show high values in comparison with Chaliyar river sediments. Ocean Islands (excluding N.Z.) show lower CIA values (54) in comparison with average CIA value for Chaliyar bedload sediments.

Table 5.3d and figure 5.7b displays the chemical composition of some selected sediments and sedimentary rocks. Average UCC has a CIA value of about 47, and average Nilambur laterite has a value of 87.5. Thus, variations of CIA between unweathered crystalline rocks (UCC) and the sedimentary rocks (average Nilambur laterite) is maximum. Although the CIA in average Nilambur laterite, Post-Archean Average Shale (PAAS) and average sediment is about 87.5, 70.4 and 72.9 respectively, for the average Chaliyar river sediment it is some what lower, about 60.5 (see Table 5.4 b). CIA values of average Chaliyar river are close but slightly lower to those of loess (CIA=63.4) and average lithic-arenite (CIA=65) while other sedimentary rocks like average sandstone, quartz-arenite show higher values and average graywacke, average arkose show lower CIA values (see Table 5.4 b). Average CIA value of LCS of the Chaliyar main stem is strikingly similar to that of the loess (for both CIA=63.4). Other sediments like average Buhwa shales of Zimbabwe and average Mount Isa Inlier Group I and Group II samples of Queensland, Australia has CIA values higher than those of the average Chaliyar river sediments. However, the highest CIA of LCS sample of Chaliyar main stem (sample H-13) and that of average Buhwa shale are almost identical (73.1 and 73.7 respectively) and fall within the spectrum of typical shale averages (about 70 to 75).

5.8.2 Chemical Index of Weathering (CIW)

In literature several workers on the geochemistry of sedimentary rocks including shales, paleosols and many soil profiles have reported that K_2O content is typically more abundant than might be predicted by comparison with basement sources (Retallack, 1986; Nesbitt and Young, 1989; Rainbird et al., 1990; Kimberly and Holland, 1992). This potassium enrichment "problem" led Harnois (1988) to propose a new weathering index, the Chemical Index of Weathering (CIW in molecular proportions) and is identical to the CIA except that it eliminates K_2O from the equation.

$$CIW = [Al_2O_3/(Al_2O_3+CaO^*+Na_2O)].100$$

where CaO* represents Ca in silicate fraction only.

Fedo et al. (1995) pointed out that this approach utilizes total aluminium without correction for Al in K-feldspar rich rocks, whether chemically weathered or not, are misleading and they yielded very high values. Most strikingly, in their study they found that unweathered potassic granite has a CIW value of 80 and fresh K-feldspar has a CIW of 100, similar to values found for residual products of chemical weathering (CIW for smectite=80; kaolinite, illite and gibbsite=100). Overlooking the above situation and citing the K-enrichment problem, numerous authors have used the CIW in preference to the CIA as weathering index (Condie et al., 1992; Maynard, 1992; Condie, 1993; Sreenivas and Srinivasan, 1994). However, study on sedimentary rocks and paleosols by Fedo et al. (1995) proved that the use of the CIW calculation to quantify chemical weathering intensity is inappropriate and should be used with caution. Since the K-enrichment is mainly seen in sedimentary rocks (shales) which is primarily a diagenetic process (K-metasomatism), similar kind of effect on unconsolidated sediments (like river sands) could be ruled out or insignificant. However, the CIW values of selected river sands including Chaliyar river and sedimentary rocks in this study show high values when compared to CIA (discussed in detail later). But the CIW and CIA values of Chaliyar river sediments are almost identical with slightly higher values for CIW (Table 5.2). Here it is discussed in detailed and compared with other river sands and sedimentary rocks.

Tables 5.2 and 5.4a tabulate the CIW value of Chaliyar river sediments and averages of different groups respectively. The CIW values are always higher when compared to CIA and it ranges between 58.2 and 74.8 with an average of 62.7. As expected the average CIW values of different groups are also slightly higher than CIA and among this the LS samples of the Chaliyar main stem show the lowest CIW and LCS show highest CIW (see Table 5.4a). As already explained the slight decrease in the CIW values in the LS when compared with other groups is mainly due to addition of less weathered materials by the downstream tributaries to the main stem. The consistent increment of CIW value of ~2 with respect to CIA in the Chaliyar main stem points that the slight decrease in CIW value for the LS especially in comparison with US and TS is not due to input of K-feldspar but more due to the addition of plagioclase carried by the downstream tributaries to the main stem sediments. This will become more clear later when Plagioclase Index of Alteration (PIA) is discussed. However, the increase in average CIW value for TS with respect to CIA is only 1.6 (for other groups i.e. US =2.1; LS and LCS=2.3) which indicates slight progressive enrichment in K-feldspar content from TS to US to LS and LCS of the Chaliyar main stem. This is reflected in the downstream spectral pattern where K_2O content shows an increasing trend while the Na_2O/K_2O show decreasing trend towards the river mouth (see Fig. 5.1i & l). Moreover, the CIW values when compared with CIA for river sediments gives information about addition of feldspars to the channel sediments as well as progressive enrichment of K-feldspar with increasing distance of transport from the source terrain. Hence it is found appropriate to use both CIW and CIA especially for river sediments.

The CIW values of selected major rivers of the world is compared with Chaliyar river sediments in Table 5.4a. Even though the CIA values of Chaliyar river sediments, 33 modern river sands and average Brazil - Peru Border main stem sands of Amazon river is almost identical (60) the CIW is high for Chaliyar river sediments and is shown in Table 5.4a. Even though the CIA values of Chaliyar river sediments, 33 modern river sands and average Brazil-Peru Border main stem sands of Amazon river is almost identical (60) the CIW is high for the latter ones when compared to average CIW for Chaliyar river. This is mainly because, with increasing distance of transport the plagioclase breaks down while the K-feldspar get enriched because they are less susceptible to alteration. This preferential removal of plagioclase significantly increases the CIW and at the same time the K_2O content is eliminated from the CIW formula. Hence it is due to the above combined factors that the CIW values for major rivers show high values when compared to CIA. However, similar kind of K-feldspar enrichment is not seen in Chaliyar river (though there is slight increase in K_2O content towards the river mouth it is insignificant when compared to world rivers) mainly because of their short flowing nature and moreover the plagioclase breakdown will be less within shorter distance of transport in rivers. The generally very high values of CIW and CIA especially for big river sands of the world (e.g. Orinoco, Amazon) are due to following reasons :

a) preferential removal of plagioclase with increasing distance of transport while there is enrichment of K-feldspar and
b) weathering of plagioclase in modern flood plains.

The latter could also be the reason for the very high CIA values for the suspended sediments (66) of the Indus river because sands show very low CIA (46) indicating no chemical weathering in source region.

Generally very high CIW for big rivers when compared with its corresponding CIA value may also be due K-metasomatism especially in modern flood plains. Though floodplain weathering (Potter, 1978), intrastratal weathering in alluvium (Walker et al., 1978) and in modern gravels (Bradley, 1970) are documented in literature the diagenetic process (K-metasomatism/enrichment) and its extent on flood plain sediments has got little attention. However such processes are well-documented in sedimentary rocks, soil profiles etc. Flood plains are major store houses of fine grained materials and will remain almost stable for 100's of years. Hence the CIW value in comparison with CIA for modern big river sands should be used with caution to infer the downstream enrichment of K-feldspar. This is because the high CIW values may be contributed by clays (illite) rather than the K-feldspar along with the CIW values especially in big rivers. However, the almost similar values of CIW and CIA for Chaliyar river sediments indicate that K-feldspar enrichment due to preferential removal of plagioclase is negligible and also that modern flood plain weathering is almost nil as flood plains are almost absent in the basin, even though minor terraces are seen in slopes of Nilambur valley.

CIW of average Chaliyar river sediments is compared with sediments/sedimentary rocks which is given in table 5.4b. Average graywacke and average arkose show almost similar CIW values (60.5 and 63.8 respectively) with that of average Chaliyar (62.7). As expected the UCC show lower CIW value (54.3) but higher than CIA value. All other sediments/sedimentary rocks shows very high CIW values when compared to CIW of average Chaliyar river sediments. It is interesting to note that the CIW and CIA of average Nilambur laterite is almost identical (88.1 and 87.5 respectively) indicating that K_2O content is negligible in source rocks or that K-feldspar are totally weathered and also that they have not undergone any K-metasomatism as in the case of Precambrian Khondalites of Kerala, reported by Sreenivas and Srinivasan (1994) which has undergone K-enrichment. Similarly very high CIA values for Buhwa shales Zimbabwe; mudstone and siltstones of Mount Isa Group I and Group II, Queensland Australia clearly indicate that these sediments have undergone potassium metasomatism. However, according to Fedo et al. (1995) the above relationship should be interpreted with caution especially using CIW.

5.8.3 Plagioclase Index of Alteration (PIA)

Fedo et al. (1995) modified the CIA equation to monitor plagioclase weathering alone which is given by the equation :

$$PIA = [(Al_2O_3-K_2O)/(Al_2O_3+CaO^*+Na_2O-K_2O)].100$$

Where CaO^* represents Ca in silicate fraction only and PIA means Plagioclase Index of Alteration (in molecular proportion). This equation is more appropriate to understand the extent of plagioclase alteration alone since K_2O is subtracted from Al_2O_3 in the numerator and denominator of the CIA equation. Fedo et al. (1995) also found that this equation yields values of 50 for fresh rocks and values close to 100 for clay minerals such as kaolinite, illite and gibbsite which is consistent with the values derived from CIA equation.

Table (5.2 & 5.4a) furnishes the PIA values for Chaliyar river sediments samples and averages of different groups respectively. As expected the PIA values are more similar to CIA values than CIW but it is slightly higher in all the samples. The PIA values ranges from 56.4 to 74.2 with an average of 61.3. However, the PIA values are slightly less than CIW and the difference between the CIW of a sample and its corresponding PIA varies between 1 and 2 while the difference between PIA and its corresponding CIA is <1 for all the samples except for sample H-13 which has the maximum CIA, CIW and PIA among all the samples, it is just the opposite i.e. difference between PIA and CIA is between 1-2. (Thus it can be generalised to a certain extent that when the PIA values are ~80 and above the difference between CIW and its corresponding PIA narrows down especially in the case of sedimentary rocks, like shale and laterite). The average PIA values of different groups in the Chaliyar river are also slightly higher than the CIA values of the different groups and lower than CIW (see Table 5.4a). The average US and the average TS has PIA values identical (61.2 and 60.5 respectively) to average Chaliyar river sediments (61.3). However, the average LCS has slightly higher PIA value (64.4) showing their more weathered nature while the average LS has slightly lower PIA value (58.4) indicating less weathered nature when compared to average Chaliyar river. The slightly lower average PIA value for the LS of the main stem in comparison with the US and TS clearly emphasize that small amount of plagioclase is contributed by the downstream tributaries to the Chaliyar main stem sediments. This also supports the view that the source regions of the downstream tributaries may be experiencing slightly warmer climate due to which they may be contributing less weathered material to the Chaliyar main stem. When average PIA values of different groups are considered except the LS of Chaliyar main stem the PIA values shows an increasing trend from tributary sediments (60.5) to US (61.2) to LCS (64.4) reflecting slight downstream weathering of plagioclase.

In comparison with the selected rivers of the world the average PIA value of Chaliyar river (61.3) closely resemble with that of modern river sands (63.3), average Brazil-Peru border main stem sands of Amazon river (63.1), and all the fractions of Meurthe river main stem, France (F2=61.9, F3=63.1, F4=61.8) (Table 5.4b). However, the PIA of F2 (coarse fraction : 0.3-0.5mm) and F4 (fine fraction : <0.1 mm) fractions are strikingly similar to the average Chaliyar river-while the PIA of F3 fraction (medium fraction : 0.1-0.3mm) are close to that of average LCS of the Chaliyar river (see Table 5.4b). Even though the PIA values of different fractions of Meurthe river, France are comparable with the average Chaliyar river sediments the CIA values differ much and is always lower for different fractions when compared with CIA of average Chaliyar river (see Table 5.4b) The significant differences between the PIA and its corresponding CIA values (PIA is higher than CIA) for Orinoco river and different fractions of Meurthe River, France suggest that a great degree of K-feldspar enrichment due to preferential weathering of plagioclase is happening in these rivers. However, in the Orinoco river this is insignificant because it is having SiO_2 content identical to average quartz-arenite (~97; see Table 5.3a) but when the absolute content of K_2O (0.25 %) and CaO (0.03 %) is considered the K_2O seems to be enriched and is found to be significant because as mentioned earlier there is vast difference between PIA and CIA for this river (PIA>CIA). Hence it supports the idea that progressive enrichment of K-feldspar at the expense of plagioclase can cause vast differences between PIA values and its corresponding CIA values, but PIA is always greater than CIA. More over the K-feldspar enrichment is reflected in high CIW values for the above rivers. Very high PIA value of 100 for Orinoco river means that plagioclase is totally absent and at the same time Al_2O_3 is less than one and whatever Al_2O_3 left is mainly due to either K-feldspar/illite. According to Johnsson et al. (1991) the mean QFR composition of Orinoco main stem sands, (QFR=95,2,3) lies near the center of quartz-arenite field. Similarly the identical PIA and CIA value (55 and 54.1 respectively) for the average Columbia river suggests that there is no significant plagioclase weathering taking place even though its CIW is slightly higher (60.5) indicating of probable K-feldspar enrichment. Hence Chaliyar river can be considered as analogous to Columbia river in its behaviour even though the CIA, CIW and PIA values are higher for Chaliyar when compared to that of Columbia river. This is mainly due to the highly weathered nature of source rocks in the Chaliyar basin while that of Columbia river they are less weathered. Similarly the Brazil-Peru Border Amazon river sediments and average Amazon river sediments are to some respect similar with the Chaliyar river sediments especially in CIA values and slightly higher values for CIW and PIA for the former two rivers. The higher CIW values for the above rivers when compared to average CIW of Chaliyar river is mainly due to K-feldspar enrichment while the increase in PIA for the above rivers when compared to PIA of Chaliyar is probably due to slightly higher amount of plagioclase weathering. This may be true because the distance traveled by these sediments in the above rivers are much higher when compared to the distance traveled by the Chaliyar river sediments, due to which progressive weathering of plagioclase occurs and at the same time K-feldspar gets enriched. Moreover these big rivers may have extensive flood plains where plagioclase weathering undergoes. The above two factors are less practical in the case of Chaliyar river because they are short flowing and flood plains do not develop due to higher gradient, heavy rainfall and high frequency of floods (bank full discharge).

PIA values of some of the sediments/sedimentary rocks are compared with the average Chaliyar river sediments in table 5.4b. As expected the upper continental crust has almost identical values of PIA and CIA (47.4 and 48 respectively) and average Nilambur laterite also show similar PIA and CIA values (88 and 87.5). This shows that the source rocks of the Chaliyar river sediments are almost devoid of K-feldspar though they may contain some plagioclase. The near absence of K-feldspar in Nilambur laterites is mainly because they are deficient in the parent rocks. The maximum PIA value is 100 (kaolinite, gibbsite) and unweathered plagioclase has a PIA of 50. Average Nilambur laterite have an average PIA value of 88, which indicates that virtually all primary plagioclase has been converted to secondary clay minerals. But however slightly lesser value of PIA for Nilambur laterites when compared to Buhwa shales, (~98 data from Fedo et al., 1996) Zimbabwe, indicates that primary plagioclase is totally weathered in shale and lower values of average PIA for Nilambur laterite is entirely due to whatever primary plagioclase left in them rather than the K-feldspar content. Although the PIA in average Nilambur laterite is about ~88, for average Chaliyar river sediment it is lower, about ~61 which suggests that the Chaliyar river sediments which have undergone fluvial transport got enriched in plagioclase while most of the weathered materials (clays like kaolinite, chlorite, gibbsite) are carried away in suspension and probably deposited in the shelf region. The essential difference between average arkose and average graywacke is the feldspar content. It is clear from the PIA and CIW values that the average arkose has slightly higher K-feldspar as well as less weathered plagioclases than the average graywacke. However, the PIA values of average graywacke and average arkose is consistently lower when compared to average PIA value of Chaliyar river sediments (see Table 5.4 b) indicating the highly weathered source rocks in Chaliyar basin. Similarly the PIA values of average Lithic-arenite (69.4) and average quartz-arenite

(73) are higher than the PIA value of average Chaliyar river sediments suggesting that plagioclase alteration is less in Chaliyar river sediments. Hence the Chaliyar river sediments may be considered as an intermediate between lith-arenites - graywacke - arkoses even though mineralogically (in terms of the %QFR data) the sediments range in composition from quartz-arenite and sub-arkoses.

5.9 Weathering trend

Weathering trends can be observed on Al_2O_3-CaO^*+Na_2O-K_2O (A-CN-K) and Al_2O_3-CaO+Na_2O+K_2O-FeO+MgO (A-CNK-FM) (Nesbitt and Young, 1984, 1989), (Al_2O_3-K_2O)-CaO^*-Na_2O (A-C-N) (Fedo et al., 1995) and (Al_2O_3-Na_2O-K_2O)-CaO^*-(FeO-TiO_2-Fe_2O_3+MgO) (A-C-F) triangular plots. The above weathering trends and a plot of the SiO_2/10-CaO+MgO-Na_2O+K_2O (S/10-CM-NK) (Vital and Stattegger, 2000) with respect to the Chaliyar river sediments are discussed below and is depicted in figure 5.8.

5.9.1 A-CN-K plot

The A-CN-K triangle can be used to infer initial compositions of source rocks. Many weathering profiles show a linear trend sub-parallel to the A-CN join in the A-CN-K triangle (Nesbitt and Young, 1984). In the absence of K-metasomatism, a line extended through the data points towards the K corner, intersects the feldspar join (see Fig. 5.9a and b) at a point that shows the proportion of plagioclase and K-feldspar of the fresh rock. This proportion yields a good indication of the type of parent rock. When the above line is constructed for the average Chaliyar river sediments it intersects the feldspar join more or less similar with that of A-type granite. As seen in the A-CN-K diagram the Chaliyar river sediment samples show a trend towards the Al_2O_3 apex indicating loss in Ca, Na and K.

The average data for Chaliyar river sediments, various group averages like average tributary, average US, average LS and LCS are plotted in A-CN-K compositional space in figure 5.9a. Also shown on the diagram are the positions of average modern river sands and some of the selected modern big rivers of the world. Though majority of the rivers plot near to the various averages of Chaliyar the major rivers of the world slightly towards the K-apex while the average Chaliyar plot more closer to the A-CN line probably indicating that they are derived from average Archean upper crust/average tonalite (not plotted in figure).

Similarly the Chaliyar average and various group averages along with post-Archean Average Shale (PAAS), UCC and other sediments/sedimentary rocks are plotted in A-CN-K diagram (Fig. 5.9b). The Chaliyar TS, US, LS and LCS show significant loss of Ca, Na and K when compared to the UCC, as they tend to plot towards the A apex. The average Nilambur laterites which are highly weathered in terms of CIA plot close to the A apex and almost on the A-CN line indicating very low K_2O in them.

5.9.2 A-C-N plot

The nature of chemical weathering can also be portrayed in A-C-N compositional space (Fig. 5.8) following the equation for plagioclase weathering (PIA - Plagioclase Index of Alteration) of Fedo et al (1995). However, in the PIA equation due to non-availability of CO_2 data it is assumed that $CaO^* \equiv Na_2O$ (see section CIA for more details). But if CaO* and Na_2O are equated the A-C-N diagram become meaningless. Hence to overcome this, correction for apatite using P_2O_5 is applied wherever data is available and CO_2 (carbonate) correction is not made and the remaining CaO is used in the A-C-N plot. Similar to the A-CN-K plot the Chaliyar river sediments show weathering trend with LCS tend to plot towards the A apex while the less weathered LS and TS slightly away from the apex.

The average Chaliyar river sediments and its various groups are compared with major rivers of the world and sediments/sedimentary rocks in Fig. 5.10a & b. The average LCS and the average Brazil-Peru border Amazon river sediments plot very close while the average LS, average US and average Chaliyar river sediments plot close to the average Columbia river and average graywacke. Note that the average Buhwa shale and average Nilambur laterite plot close to the A apex, which indicates that virtually all primary plagioclase has been converted to secondary clay minerals.

5.9.3 A-C-F plot

The data for Chaliyar river sediments are plotted in (Al_2O_3-Na_2O-K_2O)-CaO*-[(FeO-TiO_2-Fe_2O_3)+MgO] compositional space in figure 5.8. The calculation of A, C and F for this plot is as given below:

$A = [Al2O3] - [Na2O] - [K2O]$

$C = [CaO] - 10/3 \times [P2O5] - [CO2]$

$[FeO] = [FeO] - [TiO2] - [Fe2O3]$

$F = [MgO] + [FeO]$ where all oxides are in molecular proportions.

The above calculated A, C and F is expressed as a percentage of (A+C+F).

As seen in the diagram, a shift from those areas with highest CIA towards the F-apex suggests the influence of a secondary process. Moreover in this diagram there is strong discrimination among different groups of Chaliyar river sediments. They also show weathering trend especially the main stem sediments with increasing Al_2O_3 the highly weathered LCS plot towards the A apex.

Similarly the different group averages of Chaliyar as well as the average Chaliyar river sediments along with major rivers of the world and selected sediments/sedimentary rocks are plotted in A-C-F diagram (Fig. 5.11a & b respectively). All the rivers except average Amazon river, average Orinoco river show a shift towards F-apex and they all fall in a close range. However the average Amazon and average Orinoco river (not plotted in the diagram because the C component is zero) plot farthest from the F apex, that is more closer to the A-C line indicating that they have little FeO in silicate fraction even though they are derived from highly weathered terrain and also that heavy mineral concentration is very less. This may be true because petrologically Orinoco river is quartz-arenite.

In the figure 5.11b the average Chaliyar river sediments and their different group averages, UCC also show a shift towards the F apex probably due to higher FeO in silicate fraction. Note that the average quartz arenite plot very close to the A-C line indicating small amount of FeO in silicates and they closely resemble the average Amazon river sediments (compare Fig. 5.11a & b) Note that the average Nilambur laterite and average Brazil-Peru Amazon sands are not plotted because the F component is zero which suggests that iron in silicate is nil because they are highly weathered and close to the source.

5.9.4 A-CNK-FM plot

In the A-CNK-FM diagram (Fig. 5.8), similar to what is seen in A-C-F diagram, a shift from those areas with highest CIA towards the FM apex further suggests the influence of a secondary process. TS show slightly more shift towards the FM apex probably indicating a concentration of iron-bearing heavy minerals in them and moreover they are more closer to the lateritic source. Though, the samples shift towards the FM apex in the A-CNK-FM plot is only small when compared with A-C-F diagram but the shift towards the base (CNK-FM) is more stronger.

The average Chaliyar river sediments and different group averages are compared with selected major rivers of the world and sediments/sedimentary rocks in figure 5.12a & b respectively. The average Chaliyar, different group averages except average TS plot very close to average Amazon and average Brazil-Peru Amazon. It is interesting to note that modern river sands plot slightly away from the FM-apex and more towards CNK-apex than the average Chaliyar suggesting that average Chaliyar is enriched in FM and poorer in CNK when compared to modern river sediments. Similarly the average Chaliyar, different group averages except average TS plot close to average graywacke. Moreover the average LCS samples of the Chaliyar river and average Mount Isa Group II mud stone-silt stone of Australia show significant similarities. When compared to UCC the average Chaliyar show a shift towards the FM-apex while the UCC towards CNK-apex probably indicating secondary processes in the case of Chaliyar. Note that plotting of average Brazil-Peru Amazon sands in figure 5.12a and average Nilambur laterite in figure 5.12b points that they contain Fe in non-silicate minerals.

Generally in the A-CNK-FM diagram for Chaliyar river sediments (Fig. 5.8), a shift from those areas with highest CIA towards the FM-apex is well depicted. Vital and Stattegger (2000) also found similar kind of shift for lowermost Amazon sediments and attributed it to secondary processes.

5.9.5 S/10-CM-NK plot

In the S/10-CM-NK diagram (Fig. 5.8) the LS, US samples of the Chaliyar main stem are plotted towards the S/10 apex, reflecting excess quartz and very low amounts of primary clay sized material, as well as the modification of sediment composition in due to chemical weathering. The plotting of majority of TS away from the S/10 apex, like that of LCS suggests that they are poorer in quartz as well as clay but enriched in mafic minerals. The plotting of LCS away from S/10 apex is due to the antipathetic behaviour of quartz and clay content.

The average Chaliyar river sediments and different group averages in them are compared with major rivers of the world and sediments/sedimentary rocks in the S/10-CM-NK diagram (Fig. 5.13a & b respectively). The average Chaliyar and different group averages plot very close to the modern river sediments and average Brazil-Peru Amazon sediments suggesting that the quartz abundance is almost same in the above rivers. Moreover, the plotting of average Brazil-Peru Amazon sediments close to the average Chaliyar and at the same time the average Amazon away from it, more closer to S/10 apex, suggest that they are less mature. This behaviour is expected because the sediments of average Brazil-Peru Amazon represents more of the sediments of the headwater regions of the Amazon basin. Note that the average Orinoco river plots right at the S/10 apex as they are cent percent quartz. Most strikingly the average Chaliyar river sediments and different groups plot very close to average Nilambur laterite (Fig. 5.13b) suggesting that they have similar proportions of S/10, CM and NK even though they may differ in absolute abundances. Further there is much difference between the laterites and sediments in terms of other components like FeO, Al_2O_3 etc. It is also clear from the figure 5.13a & b that different sediment groups in the Chaliyar main stem plot away from the S/10 apex in the order of decreasing SiO_2 abundance. Compared to average upper continental crust (UCC) the average Chaliyar river sediments tend to plot towards S/10 apex showing a relatively marked abundance in Si with lesser amounts of Ca, Mg, Na and K.

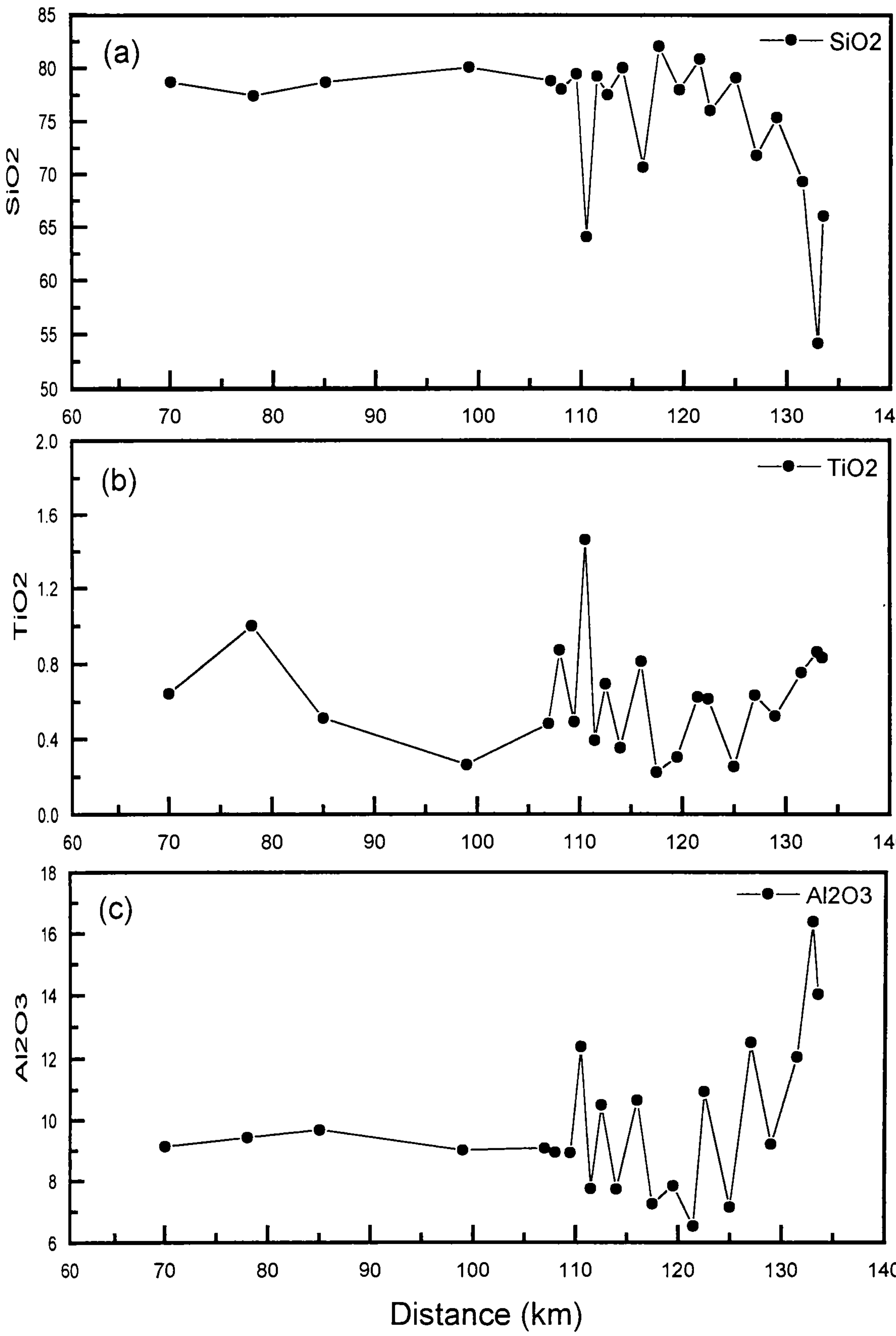
Conclusions

- The major element composition of Chaliyar bedload sediments in the main channel and the headwater tributaries is related to the mineralogical and textural characteristics of the sediments, channel morphology and bedrock lithology.
- The TS, US, LCS and LS have chemical characteristics determined by their locations in the basin, bedrock characteristics and textural and mineralogical differences.
- The TS has very high silica (average SiO_2 wt.% 70.9) reflecting the high content of quartz and high FeO(t) and MgO indicating the significant presence of mafics and opaques.

- In the main channel the SiO_2 and Al_2O_3 contents remain within a small range up to 107 km point but fluctuate highly further beyond due to the variable contents of clay in the lower reaches and inputs of feldspar to the main channel from downstream tributaries.
- The SiO_2 and Al_2O_3 variation diagrams in relation to the other major oxides reveal linear relationship that reflects the content of quartz, feldspar and clay. The variation is, however, insensitive to the differing bedrock characteristics in the upper and lower reaches of the basin and the larger inflow of quartz-poor sediments from the downstream tributaries that drain dominantly charnockitic terrain.
- The variations in CaO are influenced by the presence of clay, plagioclase feldspar and mafic minerals like hornblende and garnet in the sediments.
- The FeO(t) and MgO variations with distance show that in the upper and lower reaches of the main stem they are influenced by the bedrock characteristics, horblende being the main mafic mineral in the upstream derived from the gneissic source rocks and pyroxene in the lower reaches derived from dominantly charnockitic source rocks.
- Many of the lower reach samples appear to be immature in terms of their Na_2O content and ratios like Al_2O_3/SiO_2 and Na_2O/K_2O than the upper or middle reach samples due to the addition of plagioclase and K-feldspar by downstream tributaries to the main stem.
- The high content of CaO and to a certain extent Na_2O but very low K_2O especially in the mature sands of the lower reaches of Chaliyar main stem points to their derivation from Archean terrain.
- The Chaliyar river sediments fall in the graywacke/subarkose chemical space in standard classification diagrams.
- Climate that has influenced the extensive lateritization of the source rocks has also imparted a chemical maturity to the sediments derived there from.
- Chemical weathering indices like CIA for Chaliyar river sediments are comparable with modern rivers from tropical areas or rivers with extensive flood plain where chemical weathering is predominant.

- Triangular diagrams like A-CN-K indicate weathering trends for the source rocks such as the early complete conversion of the plagioclase to clays, transfer of FeO from the silicate to secondary oxide phases and the development of a lateritic provenance.
- Compared to the Upper Continental Crust (UCC) the average Chaliyar river sediments are enriched in Si and somewhat depleted in Ca, Na, K and Mg.
- The tectonic settings for the provenance inferred reveal continental margin sediments derived by prolonged chemical weathering of the source areas.

Fig. 5.1 Downstream variations of the bedload compositions for the Chaliyar mainstem. Major element oxide in wt.%



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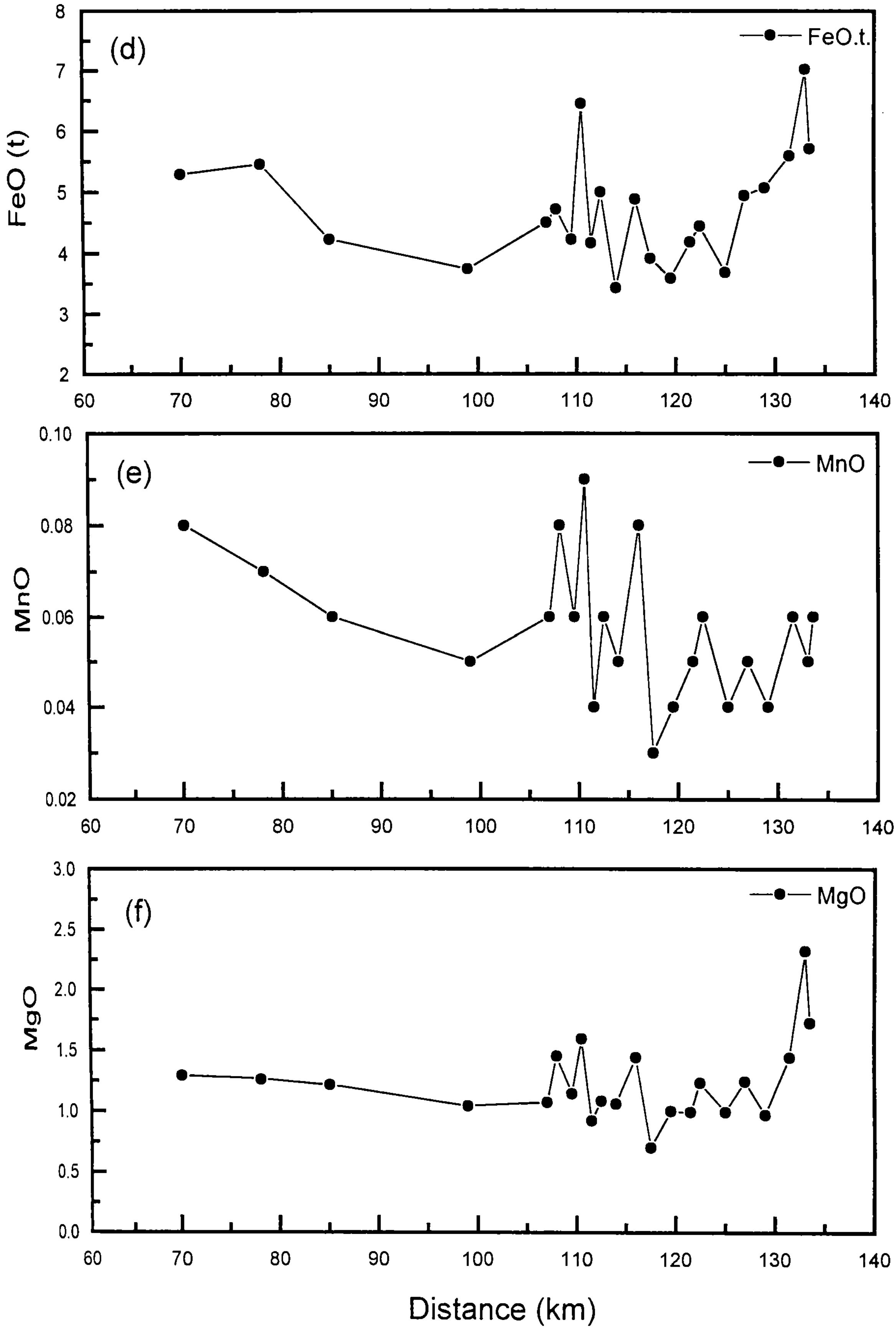


Fig. 5.1 Downstream variations of the bedload compositions for the Chaliyar mainstem. Major element oxide in wt.%

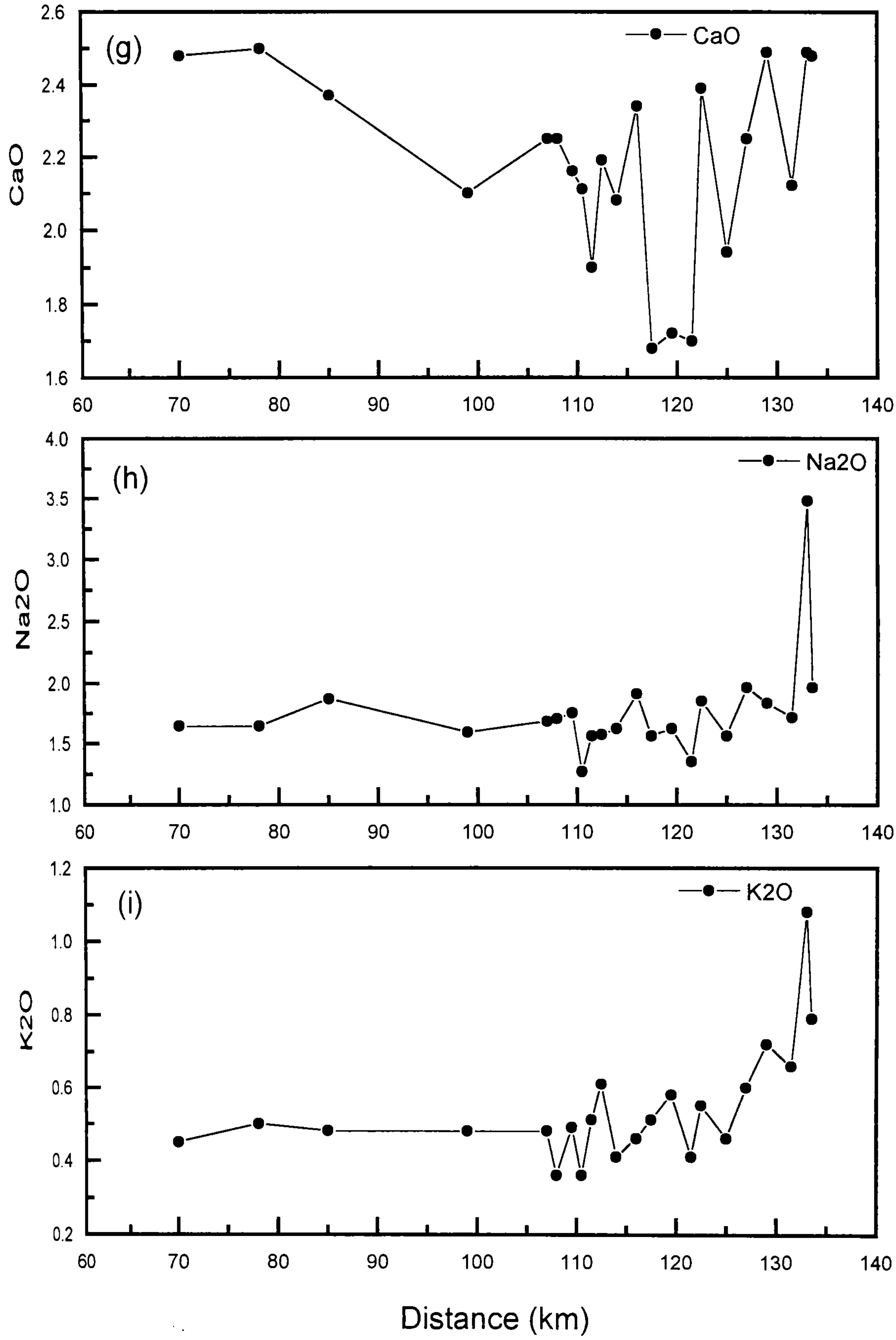
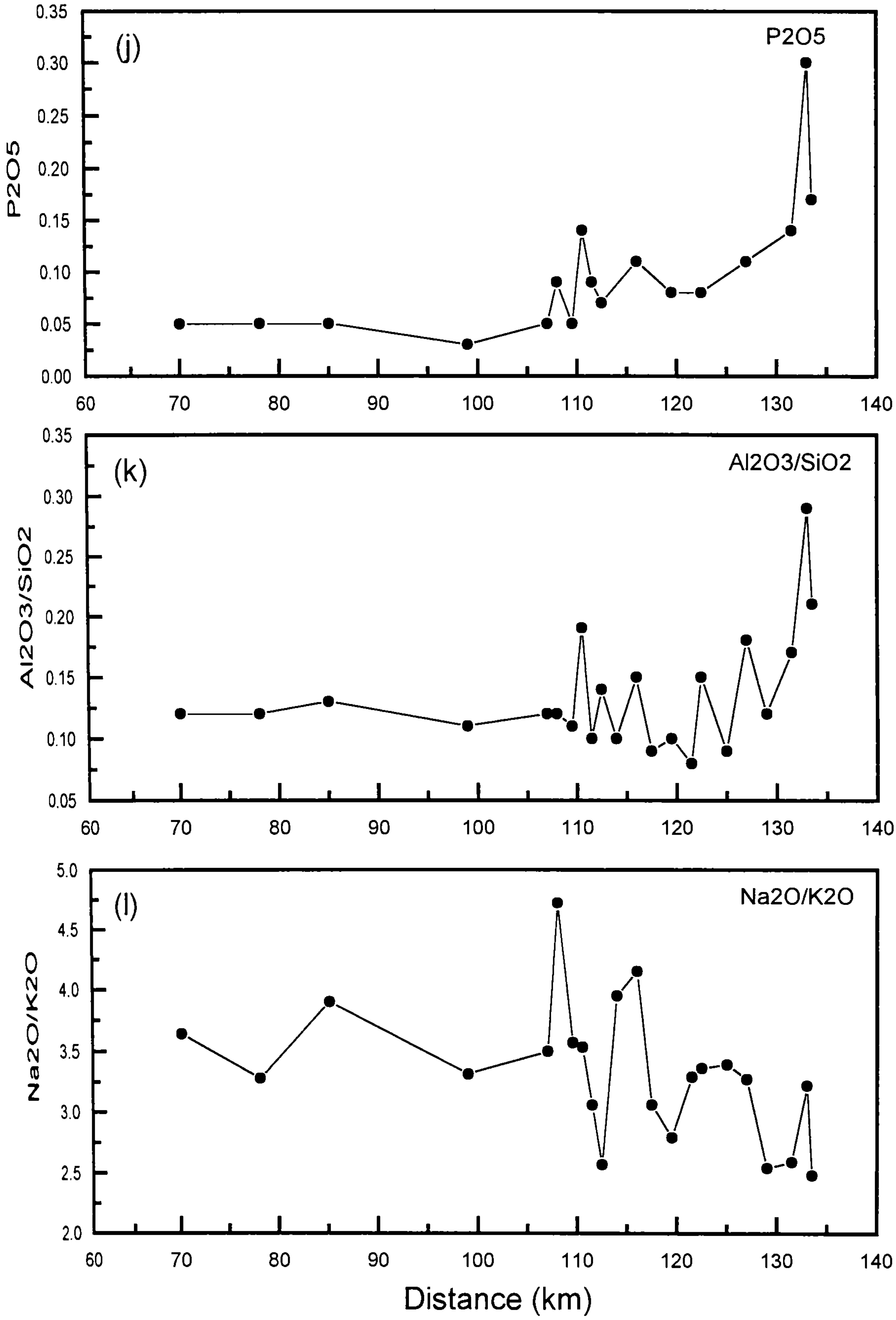


Fig. 5.1 Downstream variations of the bedload compositions for the Chaliyar mainstem. Major element oxide in wt.%



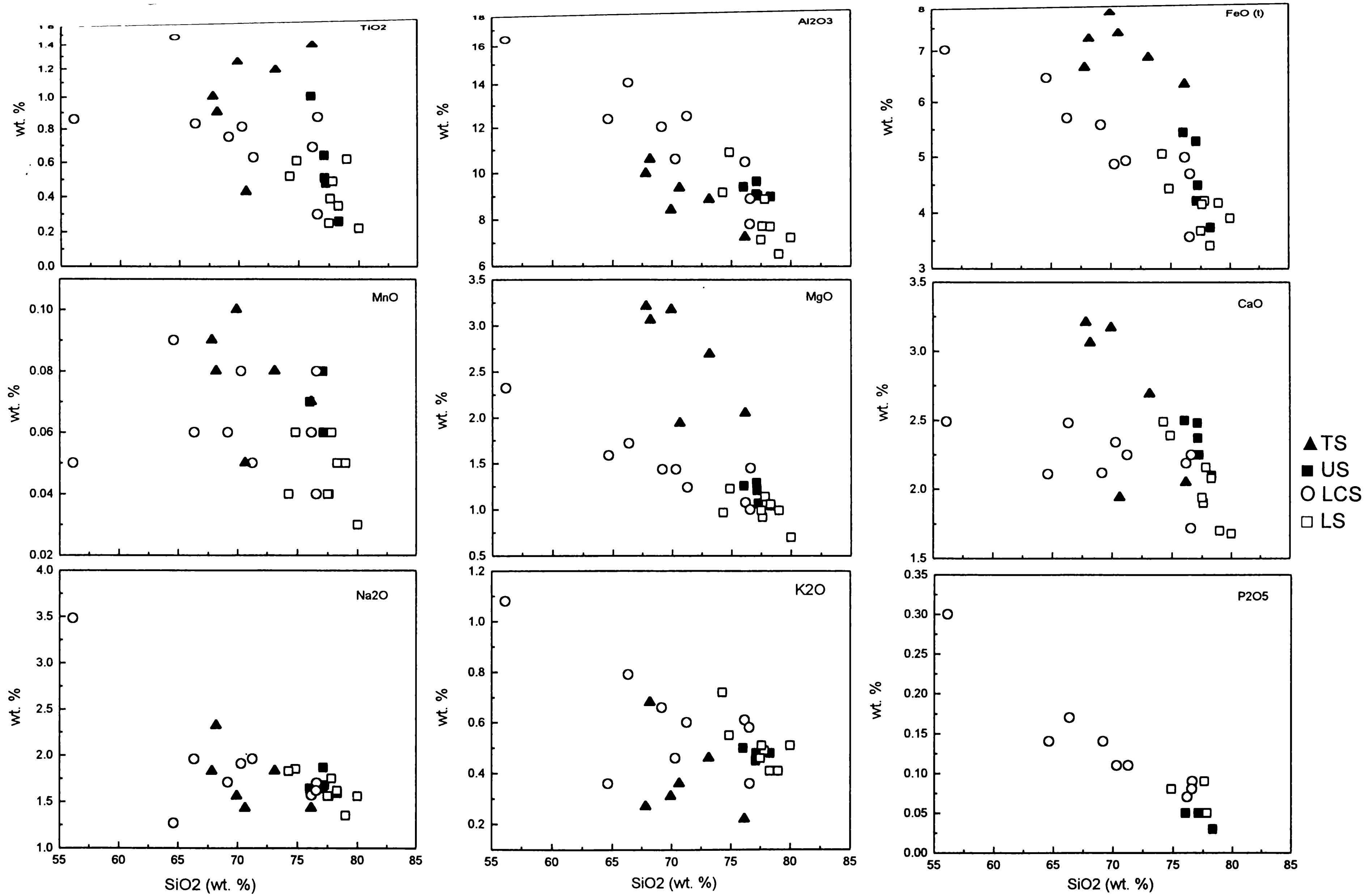


Fig. 5.2 Major Oxides (in wt. %) vs SiO2 for Chaliyar river sedimnets

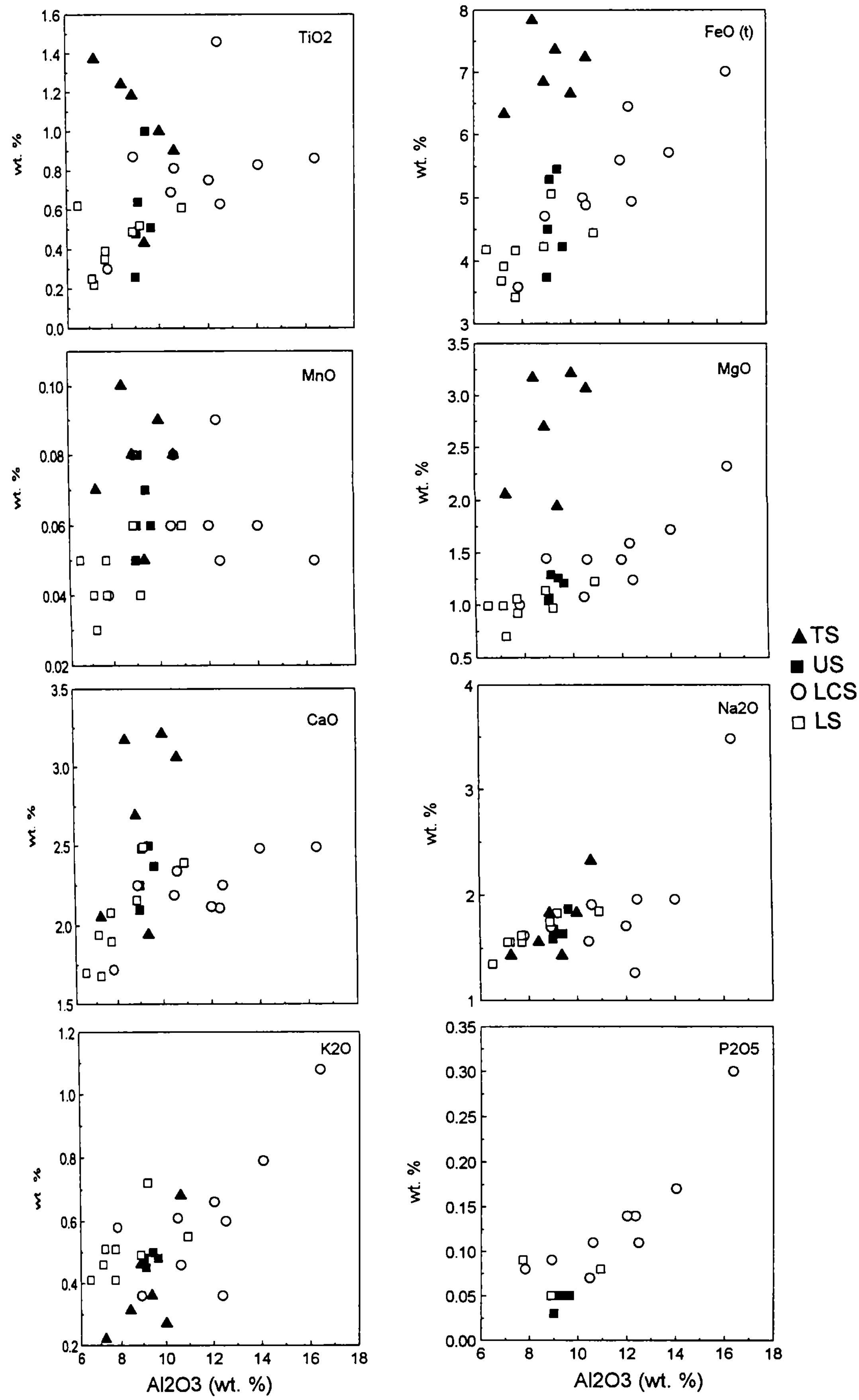


Fig. 5.3 Variation diagrams of major elements (vs) Al2O3 of the Chaliyar river sediments

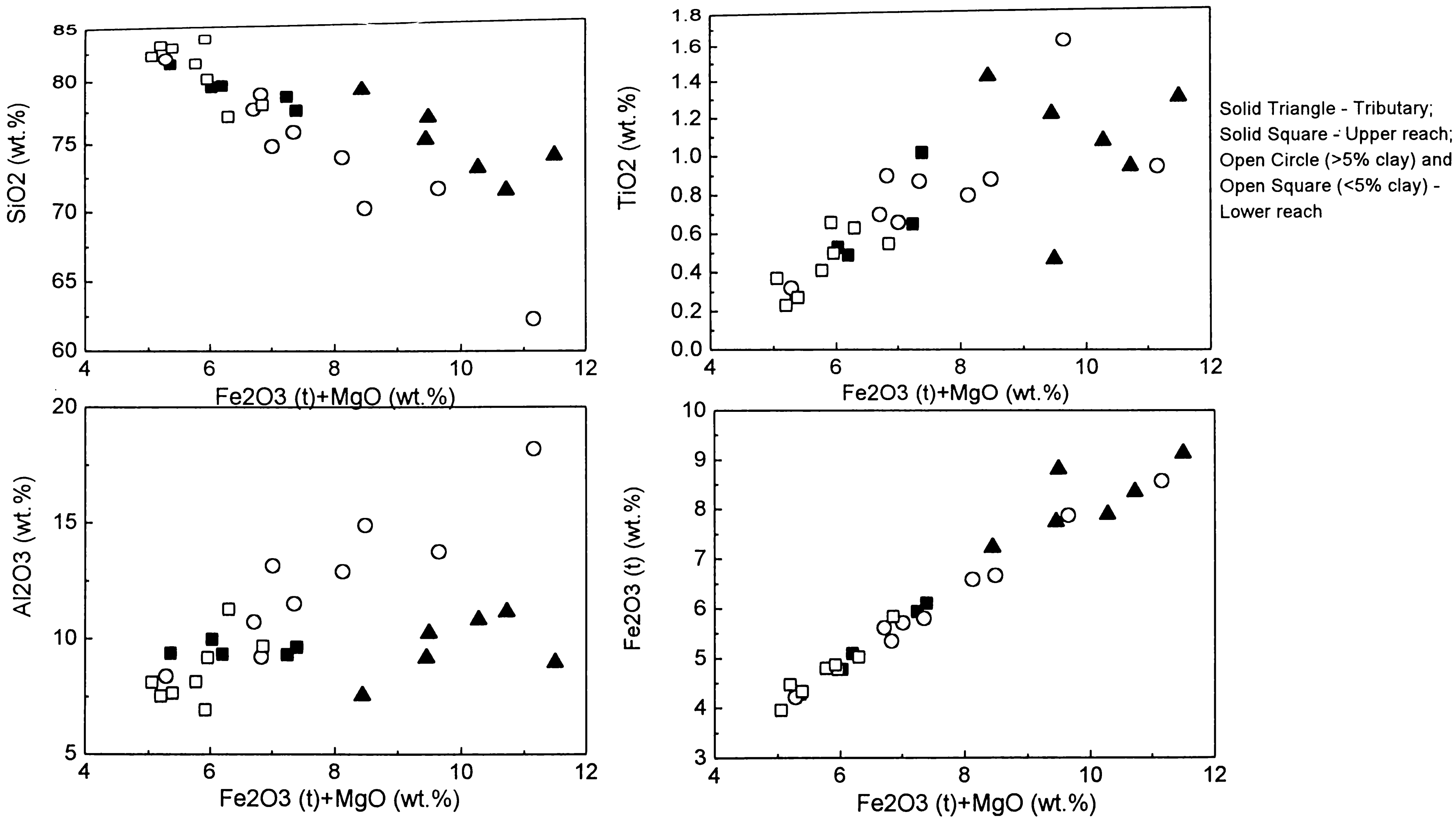


Fig.5.4 Major Oxides (in wt.%) vs Fe2O3(t)+MgO for Chaliyar river sediments

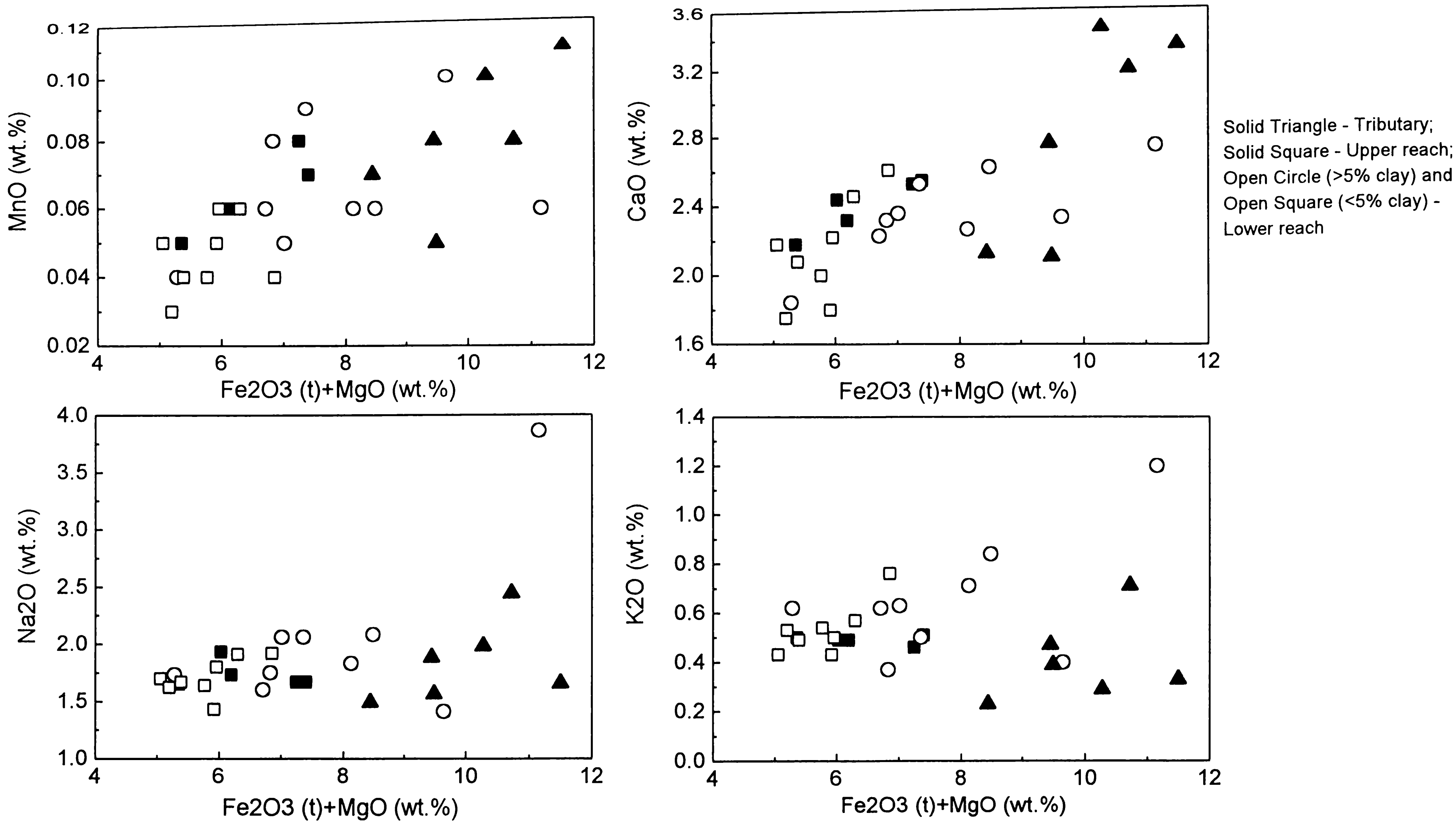


Fig.5.4 Major Oxides (in wt.%) vs Fe2O3(t)+MgO for Chaliyar river sediments

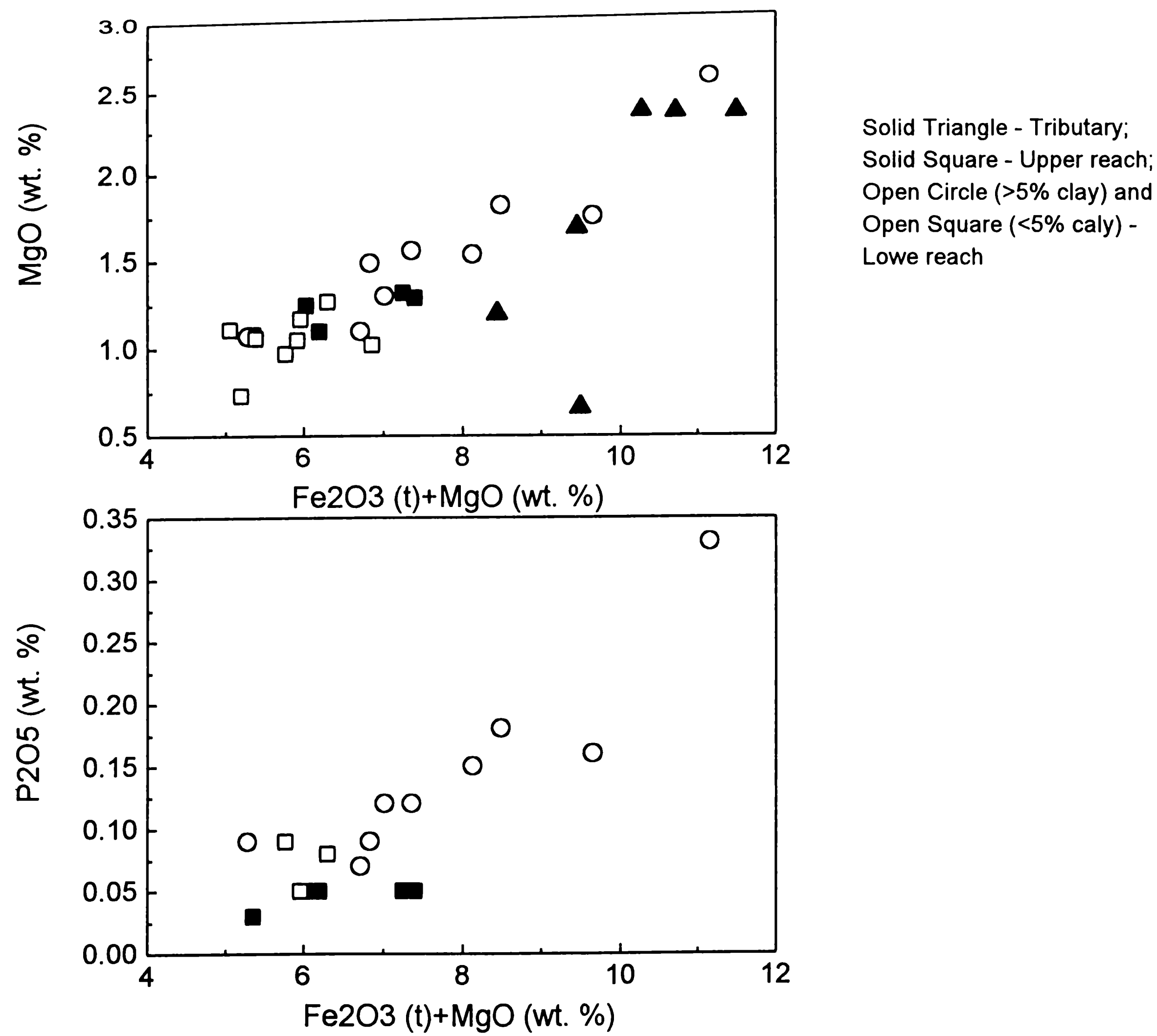


Fig.5.4 Major Oxides (in wt.%) vs Fe2O3(t)+MgO for Chaliyar river sediments

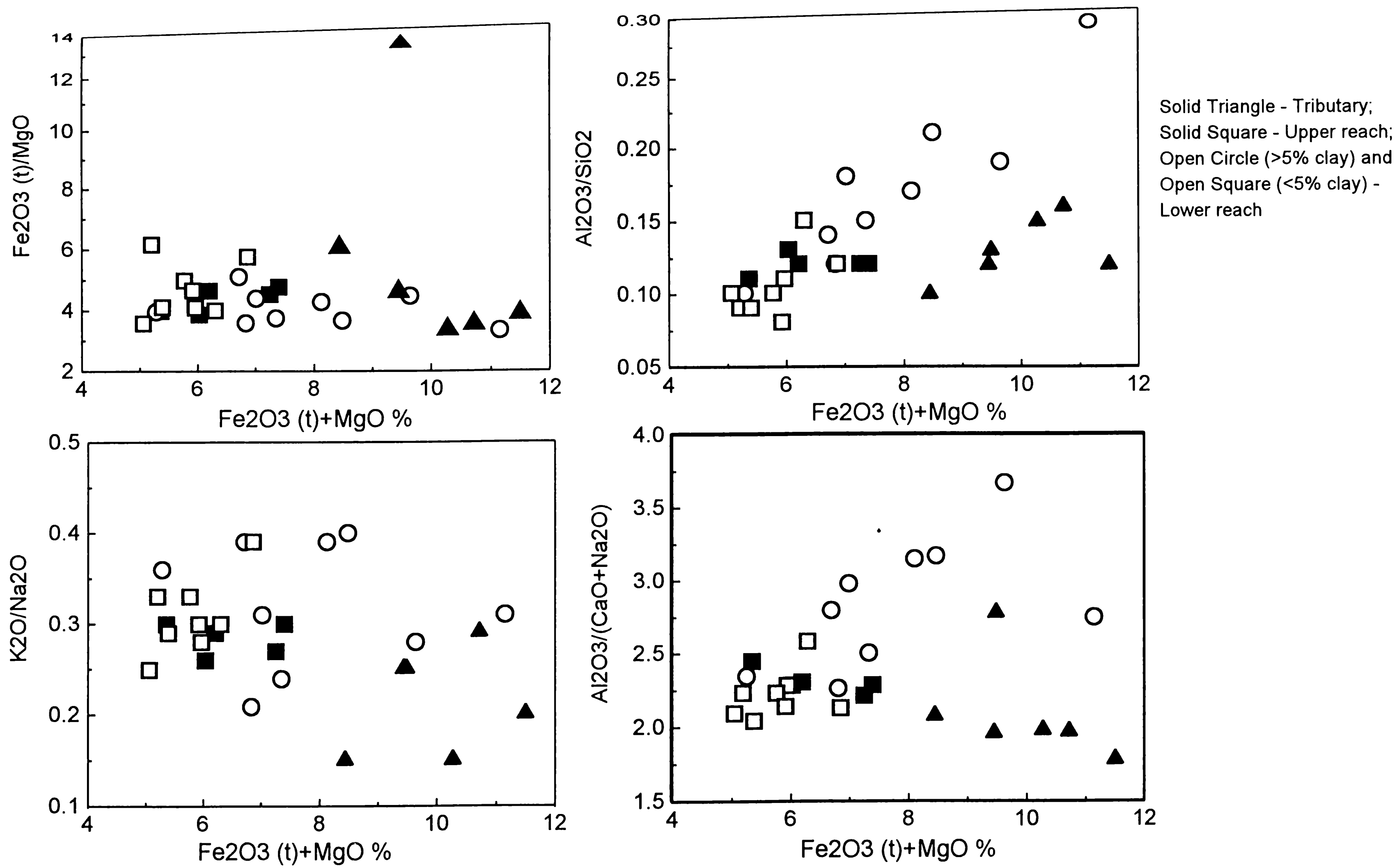


Fig.5.5 Major element ratios vs Fe2O3(t)+MgO for Chaliyar river sediments

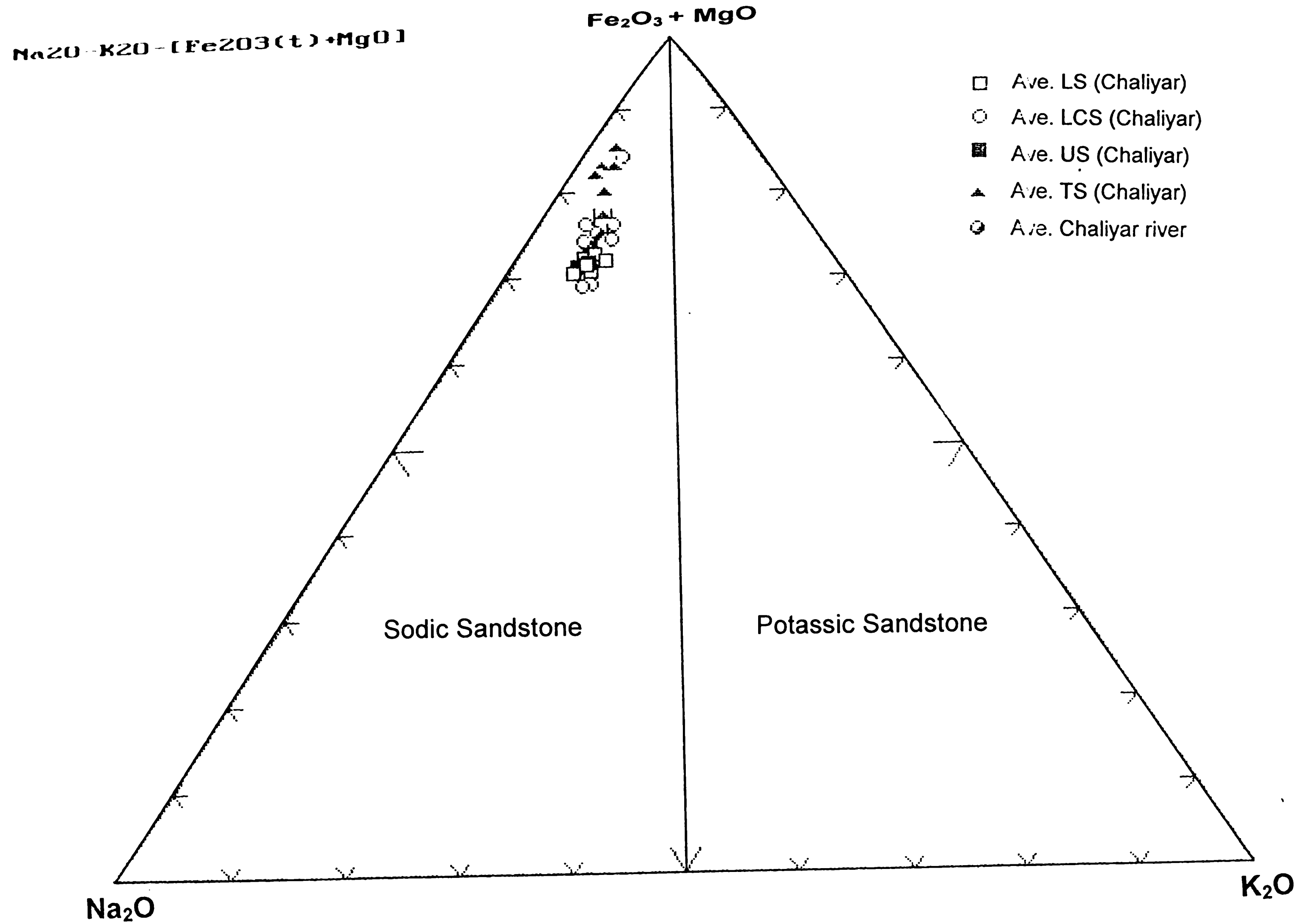


Fig. 5.6a Ternary diagram distinguishing sandstone types using Na2O-K2O-[Fe2O3(t)+MgO] (after Blatt et al., 1980).

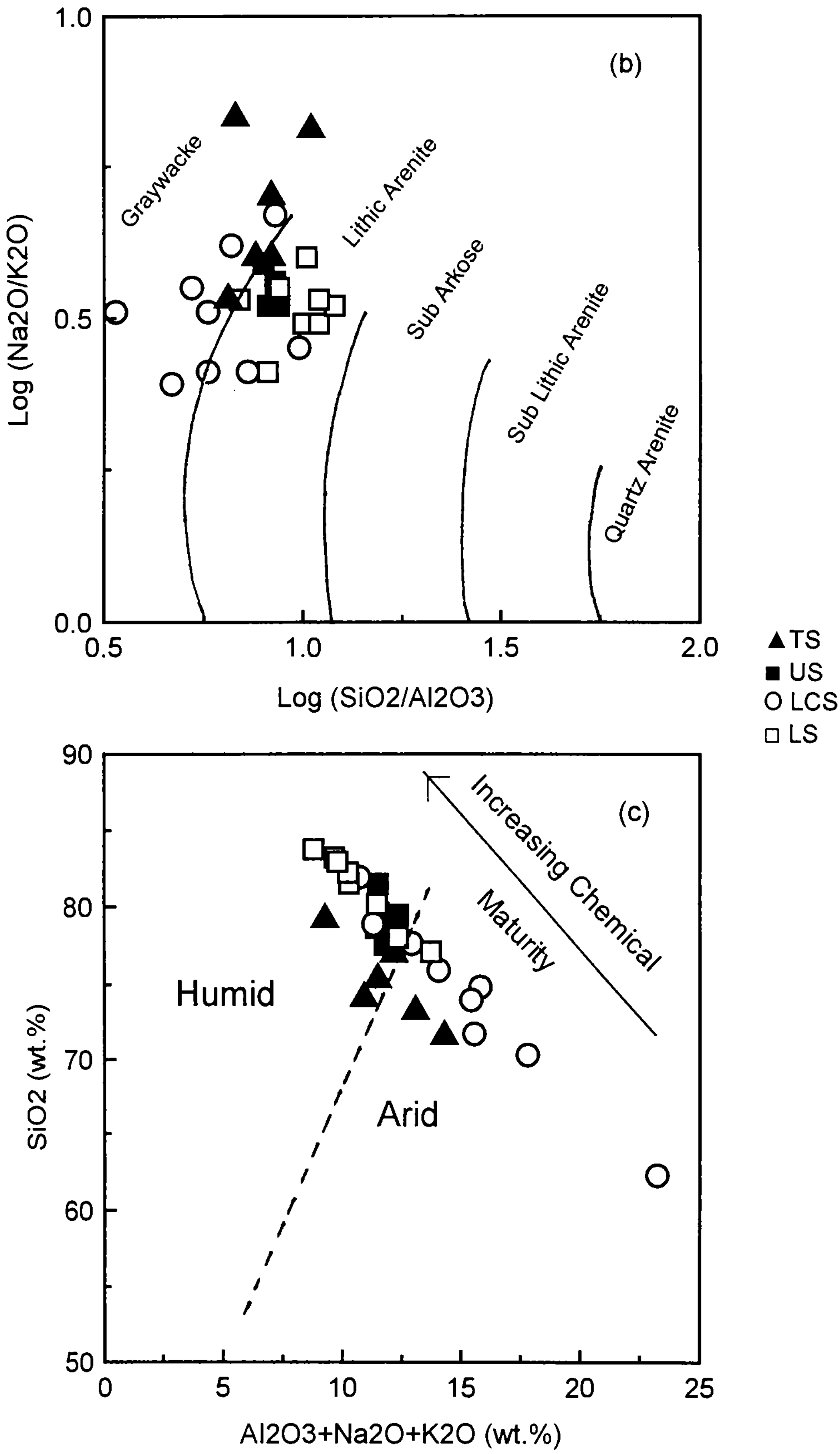


Fig.5.6 (b) Discriminating Diagram between Sandstone Types (after Pettijohn et al., 1973). (c) SiO2 and Al2O3+K2O+Na2O Binary Plot for Sandstones (after Suttner and Dutta, 1986)

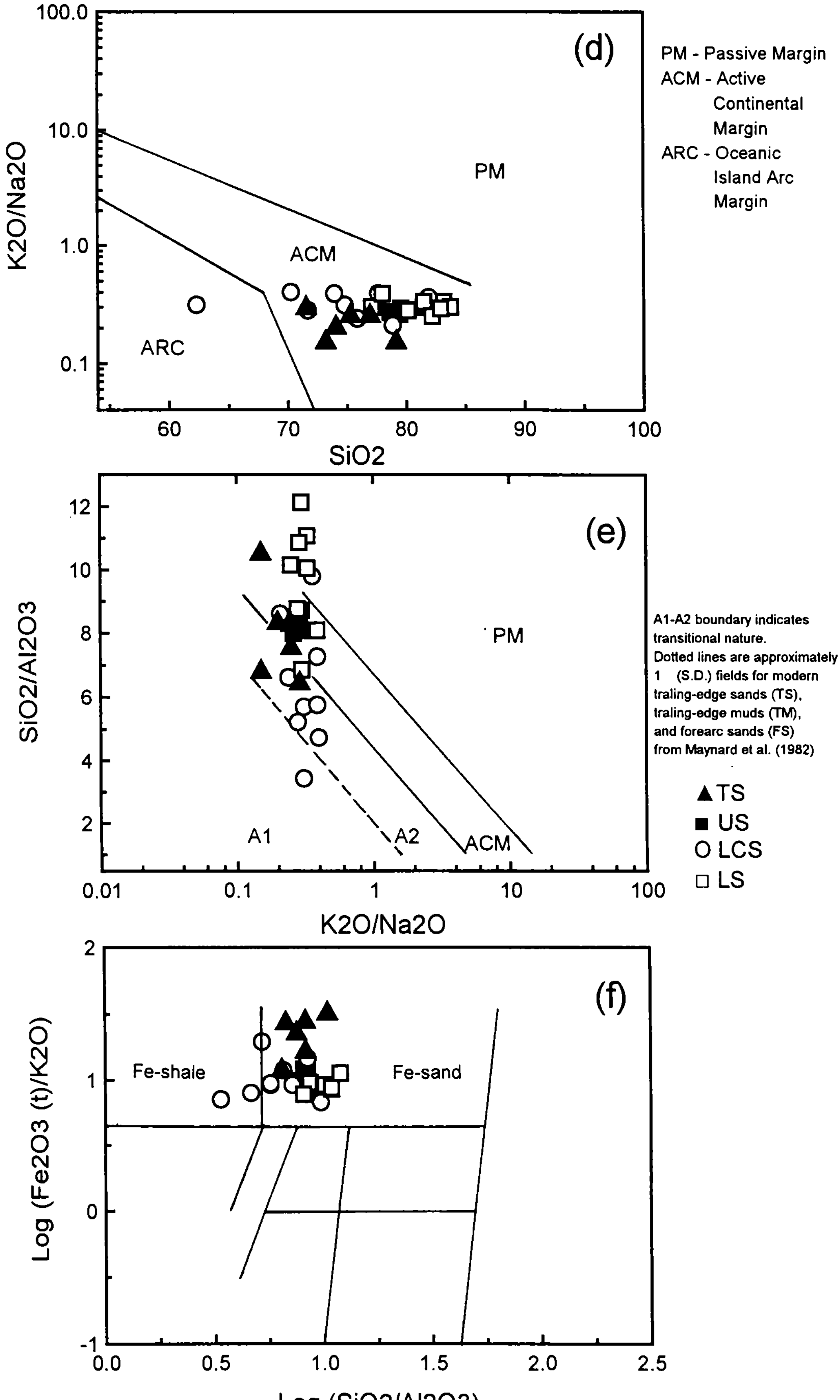


Fig.5.6 Plot of bedload sediments of Chaliyar river on the tectonic discrimination diagram from Roser and Korsch (1986) (d&e), and geochemical classification diagram from Herron (1988) (f).

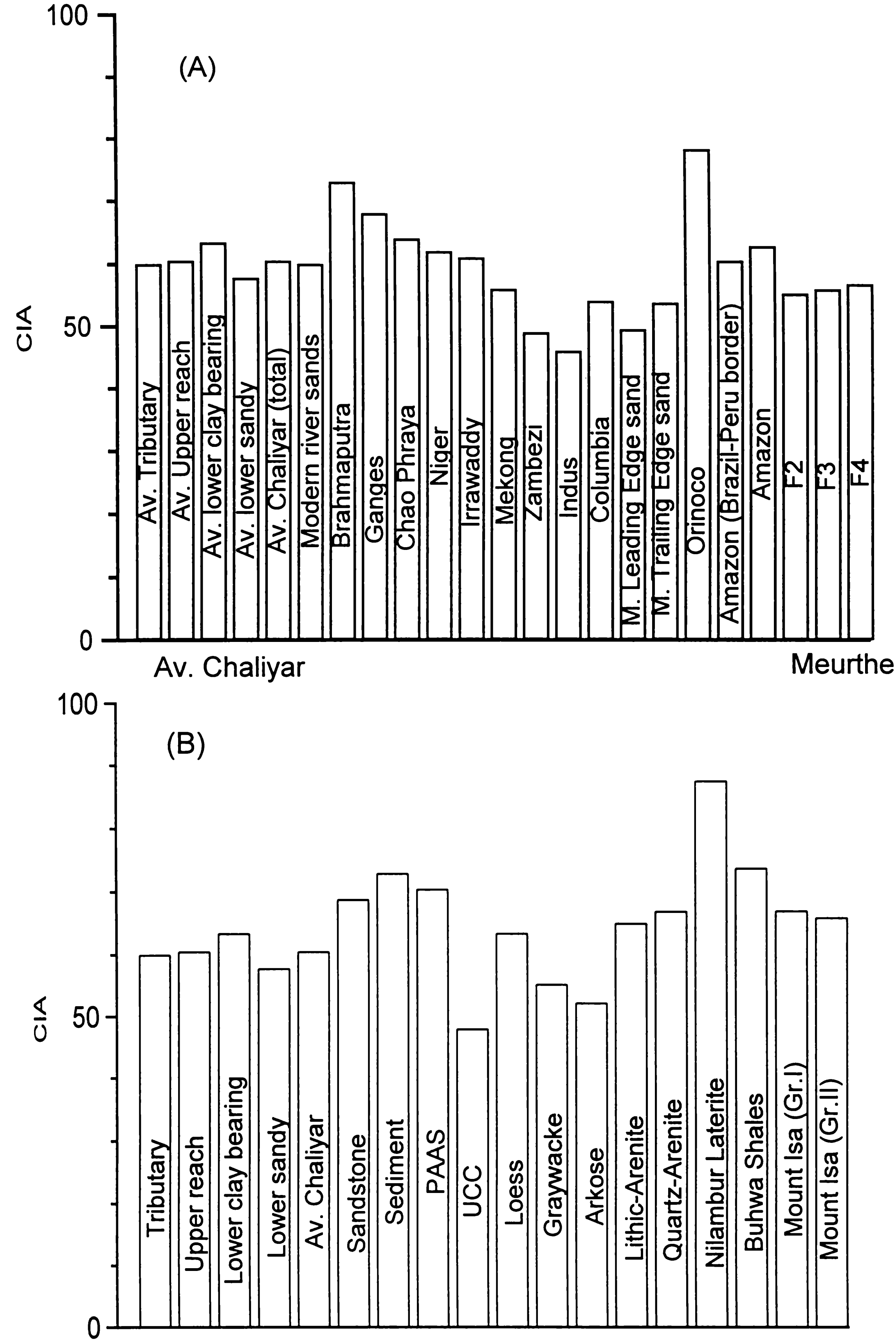


Fig. 5.7 (A) CIA for selected major rivers of the world
(B) CIA for sediments and sedimentary rocks

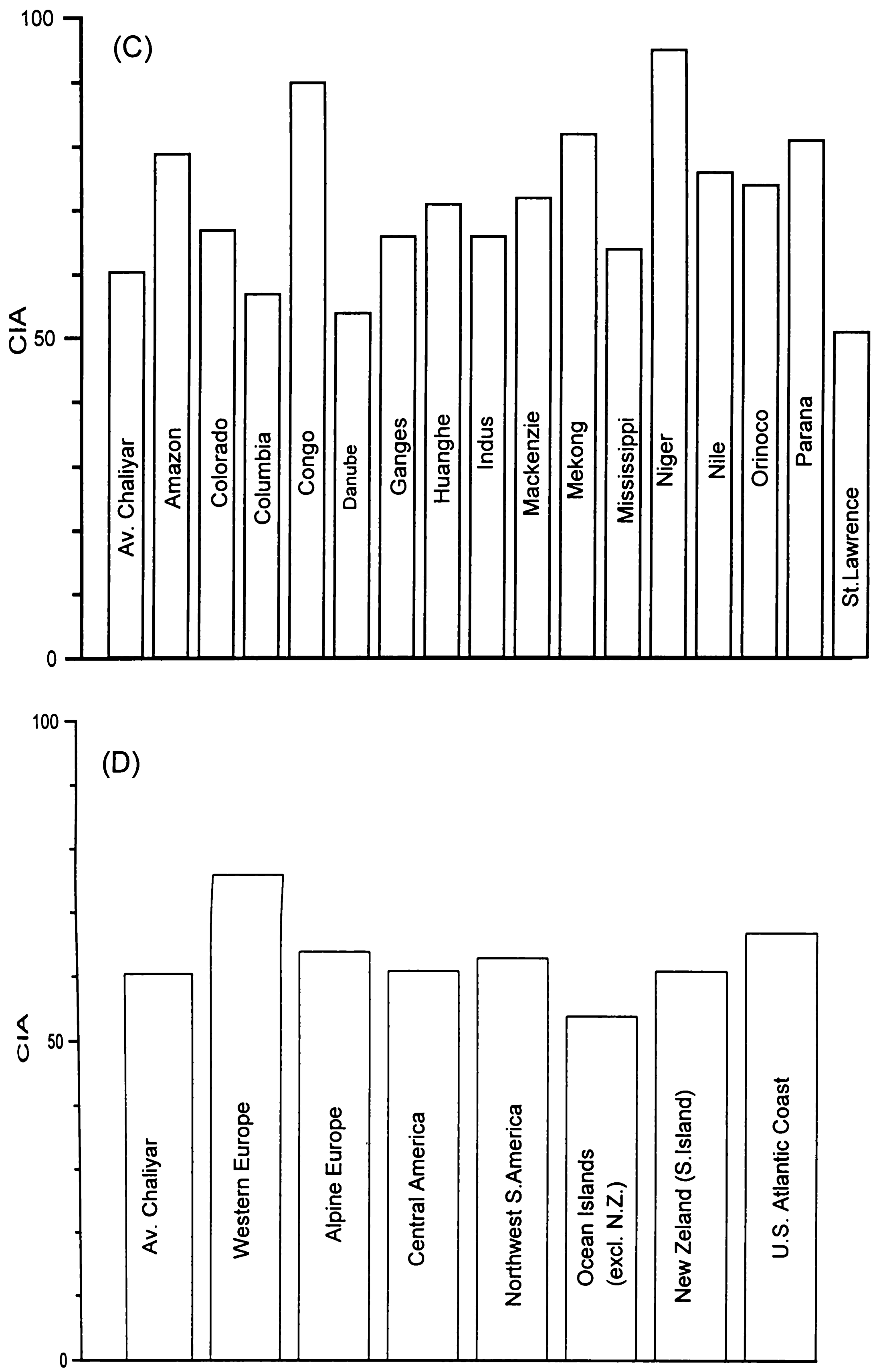


Fig. 5.7 (**C**) CIA of suspended sediments of selected major rivers
(**D**) CIA of erosional products from some major denudation regions of the world

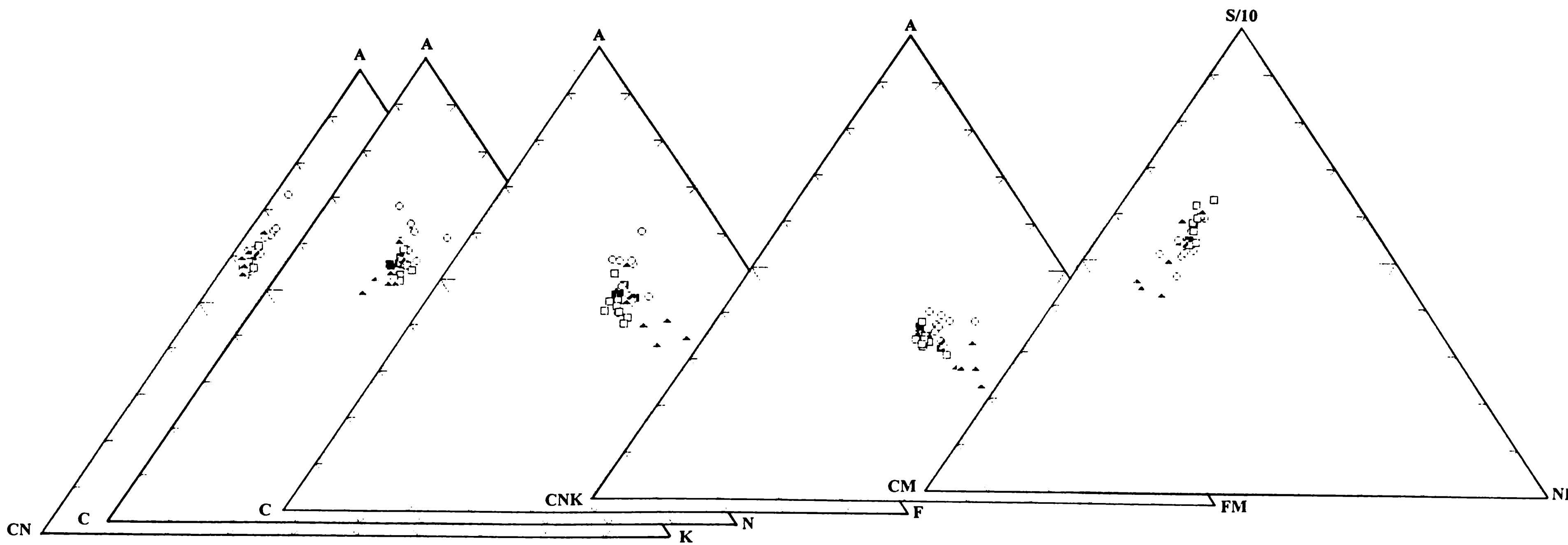


Fig. 5.8 Weathering trends on ternary plots of A-CN-K, A-C-N, A-C-F, A-CNK-FM and S/10-CM-NK showing sediment suites from the Chaliyar river.

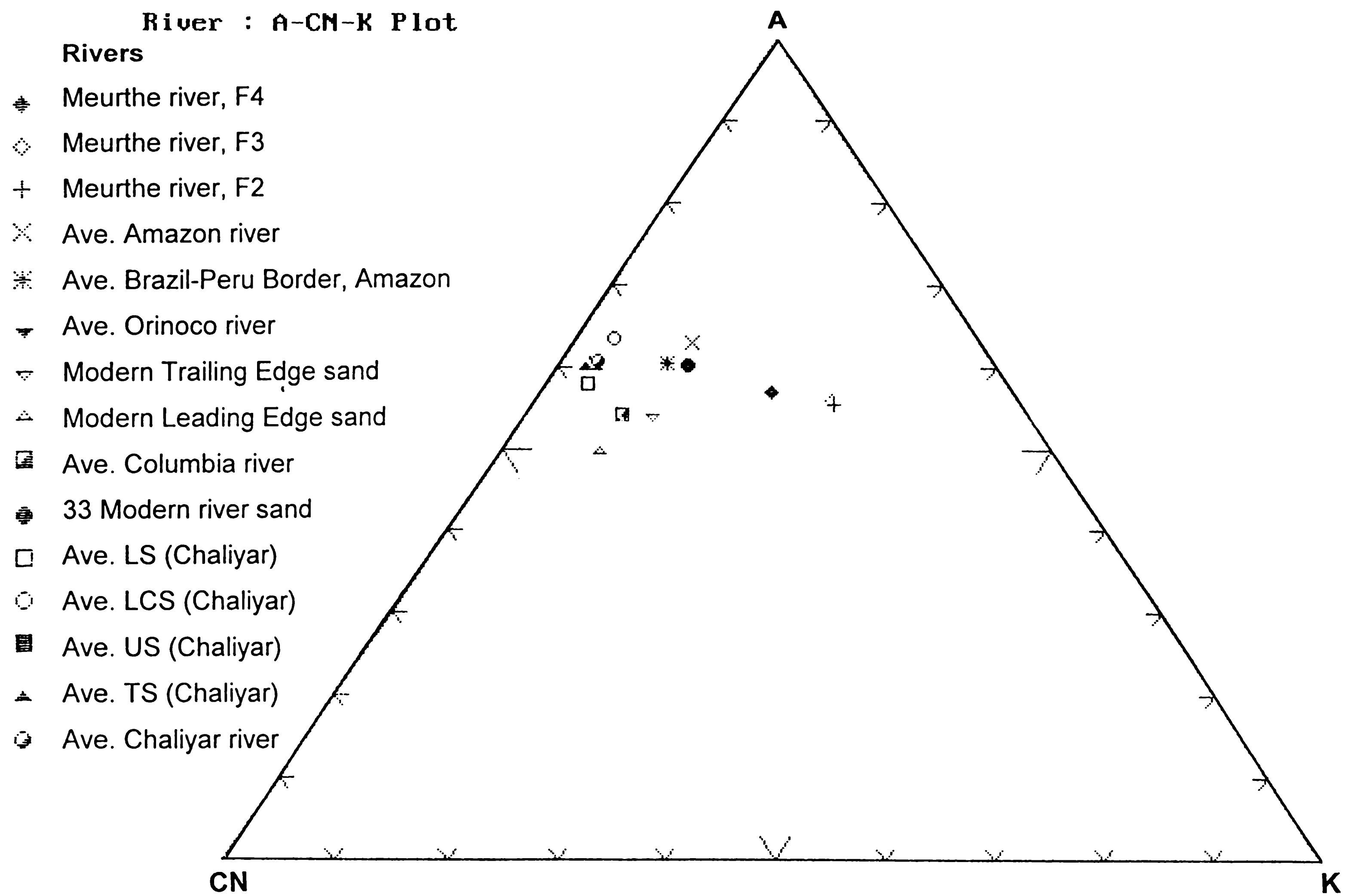


Fig. 5.9a A-CN-K plot showing simplified compositions of selected modern river sediments plotted along with sediment suites from the Chaliyar river.

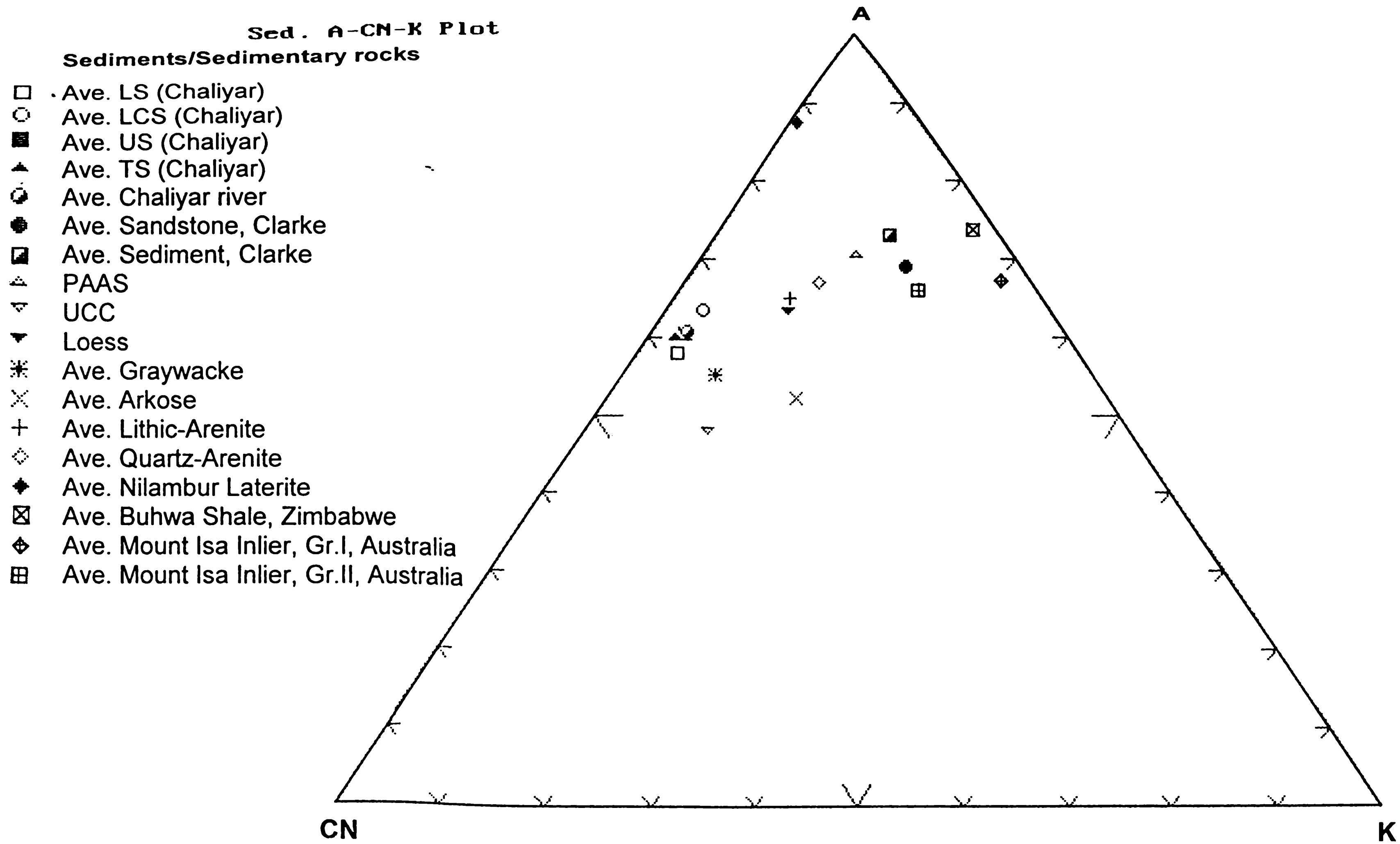


Fig. 5.9b A-CN-K plot showing simplified compositions of typical sediments/ sedimentary rock types plotted along with sediment suites from the Chaliyar river.

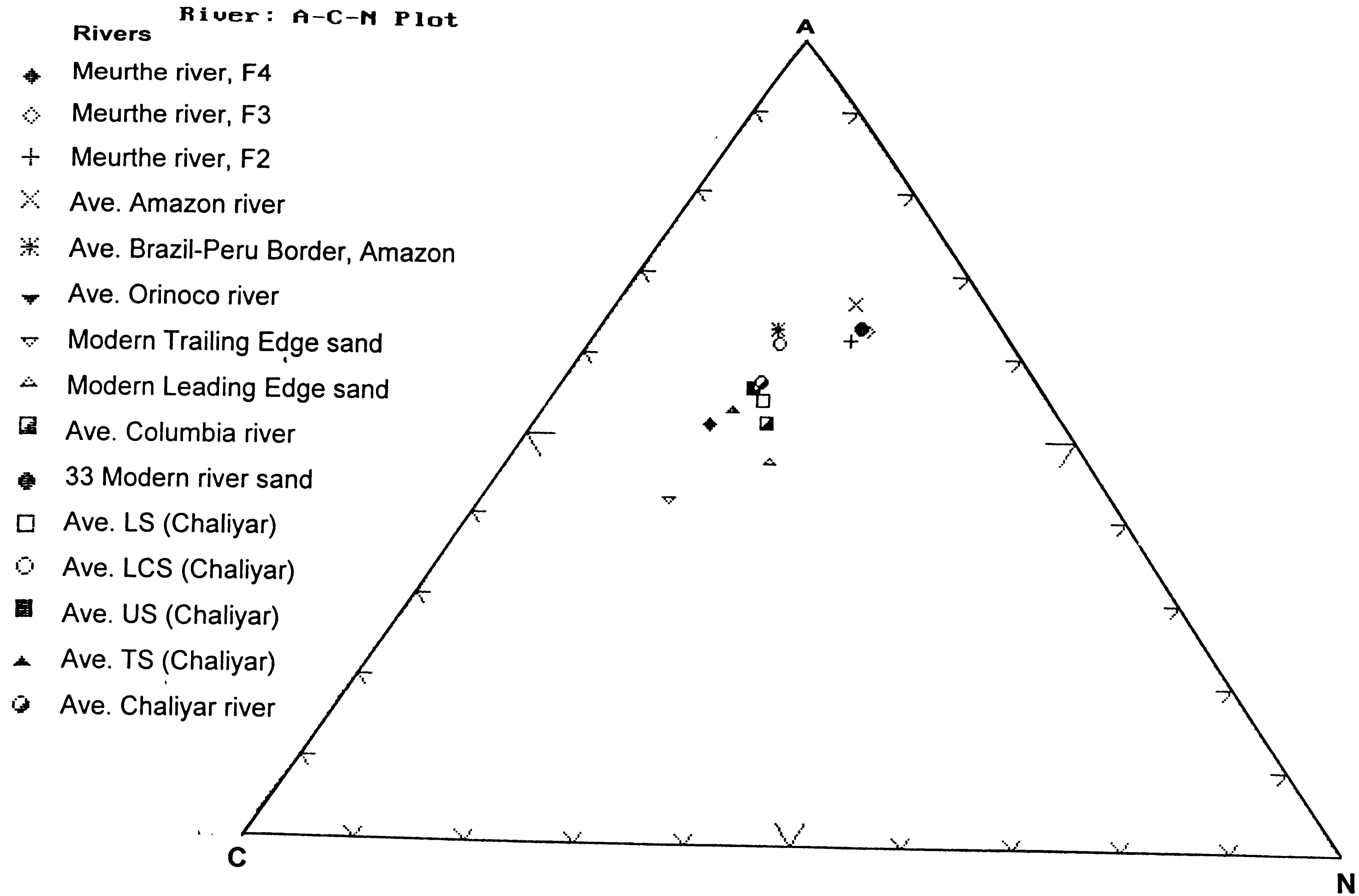


Fig. 5.10a A-C-N plot showing simplified compositions of selected modern river sediments plotted along with sediment suites from the Chaliyar river.

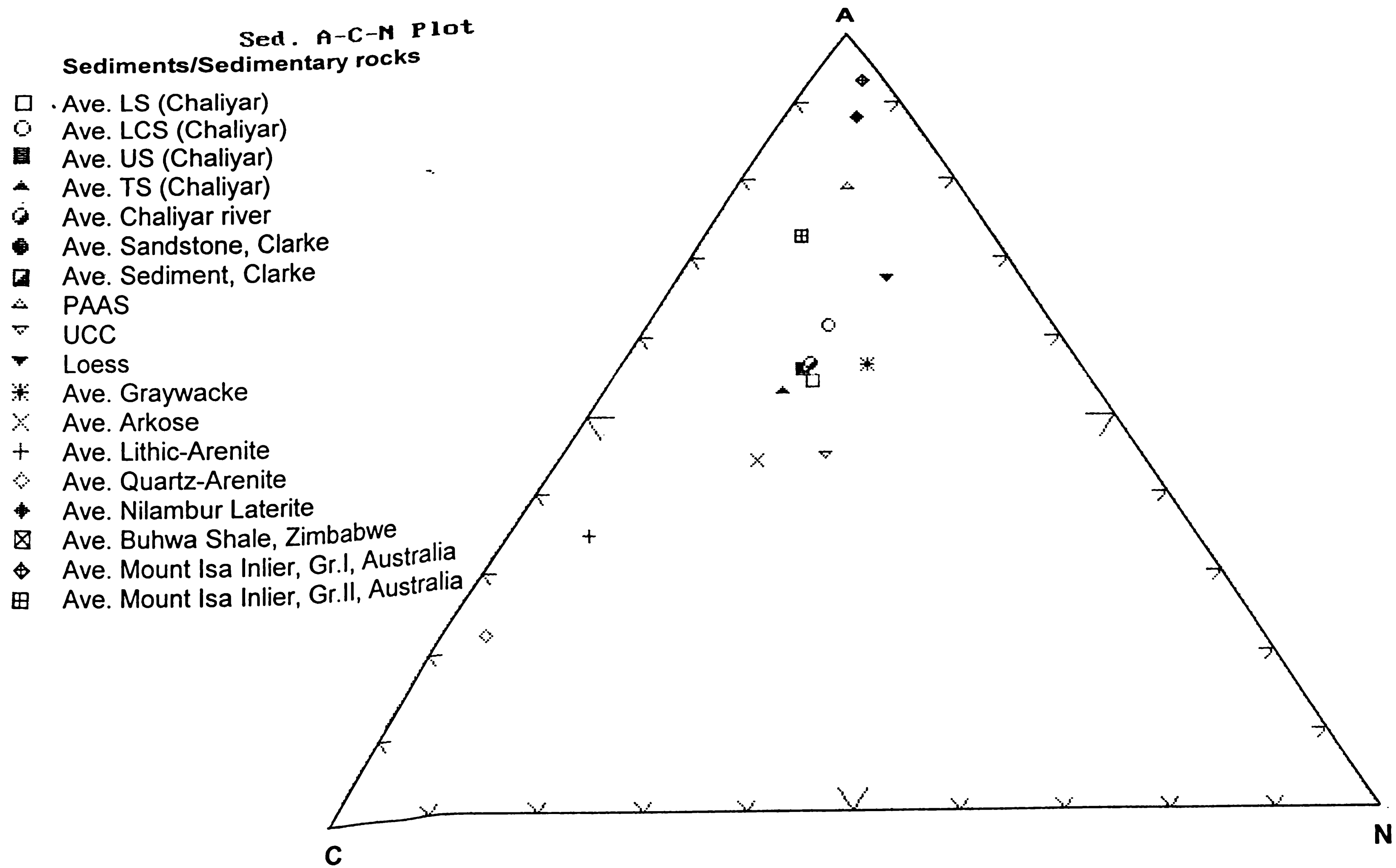


Fig. 5.10b A-C-N plot showing simplified compositions of typical sediments/ sedimentary rock types plotted along with sediment suites from the Chaliyar river.

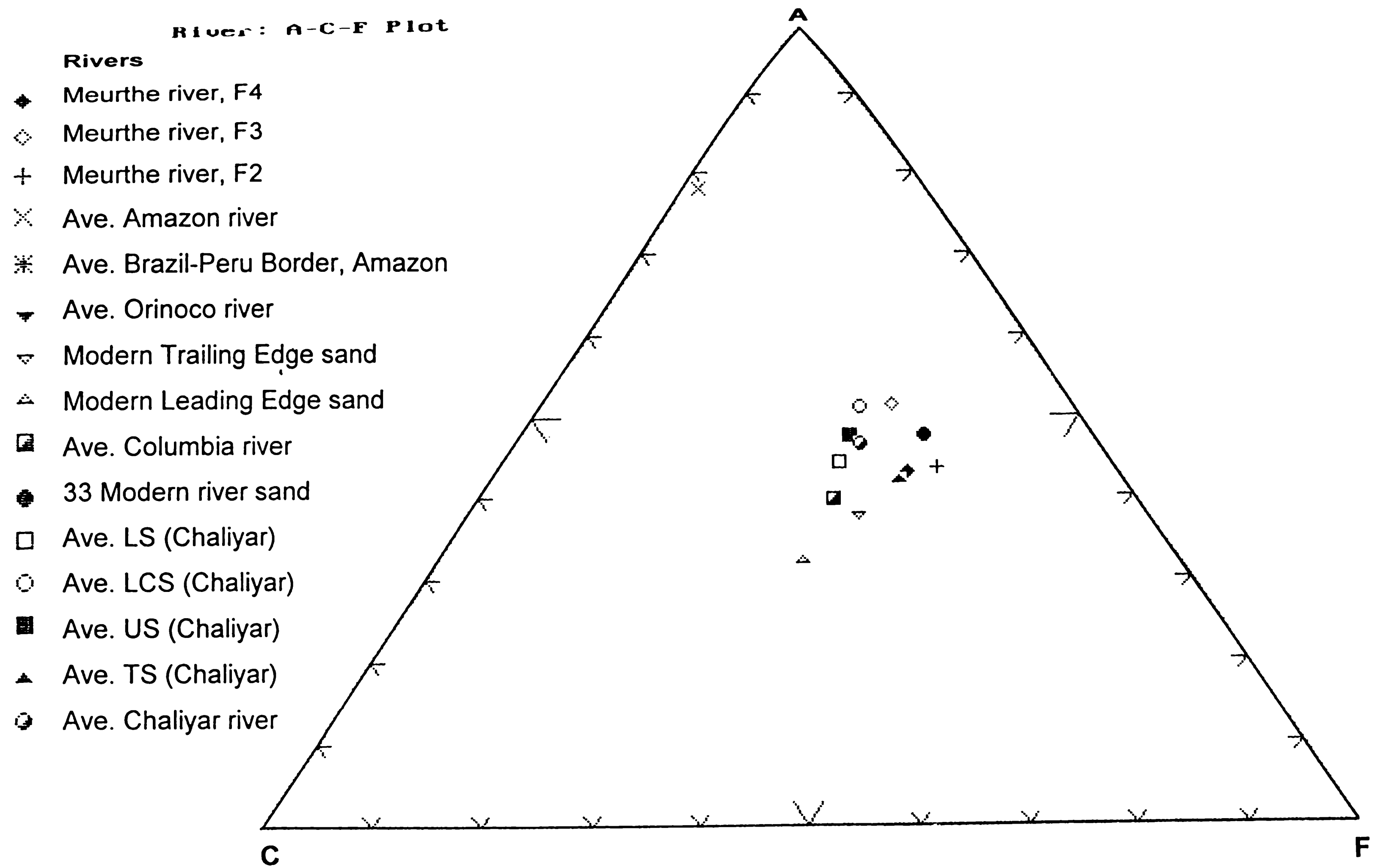


Fig. 5.11a A-C-F plot showing simplified compositions of selected modern river sediments plotted along with sediment suites from the Chaliyar river.

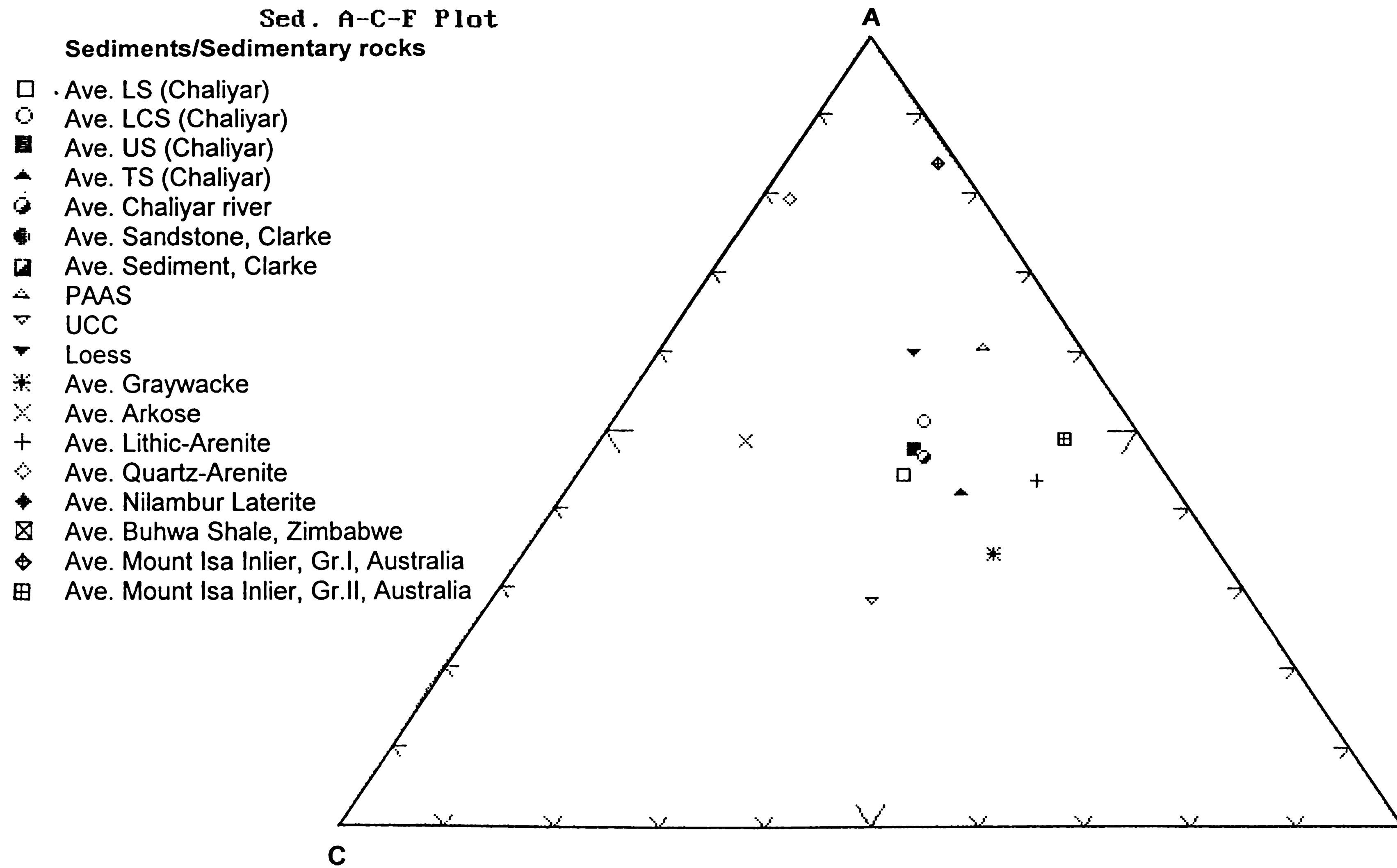


Fig. 5.11b A-C-F plot showing simplified compositions of typical sediments/ sedimentary rock types plotted along with sediment suites from the Chaliyar river.

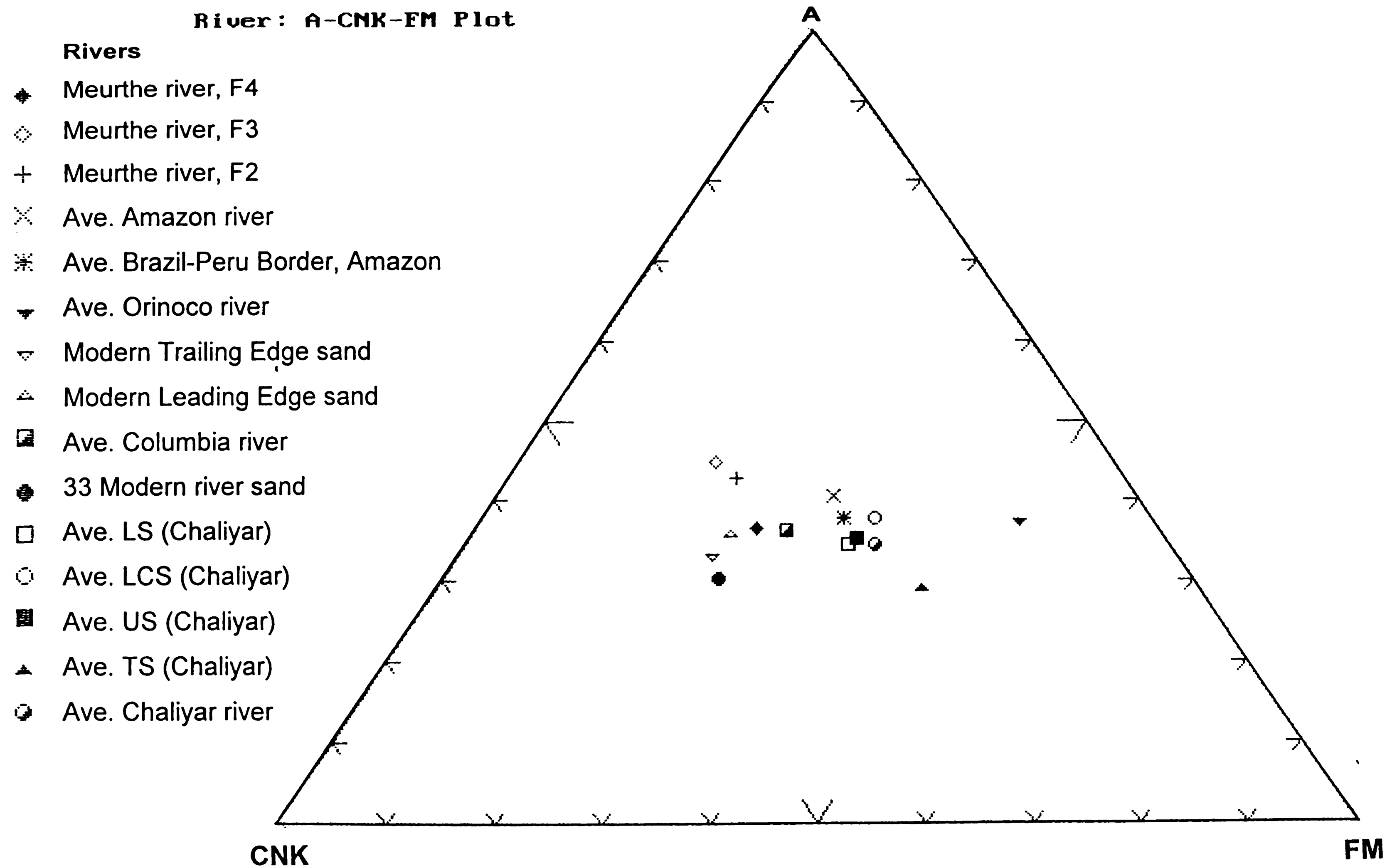


Fig. 5.12a A-CNK-FM plot showing simplified compositions of selected modern river sediments plotted along with sediment suites from the Chaliyar river.

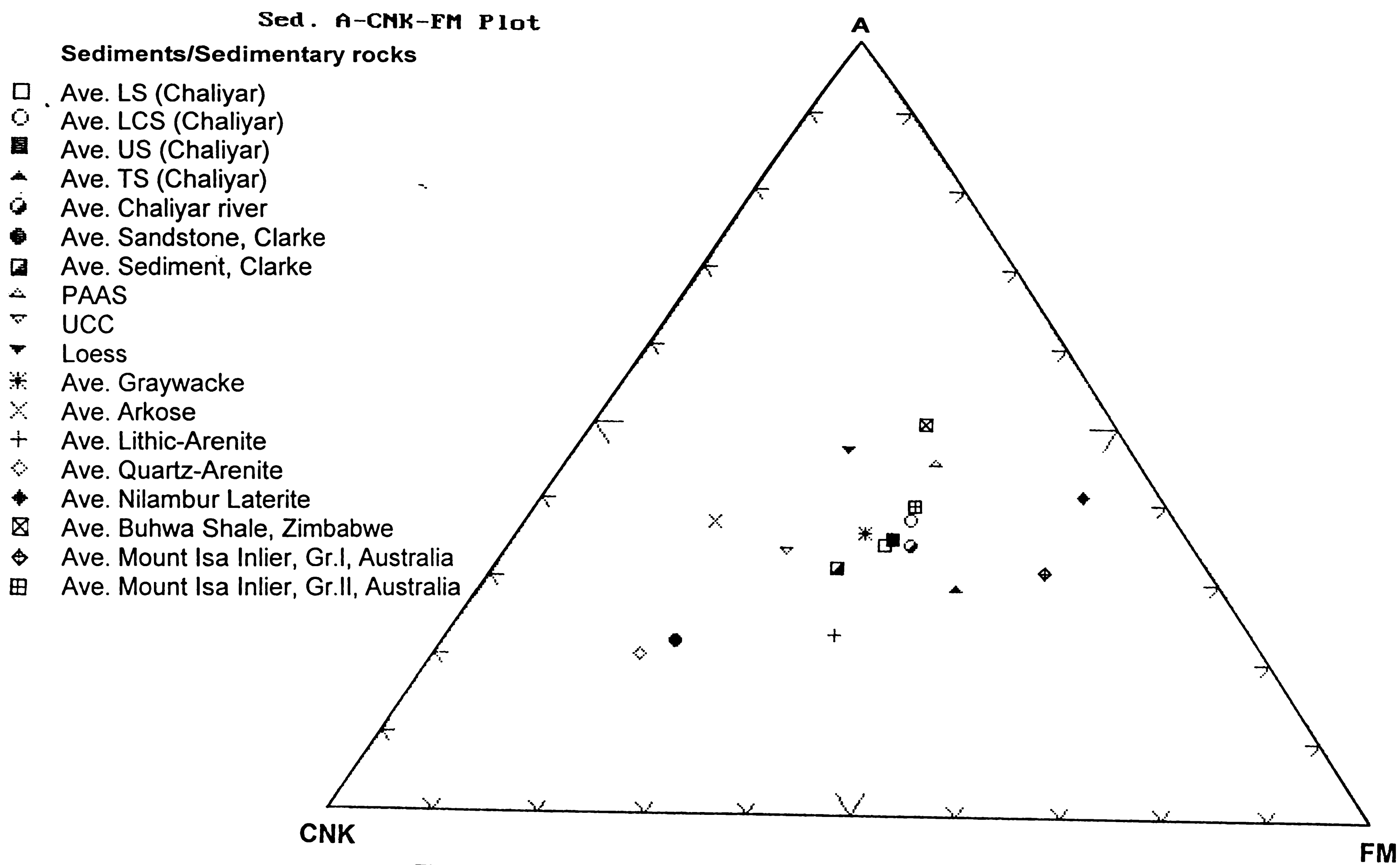


Fig. 5.12b A-CNK-FM plot showing simplified compositions of typical sediments/ sedimentary rock types plotted along with sediment suites from the Chaliyar river.

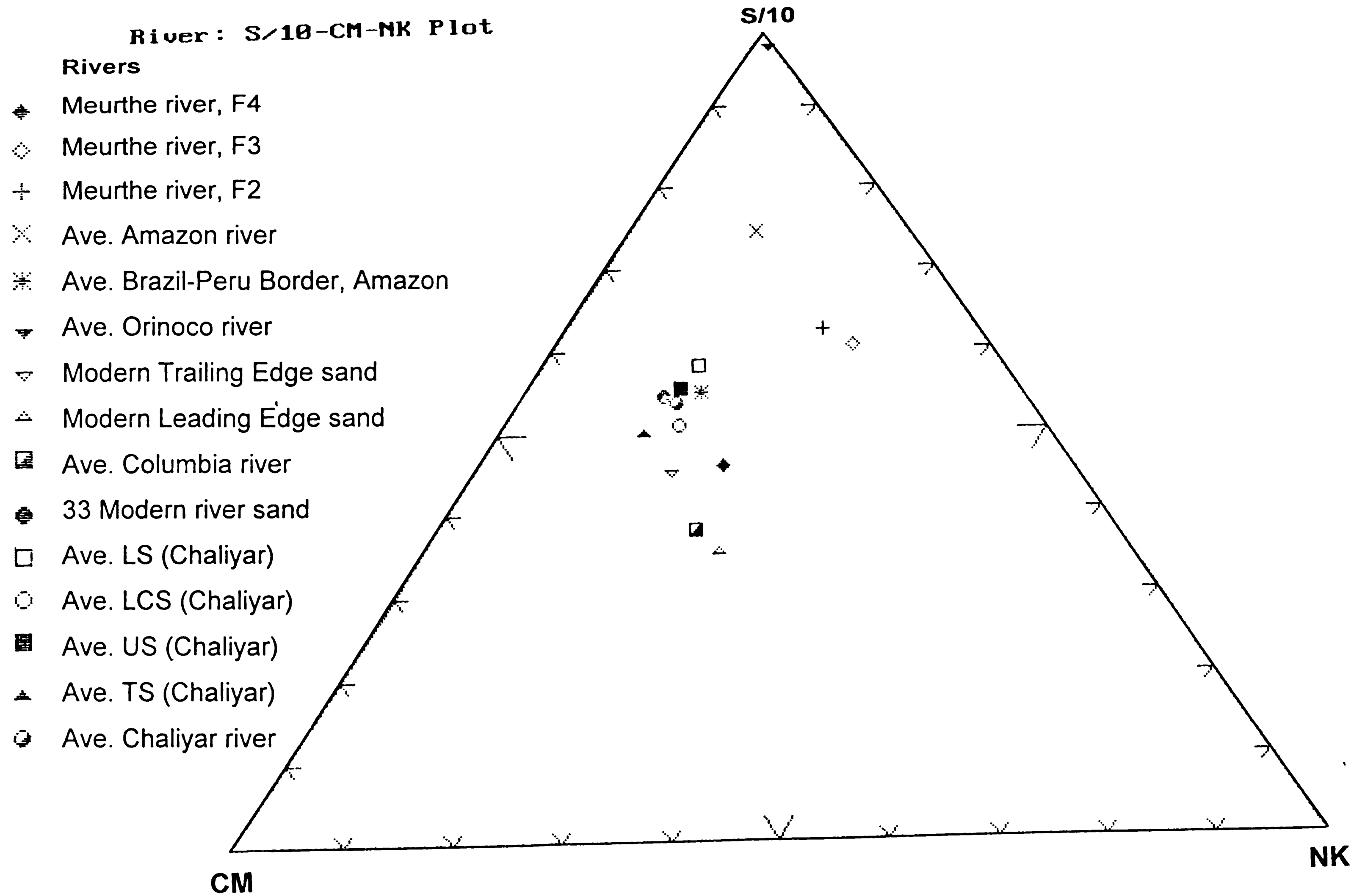


Fig. 5.13a S/10-CM-NK plot showing simplified compositions of selected modern river sediments plotted along with sediment suites from the Chaliyar river.

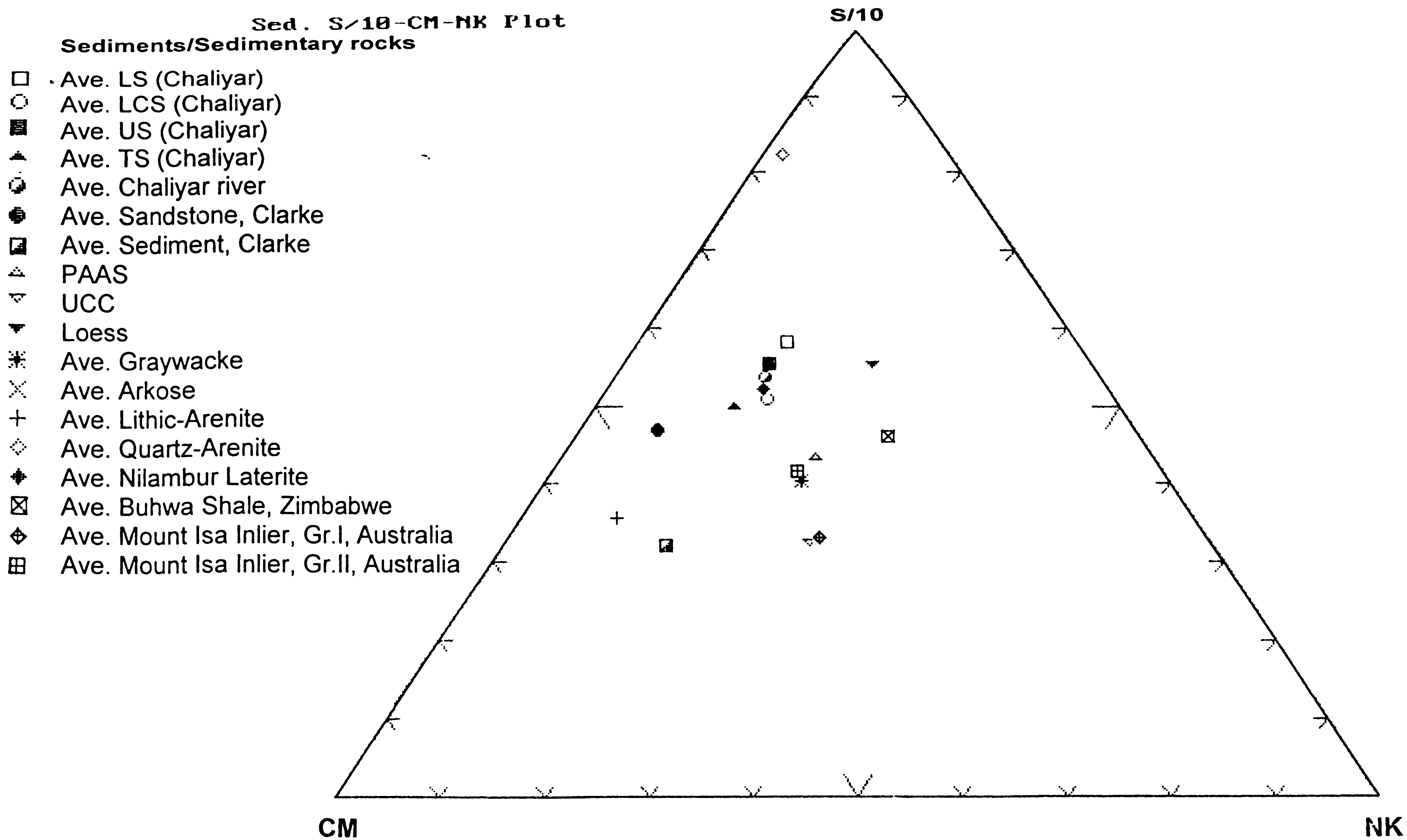


Fig. 5.13b S/10-CM-NK plot showing simplified compositions of typical sediments/ sedimentary rock types plotted along with sediment suites from the Chaliyar river.

Table 5.1 Major element content in the sediment samples of Chaliyar river. (Oxides expressed in wt.%)
(except SiO_2, Na_2O, K_2O and LOI all other oxides are analysed using ICP-AES)

Sample No (n=28)	Major Elements												
	SiO2	TiO2	Al2O3	FeO (t)	MnO	MgO	CaO	Na2O	K2O	P2O5	LOI	Total	
H-1 *	77.12	0.64	9.11	5.29	0.08	1.29	2.48	1.64	0.45	0.05	1.14	99.29	US
H-2 *	76.05	1.00	9.42	5.45	0.07	1.26	2.50	1.64	0.50	0.05	1.15	99.09	US
H-3 *	77.15	0.51	9.66	4.22	0.06	1.21	2.37	1.87	0.48	0.05	1.48	99.06	US
H-4 *	78.32	0.26	9.00	3.74	0.05	1.04	2.10	1.59	0.48	0.03	2.53	99.14	US
H-5 *	77.26	0.48	9.05	4.50	0.06	1.07	2.25	1.68	0.48	0.05	1.96	98.84	US
H-11	76.58	0.87	8.92	4.71	0.08	1.45	2.25	1.70	0.36	0.09	2.99	100.00	LCS
H-13	64.60	1.46	12.37	6.45	0.09	1.59	2.11	1.27	0.36	0.14	8.57	99.01	LCS
H-15 *	76.13	0.69	10.49	5.00	0.06	1.08	2.19	1.57	0.61	0.07	1.66	99.55	LCS
H-17	70.27	0.81	10.63	4.88	0.08	1.44	2.34	1.91	0.46	0.11	6.19	99.12	LCS
H-19	76.54	0.30	7.82	3.58	0.04	1.00	1.72	1.62	0.58	0.08	5.79	99.07	LCS
H-23 *	71.25	0.63	12.50	4.94	0.05	1.24	2.25	1.96	0.60	0.11	3.49	99.02	LCS
H-25 *	69.13	0.75	12.03	5.59	0.06	1.44	2.12	1.71	0.66	0.14	5.56	99.19	LCS
H-26 *	56.12	0.86	16.38	7.02	0.05	2.32	2.49	3.48	1.08	0.30	9.34	99.44	LCS
H-27 *	66.32	0.83	14.04	5.71	0.06	1.72	2.48	1.96	0.79	0.17	4.92	99.00	LCS
H-12 *	77.82	0.49	8.90	4.22	0.06	1.14	2.16	1.75	0.49	0.05	2.02	99.10	LS
H-14	77.62	0.39	7.73	4.16	0.04	0.92	1.90	1.56	0.51	0.09	4.03	98.95	LS
H-16	78.29	0.35	7.72	3.42	0.05	1.06	2.08	1.62	0.41	N.D.	4.02	99.02	LS
H-18	80.00	0.22	7.23	3.91	0.03	0.70	1.68	1.56	0.51	N.D.	3.38	99.22	LS
H-20	79.01	0.62	6.52	4.18	0.05	0.99	1.70	1.35	0.41	N.D.	4.29	99.12	LS
H-21 *	74.85	0.61	10.92	4.44	0.06	1.23	2.39	1.85	0.55	0.08	2.04	99.02	LS
H-22	77.50	0.25	7.14	3.68	0.04	0.99	1.94	1.56	0.46	N.D.	5.22	98.78	LS
H-24	74.30	0.52	9.19	5.06	0.04	0.97	2.49	1.83	0.72	N.D.	4.08	99.20	LS
H-28 T	76.10	1.37	7.25	6.32	0.07	1.15	2.05	1.43	0.22	N.D.	3.10	99.06	TS
H-29 T	67.77	1.00	9.99	6.65	0.09	2.19	3.21	1.83	0.27	N.D.	6.04	99.04	TS
H-30 T	70.60	0.43	9.37	7.35	0.05	0.61	1.94	1.43	0.36	N.D.	6.88	99.02	TS
H-31 T	69.88	1.24	8.42	7.83	0.10	2.23	3.17	1.56	0.31	N.D.	4.63	99.37	TS
H-32 T	68.15	0.90	10.60	7.23	0.08	2.25	3.06	2.32	0.68	N.D.	3.74	99.01	TS
H-33 TC	73.10	1.18	8.87	6.84	0.08	1.64	2.69	1.83	0.46	N.D.	2.48	99.17	TS
Average	73.49	0.70	9.69	5.23	0.06	1.33	2.29	1.75	0.51	0.10	4.03	99.14	

* Samples analysed by XRF at NGRI, Hyderabad

Table 5.2 Weathering Indices of Chaliyar river sediments

Note that where ever P2O5 data is available correction is made for CaO. Since the remaining number of moles of P2O5 corrected CaO is greater than Na2O, CaO* is assumed to be equivalent to Na2O except in sample H-26. CO2 Correction is not applied for any of the samples. Similarly in ACF diagram FeO (t) is split into Fe2O3 and FeO in the ratios seen in modern river sands. Plagioclase Index of Alteration (PIA), Fedo et al. (1995) Chemical Index of Alteration (CIA), Nesbitt and Young (1982). Chemical Index of Weathering (CIW), Harnois (1988).

Sample No.	CIA	CIW	PIA
H-1	60.8	62.8	61.5
H-2	61.4	63.6	62.2
H-3	59.2	61.1	59.8
H-4	61.0	63.3	61.9
H-5	60.0	62.1	60.7
H-11	59.9	61.5	60.4
H-12	58.6	60.7	59.3
H-13	73.1	74.8	74.2
H-14	57.7	60.1	58.3
H-15	64.3	67.0	65.6
H-16	57.2	59.2	57.8
H-17	61.1	62.9	61.8
H-18	56.0	58.5	56.6
H-19	56.8	59.5	57.5
H-20	57.2	59.5	57.8
H-21	62.1	64.2	62.9
H-22	55.9	58.2	56.4
H-23	63.8	66.0	64.8
H-24	57.5	60.4	58.3
H-25	65.5	68.2	66.8
H-26	60.5	63.2	61.5
H-27	65.8	68.6	67.2
H-28 T	59.5	60.7	59.9
H-29 T	61.3	62.4	61.7
H-30 T	64.8	66.6	65.6
H-31 T	60.7	62.2	61.2
H-32 T	55.9	58.2	56.4
H-33 TC	57.7	59.6	58.2
Average N=28	60.5	62.7	61.3

Group averages

Sample	N	CIA	CIW	PIA
Ave. TS	6	60.0	61.6	60.5
Ave. US	5	60.5	62.6	61.2
Ave. LCS	9	63.4	65.7	64.4
Ave. LS	8	57.8	60.1	58.4
Ave. Chaliyar	28	60.5	62.7	61.3

Ave. Tributary (TS) - solid triangle
Ave. Upper reach sediments (US) - solid square
Ave. Lower reach clay bearing sediments (LCS) - open circle (> 5% clay)
Ave. Lower reach sediments (LS) - open square (< 5% clay)
Ave. Chaliyar - half filled circle

Table 5.3a Major element composition of selected major rivers of the world (* recalculatrd to 100% on a volatile-free basis)

Sl. No.	Name	N	SiO_2	TiO_2	Al_2O_3	FeO (t)	Fe_2O_3 (t)	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	CO_2	LOI	Total
1	33 Modern river sands		80.15	0.42	6.43	-	-	1.29	1.18	0.05	0.85	3.32	1.19	1.20	0.06	2.10	0.96	99.20
2	Brahmaputra		-	-	11.10	-	-	-	-	-	0.87	1.22	0.87	2.36	-	1.22	-	-
3	Ganges		-	-	9.43	-	-	-	-	-	1.14	4.67	0.36	1.95	-	4.14	-	-
4	Chao Phraya		-	-	4.95	-	-	-	-	-	0.14	0.56	0.67	1.41	-	0.51	-	-
5	Niger		-	-	2.35	-	-	-	-	-	0.01	0.21	0.13	0.78	-	0.01	-	-
6	Irrawaddy		-	-	8.78	-	-	-	-	-	0.68	0.80	1.31	1.92	-	0.00	-	-
7	Mekong		-	-	5.69	-	-	-	-	-	0.65	0.57	1.25	1.37	-	0.06	-	-
8	Zambezi		-	-	7.79	-	-	-	-	-	0.01	1.47	1.98	2.08	-	0.01	-	-
9	Indus		-	-	11.41	-	-	-	-	-	1.92	8.08	1.89	2.07	-	3.99	-	-
10	Av. Columbia river sand*	68	68.69	0.83	14.41	-	4.87	-	-	0.10	2.07	3.52	3.00	2.18	-	-	-	99.67
11	M. Leading Edge sand*	15	69.00	-	15.00	-	4.10	-	-	-	1.90	4.20	3.80	2.60	-	-	-	100.60
12	M. Trailing Edge sand*	29	78.00	-	9.80	-	2.90	-	-	-	1.30	4.10	1.90	2.00	-	-	-	100.00
13	Ave. Orinoco river sand	62	96.65	0.12	0.97	-	1.01	-	-	0.02	0.00	0.03	0.00	0.25	0.04	-	0.79	99.88
14	Ave. Brazil-Peru Border main stem sands of Amz.R	3	75.32	5.46	9.94	-	-	1.65	2.59	0.06	1.2	2.03	1.3	1.52	0.07	0.35	1.69	103.18
15	Ave. Amazon River	5	89.91	0.54	5.44	-	-	1.81	0.31	0.04	0.58	0.72	0.9	0.88	0.05	0.17	0.64	101.99
16	Meurthe River main stem	(F2) 7	81.76	0.17	7.67	-	1.45	-	-	0.02	0.75	0.62	0.9	3.54	0.1	-	2.52	99.50
17	Meurthe River main stem	(F3) 7	79.45	0.25	8.95	-	1.65	-	-	0.02	0.6	0.65	1.1	4.01	0.12	-	2.85	99.65
18	Meurthe River main stem	(F4) 7	70.20	0.56	10.29	-	2.89	-	-	0.05	1.44	2.54	1.21	3.56	0.22	-	6.66	99.62

Note if Fe_2O_3 (t) is given it is first converted to FeO (t) and is expressed as Fe_2O_3 and FeO in the ratio as seen in modern river sands (this is applied for A-C-F diagram) [F2: Coarse fraction (0.3-0.5mm); F3: Medium fraction (0.1-0.3mm); F4: Fine fraction (<0.1mm)]

(1) Potter (1978); (2) to (9) Maynard et al. (1991); (10) to (12) Bhatia (1983); (13) Johnsson et al.(1991); (14) & (15) Franzinelli and Potter (1983); (16) to (18) Albarede and Semhi

Table 5.3b Major element composition of suspended sediments of selected major rivers of the world and corresponding CIA values

Rivers	SiO2	TiO2	Al2O3	FeO (t)	MnO	MgO	CaO	Na2O	K2O	P2O5	Total	CIA*
Amazon	60.20	1.23	22.90	7.45	0.14	1.96	2.36	1.11	2.28	0.40	100.03	79 (63)
Colorado	79.90	0.51	8.28	3.01	0.06	1.75	4.85	0.66	1.84	0.13	100.99	67
Columbia	64.10	1.00	16.90	6.10	0.30	2.50	3.30	2.90	2.90	-	100.00	57 (54)
Congo	58.00	1.59	25.10	10.30	0.21	1.09	1.34	0.32	1.64	0.39	99.98	90
Danube	64.90	0.71	12.10	7.19	0.08	3.53	6.39	2.38	2.51	0.16	99.95	54
Ganges	66.80	0.97	16.00	5.22	0.14	2.26	4.07	1.58	2.77	0.14	99.95	66 (68)
Huanghe	59.40	-	17.30	6.20	0.13	4.00	6.62	1.05	3.25	-	97.95	71
Indus	56.30	0.81	15.40	6.25	0.14	4.19	12.50	1.48	2.73	0.23	100.03	66 (46)
Mackenzie	67.40	0.77	15.70	5.02	0.08	0.70	5.35	0.32	4.53	-	99.87	72
Mekong	61.90	0.63	22.30	7.57	0.13	2.36	0.87	0.74	3.04	0.48	100.02	82
Mississippi	76.30	0.64	11.50	3.40	0.07	1.54	2.37	1.36	2.51	0.20	99.89	64
Niger	51.70	1.44	30.90	12.40	0.09	1.09	0.48	0.13	1.36	0.39	99.98	95 (62)
Nile	53.00	-	18.80	14.10	-	3.12	5.68	1.00	2.32	-	98.02	76
Orinoco	69.50	0.97	17.30	6.07	0.06	1.28	0.80	1.62	2.22	0.15	99.97	74 (78)
Parana	64.70	1.64	20.90	6.46	0.04	1.89	0.87	0.94	2.27	0.31	100.02	81
St.Lawrence	60.00	1.44	16.30	6.91	0.10	4.50	3.57	3.73	3.40	0.06	100.01	51

* In parenthesis is the corresponding CIA values of some river sands used in this study.
Source: McLennan (1993)

Table 5.3c Estimates of the major element composition of erosional products from some major denudation regions of the world and corresponding CIA values

Denudation Regions	SiO2	TiO2	Al2O3	FeO (t)	MnO	MgO	CaO	Na2O	K2O	P2O5	Total	CIA
Western Europe	61.90	0.93	16.00	9.48	0.45	2.01	4.71	0.72	2.53	1.13	99.86	76
Alpine Europe	53.90	0.56	11.60	5.98	0.14	2.25	21.20	1.18	2.46	0.64	99.91	64
Central America	62.50	0.90	18.80	6.63	0.09	2.70	2.86	2.84	2.68	-	100.00	61
Northwest S.America	67.10	0.66	15.70	6.82	0.12	2.57	1.91	2.03	2.82	0.25	99.98	63
Ocean Islands (excl. N.Z.)	67.80	0.64	14.40	5.63	0.09	2.99	2.36	3.53	2.41	0.13	99.98	54
New Zeland (S.Island)	62.60	0.67	18.90	5.32	0.07	2.38	3.38	2.49	3.52	0.21	99.54	61
U.S. Atlantic Coast	61.20	0.90	17.90	6.45	0.20	3.12	3.12	1.54	3.42	0.21	98.06	67

Source: McLennan (1993)

Table 5.3d Major element composition of various sedimentary rocks. (* recalculatrd to 100% on a volatile-free basis)

Sl. No.	Name	N	SiO2	TiO2	Al2O3	FeO (t)	Fe2O3 (t)	Fe2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	CO2	LOI	Total
1	Ave. Sandstone (Clarke)		78.66	0.25	4.78	-	-	1.08	0.30	-	1.17	5.52	0.45	1.32	0.08	5.04	1.71	100.36
2	Ave. Sediment (Clarke)		58.49	0.56	13.08	-	-	3.41	2.01	-	2.51	5.45	1.11	2.81	0.15	4.93	4.80	99.31
3	PAAS	23	62.80	1.00	18.90	6.50	-	-	-	0.11	2.20	1.30	1.20	3.70	0.16	-	-	97.87
4	UCC		66.00	0.50	15.20	4.50	-	-	-	0.08	2.20	4.20	3.90	3.40	-	-	-	99.98
5	Loess		76.37	0.68	13.03	3.08	-	-	-	0.07	1.13	1.10	1.89	2.25	-	-	-	99.60
6	Ave. Graywacke *	61	69.63	0.63	14.09	-	-	1.67	3.65	0.10	2.19	2.61	3.02	2.09	0.21	-	-	99.89
7	Ave. Arkose*	32	80.18	0.31	9.04	-	-	1.56	0.73	0.28	0.52	2.81	1.56	2.91	0.10	-	-	100.00
8	Ave. Lithic-Arenite*	20	72.90	0.33	8.93	-	-	4.19	1.54	0.11	2.65	6.84	0.99	1.43	0.11	-	-	100.02
9	Ave. Quartz-Arenite*	26	96.60	0.20	1.10	-	-	0.40	0.20	-	0.10	1.60	0.10	0.20	-	-	-	100.50
10	Ave. Nilambur Laterite	12	38.43	1.22	21.75	-	-	19	0.74	0.22	0.79	1.16	1.04	0.17	0.37	-	14.93	99.82
11	Ave. Buhwa Shales Zimb.	17	62.33	0.58	19.27	-	5.21	-	-	0.03	2.16	0.03	0.31	5.88	0.04	-	3.83	99.67
12	Ave. Mount Isa, Aus., Gr.I	7	52.52	0.79	16.7	-	-	13.36	1.14	0.03	3.73	0.26	0.3	6.97	0.12	-	3.94	99.86
13	Ave. Mount Isa, Aus., Gr.II	6	64.72	0.57	14.33	-	-	2.65	2.24	0.08	2.59	1.45	0.73	4.64	0.13	-	5.58	99.71

Note that where ever FeO (t) is given it is split into Fe2O3 and FeO in the ratio as seen in modern river sands. If Fe2O3 (t) is given it is first converted to FeO (t) and is expressed as Fe2O3 and FeO in the ratio as seen in modern river sands (this is applied for A-C-F diagram)

(1) & (2) Mason and Moore (1982); (3) to (5) Taylor and McLennan (1981); (6) to (9) Bhatia (1983); (10) Nair et al. (1987); (11) Fedo et al. (1996); (12) & (13) Eriksson et al. (1992)

Table 5.4a Altration indices for selected major rivers of the w

Name	N	CIA	CIW	PIA
Ave. TS (Chaliyar)	6	60.0	61.6	60.5
Ave. US (Chaliyar)	5	60.5	62.6	61.2
Ave. LCS (Chaliyar)	9	63.4	65.7	64.4
Ave. LS (Chaliyar)	8	57.8	60.1	58.4
Ave. Chaliyar	28	60.5	62.7	61.3
33 Modern river sands		60.0	68.3	63.3
Brahmaputra		73.0	-	-
Ganges		68.0	-	-
Chao Phraya		64.0	-	-
Niger		62.0	-	-
Irrawaddy		61.0	-	-
Mekong		56.0	-	-
Zambezi		49.0	-	-
Indus		46.0	-	-
Av. Columbia river sand*	68	54.1	59.4	55.0
M. Leading Edge sand*	15	49.5	54.6	49.4
M. Trailing Edge sand*	29	53.8	61.1	55.0
Ave. Orinoco river sand	62	78.2	100.0	100.0
Ave. Brazil-Peru Border main stem sands of Amz.R	3	60.5	67.2	63.1
Ave. Amazon River	5	62.8	70.5	66.4
Meurthe River main stem	(F2) 7	55.3	76.4	61.9
Meurthe River main stem	(F3) 7	56.0	76.8	63.1
Meurthe River main stem	(F4) 7	56.8	72.1	61.8

Table 5.4b Altration indices for selected sediments and sedimentary rocks

Name	N	CIA	CIW	PIA
Ave. TS (Chaliyar)	6	60.0	61.6	60.5
Ave. US (Chaliyar)	5	60.5	62.6	61.2
Ave. LCS (Chaliyar)	9	63.4	65.7	64.4
Ave. LS (Chaliyar)	8	57.8	60.1	58.4
Ave. Chaliyar	28	60.5	62.7	61.3
Ave. Sandstone (Clarke)		68.8	86.6	81.9
Ave. Sediment (Clarke)		72.9	87.8	84.6
PAAS	23	70.4	82.7	79.0
UCC		48.0	54.3	47.4
Loess		63.4	71.9	67.5
Ave. Graywacke *	61	55.2	60.5	56.3
Ave. Arkose*	32	52.2	63.8	53.5
Ave. Lithic-Arenite*	20	65.0	73.3	69.4
Ave. Quartz-Arenite*	26	66.9	77.1	73.0
Ave. Nilambur Laterite	12	87.5	88.1	88.0
Ave. Buhwa Shales, Zimb.	17	73.7	97.4	96.2
Ave. Mount Isa, Aus., Gr.I	7	67.0	96.1	93.1
Ave. Mount Isa, Aus., Gr.II	6	65.9	85.6	79.5

Chapter 6

TRACE AND RARE EARTH ELEMENT GEOCHEMISTRY

6.1 Introduction

Trace element geochemistry of river sediments provides information on provenance characteristics, processes of weathering and erosion as well as on the evolution of sediments in a basin in terms of various geochemical processes vis-à-vis fluvial transport and deposition. To cite a classic example, Taylor and McLennan (1985), based on trace element patterns, distinguished Archean and post-Archean shales that reflect weathering and erosion of undifferentiated and differentiated upper crust, respectively.

Chemical weathering of rocks is one of the major processes which modify the Earth's surface and is one of the vital factors in the geochemical cycling of elements. The significance of sediment geochemistry and its application in solving geological problems have already been discussed elsewhere (Chapter 5; section 5.2). The mobilization and redistribution of trace elements during weathering is particularly complicated because these elements are affected by various processes such as sediment recycling, dissolution of primary minerals, formation of secondary phases, redox processes, transport of material, coprecipitation and ion-exchange on various minerals (Harris and Adams, 1966; Nesbitt, 1979; Chesworth et al., 1981; Fritz and Ragland, 1980; Nesbitt et al., 1980; Cramer and Nesbitt, 1983; Fritz and Mohr, 1984; Kronberg et al., 1987; Subramanian, 1987; Middelburg et al., 1988). Nevertheless some general statements apply. Trace elements, including La, Ti, Zr, Th, Sc, V, and Co have been found to be useful discriminants of source regions, owing to the fact that they may not be strongly fractionated relative to the source by weathering and sedimentary processes (Taylor and McLennan, 1985; Bhatia and Crook, 1986).

The processes of sedimentation, including weathering, erosion, sedimentary sorting and diagenesis, essentially involve water/rock interaction and result in many fundamental chemical changes. In turn, the composition of sedimentary rocks may provide useful insights into the chemistry and nature of these interactions, including fluid compositions, fluid/rock ratios and the mechanisms of element mobility in crustal environments.

The geochemical variation in the nature of sedimentary rocks in the past, including the occurrence of mineral deposits, evaporites etc., reflect periodic changes in weathering, erosion and deposition of sediments at any given geological time brought out by eustatic and tectonic processes. The total sedimentary rock material essentially reflects recycled sediments. During each such recycling, there are chemical variations in the sedimentary column, process of weathering, erosion and riverine transport being the main agents causing chemical and physical variation in the properties of sedimentary rocks. For example, heavy metals dispersed in any source rock get concentrated in shale due to the formation of organo-metal complexes during weathering and erosion processes in the rock cycle. Thus, the surface riverine processes form the most important link in the geochemical cycling of elements individually and rock materials collectively. Observation on present day processes provides key to long term geological phenomena. Quantitatively, however, the present day surface processes are to some extent influenced by man's interference with natural geological rate processes, such as rates of weathering and erosion (enhanced by deforestation), rates of sedimentation (enhanced by dam construction), rates of metal transport (altered due to added supply by mining activities) etc. Such influence may however be evident only to a limited extent and may be confined more to the elemental abundances in the sediments. In the present study, where a large number of immobile elements are being considered, such human influences may not be significant. Hence, geochemical studies on river basins give input into the past geological processes as well as man's impact on environment.

6.2 Significance

Trace elements in solution in river water and adsorbed on suspended particles are generally deposited in estuaries and on the continental shelves or accumulate in deep sea clays. Therefore, the annual riverine input of a trace element to the oceans must be equal to the output of that element associated with marine muds. Moreover, in order to understand the geochemical budget of individual elements, the chemical composition of river-borne sediments needs to be known. The average ratio of sediment to solute load of rivers is 4:5 (Garrels et al., 1975). Thus, for flux calculations, one needs to know not only the distribution of elements in dissolved and suspended loads, but also its distribution in the bedload sediments of large as well as small rivers. In addition to this, trace and rare earth element geochemistry of modern detrital sediments from rivers acquires special importance because it helps us to understand the environment we live in today and permits us to anticipate how it may respond in the future to various anthropogenic perturbations.

6.2.1 Objectives

The purpose of the present study is to carry out a survey of trace element, especially rare earth element content in the bedload sediments of a small river like Chaliyar in order to:

a) study their concentration and distribution in the basin in relation to texture, mineralogy and the degree of transport it has undergone;
b) understand the trace and rare earth mobility in a fluvial system;
c) have a better understanding of the composition of upper continental crust over a small drainage basin; and
d) decipher the nature of provenance rocks, weathering conditions and tectonic stability of the basin, based on trace element geochemistry.

6.3 Literature Review

Several attempts have been made to estimate the average composition of river sediments (see for example, Martin and Mybeck, 1979), but the present understanding on sediment chemistry is limited as the information available is restricted only to the large sediment-carrying rivers of the world. Milliman and Meade (1983) estimated that nearly 30% of transport of sediments by world rivers takes place in the Indian sub-continent and the Asian rivers contribute about 50% of sediment flux to the world oceans. Geochemical processes have been studied in great detail in river basins by several investigators (Gibbs, 1967; Seetharamaswamy, 1970; Satyanarayana, 1973; Seralathan, 1979; Stallard and Edmond, 1983; Subramanian et al., 1985a). The overall balance between dissolved and sediment load carried to the oceans has been computed on the basis of world's major river input studies by Holeman (1968), Meybeck (1976), Martin and Meybeck (1979) and Milliman and Meade (1983).

Large amount of literature is available especially on the heavy metal contamination in rivers, estuaries and near shore environments. The fixation of heavy metals in these environments is of extreme importance due to their impact on ecosystem (Vale, 1986; Mance, 1987; Klomp, 1990; Windom, 1990). Moreover, anthropogenic contamination of the hydrosphere by heavy metals has magnified the urgency of elucidating the cyclicity of toxic metals in rivers and estuaries. Chemical analysis of river waters and sediments is being carried out for the exploration as well as environmental monitoring and management. Extensive work has been done in the world's major rivers by several investigators (Reeder et al., 1972, in Mackenzie river; Trefrey and Presley, 1976, in Mississippi river; Duinker and Nolting, 1976, in Rhine river; Gibbs, 1977b, in Amazon and Yukon rivers; Meybeck, 1978, in Zaire river; Yeats and Bewers, 1982, in St.Lawrence river; Sarin and Krishnaswami, 1984, in Ganges-Brahmaputra rivers; Qu and Yan 1990, in Chang Jiang and Don Jiang rivers). Trefrey and Presley (1976) estimated the total flux of particulate and dissolved heavy metals from Mississippi river to the Gulf of Mexico. Dupre et al. (1996) studied the chemical composition of different phases carried in the Congo river. Several researchers opined that the metal pollution assessment can effectively be carried out from sediment analysis (Forstner and Wittmann, 1983 and Allen, 1990).

The size dependent analytical study by Gibbs (1977b) showed that particle size has a strong bearing on metal enrichment in sediments. Later, this view was supported by investigations made by Williams et al. (1978), Forstner (1982), Forstner and Wittmann (1983), Lee (1985), Albarede and Semhi (1995), Vital and Stattegger (2000), Chandrajith et al., (2000).

Ramesh et al. (1989, 1990) made a through study on the mineralogical and geochemical association of metals in the Krishna river sediments. Shankar and Manjunatha (1994) studied the elemental composition and particulate metal fluxes from Netravati and Gurpur rivers to the coastal Arabian sea. Similarly, several workers have studied the trace metal concentration in the rivers and estuaries of Kerala particularly in relation to granulometry of the sediments. Murthy and Veerayya (1981) made a preliminary study on the trace element contents in the bulk sediments of the Vembanad lake. The trace metal concentration and its association in various chemical phases in the sediments of Periyar river and Varapuzha estuary have been investigated by Paul and Pillai (1983a, b). Mallik and Suchindan (1984) have analysed a few major and minor elements in the bulk sediments of Vembanad estuary. Later, Ouseph (1987) and Purandara (1990) have also studied the geochemical characteristics of a few sediment samples of Vembanad estuary. Mohan (1997) carried out a comprehensive study of the distribution and accumulation of selected trace elements in the modern sediments of Vellar river, estuary and its nearshore environments. Padmalal (1992) has studied the heavy metal content in the suspended particulates and bed sediments of Muvattupuzha river and Central Vembanad estuary, Kerala.

It is evident from the above review that geochemistry of Indian rivers are mainly studied on environmental perspective like heavy metal pollution and its impact on the ecosystem. However, studies of modern river sediments especially big rivers, and sedimentary rock geochemistry have made important contributions all over the world to interpret tectonic settings and estimates of average upper crustal composition. In many instances, provenance regions have been destroyed and the only record lies in the sediments derived from them. Each river constitutes a unique system as no two rivers are alike in terms of lithology of source areas, weathering (factors like rainfall, climate, temperature etc.), basin geometry and stage of development. Detailed trace and rare earth element analysis of modern river sediments, especially in the Indian context, is rare. An attempt is made in this chapter to determine the concentrations of trace and REE in the detrital sediments of the Chaliyar river and to interpret the effect of weathering, transport and deposition on trace elements especially REE in the fluvial system.

Trace element concentrations in sediments result from the competing influences of provenance, weathering, diagenesis, sediment sorting and the aqueous geochemistry of the individual elements (Rollinson, 1993). Due to remarkably high concentrations of these trace elements in clay-rich sediments, most geochemical studies have concentrated on these lithologies. Vital et al. (1999) successfully utilizes clay as well as heavy mineral fractions to deduce provenance. On the other hand, Chandrajith et al. (2000) carried out regional geochemical and mineralogical study on different size fractions of stream sediments in order to understand the mineralization and provenance in the Walawe Ganga river basin in Sri Lanka. Recently, Nath et al. (2000) studied the $<4\mu$ size particles from

Vembanad estuary and its near shore environments for major, trace and rare elements in order to understand the source area weathering conditions and provenance characteristics.

Rare earth elements (REE), as well as Th, Sc and to a lesser extent Cr and Co, are the most useful elements for provenance characterization, because they are among the least soluble trace elements and are relatively immobile. These elements are believed to be transported exclusively in the terrigenous component of a sediment and therefore, reflect the chemistry of their source (McLennan et al., 1980; Rollinson, 1993).

6.4 Results and Discussion

As detailed in the previous chapter, the samples of Chaliyar river have been classified into four groups, namely the tributary sediments (TS), upper reach sediments (US), lower reach clay bearing sediments (LCS) and lower reach sediments (LS) of the Chaliyar main stem. Among these, the upper reach stream sediments have the maximum number of trace elements analysed (36 including REE) while sediments from other environments the data is erratic or not complete. Though comparative study is hampered to a certain extent due to these limitations, several significant conclusions have been drawn from available data for individual elements of the different groups. These are discussed in this chapter.

As one of the important aims of this study is to get information on the upper continental crust composition over a small drainage basin, the data especially trace (except REE) and selected major elements have been normalised to mean upper crust composition proposed by Taylor and McLennan (1985). The sample locations are shown in figure 2.1.

Similarly REE geochemistry of Chaliyar upper reach sediments (US) and lower reach clay bearing sediments (LCS) of the main stem is studied in detail and they are normalised with chondritic, NASC values and compared with provenance rocks.

6.4.1 Large Ion Lithophile Elements (LILE)

Concentrations of Sr and Ba in the tributary sediments (n=6) range from 118-214 ppm, and 104-238 ppm, respectively (Table 6.1). In the Chaliyar main stem Sr ranges from 122-291 ppm while Ba ranges from 140-254 ppm (Table 6.1). It is evident from the spider plot that large ion lithophile elements Rb (data available for upper reach sediments only and it is around 8-11 ppm; see table 6.1), Sr, Ba and other mobile cations like CaO, Na_2O, K_2O are depleted relative to average Upper Continental Crust (UCC), normalized after Taylor and McLennan, 1985 (see Figs. 6.1a, b, c & d). Among this Ba, Rb and K_2O show greater degree of depletion in Chaliyar river sediments. The highest depletion is shown by K_2O which is mainly due to lower content of potassium bearing minerals in the source rocks. The second highest depletion is shown by Ba. It is interesting to note that Rb shows more depletion than K_2O in the US (see Fig. 6.1b). Like potassium, Rb will be incorporated into clays during chemical weathering, in contrast to divalent Ca, Sr, which along with Na tend to be leached (Camire et al., 1993). To sum up, the spider plots of figure 6.1, shows that samples from different environments from Chaliyar river are depleted in CaO, Na_2O, and Sr. The elements K_2O, Rb and Ba are relatively even more strongly depleted. This is mainly due to one or both of the following two reasons:

a) potassium in the source rock is very less (K_2O depletion) and which is a characteristic of many Precambrian exhumed lower crust and
b) the Chaliyar river sediments (US) are predominantly sandy in nature with only few samples (9 no.'s) having clay >5% (Rb depletion) (note that Rb is determined only for US).

In spite of the grain-size effect and varying amount of clay content these patterns do not show any significant changes in the different groups of Chaliyar river sediments especially in the large ion lithophile elements and mobile cations like CaO, Na_2O etc. The depletion of LILE in all the groups relative to the UCC are presumably due to removal of these elements from minerals during weathering. Similarly the feldspathic group (Na_2O, K_2O, Ba and Rb) from a less important component in Chaliyar river sediments because they are depleted more when compared to CaO and Sr.

6.4.2 Transition Metals

Feng and Kerrich (1990) noted that Cr, Co, Ni and Ti-V behave similarly during magmatic processes, but cautioned that they may be fractionated during weathering. In the tributary sediments Cr and Ni ranges between 234-344 ppm and

28-44 ppm respectively while in the Chaliyar main stem Cr ranges between 66-368 ppm and Ni from 21-102 ppm (Table 6.1). The average Cr and Ni content in the Chaliyar basin sediments is 216 ppm and 49 ppm respectively which is similar to Archean crust (Cr:140 ppm, Ni:90 ppm; data from Taylor and McLennan, 1981) and most other Archean shales; average Buhwa shales have Cr and Ni concentrations 284 ppm and 74 ppm respectively (Fedo et al., 1996).

The different groups of Chaliyar river sediments are normalised with transition metals of UCC and shown in figure 6.1. From the spider plots it is clear that most of the transition metals are either enriched or similar to average UCC (Fig. 6.1). However, Zn and Cu show strong depletion in US (Fig. 6.1b) while the TS and LS show minor negative Cu anomalies and Zn almost same as that of UCC (compare Fig. 6.1a & b). In the TS strongest enrichment is shown by Cr followed by V, Ca and Ni (Fig. 6.1a). However, with respect to UCC, the US show slightly higher enrichment for V when compared to other transition metal like Sc, Cr, Co and Ni (Fig. 6.1b). In the LCS of the main stem strongest enrichment is seen for Cr followed by Ni (Fig. 6.1c). Similarly with respect to average UCC, the LS show strong enrichment in Cr followed by minor positive anomalies in Ni and Co in that order, while V and Zn show almost same as that of UCC (Fig. 6.1d). The enrichment of Cr and V in US and TS and Sc in US is note worthy. While the source areas have laterite cover which bear testimony to chemical weathering of country rocks, the large amount of pyriboles, detrial ilmenite (leucoxinised), magnetite and sulphides (rare) point to a degree of mechanical weathering of the country rocks in the source areas. The high concentration of Cr and Ni may be concentrated in the heavy minerals referred above.

6.4.3 High Field Strength Elements (HFSE)

The elements Zr, Nb, Hf, Y, Th and V are preferentially partitioned into melts during crystallization and anatexis (Feng and Kerrich, 1990), and as a result, these elements are enriched in felsic rather than mafic rocks. Additionally, along with the REE's these HFSE are thought to reflect provenance compositions (Taylor and McLennan, 1985). The relative enrichment of HFSE and related trace elements and elemental differences among samples may presumably be related to the mineralogy of sediments. These elements are generally concentrated in resistant heavy mineral phases such as zircon, monazite, ilmenite, sphene, apatite, allanite and garnet. Larger variations in these minerals in coarser fractions such as in very fine sand, could result in significant variations in the abundance of elements in stream sediments (Cullers et al., 1988). For Chaliyar river the HFSE are analysed only for US (main stem samples H-1, H-2, H-3, H-4 and H-5) and is given in table 6.1.

The HFSE of Chaliyar US are normalised with UCC and is shown in figure 6.1b. In general all the HFSE show depletion when compared to UCC suggesting that the sediments are derived from HFSE-depleted source rocks. Among the HFSE, Zr and U show maximum depletion followed by Th, Hf, Nb and Y. In the US of Chaliyar main stem Zr, Nb, Hf, Ta, Y, Th and U averages approximately 24, 7, 1, 0.4, 8, 1.5 and 0.2 ppm respectively. Moreover among the above HFSE, Nb, Hf, Y, Th and U content in the Chaliyar river sediments are more comparable with the Archean upper crust (Nb=5, Hf=3, Y=15, Th=2.9, U=0.75; data from Taylor and McLennan, 1981). Thus it may be concluded that the Chaliyar river sediments are derived from HFSE-depleted Archean terrain.

6.5 Downstream variation of some selected trace elements in Chaliyar main stem

Figure 6.1e illustrates the downstream variation of Ba, Sr, Cr and Ni in the Chaliyar river main stem sediments. Similar to the mineralogical and major element spectral pattern the US samples (between 70-107 km) show a steady pattern almost constant) in the Ba, Sr, Cr and Ni contents while it fluctuates severely beyond 107 km in the downstream direction. The downstream increase (beyond 107 km) in the Ba content especially at some of the stations (e.g. H-14, H-18, H-24) again suggests that there is input of feldspar by the downstream tributaries. This is also reflected in the downstream increasing trend shown in Al_2O_3/SiO_2 ratio together with Na_2O and K_2O spectral pattern.

Even though Sr content in the Chaliyar main stem fluctuates it show decreasing trend in the downstream direction. Moreover, the positive anomalies of Ba at stations H-14, H-18 and H-24 correspond to negative anomalies of Sr. Slightly higher content of Sr in upper reaches (70-107 km) points that they are incorporated in plagioclase.

Cr content show slightly increasing trend in the downstream direction. Beyond 107 km in the downstream direction Cr content suddenly show a sharp increase probably indicating mineralogical and textural control.

The Ni content in the main stem, beyond 107 km in the downstream direction is mainly controlled by the textural characteristics. Positive anomalies of Ni in the spectral pattern corresponds to the LCS samples while the negative anomalies corresponds to the LS samples which are of sandy nature. However Ni and Cr content remains constant in the US samples (between 70-107 km).

6.6 Rare Earth Elements (REE)

Ten bedload sediment samples from Chaliyar main stem were selected for REE analysis (see Fig. 2.1 for sample locations), of which five are upper reach samples (US) and five are from lower reaches (LCS) (Table 6.2). The REE data are less variable, and display a single general trend based on curve shape (chondrite normalised) while the degree of Eu anomaly is prominent in US but has no Eu anomaly in majority of LCS (Fig. 6.2a & b).

The total concentration of fourteen rare earth elements (∑REE) in the sediment samples (note that for five US samples the fourteen REE's are analysed and for five LCS samples seven REE's were analysed) varies from 37.7 to 65.5 ppm (Table 6.2) and the mean concentrations (10 samples) is highly depleted (~0.4 times) when compared to that of the UCC (Table 6.2).

Shale-normalized REE abundances of Chaliyar river sediments define a flat pattern with approximately 0.2-0.6 (average 0.3) times North American Shale Composite (NASC) for US while it is 0.2-0.8 times for LCS (Fig. 6.2c & d respectively). The low concentration of REE in the US samples when compared to NASC is due to their sandy nature, devoid of clay minerals and rock fragments that contain high REE among the eroded materials. Similarly, the slightly higher concentration of REE in the LCS samples when compared to US is mainly due to mud content rather than rock fragments because as already explained in earlier chapters that the Chaliyar river sediments are almost devoid of rock fragments. Although their REE concentration is low, the variability in terms of bulk rare earth elements (in US samples) and LREE/HREE (average chondrite normalized LREE/average chondrite normalized HREE) ratio for samples is less (Table 6.2).

This kind of similarity among sediment samples could be attributed to the homogenization due to erosion and transportation (Goldschmidt, 1954). However, the LREE/HREE ratio is slightly less (varies between 3.21-4.30 and averages 3.71) for US samples when compared to LCS (varies between 4.78-5.70 and averages 5.31). This slight difference in the LREE/HREE ratio among the US and LCS samples may be attributed to two possible reasons:

i) the LCS samples are slightly enriched in LREE due to varying amounts of clay present and

ii) the HREE are preferentially transported in solution because they form more soluble bicarbonate and organic complexes than the LREE (Balashov et al., 1964).

The chondrite-normalized REE patterns of Chaliyar river sediments are very similar to each other,

a) being enriched in the LREE relative to the HREE,

b) fractionated LREE and flat HREE.

However, the noticeable difference is that a persistent negative europium anomaly in US samples and almost no Eu anomaly in most of the LCS samples (Fig. 6.2a & b). Moreover, the degree of enrichment in the LREE relative to HREE and the fractionation between LREE and HREE are slightly less in US samples when compared to LCS samples.

The difference in the relative degrees of fractionation among LREE and HREE is reflected in their high La_N/Sm_N ratios (ranging from 2.55 to 4.07 with an average of 3.39 for US; ranging from 4.27-4.77 with an average of 4.51 for LCS) but relatively lower Gd_N/Yb_N ratios (ranging from 1.24 to 2.01 with an average of 1.68 for US; ranging from 1.73-2.59 with an average of 2.01 for LCS) (see table 6.2). This kind of fractionation is characteristic of post-Archean sediments (McLennan and Taylor, 1991). As given above the less variability (4.27-4.77) and slightly higher average La_N/Sm_N ratio (4.51) for LCS samples suggests that they are slightly more fractionated in terms of LREE when compared to US samples. Similarly, slightly higher average Gd_N/Yb_N ratio for LCS when compared to US samples indicates that the former is more fractionated in terms of HREE also. Moreover, the samples from lower reaches of Chaliyar river have slightly elevated LREE/HREE and high La_N/Yb_N

ratios when compared to US. This is attributed to intense weathering as revealed by slightly high CIA/CIW values for majority of LCS samples. The above differences in the relative degrees of fractionation among LREE and HREE in US and LCS samples, along with their distinguishing Eu/Eu* is clearly depicted in figure 6.2e & f.

The average shale-normalized upper reach and lower reach clay bearing sediment samples are plotted together in figure 6.2g. The average of US samples define an almost flat pattern while the average LCS samples almost parallels the former but the LREE is enriched and HREE is slightly depleted in them.

In order to have a comparison of the sediments with the rocks of the source area the average REE abundances of seven samples of crystalline rocks of Wynad - Calicut region reported by Nambiar et al. (1992) is compared with the average US and LCS samples (Table 6.3 and Fig. 6.2h).

Compared to provenance rocks the US are depleted in REE's in general, to around 0.35 times in LREE and around 0.66 times in terms of HREE while it is 0.67 times in LREE and 0.63 times in terms of HREE (in this case it is Yb alone since Tb and Lu is not determined) for LCS. This could be attributed to the weathering related LREE enrichment (Duddy, 1980) and that the sediments are essentially detritals originated by the removal of clays and rock fragments from the bulk product of weathering. However, it is important to note that the HREE depletion remains almost constant in US and LCS samples while the LREE in the US samples shows slightly more depletion when compared to provenance rocks and LCS samples. Lesser depletion of LREE in LCS in comparison with provenance rocks is mainly due to varying amounts of mud present in them.

When the chondrite-normalized pattern of average sediment (average US and average LCS samples) is compared with that of the average provenance rocks, they mimic each other to a great extent (Fig.6.2h). However, the following significant differences were noted:

a) Even though the US are slightly enriched in LREE relative to HREE they show a lesser degree of rare earth element fractionation when compared to source rocks, as indicated in their La_N/Yb_N ratio. This may be due to the varying amounts of certain heavy minerals which can enhance the bulk REE and can effect the LREE/HREE ratios. In the case of LCS the LREE is more enriched relative to

HREE and they have La_N/Yb_N ratio which is comparable with that of the provenance rocks (see Table 6.3) suggesting similar rare earth element fractionation.

b) There is a negative Eu anomaly in the US, while the LCS and the provenance rocks exhibit a smooth pattern.

The negative europium anomaly especially in the Chaliyar river US indicates preferential removal of plagioclase feldspar due to weathering. Plagioclase is known to be more rapidly destroyed than either quartz or K-feldspar in weathering profiles (Nesbitt et al. 1996). The US samples have Eu/Eu* values between 0.43 and 0.69 and are comparable with the Group II samples of Queensland, Australia, which represent typical post-Archean mature sediments derived from differentiated upper continental crustal provenances (Eriksson et al., 1992). Though the rare earth elements are known to be immobile in weathering regime , Eu has slightly higher mobility than other REE's (Albarede and Semhi, 1995).

However, most of the LCS in the Chaliyar river does not have a Eu anomaly, which could be due to two possible reasons

a) addition of less weathered products by the tributaries joining the main stem along its lower reaches which is reflected in a slight increase in feldspar content (see Chapter 4) and

b) clays are essentially originated by weathering/alteration of feldspar which was having positive Eu anomaly.

The former reason is of less significance because the above samples have higher average CIA values (CIA=63, CIW=65) than US samples (CIA=60, CIW=62) indicating that the plagioclases has contributed less for the absence of Eu anomaly. Another significant point is that Eu^{2+} and Sr^{2+} has comparable ionic sizes and hence there exists a close crystal chemical relationships between them (Gao and Wedepohl, 1995). Eu^{2+} and Sr^{2+} both partly substitute Ca^{2+} and Na^{2+} in plagioclase, which is the major rock phase with high Eu/Eu*. Thus the absence of Eu anomaly in the LCS samples of Chaliyar river is mainly due to adsorption of Eu on clay sized fractions. This is also reflected in low Sr values in them while the US samples have higher Sr values and strong negative Eu anomaly. The adsorption of Eu on clays in the LCS is probably due to greater availability of Eu^{2+} in the dissolved state when compared to upper reaches.

The LCS samples have Eu/Eu* values between 0.8 and 1.03 and shows signatures similar to that of the Group I samples of Queensland, Australia (Errickson et al., 1992).

It is worth noting that, to a certain extent, the physical process of sediment sorting can determine the REE contents of sedimentary deposits if the REE's are concentrated in one or more size fractions. As may be seen in this case the US sample no. 4 (H-4) has the lowest REE content (ΣREE 37.7 ppm; average elemental concentration 2.7 ppm) whose mean grain size is 0.94∅ (see Table 3.2), while the other four samples whose mean size varies between 0.99 and 1.42∅, the ΣREE varies between 45.1 and 65.5 ppm (average elemental concentration between 3.22 to 4.68 ppm), even though all of them show moderate to well sorted character. Similarly among the LCS samples of Chaliyar river the sample no. 19 (H-19) has the lowest average REE content (5.32 ppm) whose mean grain size is 1.04∅ (see Table 3.2), while the other four samples whose mean size varies between 1.33 and 1.95∅, the average REE varies between 6.94 and 12.51 ppm, and all of them show moderately sorted character. According to Roaldset (1979), subsand-sized detrital grains of REE rich minerals can be significant in determining the REE content of continental sediments which have undergone relatively little sorting.

No substantial change in the elemental concentration is seen in samples from different locations of the channel, which has undergone different degrees of fluvial transport, implying that the REE is not mobile during fluvial transportation and reflect the stable tectonic conditions under which they have evolved. The minor differences expected between US and LCS can be explained in terms of mineralogical content (including clays) and influence of tributaries.

6.7 K vs Ba, Sr in Chaliyar river sediments

According to McLennan et al. (1983) positive correlation between K-Ba suggests that K-bearing clay minerals (illite) primarily controls the abundance of Ba in sediments. In general, the Chaliyar river sediments show positive correlation (r=0.67) between their K and Ba contents (Fig. 6.3a). However, the LCS (open circle) show a negative correlation (r=-0.58) (Fig. 6.3a). This suggests that Ba is not adsorbed in K-bearing clay minerals and moreover as discussed elsewhere (chapter 4; section 4.8) the XRD analysis has shown that in the Chaliyar river sediments the illite content is negligible when compared to other clay minerals like kaolinite and chlorite. At the same time there exists a strong positive correlation between K and Ba in TS (r=0.98) (solid triangle), US (r=0.73) (solid square) and in LCS (r=0.97) (open square). This implies that Ba is mainly incorporated in K-feldspar because the above sediment samples are mainly gravelly and sandy in nature with little amount of clay.

K vs Sr for Chaliyar river sediments does not show any significant relationship however, in the US they show moderate negative correlation (r=-0.32) (Fig. 6.3 b). Similarly Ba show moderate positive correlation with Sr (r=0.33) in the US while in tributary and LCS and LS Ba do not systematically vary with Sr (fig. 6.3 c).

6.8 Mafic trace elements (Cr, Ni, Co and V)

In magmatic processes Cr, Ni, Co and V-Ti generally have similar behaviour: however, during weathering they may be mutually fractionated. In the Chaliyar river sediment samples Cr and Ni contents co-vary with MgO (see Fig. 6.3d & e) except in LS (open square) where Cr varies negatively with MgO (r=-0.67) (Fig. 6.3d). When plotted the individual groups show significant positive relationship. In the MgO-Cr plot the US show moderate positive correlation (r=0.38) while the TS and LCS (excluding the value in sample H-15=358 ppm) show strong positive correlation (r=0.69 and 0.86 respectively) (Fig. 6.3d). Similarly in the MgO-Ni plot the US show moderate positive correlation (r=0.43) while the TS, LCS and LS show strong positive correlation (r=0.94, r=0.76 and r=0.80 respectively) (Fig. 6.3e). It is also important to note that in MgO-Cr and MgO-Ni plots the different groups of sediment samples in the Chaliyar basin are clearly distinguishable with almost no overlapping of fields of different groups.

The V content is also well correlated with MgO (by excluding the values of samples H-3 and H-4) in the Chaliyar river (Fig. 6.3g). In general they show positive correlation (r=0.53). In this plot also the different groups show clear distinction from one another (note that V is not determined for LCS). In figure 6.3 k, V content in different groups are positively correlated with Al_2O_3 (in tributary the V content in sample H-31 is not considered for correlation). However, V is positively correlated with TiO_2 in LS (r=0.75) while it is negatively correlated with US (r=-0.51) (Fig. 6.3j). TS samples does not vary systematically. Among the different groups the LS samples show significant positive correlation between V and TiO_2, V and Al_2O_3 (r=0.75, r=0.62 respectively). According to Feng and Kerrich (1990) the positive correlation of V with Al_2O_3 and TiO_2 abundances is interpreted to indicate their co-enrichment during the weathering process.

The Co content is well correlated with MgO (Fig. 6.3f) (note that for LCS samples the Co content is not determined). TS show maximum content of Co followed by US and LS. In general the Chaliyar river sediments show strong positive correlation (r=0.80) between Co and MgO. Moreover, when the individual groups are plotted the LS samples show moderate positive correlation (r=0.44) while the TS and US show significant positive correlation (r=0.73 and r=0.94 respectively). In this plot also the different groups are very distinct with no overlap between the fields of different groups of samples.

Co vs TiO_2 and Co vs Al_2O_3 were plotted and is shown in figure 6.3l & m respectively. In general, Co shows significant positive correlation (r=0.93; n=17) with TiO_2 and moderate positive correlation with Al_2O_3 (r=0.39) (n=17) (note Co is not determined for LCS). However, when different groups are plotted individually in Co vs Al_2O_3 diagram (Fig. 6.3m) LS samples strong positive correlation (r=0.95; Co content in sample H-20 is not considered for correlation), US samples show moderate positive correlation (r=0.48) while the TS show negative correlation (r=-0.29). Significant positive correlation exists between Co and TiO_2 in different groups of Chaliyar river sediment samples (TS: r=0.92; US: r=0.66; LS: r=0.99). Like V, the positive correlation between Co vs TiO_2, Al_2O_3 is believed that V and partially Co were variably concentrated by weathering processes (Feng and Kerrich, 1990).

The pronounced negative correlation between MgO and Cr, moderate positive correlation between MgO and Co, suggest that the LS samples might have been derived from source regions having different nature and contents of mafic mineral assemblages.

Cr content is well correlated with Ni abundances except in the LS (open square) of the Chaliyar river (Fig. 6.3h). When plotted the LS show negative correlation between Cr and Ni (r=-0.7) while in the TS, US it shows moderate positive correlation (r=0.48, r=0.36 respectively) and the LCS show strong positive correlation (r=0.86) (note that the above 'r' value for LS is got by excluding the Cr content in the sample H-15). In the Cr vs Ni plot the different groups of samples are clearly distinguishable and all of them have separate fields with no overlapping between them. It is also important to note that the Cr is higher in TS and LS (solid triangle and open square respectively), the LCS have intermediate Cr and high Ni content (open circle) while the US have minimum Cr values (solid square) (see Fig. 6.3h). The pronounced negative correlation (r=-0.7) between Cr and Ni for LS of the Chaliyar river again supports the idea that these sediments are derived from source rocks having slightly different composition, as deduced above from MgO-Cr and MgO-Co relations (Fig. 6.3d & f respectively).

As mentioned earlier the Cr and Ni contents in the Chaliyar river sediments are similar to the Archean crust and most other Archean shales (e.g. Buhwa shales in Zimbabwe). The important Archean stable shelf deposits in South Africa include the Witwatersrand Super Group (West Rand Group, Wronkiewicz and Condie, 1987) and the Mozaan Group (Wronkiewicz and Condie, 1989) on the Kaapvaal Craton, and the Beitbridge Group within the granulite-facies Central Zone of the Limpopo Belt (Taylor et al., 1986; Boryta and Condie, 1990) and Phyllites from Buhwa Greenstone Belt, Zimbabwe (Fedo et al., 1996). It is useful to compare the geochemistry of these deposits with the Chaliyar river sediments in order to assess regional source area conditions.

Fields representing the different stable-shelf deposits, along with Chaliyar river sediment data, are plotted in figure 6.3i (note that the fields in the above figure is taken from Fedo et al., 1996). The Chaliyar river sediment data for Cr vs Ni is atypical of Beitbridge Group deposits and Buhwa shales, but they show slightly lesser range in Ni content, similar to the Buhwa shales. Moreover, the LCS (open circle) of Chaliyar river, almost overlap with the Beitbridge Group pelites (see Fig. 6.3i). However, the range in Cr and Ni content in the sediments of Chaliyar river is almost identical with that of the Buhwa shales from Zimbabwe (Buhwa shale data from Fedo et al., 1996).

6.9 Heavy mineral addition and trace and rare earth elements in Chaliyar river sediments

Plot of Yb_N vs Gd_N/Yb_N illustrate the effects of concentrating zircon on sedimentary pattern. According to McLennan (1989) sandstone is having a REE pattern parallel to shale (PAAS) but with lower overall abundances by a factor of five. When the Chaliyar river sediments are plotted in the above diagram (Fig. 6.4 a) they show strong negative correlation (r=-0.7) between Yb_N and Gd_N/Yb_N suggesting that there is zircon addition by sedimentary processes. However, the zirconium concentration in Chaliyar river sediments (Zr data available only for US samples) are several times lower than the zirconium concentration of an average sandstone. Hence, the above plot for Chaliyar river sediments may not be directly relatable with the plot of McLennan (1989) but the negative correlation between Yb_N and Gd_N/Yb_N is an indication of zircon addition in Chaliyar river.

The effect of concentrating monazite on sedimentary environment is perfectly understood in Gd_N vs Gd_N/Yb_N plot (McLennan, 1989) wherein a positive correlation suggests monazite addition assuming initial Th abundances for both sandstone and shale of 10 ppm. In general, the Chaliyar river sediments does not vary systematically in Gd_N vs Gd_N/Yb_N plot (Fig. 6.4b). When the US and LCS (solid square and open circle respectively) are plotted independently the former show moderate positive correlation (r=0.26) between Gd_N and Gd_N/Yb_N, while the latter show negative correlation (r=-0.49) suggesting that in the US there is small amount of monazite addition taking place. However, in the Chaliyar river sediments the Th content is several times less when compared to average sandstone and hence direct relationship cannot be established.

Allanite addition by sedimentary processes is shown by La_N vs La_N/Yb_N plot (McLennan, 1989) in which a positive correlation suggests allanite addition by sedimentary processes and the initial concentration of Th is taken as 10 ppm for both sandstone and shale. However, as mentioned earlier the Chaliyar river sediments have Th content several times lesser than the average Th values of sandstone. Hence the relationship may not be directly compared with the above plot.

However, when the US samples (solid square) are plotted in the La_N vs La_N/Yb_N diagram (Fig. 6.4c) (note that for the LCS the value for La is nor determined) they show moderate positive correlation (r=0.32) suggesting a small scale addition of allanite.

6.10 Eu/Eu* plots

The Chaliyar US and LCS samples are distinguished on plot Eu/Eu* vs Gd_N/Yb_N (Fig. 6.4d). The LCS samples display post-Archean affinities but with higher Eu/Eu*, Gd_N/Yb_N ratios and are less mature than US samples, similar to Group I samples of Queensland, Australia (Eriksson et al., 1992). The LCS vary slightly more especially in Eu/Eu* (0.8-1.03) and to a lesser extent in Gd_N/Yb_N ratios (1.73-2.59) and probably reflect variable proportions of different local sources. Thus the LCS samples are attributed to dilution of mature, post-Archean sediments by addition of sediments from local sources having slightly different chemical composition to produce a less mature sediments.

The Chaliyar US samples represent typical post-Archean mature sediments derived from upper continental provenances and are strikingly similar to the Group II samples of Queensland, Australia (see Fig. 6.4d & e; fields taken from Eriksson et al., 1992). In the US samples the Eu/Eu* (0.53-0.69) and Gd_N/Yb_N varies less (ranges between 1.24-2.01) which are typical characteristics of post-Archean mature sediments derived from differentiated upper continental crust with no dilution by local sources. It is important to note that in the Eu/Eu* vs Gd_N/Yb_N plot (Fig. 6.4d) one of the LCS sample plot in the Group I field while other samples shows signatures similar to Group I. Moreover, among the LCS one of them show Gd_N/Yb_N >2 (sample H-19 has 2.59) while others have values around 1.75-2.0 similar to US (1.25-2.0). However, compared to US the LCS samples are having slightly higher Gd_N/Yb_N ratio.

Similar to the above plots the Chaliyar US and LCS samples (solid square and open circle respectively) are well distinguished in the plots of Eu/Eu* vs CIW, Eu/Eu* vs Sr and Eu/Eu* vs CIA. In the Eu/Eu* vs CIW plot the LCS of Chaliyar river which are represented by five samples (open circle) show a considerable spread in CIW values and Eu/Eu* ratios while the US samples (solid square) show less spread especially in CIW values (Fig. 6.4f). Moreover as already explained the Eu/Eu* values for LCS are higher when compared to US samples. Both exhibit negative

Eu/Eu*-CIW correlations, with apparent linear correlation coefficients of -0.63 and -0.59 for the US and LCS respectively. The US samples with average CIW=62 (lesser than LCS samples) almost invariably correspond to significant negative Eu anomalies (Eu/Eu*=0.53 to 0.69). In contrast, the LCS samples with average CIW=65 (slightly higher than US samples) show a wide range in Eu/Eu* ratios, from 0.80 to 1.03 and in CIW values, from 56.8-73.1. This slightly wide range reasonably reflects variable, lithologically dependent Eu/Eu* values of plagioclase rich sediments (plagioclase addition) in the lower reaches. However, slightly higher average CIW values for the above samples probably indicate that higher Eu/Eu* values is mainly due to adsorption of europium in the finer particles like clay. Hence LCS without Eu anomalies usually have slightly higher average CIW values (65).

The negative Eu/Eu*-CIW correlation is accompanied by positive Eu/Eu*-Sr correlation in LCS (Fig. 6.4g; r=0.42). Even though, in the US, Eu/Eu*-CIW show negative correlation they does not vary systematically in the Eu/Eu*-Sr plot. The positive correlation between Eu/Eu* and Sr especially in the LCS (open circle) indicates the close crystal chemical relationships between Eu^{2+} and Sr^{2+}, which is a result of comparable ionic size. Eu^{2+} and Sr^{2+} both partly substitute Ca^{2+} and Na^{2+} in plagioclase, which is the major rock phase with high Eu/Eu* (Gao and Wedepohl, 1995). It is important to note that the US samples is having higher Sr content when compared to LCS samples even though the former consists of essentially of sand while the latter contains variable proportions of mud.

The US having negative Eu anomalies are characterised by lower average CIW values (CIW=62). LCS samples having slightly higher average CIW values (CIW=65) do not show any significant Eu anomaly. The above characteristics is unique and the above differences may be brought about by grain size effect.

A clear correlation exists between CIA and Eu/Eu* for sediments from upper (US) and lower reaches (LCS) (Fig. 6.4h). Both exhibit negative Eu/Eu*-CIA correlation with linear apparent correlation coefficient (r) of -0.68 and -0.65 for the US and LCS respectively which is quite similar as in the case of CIW. Similar kind of negative correlation between Eu/Eu* and CIW, Eu/Eu* and CIA, and positive correlation between Eu/Eu* and Sr for Archean pelites, graywackes/sandstones and young deep sea sediments has been reported by Gao and Wedepohl (1995). From this it can be concluded that modern river bedload sediments from Chaliyar river are also comparable with respect to the above discussed correlation.

6.11 Provenance and crustal abundances

In order to identify the effect of sedimentary processes and thus, to enable separating them from the provenance and crustal signatures, a series of elemental plots are shown below. The elements Th, La, Sc, Zr, Hf, Ta, Nb and Cr are compared in various scatter plots (Fig. 6.5). Both strongly incompatible elements (Th) and strongly compatible elements (Sc and Cr) as well as those related to dense-minerals (Hf, Zr, Ta and Nb) are represented (note that the above elements are analysed for US and hence study is restricted only to samples H-1 to H-5 in the Chaliyar river main stem).

Coherent behaviour between REE (La) and Th has been shown by McLennan et al. (1980). A positive correlation between Th and light REE (expressed as La) can be observed in figure 6.5a. The Chaliyar US plot between the estimated average UCC and La/Th ratio of 10. In the US samples La/Th ratio ranges between 4.6 and 9.7 with an average of 7.7. The Archean shale has generally higher La/Th ratios (3.6±0.4) than the post-Archean shale (2.7±0.2) (Taylor and McLennan, 1985). The US samples which are predominantly coarse sand and showing moderate to well sorted character has high La/Th ratios, heavily reflects the provenance rather than the effect of grain size.

According to Taylor and McLennan (1985) the Th/Sc ratio is a much more sensitive index of average provenance composition than is the La/Th ratio. In the Chaliyar US samples the Th/Sc ratio ranges between 0.1-0.16 with an average of 0.12 (Fig. 6.5b). Taylor and McLennan (1985) noted that the Th/Sc ratio is fairly constant in UCC and post-Archean fine grained sedimentary rocks at about ~1.0. However, there is significant similarity in Th/Sc ratios of Chaliyar US samples (averages 0.12) and Archean upper crust (0.12) (data for Th and Sc for Archean upper crust is taken from Taylor and McLennan, 1981).

Zr and Hf are important constituents of the heavy mineral zircon. Zircon generally occurs as an accessory mineral in wide compositional range of igneous and metamorphic rocks and is usually ubiquitous in all felsic igneous rocks. Zircon is a very robust mineral and is often resilient to chemical and mechanical destruction.

Therefore detrital zircon grains can be effectively used to trace back their sources. Zr and Hf are very similar crustal incompatible elements and hence can be used to differentiate between different crustal processes. In the Chaliyar US samples Zr and Hf show significant positive correlation (Fig. 6.5c). Moreover they plot above the UCC having a Zr/Hf ratio of about 40. The Zr/Hf ratio in the samples ranges between 17.87 to 21.61 with an average of 20.06. The value of Zr/Hf ratio in most crustal rocks lie close to 40 (Brooks, 1970; Murali et al., 1983). In mid oceanic ridge basalt and oceanic island basalt, this ratio has been estimated to average 36.6±2.9 (Jochum et al., 1986). However, the Zr/Hf ratio is known to increase with increasing alkalinity (Pavlenko et al., 1957) and increasing degree of silica undersaturation (Dupuy et al., 1992). In the Archean upper crust the Zr/Hf ratio is about 33 (Zr and Hf data for Archean upper crust is from Taylor and McLennan, 1981). The occurrence of similar ratios of Zr/Hf in Chaliyar US samples presumably provide evidence that the zircon in sediments are of single origin (i.e. Precambrian crystallines).

In figure 6.5d Ta is plotted against Nb. They show positive correlation (r=0.58), indicating a close geochemical association in Chaliyar river sediments. This presumably reflects the occurrence of Ta- and Nb- bearing minerals such as niobian rutile and fergusonite (Yt Nb Ta O_4) in sediments. However, the presence of Ta in trace amount (ranges between 0.22-0.64 with an average of 0.42) when compared to Nb (ranges between 4.92-10.39 with an average of 7.77) suggests that niobian rutile may be the dominant mineral rather than fergusonite. The Nb/Ta ratios of the US of Chaliyar river ranges between 12-27 with an average of 20.15. The above average ratio are similar to the Nb/Ta ratios (lie between 10 and 20) of the stream sediments of the Walawe Ganga Basin, Sri Lanka (Chandrajith et al., 2000). However, the absolute content wise the stream sediments of the Walawe Ganga Basin has very high Ta and Nb in all size fractions while in Chaliyar US (bulk) it is considerably low.

In figure 6.5e, Th/Sc is plotted against Zr/Sc. This diagram evaluates the role of heavy mineral concentrations especially zircon during sedimentary sorting. According to McLennan et al. (1993), the Th/Sc ratio is a sensitive index of the bulk composition of the provenance, and the Zr/Sc ratio is a useful index of zircon enrichment. Zircon enrichment (low Zr/Sc ratio when compared to UCC; see Fig.

6.5e) cannot be observed in the Chaliyar US. The value of Zr/Sc and Th/Sc ratios in Archean upper crust is 4 and 0.12 respectively (data from Taylor and McLennan, 1981). The above Th/Sc ratio is identical to the average Chaliyar sediment samples (average: 0.12) while the Zr/Sc ratio averages 2.06 which is slightly lower when compared to the Archean upper crust. However, the Zr/Sc ratios of US samples of Chaliyar river main stem show signatures similar to that of Archean upper crust. Even though, Chaliyar US samples show low values of Zr/Sc ratio when compared to UCC and Archean upper crust the horizontal (parallel to the x-axis) trend for samples increasing Zr/Sc ratios, to a lesser extent reflects sedimentary sorting and recycling.

The Cr/Th ratio has been used by Condie and Wronkiewicz (1990) as a provenance indicator , based on the fact that it correlates with the Sc/Th ratios. The Cr/Th ratio of the US of the Chaliyar river (Fig. 6.5f) trends to be higher than the estimated ratio for the UCC but they show significant positive correlation with Sc/Th ratio. The Cr/Th ratio for US samples ranges from 22.24 to 85.43 with an average of 61.35 while the Sc/Th ratio ranges between 6.45 to 10.53 with an average of 8.71. The above average ratios for Chaliyar US (bulk) are almost identical with respect to that of the Archean upper crust (Cr/Th=48.28 and Sc/Th=8.62 for Archean upper crust; data from Taylor and McLennan, 1981).

During weathering, there is a tendency for an elevation of Th/U ratio above upper crustal igneous values of 3.5 to 4.0 (McLennan et al., 1993). Moreover, Vital and Stattegger (2000) noted that weathering trends can be followed in the plot of Th/U vs Th (Fig. 6.5g). Chaliyar US samples show Th/U ratios ranging from 5.9 to 7.3 (average: 7.46), except in the sample H-2 (upto 11). Even though, the US samples are sandy in nature the Th/U ratio show significant positive correlation (r=0.99) with Th. The above trend (see. Fig. 6.5g) may be due to intense weathering in source area.

LREE/HREE, when plotted against the Th/U ratio, tend to show significant positive correlation (r=0.94) in the US (Fig. 6.5h). It is seen that as the LREE/HREE ratio increases the Th/U ratio also increases, indicating a close geochemical association in sediments. The above trend may also be interpreted as a weathering effect. In the LREE/HREE vs Th/U plot it is clear that the Chaliyar US have lower

LREE/HREE ratios, except sample H-2 (similar to that of UCC), while Th/U ratio is enriched in all the samples when compared to UCC.

Conclusions

- The Chaliyar river sediments are depleted with respect to Upper Continental Crust (UCC) in LILE, like Ba (range: 104-254 ppm), Sr (range: 118-291 ppm) and Rb (range: 8-11 ppm), which when considered along with the depletion in major elements like K, Ca and Na reflect the LILE depleted nature of the provenance modified by weathering.
- The transition metals like Ni, Cr, Cu, Zn, V and Co are either enriched or similar to that of the UCC. The enrichment of Cr and V in TS and US is suggestive of their enrichment in the soil and weathered products in the source area. From their correlation with TiO_2 and Al_2O_3, it is inferred that V and partially Co are variably concentrated by weathering processes.
- The average Cr and Ni contents in the Chaliyar basin sediments are 216 ppm and 49 ppm respectively and are consistent with an Archean crustal source.
- Content of the HFSE and ratios among them are also consistent with an Archean upper crust source.
- Ni is lower in sandy sediments and higher in clay bearing sediments while Cr abundance is controlled by the proportion of mafic minerals.
- The slight difference in mafic mineralogy of source regions of the upper and lower parts of the basin is reflected in the contents of several trace elements in samples from the two regions.
- The average REE in individual samples from the upper reach bedload sediments are lower (2.7 to 4.68 ppm) when compared to the lower reach (5.3 to 12.5 ppm). The upper and lower reach samples are distinguished on plots Eu/Eu* vs La_N/Sm_N and Eu/Eu* vs Gd_N/Yb_N. The Eu/Eu* values range from 0.53 to 0.69 for upper reach samples while the lower reach samples it ranges from 0.8 to 1.03. The lower reach sediment samples have elevated average $LREE_N$ /average $HREE_N$ and La_N/Yb_N ratios when compared to upper reach samples that are attributed to intense weathering in the source area.

- The highly fractionated chondrite-normalized REE patterns of the average upper reach as well as lower reach sediments mimic that of the average provenance rocks but for the presence of significant negative Eu anomaly in the upper reach sediments that is suggestive of preferential removal of plagioclase during weathering. However, the lower reach samples have Eu/Eu* values close to unity, consistent with increments in feldspars contributed by tributaries.
- Trends in the enrichment of heavy minerals like zircon, monazite and allanite in the sediments are reflected in behavior of certain selected REE pairs.

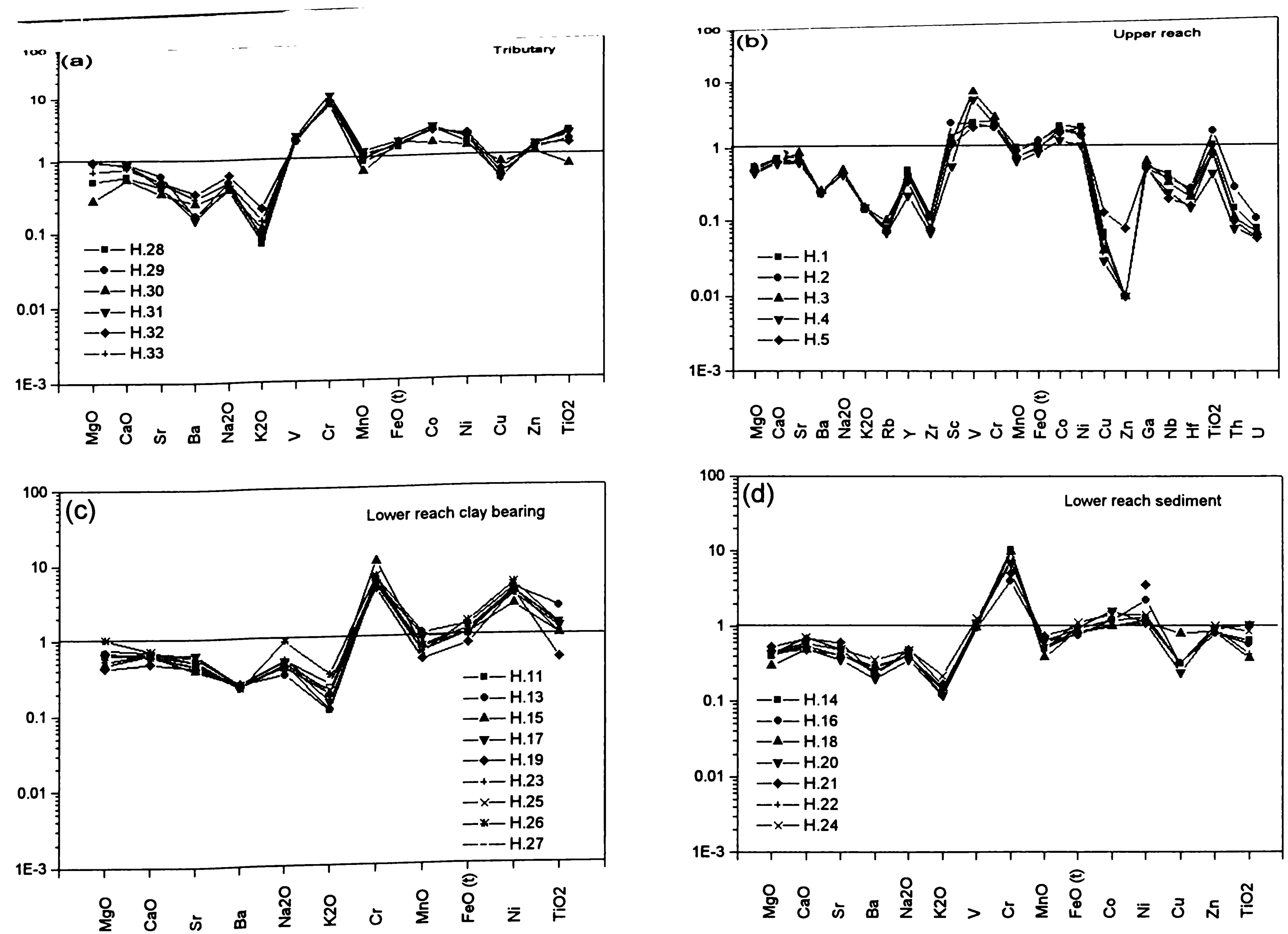


Fig. 6.1 Spider plot of different groups of samples from Chaliyar river normalised to UCC

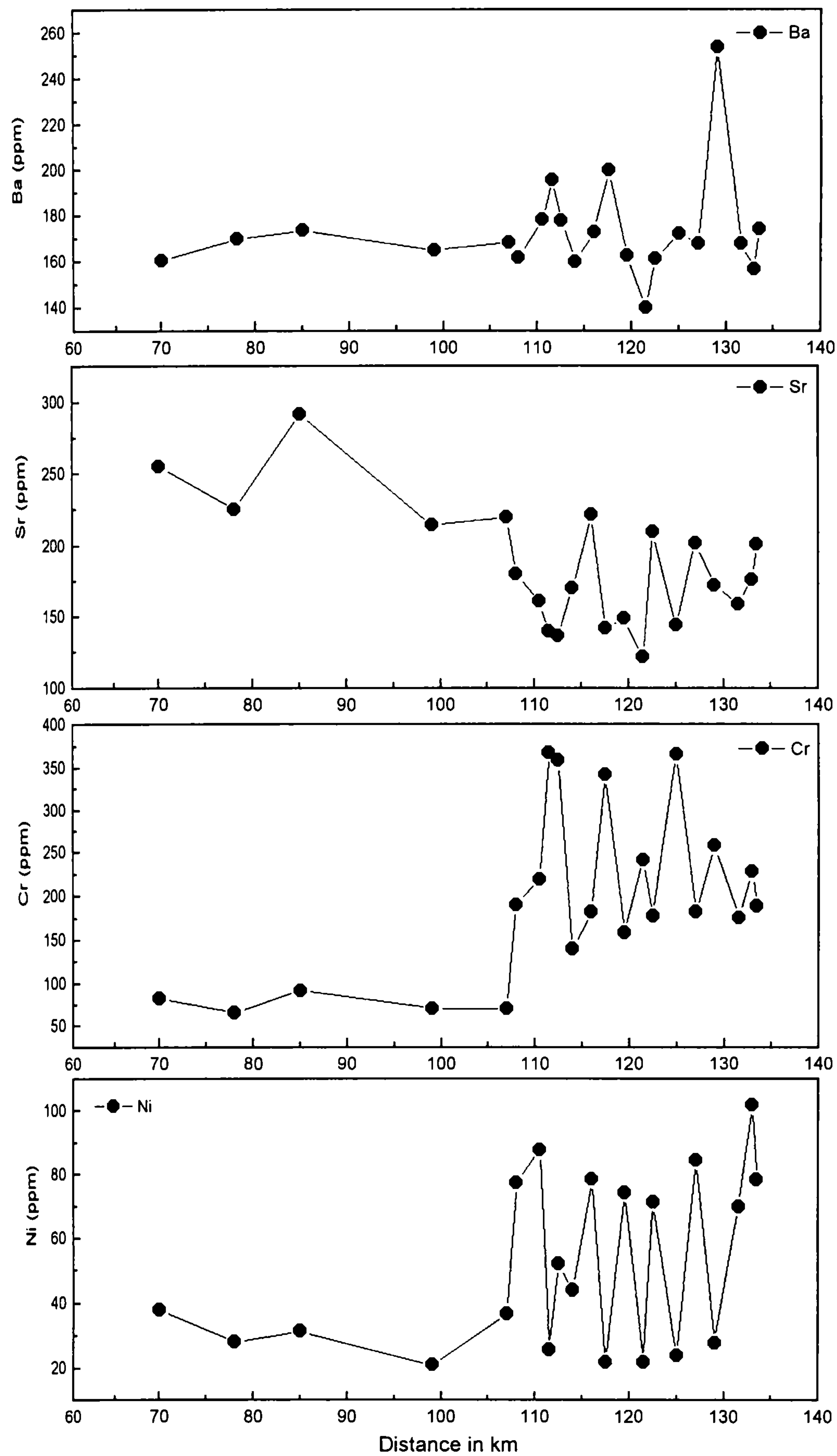


Fig. 6.1 (e) Down stream variation of some selected trace elements in the Chaliyar river sediments

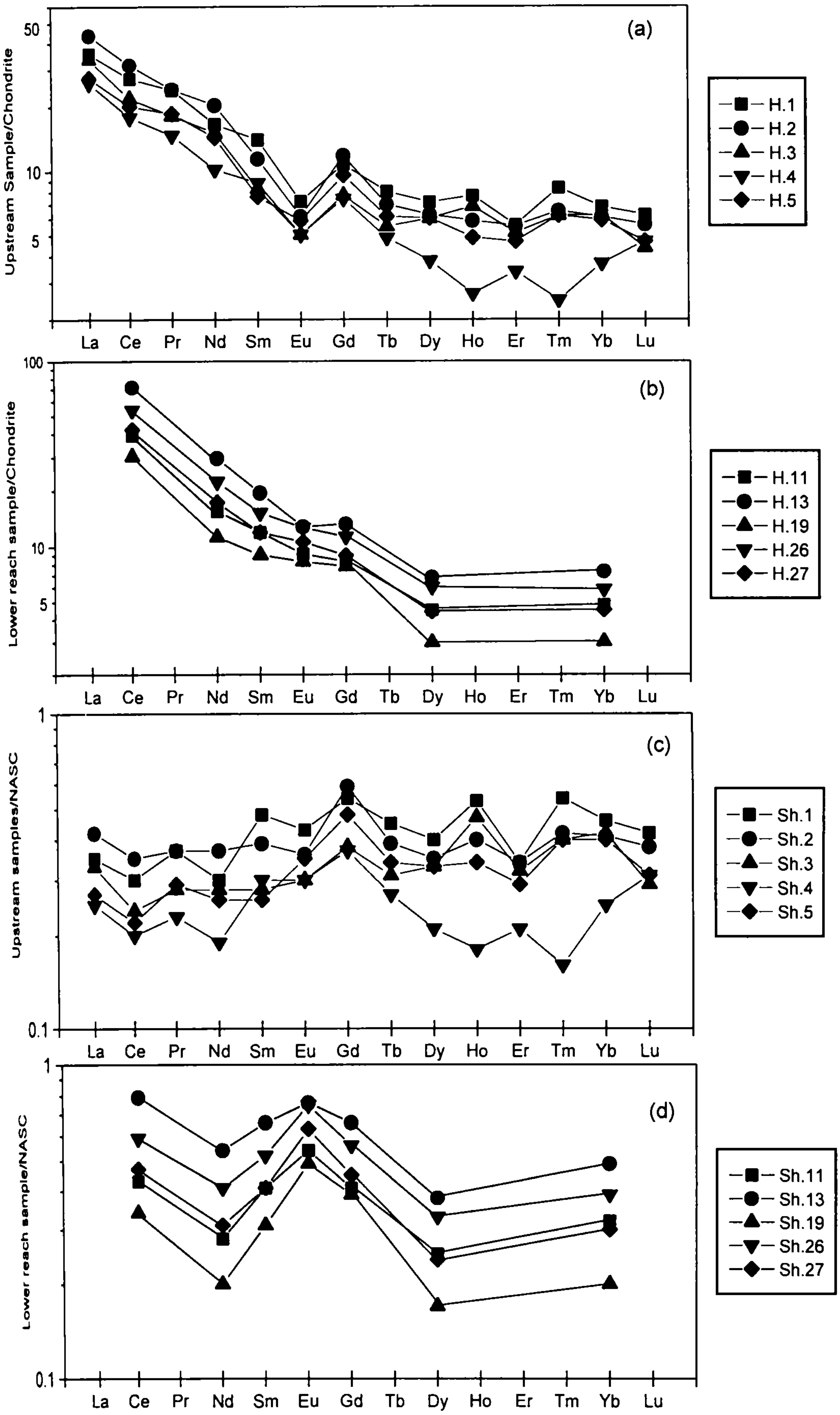


Fig. 6.2 Chondrite-normalised REE pattern of Chaliyar river sediments (a) Upstream (b) Lower reaches
Shale-normalised REE pattern of Chaliyar river sediments (c) Upstream (d) Lower reaches

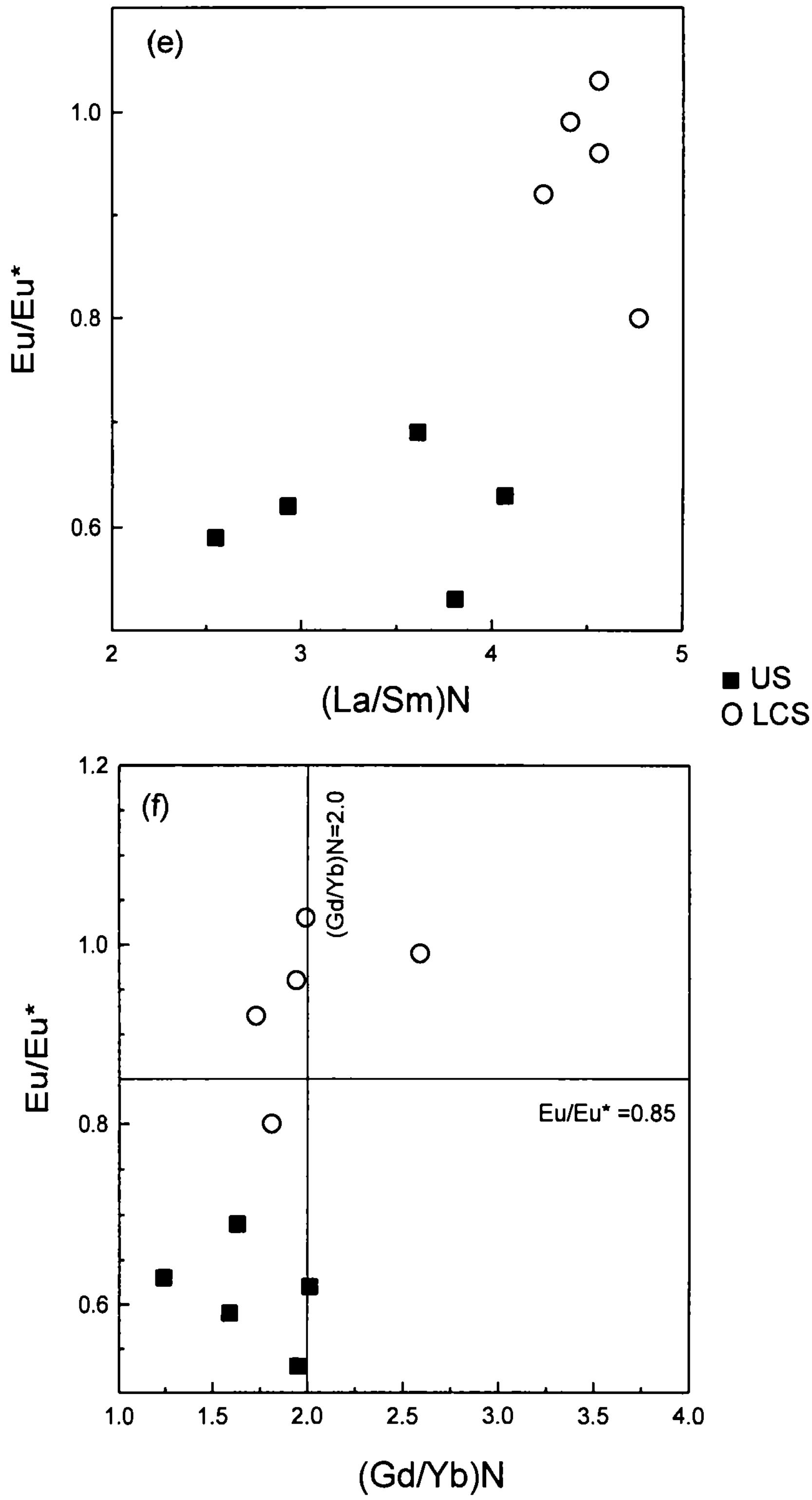


Fig. 6.2 (e) Eu/Eu* vs (La/Sm)N
(f) Eu/Eu* vs (Gd/Yb)N

Table 6.3

Average REE contents in stream sediments and provenance rocks

REE (ppm)	La	Ce	Sm	Eu	Tb	Yb	Lu	(La/Yb)N
Sediment (upstream)	10.30	19.13	1.96	0.43	0.30	1.20	0.16	5.90
Sediment (lower reach)	*19.03*	38.29	2.64	0.97	-	1.06	-	12.11
Provenance	30.96	54.13	5.05	1.33	0.62	1.68	0.16	14.44

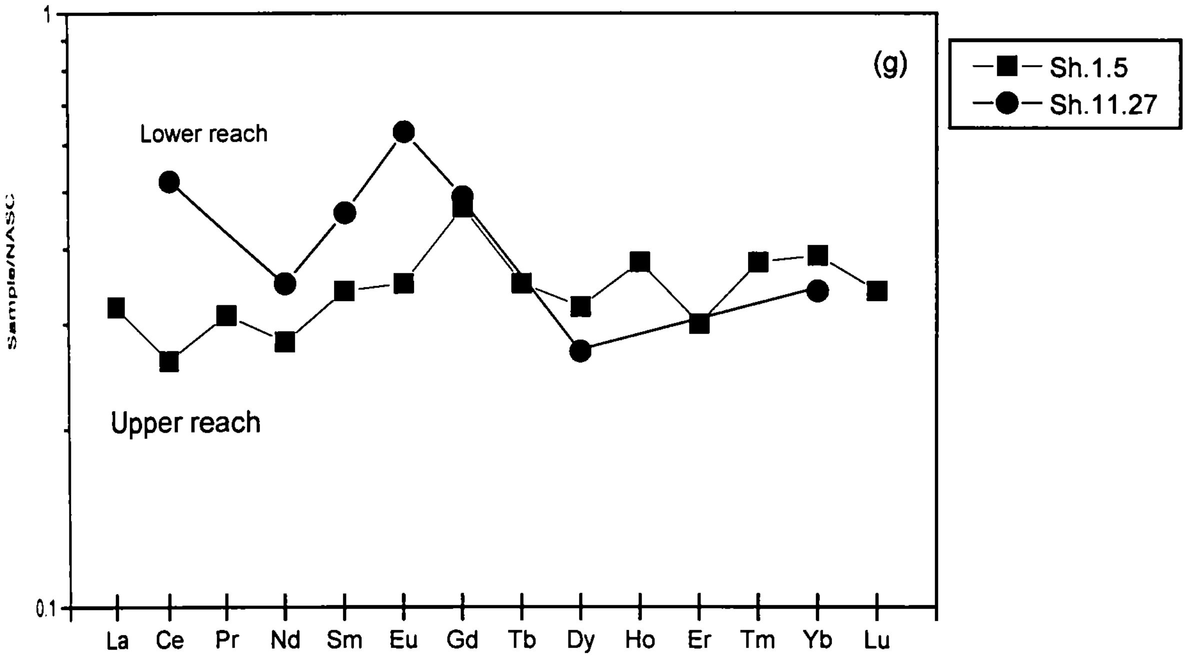


Fig. 6.2g NASC – normalized REE pattern of average upper and lower reach Chaliyar river sediments.

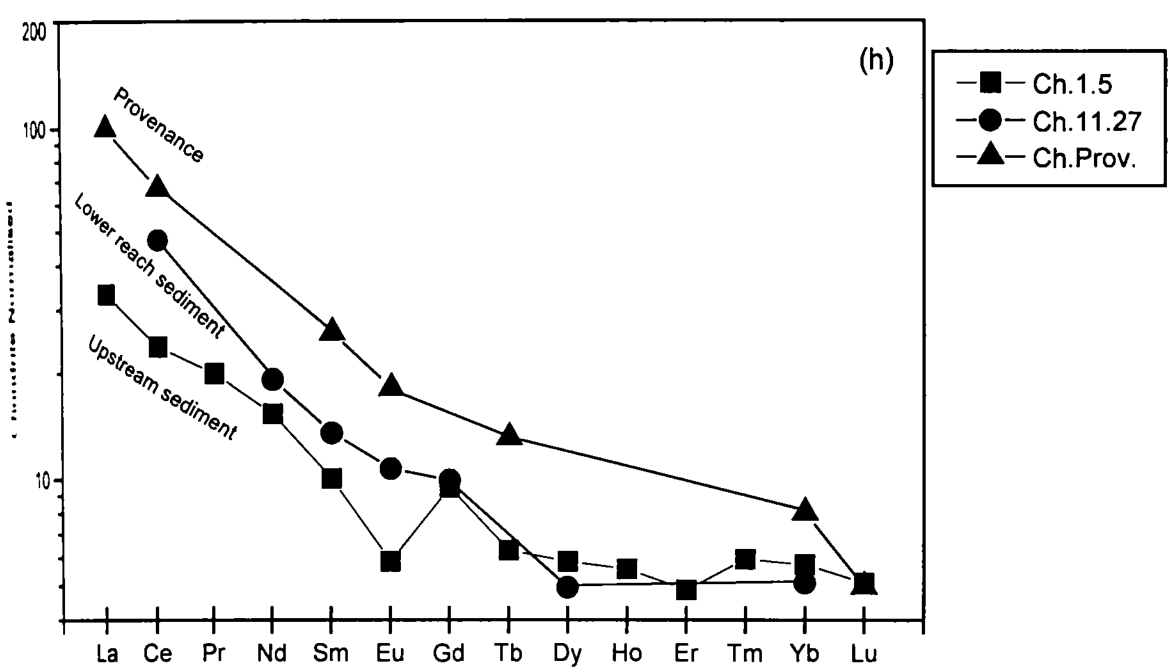


Fig. 6.2h

Chondrite-normalised REE pattern of average sediment of Chaliyar compared with that of average provenance rock

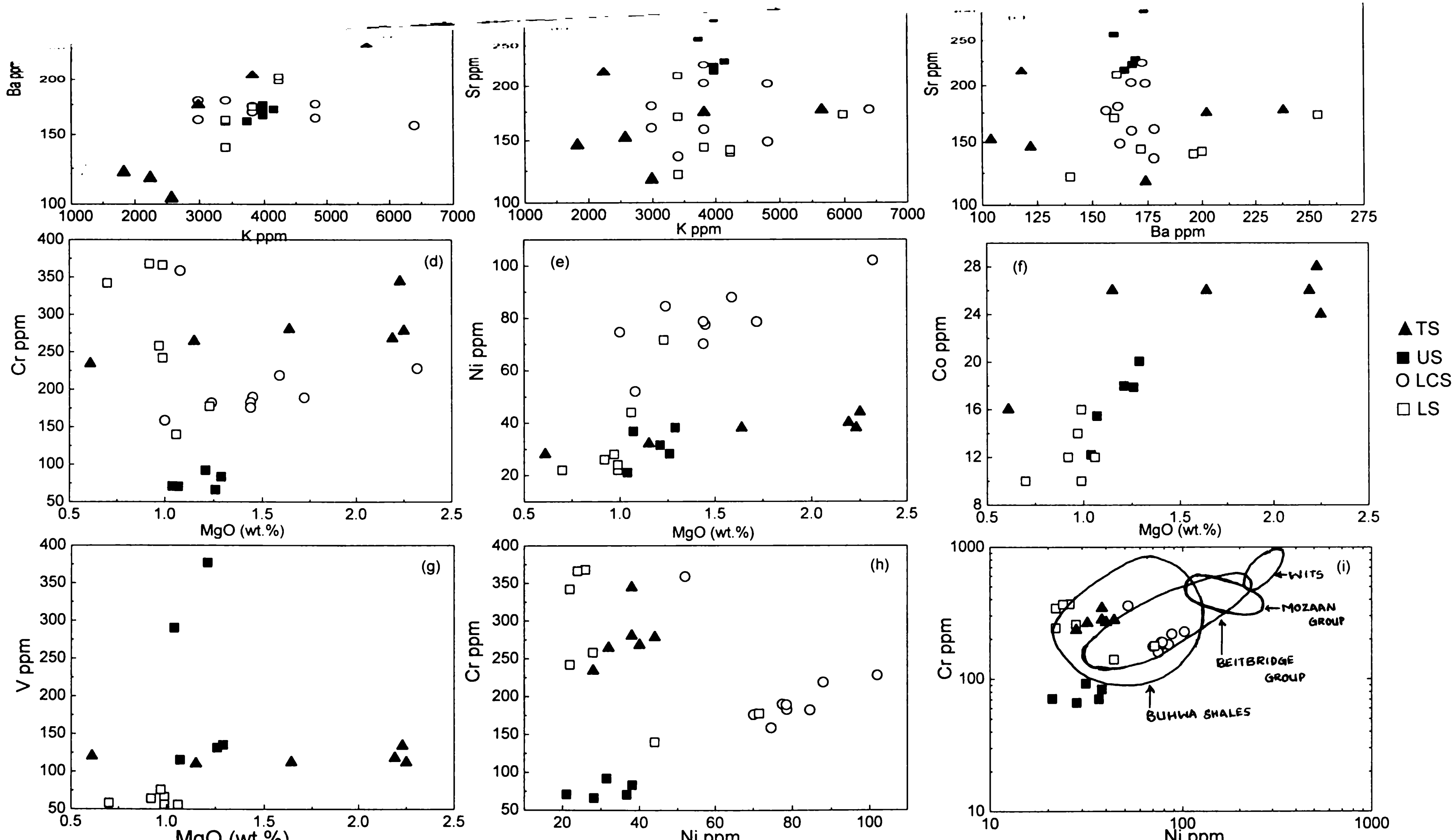


Fig.6.3 Plot of K-Ba, K-Sr and Ba-Sr (a,b and c); Plot of specified ferromagnesian trace elements against MgO content for Chaliyar river sediments (d-h); (i) Distribution of Cr and Ni in Chaliyar river sediments. Fields taken from Fedo et al. (1996)

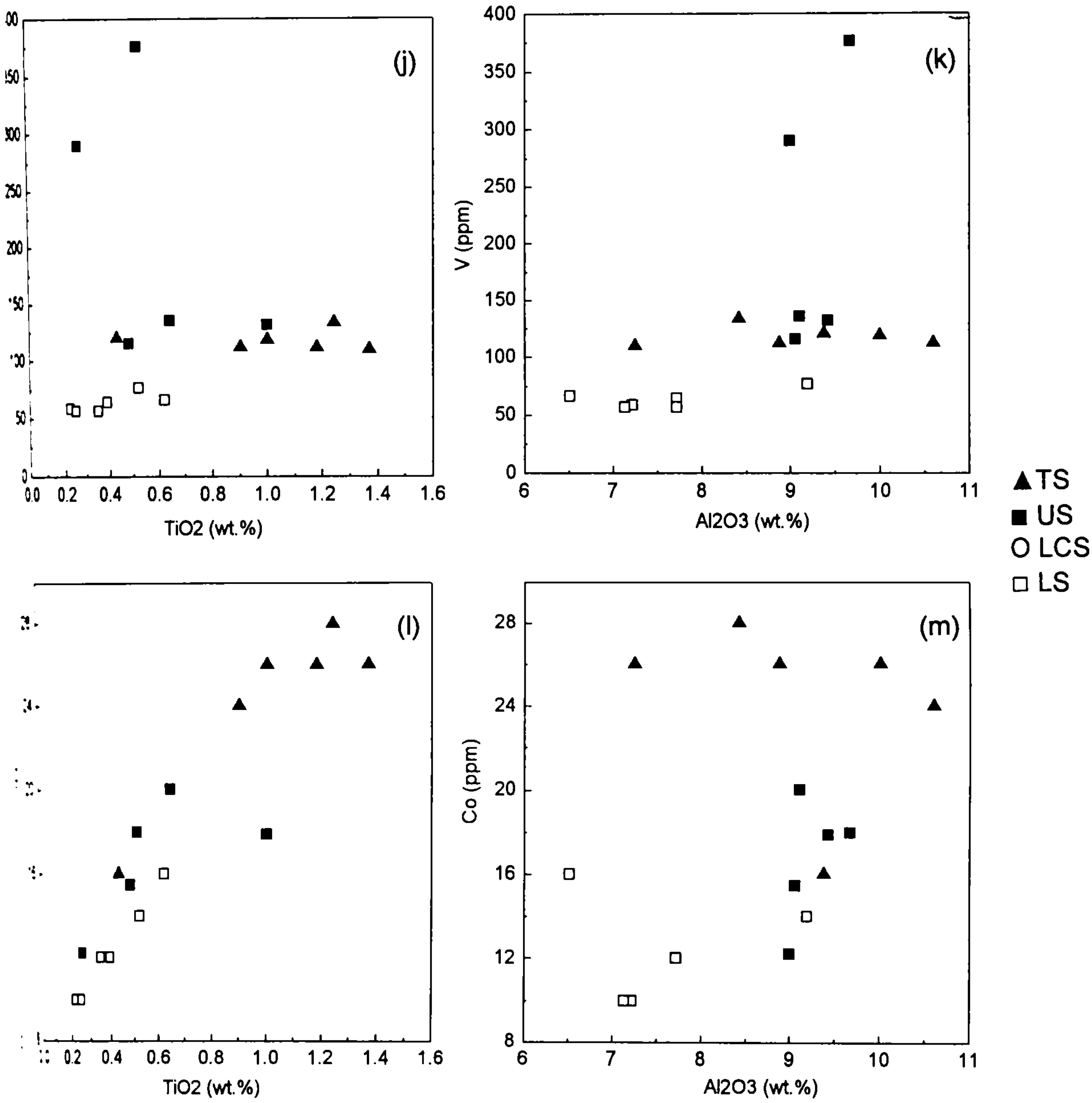


Fig. 6.3 TiO_2-V, Co and Al_2O_3-V, Co plots for Chaliyar river sediments.
(note that V and Co is not determined for lower reach clay bearing sediments (LCS)

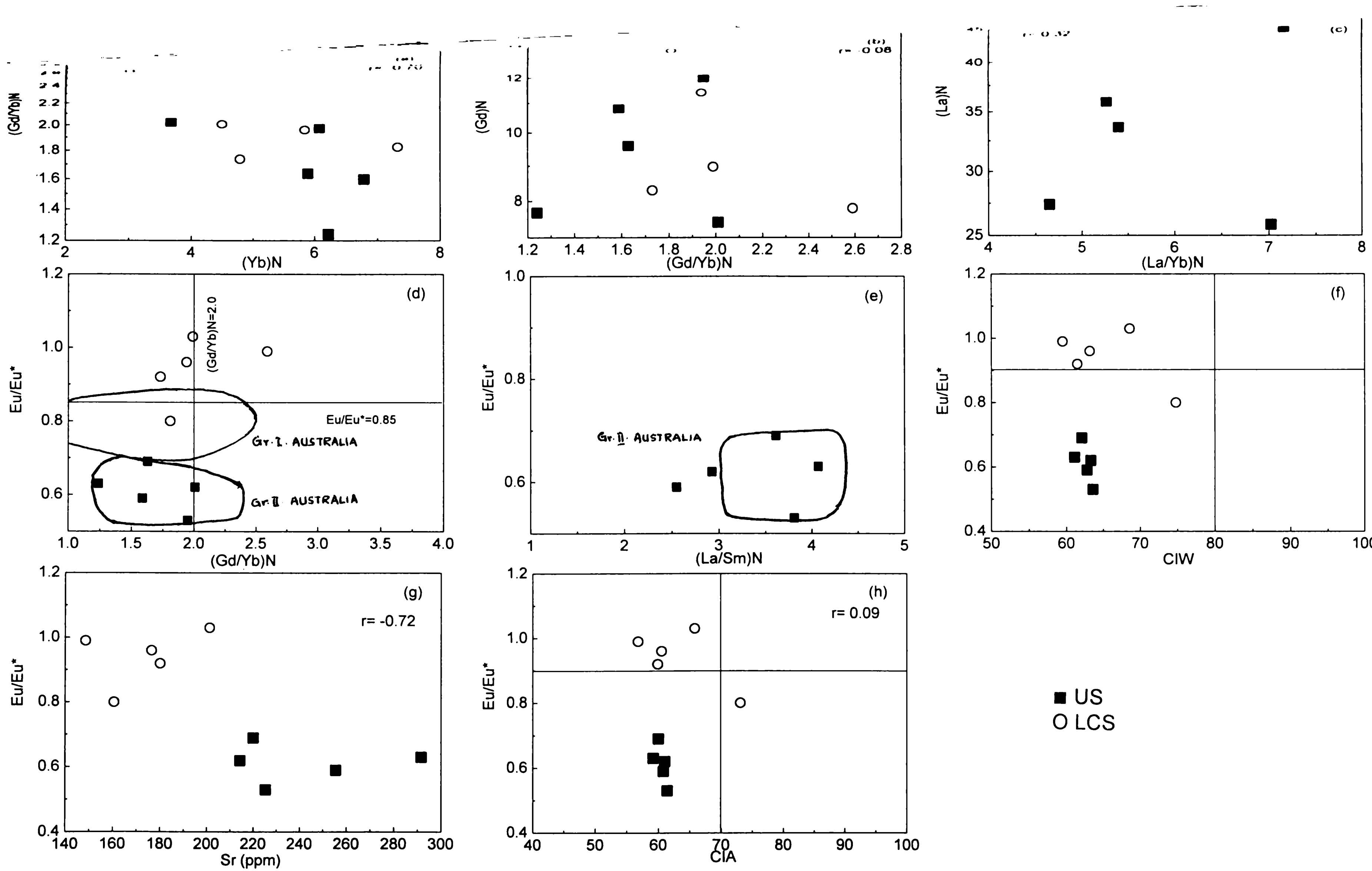


Fig.6.4 Plot of : (a) (Gd/Yb)N vs (Yb)N (Zircon addition); (b) (Gd)N vs (Gd/Yb)N (Monazite addition; (c) (La)N vs (La/Yb)N (Allanite addition); (d) Eu/Eu* vs (Gd/Yb)N; (e) Eu/Eu* vs (La/Sm)N; (f) Eu/Eu* vs CIW; (g) Eu/Eu* vs Sr (ppm); (h) Eu/Eu* vs CIA correlations for Chaliyar river sediments

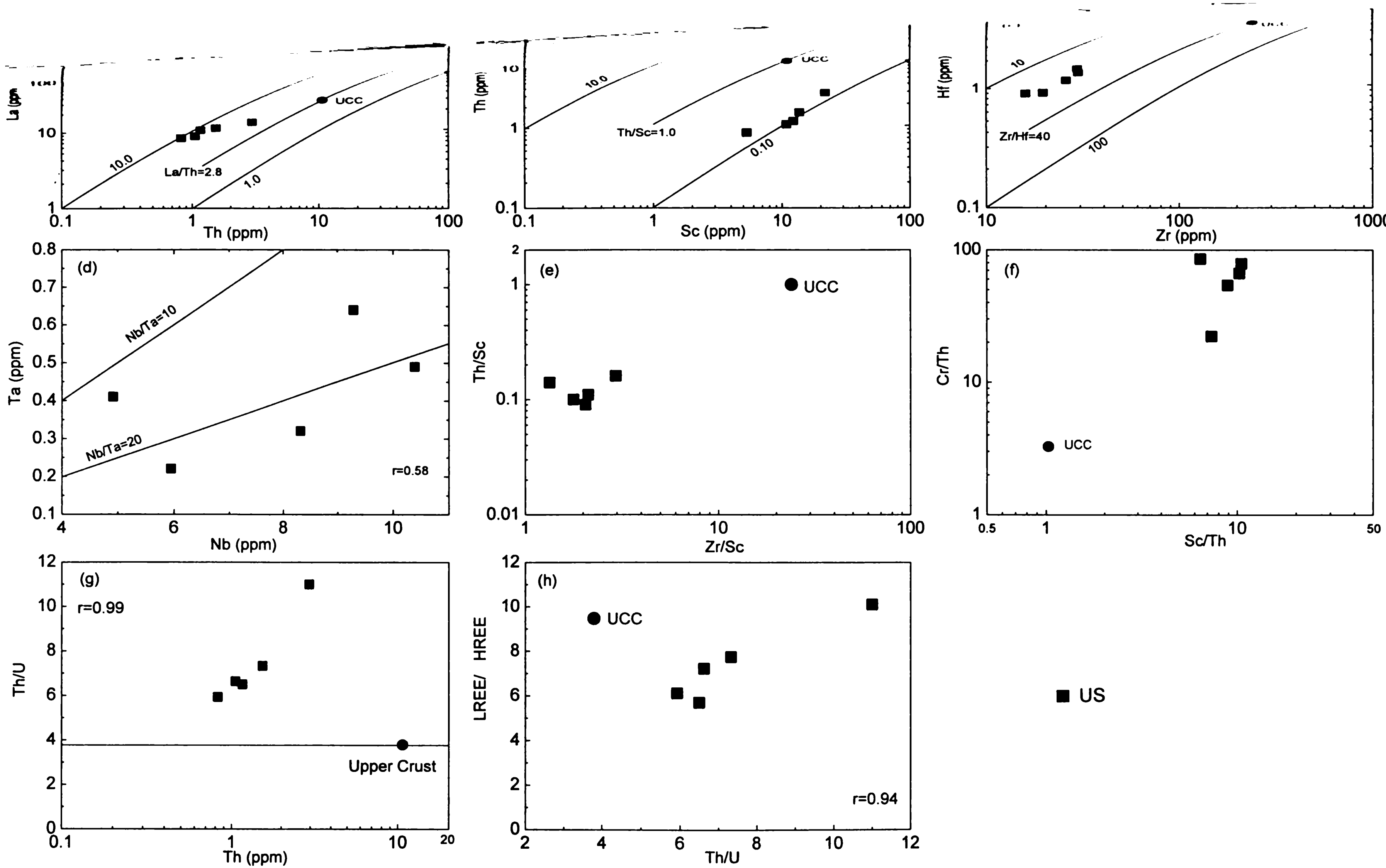


Fig.6.5 Plot of (a) La (ppm) vs Th (ppm); (b) Th (ppm) vs Sc (ppm); (c) Zr (ppm) vs Hf (ppm); (d) Nb (ppm) vs Ta (ppm); (e) Th/Sc vs Zr/Sc; (f) Cr/Th vs Sc/T Weathering trends diagrams (g) Th/U vs Th (ppm); (h) Th/U vs LREE/ HREE for Chaliyar river sediments. UCC = Upper Continental Crust

Table 6.1 Trace element concentrations (in ppm) in the bulk sediments from Chaliyar river (N.D. - Not Determined)

Sample No	H-1	H-2	H-3	H-4	H-5	H-11	H-13	H-14	H-15	H-16	H-17	H-18	H-19
Sc	13.75	21.85	12.32	5.35	10.88	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
V	135	131.7	376.7	290.1	115.6	N.D	N.D	64	N.D	56	N.D	58	N.D
Cr	83.22	66.06	91.98	70.91	70.4	190	218.7	368	358.6	140	182.8	342	158.6
Co	20.04	17.88	17.99	12.21	15.47	N.D	N.D	12	N.D	12	N.D	10	N.D
Ni	38.17	28.2	31.51	21.08	36.77	77.47	87.89	26	52.02	44	78.6	22	74.59
Cu	1.72	1.56	1.1	0.76	3.31	N.D	N.D	8	N.D	8	N.D	20	N.D
Zn	0.28	0.35	0.4	0.41	4.29	N.D	N.D	42	N.D	42	N.D	44	N.D
Ga	10.05	9.06	11.34	9.1	9.32	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Rb	9.1	8.62	10.73	7.77	8.04	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Sr	255.5	225.3	291.7	214.3	220	180.1	160.6	140	136.5	170	221.8	142	148.6
Y	10.78	9.22	8.61	4.86	7.44	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Zr	29.45	29.17	25.56	15.9	19.45	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Nb	10.39	9.29	8.32	5.95	4.92	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Cs	<0.01	<0.01	0.11	<0.01	<0.01	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Ba	160.2	169.8	173.6	164.9	168.4	161.7	178.1	196	177.8	160	172.7	200	162.6
Hf	1.42	1.57	1.19	0.89	0.9	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Ta	0.49	0.64	0.32	0.22	0.41	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Pb	10.29	<0.01	<0.01	<0.01	<0.01	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Bi	31.96	66.32	30.8	64.93	55.41	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Th	1.54	2.97	1.17	0.83	1.06	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
U	0.21	0.27	0.18	0.14	0.16	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D

Sample No	H-20	H-21	H-22	H-23	H-24	H-25	H-26	H-27	H-28 T	H-29 T	H-30 T	H-31 T	H-32 T	H-33 TC
Sc	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
V	66	N.D	56	N.D	76	N.D	N.D	N.D	110	118	120	134	112	112
Cr	242	177.3	366	182	258	176	228	189	264	268	234	344	278	280
Co	16	N.D	10	N.D	14	N.D	N.D	N.D	26	26	16	28	24	26
Ni	22	71.53	24	84.5	28	70.1	102	78.5	32	40	28	38	44	38
Cu	6	N.D	8	N.D	8	N.D	N.D	N.D	12	14	20	12	16	12
Zn	48	N.D	48	N.D	52	N.D	N.D	N.D	72	64	58	76	72	74
Ga	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Rb	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Sr	122	209.8	144	202	172	159.1	176.5	201.2	146	214	118	152	176	174
Y	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Zr	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Nb	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Cs	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Ba	140	161.3	172	167.7	254	167.8	156.4	174.1	122	118	174	104	238	202
Hf	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Ta	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Pb	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Bi	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Th	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
U	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D

Table 6.2 REE content (in ppm) in the upstream sediments from Chaliyar river, northern Kerala.
(in paranthesis are chondrite normalised value)

Sample No.	H-1 ppm		H-2 ppm		H-3 ppm		H-4 ppm		H-5 ppm	
La	11.10	36	13.50	44	10.41	34	8.01	26	8.49	27
Ce	21.91	27	25.45	31	17.66	22	14.45	18	16.20	20
Pr	2.93	24	2.95	24	2.22	18	1.80	15	2.27	19
Nd	9.95	17	12.22	20	9.10	15	6.12	10	8.64	14
Sm	2.74	14	2.23	11	1.61	8	1.72	9	1.48	8
Eu	0.53	7	0.45	6	0.37	5	0.37	5	0.43	6
Gd	2.79	11	3.07	12	1.99	8	1.92	7	2.48	10
Tb	0.38	8	0.33	7	0.26	5	0.23	5	0.29	6
Dy	2.30	7	2.01	6	1.93	6	1.22	4	1.94	6
Ho	0.55	8	0.42	6	0.49	7	0.19	3	0.35	5
Er	1.17	6	1.16	6	1.08	5	0.71	3	0.98	5
Tm	0.27	8	0.21	6	0.20	6	0.08	2	0.20	6
Yb	1.42	7	1.27	6	1.30	6	0.77	4	1.23	6
Lu	0.20	6	0.18	6	0.14	4	0.15	5	0.15	5
ΣREE	58.24	-	65.45	-	48.76	-	37.74	-	45.13	-
Average REE	4.16		4.68		3.48		2.70		3.22	
(LREE/HREE)N	3.40		4.30		3.38		4.26		3.21	
(La/Sm)N	2.55		3.81		4.07		2.93		3.61	
(Gd/Yb)N	1.59		1.95		1.24		2.01		1.63	
(La/Yb)N	5.27		7.16		5.40		7.02		4.65	
Eu/Eu*	0.59		0.53		0.63		0.62		0.69	

REE content (in ppm) in the lower reach sediments from Chaliyar river, northern Kerala.
(in paranthesis are chondrite normalised value) Italic values are extrapolated

Sample No	H-11 ppm		H-13 ppm		H-19 ppm		H-26 ppm		H-27 ppm		Mean ppm	UCC (*) ppm	
La	*15.81*	*51*	*28.83*	*93*	*12.40*	*40*	*21.39*	*69*	*16.74*	*54*	10.30	30.00	97
Ce	31.67	39	57.93	72	24.51	30	43.37	54	33.99	42	28.71	64.00	79
Pr	-	-	-	-	-	-	-	-	-	-	2.43	7.10	58
Nd	9.32	16	17.78	30	6.75	11	13.37	22	10.38	17	10.36	26.00	43
Sm	2.33	12	3.79	19	1.76	9	2.97	15	2.33	12	2.30	4.50	23
Eu	0.67	9	0.94	13	0.61	8	0.93	13	0.78	11	0.61	0.88	12
Gd	2.15	8	3.43	13	2.02	8	2.93	11	2.32	9	2.51	3.80	15
Tb	-	-	-	-	-	-	-	-	-	-	0.30	0.64	14
Dy	1.45	5	2.19	7	0.96	3	1.94	6	1.42	4	1.74	3.50	11
Ho	-	-	-	-	-	-	-	-	-	-	0.40	0.80	11
Er	-	-	-	-	-	-	-	-	-	-	1.02	2.30	11
Tm	-	-	-	-	-	-	-	-	-	-	0.19	0.33	10
Yb	1.00	5	1.53	7	0.63	3	1.22	6	0.94	4	1.13	2.20	11
Lu	-	-	-	-	-	-	-	-	-	-	0.16	0.32	10
ΣREE	-	-	-	-	-	-	-	-	-	-	-	-	-
									Total		62.52	146.37	-
Average REE	6.94		12.51		5.32		9.53		7.45		4.47		10.46
(LREE/HREE)N	4.78		5.70		5.63		5.12		5.33				5.46
(La/Sm)N	4.27		4.77		4.41		4.56		4.56				4.19
(Gd/Yb)N	1.73		1.81		2.59		1.94		1.99				1.39
(La/Yb)N	10.66		12.67		13.24		11.88		12.10				9.19
Eu/Eu*	0.92		0.80		0.99		0.96		1.03				0.65

* After Taylor and McLennan (1985)

$Eu/Eu^* = Eu_N/[(Sm_N)(Gd_N)]^{1/2}$

Subscript N referes to chondrite-normalized ratios; normalizing factors recommended by Brynton (1984).

Chapter 7

NATURE AND DISTRIBUTION OF GOLD

7.1 Introduction

Gold placer deposits, including fossil placers are the result of the weathering and mechanical transportation of primary deposits and the re-distribution and concentration of gold by fluvial or eolian processes. Dispersal of gold grains from their primary source regions by mechanical transport in the fluvial systems, and their accumulation in geomorphic units can make substantial change on the morphology and chemical nature of the gold grains.

During transport the original crystalline gold is deformed and comminuted on the stream bed in the frequently agitated gravels on the bed and to a lesser extent in the load suspended in the water above the bed (Parker, 1974). The decrease in the particle size is rapid till equilibrium is reached between gold particles and the stream load. The comminution of gold particle also ceases when the particles have moved in the gravel layer below the zone of transportation. However, some fine gold is transported at all stages to the sea. Therefore, the morphological characteristics of placer gold evolve during fluvial transport as a function of transport distance and fluvial dynamics (Ramdohr, 1965; Yeend, 1975). Numerous studies have addressed these characteristics, interpreting them in terms of economic implications (Fricker and Minehan, 1986; Giusti, 1986), particle origin (Bowles, 1988; DiLabio, 1991; Youngson and Craw, 1993, 1995, 1996, 1999; Eyles, 1995), source type (Knight and McTaggart, 1986, 1989, 1990), or placer-source relationships (e.g., Hallbauer and Utter, 1977; Tishchenko, 1981; Nelson et al, 1990; Herail et al., 1990; Knight et al., 1994; Knight et al., 1999). Quantitative or qualitative data are fitted into classification schemes based on various particle parameters such as size, shape, outline, roundness, flatness, sphericity, or surface texture. Many of these classification schemes were originally intended for silicates and assume a limited number of primary shapes (e.g., Zingg, 1935; Powers, 1982) or require prior assumptions about particle history (e.g., Averill, 1988; DiLabio, 1991).

The shape of placer gold particles has been used to characterize gold for at least a century (e.g., Boyle, 1979, p. 336) and it has also been used in arguments about the source of placer gold with less flat, more equant gold particles accepted as being nearer the lode source (e.g., Fisher, 1945; Gorbunov, 1959; Yablokova, 1972; Hallbauer and Utter, 1977; Fedchuck et al., 1983). However, there are very few comprehensive studies on the relationship between the distance of transport and the change in particle shape (Tishchenko and Tishchenko, 1974; Yeend, 1975; Tischenko, 1981; Herail et al., 1989). Shape has been used as an exploration tool (e.g., Averill and Zimmerman, 1986; Sauerbrei et al., 1987; Grant et al., 1991). Despite this common usage there are few comprehensive studies on the implications of morphology of gold particles on the relationship between the distance of transport and the change in gold particle shape in a fluvial system, where the particles have been modified by lateritization processes.

The shape (three-dimensional) and outline (two-dimensional) of undeformed and slightly deformed gold particles are infinitely variable. Unlike silicates, gold is malleable, and flattening as well as rounding during transport change its shape and outline. Flattening and rounding lead to specific entrainment and settling properties (Shilo and Shumilov, 1970) so that gold behaviour in fluvial systems is fundamentally different from that of most silicates. Moreover, current shape description systems (e.g., Zingg, 1935; Folk, 1974; Briggs and Winkelmolen in Willetts and Rice, 1983) or Corey, Wentworth, and Heywood address shape factors designed primarily for minerals which fracture or, cleave and maintain simple shapes. Gold, however, has a wide variety of complex shapes in the lode (e.g., Weining, 1960; Kang and Hwang, 1974). Because gold is malleable and ductile, lode gold as well as lateritic gold shapes deform, when stressed in fluvial environment, into different complex shapes. Traditional shape descriptors, therefore have limitations when applied to gold (Tourtelot, 1968; Tourtelot and Riley, 1973; Willetts and Rice, 1983).

Shape factors, when applied to gold, are used in transport settling equations to model placer formation. But, the variety of shapes and limited testing (Tourtelot, 1968; Shilo, 1970), raise doubts on the 'correct' shape factor to use. The possibility that entrainment is more important than settling in hydraulic sorting (Slingerland, 1984) further complicates the selection of the correct shape factor. The differences in shape factor have not yet been fully quantified because of the absence of any geologically well-constrained database of changing gold characteristics and behaviour in fluvial systems. However, much of the available data are derived from fragmented ancient placers with unknown source relationships, from areas where placer-source relationships are complicated by glacial influence or source area complexity, or from placers in which the distance from source is relatively short (e.g., Hallbauer and Utter, 1977; Utter, 1980; Tishchenko, 1981; Nelson et al., 1990; Knight et al., 1994). Hence, interpretation of detrital gold morphology for placer-source relationships and exploration purposes is currently hampered by the need to adapt silicate transport models. An empirical shape classification system proposed by Knight et al. (1994) is found to be comparatively more useful to study particle history because it is based on the observed variation in gold particle morphology. Recently comprehensive studies on the relationship between placer gold particle shape, rimming, transport distance (Knight et al., 1999) and variation in placer style, gold morphology, gold particle behaviour (Youngson and Craw, 1999) along two different fluvial systems have been carried out, the results of which may form the basis for more quantitative studies of these parameters and their use in placer formation modeling.

Most placer gold particles have a partial to complete zone, or rim, of nearly pure gold at their outer surface (Desborough, 1970; Boyle, 1979; Groen et al., 1990; Knight and McTaggart, 1990). Often fluvial transport of gold grains can enhance their purity by leaching out silver (Grant et al., 1991). However, the mechanisms that chemically refine gold in the supergene environments are an important factor by which pure gold nuggets are found in laterites and soils (Mann, 1984; Wilson, 1984). Santosh and Omana (1991) identified gold grains associated with weathered lateritic profiles of Nilambur as one of the best examples of the process of natural purification and concentration of gold, wherein chemical dissolution, migration and repricipitation attended laterite formation under tropical weathering conditions. They also concluded that chemical refinement of gold in the supergene environments prior to their transfer into the fluvial system may result in the accumulation of very high purity gold in placers.

7.2 Present Study

In this chapter an attempt is made to understand the gold concentration and its distribution in the Chaliyar river and its major tributaries. Studies are focused on gold grains from the major tributaries and upper reach sediments of Chaliyar river, closer to the Wynad Gold Fields, to develop a rapid method for the estimation of the critical shape parameters for placer gold particles. Various quantitative parameters such as flatness indices and their relationship with transport distance are discussed. The chemistry of gold particles from tributaries as well as from the main stem of Chaliyar are studied in order to identify the source characteristics of gold particles and their changes with increasing distance of transport. The results of this study are used as a framework to comment on the deformation of gold, the evolution of the shape and the formation of the rims in the fluvial environment. A preliminary attempt is made to understand the relationship between the shape and other characteristics of gold grains with their progressive evolution as placers in the fluvial environment. To understand the above factors a semiquantitative study of various physical features like shape, outline, roundness, flatness index (quantitative), rim characteristics of gold particles from different locations of Chaliyar river under high magnification is carried out.

7.3 Literature review

The occurrence of gold in the region around Nilambur, commonly referred to as the Wynad Gold Field (WGF), has been known for several decades (Mahadevan, 1965; Sawarkar, 1980; Ziauddin and Narayanaswami, 1974). One of the principal modes of deposition of gold is as placers along the first-order streams in the region of which the river Chaliyar is the major one. Offshore concentrations of gold in the marine sediments where Chaliyar meets the sea are known (Michael et al., 1989).

Although the mechanisms of gold precipitation from hydrothermal solutions at elevated pressure and temperature leading to the formation of primary gold deposits have been extensively studied all over the world, the nature and physicochemical parameters, governing supregene gold genesis are poorly known (Wilson, 1984; Radhakrishna, 1989). Moreoever, the supergene gold in the Nilambur laterites is known to have contributed gold placers in Nilambur valley (Chaliyar river and major tributaries in the upstream) but the changes in the physical and chemical parameters in gold particles which have undergone fluvial transport have not been understood.

Conventional knowledge holds that larger, more equant and less flat grains of gold in a placer indicate a lode source close by (Gorbunov, 1959; Boyle, 1979; Slingerland, 1984). Gold shape (Yeend, 1975; Herail et al., 1989) and size (Antweiler and Lindsay, 1968; Yeend, 1975) change with distance of transport. The work of Yeend (1975) showed that both the velocity of transport and the host sediment particles size is important in the comminution of gold particles. The larger the host sediment particle size the more efficient the comminution process. The photographs of gold grains by Yeend (1975) show that the gold develops a very smooth surface when abraded with dry sand, a pitted surface with pits to 1 micron when abraded with wet sand and cobbles, and scratched wider than 10 microns when abraded with cobbles and water only. He did not discuss flattening. Fisher (1945) describes particles 8 km (5 miles) from the source as rough and nuggety, at 13 km (8 miles) they are small nuggety and water worn, at 17.5 km (11 miles) fine granular and at 40 km (25 miles) fine scaly. Unfortunately these terms are imprecise. Tishchenko and Tishchenko (1974), and Tishchenko (1981) have demosntrated that the flatness of gold particles increases downstream. Tishchenko (1981) showed that from a particular lode source, the flatness increases while the size decreases in a downstream direction from the lode. Furthermore, flattening was dominant in the 1 to 2 mm size while particles between 8 to 16 mm and less than 60 microns underwent little flattening. He concluded that flattening was greatest in the high energy environment and that the change in the size-flatness relationship was in part the result of sorting during fluvial transport. Tishchenko (1981) also postulated that the reason for finding a higher proportion of folded particles in fossil placer was probably due to the fact that these particles had been in the fluvial environment for a long time. In agreement with Tishchenko, Utter (1980) concluded that the minimum grain diameter below which abrasion of detrital gold would not take place is 32 microns. Giusti (1986) describes the sequence needed to form a complexly folded particle from a placer. Antweiler and Lindsey (1968) report that the average weight of a 0.125 mm particle is halved over 640 km (400 miles) but does not discuss the mechanism. Herail et al. (1989) describe the systematic linear change is flatness with distance over 100 km in Bolivia. Knight et al. (1999) described an empirical shape classification system for gold particles using flatness, roundness and outline shape. According to them the shape characteristics of placer gold in the 0.2 to 1.5 mm range can be used to estimate the distance of transport of placer gold from its source. They concluded that flatness is the most reliable parameter to estimate distance of transport, particularly for distances greater than about 3 km, from the source. On the other hand, roundness is a more sensitive estimator for distances less than 5 km. Moreover, fluvial transport gold particle shape changes by increasing its flatness and decreasing its roundness.

Shape has been used in some areas as an exploration tool to locate lode gold occurrences. Fedchuck et al. (1983) used shape and chemical composition to distinguish between gold of different origins including lode sources (bedrock sources), supregene sources (oxidized ore sources) and precipitated sources (surficial sources). Grant et al. (1991) used morphology and chemistry of transported gold grains from laterite and glaciated terrain as an exploration tool. Hallbauer and Utter (1977) established a relationship between morphology and fineness of gold particles and the distance over which they have been transported in recent alluvial placer deposits. They successfully used the above parameters to estimate the distance of transport for the fossil placers of the Witwatersrand and concluded that most of the gold particles have undergone transport which ranges from 10 to 30 km. Yablokova (1972), described the uniformity of gold shape over 25,000 km^2 and used the results to discuss the origin of gold particles. Averill and Zimmerman (1986) and Sauerbrei, Pattison and Averill (1987) have successfully used the shape of gold particles recovered from glacial till to determine the distance and direction to a buried lode source. Youngson and Craw (1999) described the morphological evolution of gold particles during 180 km of fluvial transport from vein sources.

Gold occurs in a wide variety of shapes in lodes (Weinig, 1960; Kang, 1974). Because of its malleable and ductile nature, gold occurs in placer deposits in a still greater variety of shapes which commonly differ from the original shape(s) in the source lode(s). Current shape description systems are designed primarily for minerals which fracture or cleave rather than deform and as a result are inadequate to describe gold shapes. Examples of shape classification systems include the Zingg system (Zingg, 1935) and shape factors such as the Corey, Wentwroth, and Heywood shape factors, and the Sneed and Folk, Briggs and Winkelmolen shape classification systems (Willetts and Rice, 1983). These classification systems either ignore (e.g., Zingg) or do not separate out (e.g., Briggs) the roundness of gold particles, and are time consuming to use. Tourtelot and Riley (1973) point out that shape factors using length × breadth in the denominator (as in Corey) cannot distinguish between particles having different elongations. Tourtelot (1968) notes that the Corey shape factor is often used because of the ease of measuring the required parameters. Herail et al. (1990) and more recently Youngson and Craw (1999) used Cailleux flatness index (Cailleux and Tricart, 1959) which is similar to the Shilo flatness index (Shilo and Shumilov, 1970) in order to study gold particle behaviour downstream in a fluvial system.

Shape factors provide a variable which, when inserted in transport or settling equations, allows for adequate descriptions of the hydraulic behaviour of low density minerals of restricted shape variability. The validity of these shape factors for the description of the hydraulic behaviour of gold particles has had limited testing for simple shapes (Tourtelot, 1968; Shilo, 1970) and has not been tested for unusual or complex shapes. Even for the simple shapes there is still some argument about which of these shape factors is the 'correct' shape descriptor. The possibility that entrainment sorting is more important than settling in hydraulic sorting (Slingerland, 1984) further illustrates the importance of gold shape during the formation of placer deposits.

Several notable studies on the chemistry of gold especially lateritic gold/ gold from weathering profiles of Nilambur have been carried out by Santosh and Omana (1991), Santosh et al. (1991), Santosh (1994). Santosh et al. (1992) noted that the lowest fineness values (and highest silver content) are exhibited by gold grains from primary veins, with a range of 921-975 (maximum near 960). The supergene gold grains show a marked increase in fineness, with a range of 982-1000 (maximum around 995). Fineness levels are further enhanced in the placer gold, with most values above 995 (range 985-1000). Knight and McTaggart (1986, 1988, 1989, 1990) studied the composition of placer and lode gold particles in the 0.1-1.0 mm size range from the Cariboo, Bralorne and Fraser river areas of southern British

Columbia. They found that most placer particles have a nearly pure gold rim surrounding or partly surrounding a core of varying composition. They concluded that the core composition is unchanged by its passage from the lode to the placer and that the placer gold composition can therefore be used to identify the lode source of placer gold. Hallbauer and Utter (1977) noted gold particles in recent placers show a characteristic increase in fineness with increasing distance of transport because of the leaching of the silver from them. Grant et al. (1991) opined that significant variation in the fineness of gold grains extracted from a given sample suggests multiple sources; a restricted range in fineness suggests a single source. Moreover, according to them gold grain morphology is a less reliable indicator than gold grain fineness in determining whether a single source or multiple sources have contributed gold to a sample. However, morphology is an effective tool in identifying proximity to source. The silver content or fineness of Witwatersrand native gold has been studied by various authors (e.g., Hallbauer and Utter, 1977; Utter, 1979; Hirdes, 1979; Erasmus et al., 1980; Hallbauer, 1981a and 1981b; Hirdes and Saager, 1983; Von Gehlen, 1983). Knight et al. (1999) measured Au, Ag, Cu and Hg contents in vein samples and these characteristic geochemical signatures were compared with the placer gold composition in order to understand the nature and genesis of placer and lode gold deposits in the Klondike District, Yukon Territory, Canada.

Placer deposits, which are the most important from the economic point of view, are concentrations of relatively dense detrital minerals that accumulated in fluvial, marginal marine, or eolian environments as a result of sediment transport mechanics. They have been mined in many parts of the world for thousands of years and still constitute the most commonly, and volumetrically the largest, exploited type. Despite the important historical and present day economic significance of placer deposits, relatively little research has been conducted into the nature and formational processes of fluvial placers. This is because most individual deposits are or were small and mines were short lived. An exception to this is the huge Witwatersrand paleoplacer deposit in South Africa because it is Archean in age and has been subjected to metamorphic overprints. The genesis of Witwatersrand paleoplacer deposit was however considered enigmatic (Minter and Craw, 1999).

7.4 Gold in Nilambur

Since time immemorial, the Nilambur valley and adjoining regions have been known for winning gold from the river bed. The auriferous quartz reefs have been mined to recover primary gold for several years, starting in latter part of the 19th century. Several exploration programs are under way and have demarcated potential targets for further gold recovery (Anthraper et al., 1985). This region is considered to be one of the potential sites for India's future gold recovery programmes (Radhakrishna and Curtis, 1991).

The lode-gold mineralization is mainly restricted to the quartz veins filling shear-fractures, where it occurs as thin films and fine disseminations. Tiny inclusions of gold occur within pyrite. The mean grain-size of primary gold is about 200 microns and shows typical angular grain contours. The primary gold is allied with upto 8 wt. percent silver.

Prolonged weathering under tropical climatic conditions has deeply penetrated into the crystalline rocks, with the development of a thick (up to 30 m) laterite cover. Grains and nuggets of gold are recovered from the various zones in the weathering profile (Omana and Santosh, 1991; Santosh and Omana, 1991). Gold grains from various zones of weathering have distinctly different shapes, and there is direct correlation between the grain morphology and degree of weathering (Santosh and Omana, 1991). Gold grains toward the upper (highly to completely weathered) horizons are usually nearly spherical or ovoid, grains recovered from lower saprolitic and clayey horizons tend to be irregular, elongated or polygonal. Regular grain contours and rounded faces are typical of the upper horizons, whereas those from the lower horizons include xenomorphic grains with plane faces and jagged contours. The surficial texture of fold grains also varies markedly with depth. Grain-size measurements indicate a threefold to fourfold increase in the size of gold in the supergene environment (up to 800 μm) compared to the primary gold (200 μm) (Santosh and Omana, 1991; Omana and Santosh, 1991). Average grain size was found to increase from top to bottom within individual laterite porifles. EPMA of supergene gold from Nilambur area gave fineness values ranging from 991 to 999 (Santosh and Omana, 1991) suggesting that they are exceedingly pure gold.

There are two types of gold-bearing gravels in the Nilambur region: (1) older gravels that form terraces at higher altitudes and (2) recent gravels that form terraces along the bends of stream course. The older gravels and pebble beds occupy the apex and flanks of isolated lateritized mounds, and extend to several kilometers, with variable widths of upto 1.5 km. The recent level terraces occur along the meandering courses and sharp bends of the stream and are gold rich. In the older terraces, the Au concentration varies according to the disposition of the terraces, with generally the top levels being richer in Au. Earlier prospecting work (Sawarkar, 1980) fixed the tenor of Au around 0.1 g/m^3, but it is expected to be more in the recent gravels. Santosh et al. (1992) observed that there is a striking morphological similarity between gold grains from the placers and those from the laterites. In the latter case, the grain surfaces are pitted, and within these etch pits or chemical corrosion cavities are developed finescale growth patterns of pure gold such as filaments, leaves, sponges and arboroscent dendrites. Many of these features are preserved in the placer gold, which additionally shows striations and abrasions on the grain surface. Some grains contain remnants of powdery ferruginous/silica precipitated materials within voids, suggesting lateritic derivation. In contrast, the primary gold grains from the quartz veins have a markedly different morphology, characterised by angular grain contours and lack of surface irregularities like etch pits or striations. According to Santosh et al. (1992) gold grains from the placer also show large grain size, clustering around 400-600 μm. Moreover, the microprobe data shows fineness levels are further enhanced in the placer gold, with most values above 995 (range 985-1000).

7.5 Results and discussion

7.5.1 Concentration of gold in sediments

The gold estimation in sediment samples is carried out by Neutron Activation Analysis and the analytical procedure followed is given in the chapter 2. The concentration of gold in the bulk sediments of Chaliyar main stem as well as major tributaries in the headwater regions are given in table 7.1. The downstream variation of Au concentration in the main stem is given in figure 7.1a. The major tributaries and their confluences show gold variation from 0.004 to 0.009 μg/g which is less when compared to the upper and lower reaches of the main channel. The highest concentrations of gold is seen in the upper reach bulk sediments (H-1 to H-5) and it varies from 0.09 to 0.53 μg/g (averaging around 0.3 μg/g). The highest concentration of 0.53 μg/g is seen in sample H-3 which differes from other samples in being well sorted. In the lower reaches the gold concentration in the bulk sediments varies from 0.005 to 0.04 μg/g which is slightly higher than the tributary sediments. Approximately 10 km upstream from the mouth of the river in the main channel, one of the samples (H-24) shows 0.04 μg/g of gold in the bulk sample. This is a clear indication that a notable amount of gold is being transported to the nearby offshore areas as speculated earlier. From the above data it can be inferred that the major trunk of the Chaliyar river from Nilambur to Edavannapara (between 70 to 107 km; ~40 km) can be regarded as suitable prospecting site for a potential large source of uniform low-grade gold deposits, which can be of economic importance. It can also be deduced that 40 km stretch from Nilambur to Edavannapara (i.e., the region between sampling locations H-1 to H-5; see Fig. 2.1) is having optimum hydrodynamic conditions for the deposition of gold particles in the river sediments.

Unlike the primary gold deposits of Nilambur area and the placers along the lower order streams in the valleys which are heterogenous and are highly localised the auriferous sands in the lower reaches of Chaliyar river have the advantage of being a larger source of more uniform grade. This may be relevant in an emerging context of increasing viability of low grade gold deposits. The main channel of the Chaliyar river carries around 3.3×10^5 metric tonnes of sediment per year (as per the Water Year Book 1993-94 of Central Water Commission). If the average value of 0.30 μg/g of Au in the bulk sediments (note the upper reach Au concentration is considered because gold particles are entrained, which is discussed later in the chapter), as now estimated is taken as a guide, the metal being transported by the river annually may be around 100 kg (or of the order of several tens of kilograms). The present work is of a preliminary nature but the results do underline the need for systematic sampling and estimation of gold values in the sediments on a much larger scale.

7.5.2 Comparison between sediment texture, gold concentration and size of gold particles

Textural parameters like phi mean and standard deviation of the sediment samples are plotted against Au concentration (Fig. 7.1b & c). Au shows weak positive correlation (r=0.2) with phi mean size (see chapter 4; Table 4.4, correlation matrix) and a negative correlation with standard deviation except in tributary samples. The above relationship suggests that sorting as well as phi mean size, to a certain extent has influenced the distribution of gold in sediments. Moreover, the highest concentration of Au (0.53 μg/g) in sample H-3 shows a well sorted character and this could be attributed to two possible reasons :

i) reworking of upstream sediments in the active fluvial system and

ii) entrainment sorting of gold grains from upstream sites.

A comparison of the concentration of gold in the bulk samples and the respective finer fractions in samples H-1 to H-5 (-60 mesh; fine sand and below) (see Table 7.2) shows that in three out of five cases the finer fractions contain very low concentration of the metal indicating preferential accumulation of it in coarser (+60 mesh; medium sand and above) fractions possibly due to the high density of gold (hydraulic equivalent-size relationship) and also may be greater size of (>0.5 mm) gold particles in the laterite.

Hammering is the main cause of shape change in fluvially transported gold particles. Abrasion had its most marked effect on surface texture. Hammering and abrasion both increase the mass (size) and increase the roundness of the gold particles. Size measurements of ~250 gold particles from different locations of Chaliyar river reveals that the size varies between 0.12 to 1.2 mm (average: 0.36 mm). However, the gold particles in the laterites as reported by earlier workers are measured around 0.5 mm and hence the reduction in the mean size of the gold particles in the Chaliyar river sediments could be attributed to fluvial transport. At the same time reduction in the size is not that much pronounced to concentrate the gold particles in the fine sand (-60 mesh). In addition, the reduction in average mean size could also be due to the fact that laterite derived secondary nuggets are highly unstable.

7.5.3 Mineralogical control on gold concentration in sediments

When the samples in the upper reaches i.e., between 63-108 km are considered, sample H-3 has the highest amount of opaques (7%) and as mentioned in the earlier chapter (see chapter 3) this sample is well sorted in nature and its gold value in the bulk sediments is also distinctive. Thus the textural characteristics in conjunction with mineralogical maturity (high mean size, well sorted nature, high content of quartz and opaques, notable amount of other dense minerals, heavy mineral control and least amount of feldspar among the upper reach samples) point that the high gold values in the sample could have been partly due to the intrabasinal reworking of sediments or probably brought about by the reworking of terrace sediments which are seen mainly in lower order streams. Sawarkar (1980), Anthraper et al. (1985), Nair et al. (1987) have reported that the older terrace sediments and recent stream gravels in the Chaliyar basin contain large proportion of gold. In addition to the gold carried by the bedload from the headwater regions, the reworked sediments from the terrace and within the active channel might have also contributed for this high concentration of gold in this sample.

The highest heavy mineral content beyond 107 km in the downstream direction of Chaliyar main stem is noticed in location H-13 (22.09 wt. %) and it has the highest gold concentration (0.04 ppm) among the lower reach samples, even though they are moderately sorted and their mean size falls in the medium sand category. Similarly the lowest heavy mineral content is seen in sample H-22 (8.99 wt %) and the gold content in it is second lowest (0.006 ppm) showing poorly sorted nature and its mean size displays that it is coarse sand.

In addition to the above characteristics, moderate positive correlation between mean size and Au concentration as seen in the table 4.4 (see chapter 4, correlation matrix) also point to a textural and mineralogical control in the deposition of gold particles.

7.5.4 Relationship between Au and selected trace elements

The scatter plots between Au vs Cr, Ni, V, Co, Cu, Zn and TiO_2 in Chaliyar river sediments are given in figure 7.1d. In general, the Au vs V show a tendency for positive correlation while Au vs Cu show a negative correlation in sediment samples. However, the most significant and notable result is that the concetration of Au and the other trace elements in the four groups of samples within the basin [namely tributary (TS), upper reach (US), lower reach clay bearing sediments (LCS) and lower reach sediments (LS)] show a distinct character. Each of the above sets of samples show separate fields with minimum amount of overlapping among groups as well as between individual samples. Among the different groups the upper reach sediment samples show highest Au and lowest Cr, Cu and Zn. Even though the Au concentration in other groups does not show much difference the trace elements are very distinct in nature. The minimum variation of Au is seen in tributary samples. Thus the textural and mineralogical identity of the four groups of riverine sediments is also reflected in their distinctive chemistry.

7.6 Fluvial gold particle size, shape/morphology and surface texture

7.6.1 Particle size

The size distribution of gold particles from different locations namely tributary and upstream trunk placers of Chaliyar river is given in table 7.3. The maximum size of fluvial gold particles rises to 1.14 mm (sample no. L11) within the first few kilometers downstream of proximal placers of the Punna puzha tributary itself, then generally decreases further downstream in the upper reaches of the Chaliyar main stem (see Fig. 7.2 for sample locations). The increase in maximum gold size in the first few kilometers downstream from primary sources is contrary to most (if not all) of the previous literature on placer deposits (e.g., Lindgren, 1911, 1928; Boyle, 1979; Slingerland, 1984). Maximum gold particle size has always been suggested to occur adjacent or very close to primary sources, with progressive downstream decrease from there (Youngson and Craw, 1999). The progressive size increase phenomenon observed in the Chaliyar river especially from the proximal placers of Punna puzha tributary to first few kilometers downstream of the same tributary may arise where weathering processes are predominantly chemical but not in areas where uplift and/or erosion rates are low. Since, Nilambur valley has extensive laterite cover signifying tropical/chemical weathering, in such areas, most gold is released as free particles in the eluvial and colluvial environments, and comparatively little gold enters the fluvial system as inclusions within the host sulphides.

Most of the gold grains entering the bedload sediments of Chaliyar main stem from the headwater tributaries namely Punna puzha, Chali puzha and Karim puzha are smaller than about 0.9 mm (see Table 7.3; sample no. L10,9). Published literature indicates that gold particles recovered from weathering profiles in the Nilambur valley measure, with most values lying around 0.4-0.7 mm with few large grains 1 mm or more while primary grains measure up to 0.2 mm. Gold grains from fluvial placer also show high grain size, clustering around 0.4-0.6 mm. The source of some of the gold particles in the location no. L5 is uncertain but they are typically irregular and are probably derived from minor local sources on the valley sides suggesting particles undergoing very little fluvial transport. The rate of downstream decrease in the gold particle size is more or less uniform from tributaries to Chaliyar main stem, but much more significant at the downstream limit of sampling for this study (sample no. L5). At the downstream limit of trunk placers (Fig. 7.2) particles are typically less than 0.4 mm (see Table 7.3). The following describe the evolution of gold shape (in terms of various shape parameters as it passes downstream through each placer type, namely,

(i) proximal parts of tributary placers (considered to be very near to the lode/lateritic source), followed by
(ii) placers in the first few kilometers downstream from the above and finally
(iii) the placers in the upper reaches of Chaliyar main stem/trunk placers.

7.6.2 Particle shape and surface texture

Gold particles in proximal parts of tributary placers, which are considered to be near to the lode/lateritic source, are relatively undeformed and have infinite variety of shape in three dimensions (Plate 7.1 A, B, C). Similarly, some of the locations in upper reaches of trunk placers also show the above characteristics (Plate 7.1 D, E). As a result, they are virtually impossible to describe in terms of limited category shape classification systems such as those commonly used for silicates (e.g., Zingg, 1935; Sneed and Folk, 1958; Powers, 1982). In addition to this the tributary placer locations, which are considered to be near the source, also consists of gold particles derived from weathering profiles and were characterised by near-spherical or ovoidal shapes (Plate 7.1 F), elongated or rod shaped (Plate 7.1 G, H), irregular and polygonal (Plate 7.2 A, B). Shape descriptors become easier to apply farther downstream, in and below the zone where the tributary river gradient decrease toward the trunk river slope. In this zone (sample no. L11), which is marked by the first appearance of significant flattening (Plate 7.2 C, D), bending and to a certain extent folding of gold particles (Plate 7.1 H; Plate 7.2 E), begin to converge toward a limited number of more two-dimensional shapes. In the Punna puzha tributary, this zone occurs approximately 15 km downstream from proximal placer sources. Initiation of folding and flattening in this zone is followed by a progressive downstream increase in the proportions of discoid and folded particles just below the confluence zone of the major tributaries (Plate 7.2 F, G, H; Plate 7.3 A, B). Gold in the downstream limit of sampling for this study, i.e., distal parts of upper reaches of the Chaliyar trunk placers consists predominantly highly flattened, commonly folded, elongate or irregular particles produced by folding of discoids, and less abundant sub-spherical or rod-shaped particles (Plate 7.3 C, D, E, F, G, H; Plate 7.4 A, B). The L5 sample, which is downstream of Nilambur, is anomalous, containing a higher than predicted proportion of angular particles co-existing with flattened, folded and rounded particles (Plate 7.1 E; Plate 7.4 C, D, E, F, G). This could be attributed to contributions from local primary sources in Nilambur (reported by earlier workers) and by Vadapuram river, a small tributary joining the main stem near Mambad. The causes for progressive shape changes beyond the sample location L5, in decreasing order of importance, are flattening, folding and rounding of particles (Plate 7.4 H; Plate 7.5 A, B, C, D, E).

Hammering is the main cause of shape change in fluvially transported gold particles affecting both roundness and flattening. Not only does it flatten particles but it also contributes to the increase in roundness (Plate 7.7 A, B, C, D, E). Hammering and abrasion decrease the size of the particles by removal of material and breakage. The switch from hammering causing only flattening to hammering causing flattening, folding, and breakage is thought to increase with distance of fluvial transport of gold particles. Particle breakage commonly occurs along fold hinges or on folded gold particles which have already been highly flattened (Plate 7.5 A, F, G; Plate 7.2 G). In the present study there is insufficient evidence to indicate that particle breakage occurs anywhere other than in the distal parts of trunk placers.

Surface texture is an aggregate of hammering, abrasion, and smearing, and is thought to preferentially record the latest transportation event (Plate 7.4 C; Plate 7.5 H; Plate 7.6 A & B; Plate 7.7 B). Several incipient growth patterns on surface of gold particles resulting from low temperature chemical precipitation were observed during the present investigation, including those described by Nair et al. (1987), Santosh and Omana (1991) for supergene gold. Freyssinet et al. (1989) also described similar texture within the deep chemical-corrosion cavities of spherical and oval grains from supergene gold occurrences that typify chemical precipitation. The placer gold nuggets from Chaliyar river possess spongy, botryoidal or mossy forms with porous, filamental, dendritic or tuft-like internal textures (Plate 7.6 C). Minute filaments, tufts or dendrites of gold were found to grow attached to iron-oxide/grain cavities (Plate 7.6 D). Such `arborescent dendrites' are considered to typify secondary chemical precipitation (Freyssinet et al., 1989). Within deep etch pits of flattened and rounded grains, the growth of small petals of leaves of secondary gold with contrastingly high purity as indicated by their bright luster has been observed (Plate 7.6 A). The most spectacular growth of secondary gold was observed as bright coatings of "painted" gold over dull primary grains (Plate 7.6 E, F, G). The contrast in the luster of the metal and "spray-painted" appearance of such precipitations distinguish them from the dull primary grains over which they are usually developed (Plate 7.4 B; Plate 7.6 H). The neoformed painted gold is characteristically different from host grain and they indicate secondary precipitation of gold with increased fineness. They also represent products of natural purification through chemical-dissolution in the fluvial environment and or processes attending weathering.

7.7 Empirical shape classification of gold grains

The shape of a gold particle can be described by three parameters viz., (1) the degree to which the particle is flattened (flatness), (2) the degree to which the particle is rounded (roundness), and (3) the outline shape of the particle as it lies on its preferred side (outline) i.e., the side with the largest surface area. One other feature related to shape is the texture of the surface. For the smaller particles it is important to maintain the distinction between terms describing roundness and those describing surface texture. Surface texture features are those which affect the appearance of the surface but not the shape of the particle. Terms used to describe surface texture include matte, mirror-like, scratched, pitted. As the particles become smaller, the features affecting roundness approach that of features affecting surface texture. This relationship seems to become particularly important for particles less than about 200 µm in size when, as DiLabio (1990) pointed out, the shapes are more easily described from secondary electron images. The terms angular and rounded are used as descriptors for roundness, however the term angular can also be used to indicate the size of the angle between adjacent surfaces (Pettijohn, 1975). This distinction is important in describing the shape of gold grains.

The Empirical Shape Classification System proposed by Knight et al. (1999) combines roundedness and flatness to form nine shape classes each labeled by a three-digit number (Fig. 7. 3a). Four outline shape classes (after Knight et al., 1994) were also used along with shape to classify the gold particles, each labeled by a two digit number (Fig. 7.3b). Note that in addition to the above four outline shape classes, a new class which is a combination of complex and elongate outline is also introduced in the present study, which is labeled with a two-digit number (70) and is assigned the name complex-elongate. A particle is uniquely classified by adding the three and two-digit numbers. Particle roundness and outline were usually determined under a binocular microscope. Particles were classified empirically by comparison to charts (for roundness and outline shape), while flatness estimates were based on arbitrary limits. The roundness classifications have three classes, which were adapted from the six category scheme of Powers (1982) (Fig. 7.3a).

The sample means for classed data (roundness and flatness) were calculated by using the equation for averaging classed data (Folk, 1974):

Mean= (SUM[f×m])/n

Where :

f= frequency of each grain-size grade (or class) present

m= midpoint of each grain-size grade (or class mark)

n= total number of particles in sample

The mean data for these two parameters (flatness & roundness) are presented on plots which use the total range (0-100%) for individual particles, therefore the minimum and maximum values for the mean are the minimum and maximum class marks, 16.67 percent and 83.33 percent respectively. Based on this method it is demonstrated that for an adequate number of gold particles at a sample site there is a semi-quantitative realtionship between average shape (flatness and roundness) and the distance of transport of particle from the tributaries (assumed to be closer to the lode/lateritic source) to the Chaliyar main stem.

Certain trends are noticed in grain-shape modifications due to transport in Chaliyar river, from tributaries to main stem especially in roundness, flatness indices (which is discussed later in this chapter) and outline characteristics .

Recent study by Knight et al. (1999) on gold particles from lode deposits and placer deposits in the Klondike district, Yukon Territory, Canada has shown that a relationship does exist and has documented its general nature, between three variables namely roundness percent, flatness percent (empirically classified) and distance of transport from lode/source. However, studies on the placer gold in the Chaliyar river sediments cannot be related in similar way due to following reasons:

(i) involvement of multiple sources with different cycles of gold transport,

(ii) primary gold particle shape (lateritic source), mass etc.,

(iii) restricted ranges of average flatness and roundness percentages suggesting particle undergoing shape unification in weathering zone and

iv) particle entrainment and retention in trunk placers.

Knight et al. (1999) concluded in their studies on lode and placer gold in the Klondike district of Canada that since lode and placer gold particles can be distinguished from each other, and the lode and placer gold characteristics may be used to delimit lode gold source areas. This procedure was attempted on the present samples. However, based on the empirical classification study the placer samples from Chaliyar river cannot accurately specify/estimate the general location of the lode source (Fig. 7.2). This is mainly due to the fact that the placer samples are mainly derived from lateritic source; though one of the major tributary, Punna puzha (see Fig. 7.2 for location of samples) has angular and complex grains along with rounded and elongate particles. It is therefore not possible to estimate the actual distance of transport from source because the relative contributions from multiple sources is unknown and the particles might have under gone more than one cycle of fluvial transport in the placer deposits of Chaliyar river.

7.7.1 Outline shape, roundness and flatness

Representative samples from major tributaries in the headwater regions and upper reaches of the Chaliyar main stem were mounted on stubs and photographed using SEM. In total ~ 250 gold particles from 7 locations was classified into roundness (Fig. 7.5) and outline shape (Fig. 7.4) by studying under binocular microscope and SEM.

Particle outline

Since majority of the gold particles in the tributaries are drived from laterites the branched particles are totally absent. Moreover, due to shape unification in weathering zone a new class namely complex-elongate type of particles are seen in the tributaries (Fig. 7.4). The placer gold particles in proximal regions of source area exhibit complex outlines and it predominates in the tributaries (Fig. 7.4a, b & c). The outline modification in the downstream sample (sample no. L11) of Punna puzha is shown in figure 7.4d. At this site all the shape classes are present in nearly equal amounts except complex and elongate outline. This is due to progressive transport induced shape modification in transition/just upstream of the confluence zone.

In the upper reaches of the trunk river system the placers show major shape transformation (Fig. 7.4e) were the complex outline slightly dominates when compared to other outline classes. This is mainly due to the mixing up of gold particles having different proportions of outline shape classes to the main trunk. However other outline shape classes like equant, elongate and complex-elongate also show increasing trend with increasing distance of transport from tributary to main stem. Figures 7.4f & g show progressive increase in the proportion of equant and elongate outlines. Even though, the above trend is noticed in the main stem, the consistent or uniform percentage of complex grains in all the samples in the main stem (Fig. 7.4e, f & g) probably reflects some input from the local veins having particle with complex outline.

Particle roundness

Gold particle rounding results mainly from abrasion of particle edges and in-folding of delicate protrusions and thin edges into cavities produced by plucking or crushing of ore mineral inter growths (Youngson and Craw, 1999). As already mentioned, the gold grains from various zones of weathering from Nilambur have been reported to possess distinctly different shapes, and there is a direct correlation between the grain morphology and degree of weathering according to Santosh and Omana (1991). Gold grains toward the upper (highly to completely weathered) horizons are reported to be nearly spherical or ovoid, grains recovered from the lower saprolitic and clayey horizons tend to be more irregular, elongated or polygonal. Regular grain contours and rounded faces are typical of the upper horizons, whereas those from the lower horizons include xenomorphic grains with plane faces and jagged contours.

Based on the results of the study by Youngson and Craw (1999) on placers in Otago, New Zealand, in the first 10 km of primitive placers, the degree of rounding is minor, especially for smaller particles having size < 3 mm, and few particles advanced beyond the subangular stage. However, in the tributaries of Chaliyar river the particles show greater degree of rounding and they advance beyond the subangular stage consisting of higher proportion of sub-rounded particles (Fig. 7.5a, b, c & d). In addition to this, the tributary placers maintain a small proportion of rounded and well rounded particles along with the angular and very angular grains. As with particle outline, the gradual release of gold from weathering zone and additional inputs from vein sources and the existence of angular particles along with rounded ones in all the tributary placers suggest that there is shape modification in the weathering profile. The above phenomena become a problem for estimating the distance of transport the particles has undergone from the source.

More notable rounding appears in the upper reaches of the Chaliyar main stem, where significant flattening and outline modification begin to occur. Though, sub-rounded and rounded particles show an increase in the main stem when compared to tributary placers (Fig. 7.5e, f & g). The persistance of sub-angular grains and smaller proportion of angular particles in the main stem may be due to following factors :

i. particle entrainment and retension

ii. additional inputs from local weathering zone/vein sources and

iii. > 10 km from the source particles undergo greater degree of flattering with a less progressive increase in roundness downstream.

Though in the tributary placers the source characteristics of particles (shape) has played an important role for the non-relation with distance the placers in the main trunk, gold entrainment and retension due to particle folding and flattering has contributed for the inconsistent or deviation from general nature of continous particle-shape evolution with increasing distance of transport from the source.

7.7.2 Flatness vs Roundness plot based on empirical data

Based on the results of the empirical shape classification system, the average flatness and roundness percentages for gold particles from 7 selected samples were determined and plotted in figure 7.6. Note that from the figure it is clear that the tributary placers show an increasing trend in flatness and roundness percentages even though they are from different tributaries and moreover their distance from source is not precisely known. In the figure 7.6 the sample no. L14 and sample no. L11 are from the tributary Punna puzha. However, the sample no. L14 is more closer/proximal to the source while sample no. L11 is ~ 10 km downstream/near to the confluence zone (see Fig. 7.2 for sample location).

In the trunk placers, though the roundness is high the average flatness percentage show a decreasing trend in gold particles. However, there is a gradual decrease in roundness along with flatness percentage. Particle flatness in sample no. L10, 9 and L 8, 7, 6 is almost identical, the roundness show a slight decrease for sample no. L10, 9. The most striking is the significant decrease especially in flatness and to a certain extent in roundness for sample no. L5 which is farthest from the source suggesting that the gold particle entrainment and retension, brought about by particle folding, flattening and rounding have played an important role in the evolution of gold grain shape in the upper reaches of the main stem. In addition to this the decrease in flatness percentage and to a certain extent roundness percentage are further due to mixing up of multiple sources, which have undergone varying degrees and different cycles of gold transport in the fluvial systems and also due to minor inputs from local weathering zones/lode sources. The anomalous decrease in flatness and roundness percentages in sample no. L5 (Fig. 7.6) again reflect minor local source influence.

From the above results it is concluded that the empirical shape classification based distance estimation of placers from source does not hold good or is hampered due to variable source contributions and it can be deduced that distance estimation using flatness/roundness percentages is not effective in a dynamic and complex system as in the Chaliyar river basin. Certain trends, however are noticed in grain shape modification due to transport and effects of entrainment partially. Moreover, the average flatness and roundness percentages show restricted ranges of around 47 to 50 and 45.5 to 57 respectively which invariably suggest that gold particles have undergone shape unification in weathering zone and are derived principally from lateritic source.

7.8 Quantitative studies on shape of placer gold particles

Representative gold particles from 7 samples were considered for the purpose of quantitative studies on shape of placer gold particles. The minimum number of particles in a sample is 14 while maximum is 45. In total 250 gold particles from 7 locations are studied (see Fig. 7.2 for sample locations). The long (a), intermediate (b), and small (c) axes of individual gold particles were measured using a graduated eyepiece on a binocular microscope. All measurements are at near right angles to one another. Summary of the particle size are given in table 7.3 (see Appendix 7.5 for individual particle size data of gold grains).

In order to verify the results of the empirical system, the results for the 7 selected samples were compared with those of quantitative classification systems. The empirical outline classification (Fig. 7.3b) can be compared with the quantitative Zingg (1935) classification. The relationship between outline and shape as quantified by Zingg (1935) and the empirical classification system is illustrated in figures 7.7a, b, c & d. There is good correspondence between the empirical outline shape classification system (i.e., 2 digits) and the Zingg classification. Knight et al. (1994) also reported similar correspondence for Klondike placers. It may be noted that though the outline 70 (complex-elongate) is not present in the previous studies they show signatures of complex and elongate outline shape classes in the Z[illegible] classification diagram and they plot in the 'C' quadrant which represents [illegible] shape (see Fig. 7.7d and 7.8).

No fundamental relationship between outline shape and other parameters such as flatness was seen. This again supports the view that the principal use of outline shape is to compare very near source placer gold shapes to lode gold shapes, as illustrated by Petrovskaya (1973) and Knight et al. (1999). A further potential usefulness of the outline shape classification is given by comparison between the distribution shown in figure 7.8 and the striking similarity between the Zingg shape distribution reported by Minter et al. (1993, Fig. 13) for particles from the Witwatersrand gold deposits and that Zingg shape distribution for the 14 samples from the Klondike (Knight et al., 1994; part 2, Fig. 12). The similarities between these three (the Precambrian placer setting, Quarternary placer setting of Klondike and Modern placer setting used in this study) are worth discussing.

7.8.1 Cailleux flatness index

The long (a) intermediate (b) and small (c) axes of gold particles were used to calculate the Cailleux flatness index (flatness index = (a+b)/2c) (Cailleux and Tricart, 1959). This index is a measure of the transport induced mass redistribution (i.e., shape change) of malleable particles by progressive hammering and/or folding in the fluvial system. It was used by Herail et al. (1990) for Bolivian placer gold, Youngson and Craw (1999) for Otago placers and is similar to the Shilo flatness index (flatness index=[(a+b/2c)-1] (Shilo and Shumilov, 1970), in which the subtraction of 1 is designed to give a flatness index of zero for a cube or sphere. A formula published by Knight et al. (1994) [flatness index=[(a+c)/2c)-1] to describe Klondike placer gold is not used in the present study for reasons outlined by Youngson and Craw (1999).

7.8.2 Particle flatness

Gold particles sampled from the major tributaries of the Chaliyar river have Cailleux flatness index values between 1 and 18. However, the most dominating flatness index lies between 1 and 6 for tributary samples (Fig. 7.9a, b & c). The above flatness index maxima for majority of gold particles in the tributary placers are comparable with the flatness index maxima of <7 reported by Youngson and Craw (1999) for the proximal parts of the primitive placers in the rivers of Otago. Youngson and Craw (1999) also noted that there is no evidence for significant particle flattening within the first 10 to 15 km of transport in the primitive placer system. However, smaller proprotion of flattened grains is seen in tributaries especially in sample no. L

11 (Fig. 7.9d) which is just above the confluence zone of main stem and it can be attributed to progressive increase in flatness index due to transport. Consistent higher flatness index values in lower Punna puzha (Fig. 7.9d) can be attributed to stream transport as some of this gold has been transported fluvially from the upper Punna puzha (Fig. 7.9a).

Flatness is more pronounced and maintains a uniform proportionality between higher and lower flatness index in the upper reaches of the trunk placers, where flatness index maxima increase toward values of about 22 at the penultimate sampling point of this study (Fig. 7.9e & f). Only a small proportion of particles in the main stem samples have a flatness index of <6 (e.g., sample no. L 10, 9 & L 8, 7, 6; Fig. 7.9e & f). Based on the studies carried out on Otago placers by Youngson and Craw (1999), significant flattening begins to occur in the transition zone, after about 15 km of transport and flatness index maxima increase to >20. Moreover, they noted that in downstream limit of the trunk placers flatness index maxima increase progressively toward values of about 45. But the upper reaches of the Chaliyar main stem placers have flatness index maxima of 22 (Figure 7.9f) (higher proportion of particles in the flatness index range 7-14) and this suggests that the particles have reached its critical flatness index maxima beyond which the particles cannot flatten and they start to fold and gets rethickened or break into still smaller particles. In addition to this the gold particle size ranges between 0.12-1.2 mm which is comparatively less when compared to Otago placers where the maximum size ranges upto 8 mm (a-axis). The above short range of size could be one of the reasons for the lower flatness index maxima for Chaliyar trunk placers. Moreover, most of these are flattened particles which have been rethickened by folding (see Plates 7.2; 7.3;7.4; 7.5).

As with roundness and outline, flatness index distribution is slightly anomalous for the sample no. L5 (Fig. 7.9g) again presumably reflecting minor local source influence and entrainment sorting. The flatness index distribution in L5 is strikingly similar to L12 (Karim puzha tributary). Some of the gold particles in this are not folded and show little evidence for any significant flattening and fluvial transport (see Plate7.4 E & G). These latter particles are probably derived from either local primary or relatively proximal placer sources or the flattened particles might have got folded and rethickened to attain subcritical flatness index which felicitated for the retension of gold particles in this zone. Some particles are morphologically similar to tributary placers and placers on valley flanks (see Plate 7.1 E).

7.8.3 Particle folding

The presence or absence of folded particles have noted for all samples to determine where this phenomenon first appears. Although reflattening after folding commonly removes much of the evidence, folding can nevertheless still be recognized from certain morphological features (see Plate 7.2 H; Plate 7.5 E & F).

Folded particles are not present in any of the samples from high gradient parts of tributaries (samples L14, L13, L12 and L11). The presence of folded particles is first noted 15 to 20 km downstream from the above tributary placers in the Chaliyar main stem. That is, it commences more or less concurrently with the onset of significant flattening in the upper reaches of main stem. The population of folded particles increases particularly in the downstream limit of sampling for this study. Some particles have been multiply folded without flattening occurring between folding events (see Plate 7.5 A).

According to Youngson and Craw (1999) the increase in the proportion of folded particles in the lower reaches of the trunk river system is probably due to the enhanced susceptibility to folding that results from the extreme flattening associated with relatively long-distance transport. Similar conclusions were also made by Tishchenko (1981), who suggested that a high proportion of folded particles in some recycled Siberain placers is due to significant transport (and presumably flattening) in previous placer cycles.

7.8.4 Cailleux flatness index vs a-axis length

Figure 7.10 shows positive correlation between flatness index and a-axis length for all gold particles in Chaliyar river. However, flatness index vs b-axis length does not show significant relationship (Fig. 7.10) for gold particles. This suggests that as the particles undergo flattening due to hammering and with increasing degree of fluvial transport the a-axis length also increases. But Youngson and Craw (1999) found no correlation between the distribution of flatness index values and lengths of the a-axis or the b-axis of particles in either primitive or trunk placers of Otago river system (cf. Fig. 8 B). The positive correlation between flatness index and 'a', to a certain extent 'b'-axis, for gold particles in placers of Chaliyar river could be attributed to smaller ranges in lengths of 'a' and 'b'-axis. At the same time the lack of correlation for the Otago placers may be due to wide range in the minimum and maximum values for 'a' and 'b'-axis. Tishchenko (1981) noted that flattening of gold particles is more significant in the <2 mm size range in the eastern Siberian placers.

Figure 7.11 illustrates the relationship between Cailleux flatness index and a-axis length for gold particles in tributary and upper reaches of the Chaliyar main stem placers. In tributary samples (L14, L13, L12 and L11) it is noticed that majority of the particles show an a-axis length of < 0.5 mm and a flatness index of <6. Slightly higher values for a-axis length and flatness index for gold particles in sample L11 (Fig. 7.11d) are due to flattening of gold particles with increasing distance of transport from proximal placers (Fig. 7.11a). Note that samples L14 and L11 are from the tributary Punna puzha and L14 is closer to the source.

The gold particles in the upper reaches of the Chaliyar main stem (sample L10, 9 & L8, 7, 6) show a gradual increase in flatness index as well as a-axis length (Fig. 7.11e & f). Significant number of gold particles have flatness index >6 and moreover, greater number of gold particles have a-axis length >0.5 mm. However, the sample no. L5 (Fig. 7.11g) which is the downstream limit of sampling for this study, the a-axis length and flatness index distribution of individual gold particles are anomalous, again reflecting entrainment sorting and reflecting minor local source influence. As already seen in the flatness index vs a-axis length plot the positive correlation is more clear in the 7 samples (see Fig. 7.11).

As a particle of given mass moves downstream in transition and trunk placers it is progressively flattened, enhancing its entrainment potential at lower values of river gradient and bed roughness. The settling velocity of gold is independent of flatness for flatness index >15 (Shilo and Shumilov, 1970), so entrainment potential is probably more important than settling properties for hydraulic sorting and dispersal of gold in river systems (cf. Grigg and Rathburn, 1969). In the present study the gold particles have a restricted size range between 0.12 to 1.2 mm (average: 0.32 mm), which may considerably reduce the flatness index and in turn the independency of settling velocity of gold particles. Based on the results of the studies carried out by Youngson and Craw (1999) on Otago placers, they suggested that when a critical flatness index is attained, gold particles may be reentrained and transported to lower energy parts of the fluvial system where higher flatness index values are in equilibrium. Again, for fixed particle mass, flattening increases both the size and surface area to volume ratio of particles. This adds buoyancy (Krumbein, 1942) which facilitates entrainment and allows increasingly nonspherical particles to be transported to lower energy parts of the fluvial system than they would had flattening not occurred.

According to Youngson and Craw (1999) in the transition zone and trunk placers, hydraulic sorting of gold becomes increasingly more dependent on shape change, and mass and/or size reduction due to particle abrasion, flattening, folding or breakage during transport (cf. Fig. 10). This kind of modification of particles is reflected in sample no. L5 of Chaliyar main stem by general increase in roundness (Fig. 7.5g), and in the proportion of equant and elongate particles (Fig. 7.4g).

7.9 Shilo and Corey shape factors

In order to verify the results of the empirical system, the results for the 7 selected samples were compared with those of quantitative classification systems. Moreover, because of the empirical nature of the classification scheme it is necessary to establish its reliability. This can be done by comparing the empirical shape classifications for individual particles with that of a more quantitative method. There are basically two groups of shape factors represented by the Corey and Shilo shape factors. However, there is no simple quantitative measure for roundness but the empirical flatness can be compared to the Shilo and Corey shape factors. The plot of Shilo versus Flatness percent (Fig. 7.12a) for individual data shows a reasonable spread in the estiamted flatness for the thick and intermediate particles, however there is a significant spread for thin particles. The relationship between the flatness percent and the Shilo shape factor is curvilinear for gold grains from Chaliyar river. However, for Klondike placers (Knight et al., 1994, part 2, Fig. 2 & 5) the gold placers show a linear relaionship. This provides a simple method of quantifying and checking the empirical classification system. Figure 7.12a indicates that the thick particles (<33.33 flatness) have a Shilo value from 0 to 3, intermediate (33.3 to 66.67 flatness) from 3 to 6 and thin (>66.67 flatness) from 6 to same large value around 15. Fortunately in this study there were very few particles with a Shilo value 0 to 3 and >9. Knight et al. (1994) proposed that where a significant number of particles have a Shilo >9 it would be necessary to add one or more flatness categories to maintain the linear relationship between the empirical flatness and Shilo classifications. Figure 7.3 also provides a comparison of Shilo values for a flattened sphere of a fixed diameter for the empirical shape classes.

Because the conclusions in this study are based on averaged data the reliability of the averaged empirical classification data is checked by comparing it with averaged Shilo data for 7 samples. A comparison of the curve on the Shilo versus Corey plot (Fig. 7.13) of the individual particle data with the curve for the averaged Shilo versus Corey data (Fig. 7.14) reveals an offset which indicates that the mean may not be the best method of averaging this kind of data. Because of the restricted range in the empirical flatness percent for particles in 7 samples the Flatness versus Shilo plot (Fig. 7.12b) for the averaged shape data does not show any relationship. However, when a line is constructed which passes through 16.6% on the flatness axis at Shilo=0 (because of the method of calculating the means) as well as through maximum number of data points in the plot, it is found that the empirical classification system commonly underestimtaes the flatness as shown in figure 7.12b.

The flatness versus Corey plot for individual particles (Fig. 7.15a) shows that the Corey factor is linear with respect to flatness. Similar to flatness versus Shilo plot for averaged data (Fig. 7.12b) the flatness versus Corey plot for averaged data (Fig. 7.15b) does not show any relationship. However, in the figure 7.16a & b (flatness vs Shilo and Corey) Shilo shows a curvilinear relationship while Corey has linear relationship with flatness respectively. As a result in the present study the Corey shape factor is the preferred comparison with the empirical classification system. Approximate Corey values for the empirical shape classes are shown in figure 7.3. Based on the studies on Klondike placers Knight et al. (1994) noted that the flatness shows a curvilinear relationship with Corey and linear-relationship with Shilo.

Thus the comparison of individual and averaged flatness data for the 7 samples show that to a certain extent there is a smooth relationship between the two methods implying that the empirical method is valid. However, as discussed earlier the empirical shape classification system based distance estimation from source for placers is not a reliable method in the present study. The results of the present study agrees with the view of Knight et al. (1994) that the eye (the empirical shape classification) is capable of compensating for the change in flatness with size and is therefore able to classify individual particles for flatness in a similar way to the Shilo, Corey and related shape factors. In addition to this it is concluded that the empirical classification system provides data which can be reliably used to draw conclusions about gold particle shape.

7.9.1 Variation of Shilo and Corey shape factors with distance

The mean Shilo and Corey shape factors of gold particles from different locations of Chaliyar river is presented in table 7.3. In general, the mean Shilo and Corey shape factors for placer gold particle in the Chaliyar river fall in the intermediate flatness range (compare Table 7.3 with Fig. 7.3a). Mean Shilo shape factor for gold particles ranges from 2.68 to 5.19 (Table 7.3). The tributary placer samples except L11 show almost uniform mean Shilo value (range: 3.08 to 3.51). Among all the tributary samples the proximal placers in Punna puzha shows minimum mean Shilo factor (3.08) which is primarily due to less deformed/ less flattened particles and they show source inherited shape characteristics. The Punna puzha placer sample L11 shows maximum mean Shilo value of 5.19 and this is approximately 15 km downstream from proximal Punna puzha placer sample L14. This is mainly due to transport induced flattening of gold particles where they become more of two dimensional nature (eg., lenses, discoids, plates). The slight decrease in the mean Shilo value (4.91) in the Chaliyar main stem sample L10,9; which is just below the confluence zone of major upstream tributaries, is probably due to mixing up of particles that have undergone different degrees of fluvial transport. However, among the main stem samples, L8,7,6 shows the maximum mean Shilo value (5.16) which is due to flattening of particles with increasing distance of transport. Beyond this, at the downstream limit of sampling for this study, mean Shilo values show a drastic decrease (L5=2.68, L4=2.91), less than mean Shilo values of tributaries, which is brought about by particle folding and thickening. In addition to this, inputs from local weathering zone/vein sources have also played an important role in the decrease in Shilo values.

The mean Corey shape factor for gold particles ranges between 0.24 to 0.39 (Table 7.3). Among the tributary samples Chali puzha has the maximum mean Corey value (0.39). However, from the proximal placers in the Punna puzha tributary to approximately 15 km downstream the Corey value, 0.35 reduces to 0.26. The above decrease is brought about by the progressive hammering induced flattening of gold particles. The Corey value of gold particles further decreases when it reaches the Chaliyar main stem (see sample number L10,9=0.24). Beyond this, the mean Corey shape factor gradually increases and at the downstream limit of sampling (sample number L5, L4) for the present study the values are identitical with that of the proximal tributary placers. This can mainly be attributed to the following processes:

a) inputs of gold particles from local weathering zones/veins;

b) folding and rethickening of flattened particles; and

c) entrainment and retension of gold particles in the main stem.

7.10 Geochemical characteristics of placer gold in Chaliyar river

Representative gold grains from major tributaries and Chaliyar main stem have been analysed for Au, Ag, Cu, Fe and other platinum group elements by EPMA. The results of the analysis are presented in table 7.4 (see Appendix 7.1 and 7.3 for detailed data). At least three points were analysed in each grains. The results also underline the observations made by other workers that the placers in the Nilambur valley are mainly contributed by laterization processes and moreover they show very high purity with Au of 100%. However, certain interesting observations are also made using back scattered imaging of polished sections which is supported by grain chemistry which are discussed later in this chapter.

Recently Santosh and Omana (1991), and Santosh et al. (1992) have reported that the primary gold grain yielded the value of 85.2 to ~ 90% Au and ~ 8 to 13% Ag. Similarly, the secondary gold grains from weathering profiles have Au values between 99.91% to 99.93% (Santosh and Omana, 1991). Santosh (1994) and Santosh et al. (1992) also reported similar results for supergene gold grains from Nilambur laterite.

In the present study, the placer gold particle from Punna puzha (Grain 1) yielded Au values between 94.35 to 99.32% with 1.84 to 2.35% Ag (see table 7.4). Two grains were analysed from Karim puzha. Grain 1 yielded Au between 97.16-

99.30% and Ag between 0.63-0.99%, while in Grain 2 Au ranges between 99.94 to 99.93% and Ag between 0.03 to 0.10% (see table 7.4). Gold particle from Chali puzha (Grain 1; Table 7.4) has Au content in the range 98.96-99.93% and Ag ranges between 0.03-0.18%. Gold particle from Nilambur (main stem) (Grain 1, Table 7.4) has yielded gold values of 98.15 to 98.23% and Ag ranges between 1.68-1.73%. Santosh et al. (1992) recently reported pure placer gold in the Nilambur valley and they found that the fineness values for gold particles are above 995. Similar high purity gold placers have been reported from Klondike (Knight et al., 1999), fossil placers of the Witwatersrand (Hallbauer and Utter, 1977), Ivory Cost (Grant et al., 1991), Western United States (Desborough, 1970). Apart from the analysis of spongy gold in gossans at Kalgoorlie reported by Wilson (1984), with 99.91% Au and 0.09% Ag, the high gold concentrations observed are exceedingly rare. The average fineness value (1000 Au/Au+Ag) is 950 for most weathered ore bodies carrying pure gold (Wilson, 1984) and it ranges from 947 to 957 in the laterite profiles of southern Mali (Freyssinet et al., 1989) and from 919 to 929 in lateritic soils at Mato Grosso, Brazil (Michel, 1987). The Nilambur laterite gold has fineness values from 991 to 999 (Santosh and Omana, 1991), well above the previously reported values. A comparable occurrence is at Edna May mine in Western Australia, reported in Webster and Mann (1984); it should be noted, however, that significant differences exist in the gross chemistry of laterites with varying ages and formational histories. The Western Australian laterites, for example, are "fossil laterites" formed in a saline-arid environment; in southern India, present-day laterite formation occurs through tropical weathering processes.

In well-polished surface, the differences in reflectivity and/or colour of gold surfaces, indicate variations in composition. This has been documented on a quantitative basis by Eales (1967, 1968), Desborough (1970) and most recently by Knight et al. (1999) for Klondike placers. In the present study it is found that one can distinguish optically and quantitatively as little as 5 and 8 weight percent silver between two adjacent areas in a single grain (Grain 2 in Punna puzha - tributary and Grain 1 in Arikkode - main stem respectively) and moreover the contact between two adjacent areas of differing composition is gradational (Table 7.4; Fig. 7.17 & 7.18). However, gradational variations are more subtle in figure 7.17 (Grain 2 in Punna puzha) than in figure 7.18 (Grain 1 in Arikkode - lower limit of sampling in main stem) and hence more difficult to evaluate microscopically. Microscopic study of polished sections of each gold grain was done prior to electron microprobe analysis.

Table 7.4 shows the analytical results of core and rim in gold particles from Punna puzha tributary (Grain 2) and Arikkode-main stem (Grain 1). The Au in the rim ranges from 99.12-99.62% and Ag 0.35-0.83% in the Punna puzha while in the core Au ranges from 93.44-94.46% and Ag 5.29-6.24% (see Table 7.4; Grain 2- Punna puzha). In the Arikkode gold particle (Grain 1; Table 7.4) the Au varies between 98.03-99.68% and Ag 0.26-1.88% in the rim. The core of the grain yielded Au 91.99-92.45% and Ag 7.44-7.96%. This high content of Ag in core is strikingly similar to the Ag content in the lodes of Wynad gold deposits.

In addition to Au, Ag association in the core of the placer particles, trace quantities of Cu is also present (Cu up to 0.27%; see Appendix 7.2 for more details) especially in Grain 2 of Punna puzha. It is also noticed that there is a higher content of Cu in gold particle of Chali puzha (Grain 1: Cu up to 0.87%; see Appendix 7.2).

Primary suphide inlcusions of minerals such as pyrite, galena and chalcopyrite which range from 0.002 to 0.5 mm in diameter occur within placer gold grains from several localities (Desborough, 1970). These attest to the preservation of the original composition of the gold grains because unprotected or exposed sulfides are readily altered to other phases or entirely decomposed in the placer environment. Ramdohr (1965, p. 88) observed sulphides in gold in the Rhine river and reached the same conlusions regarding the protection of sulfides from weathering.

The ubiquitous occurrence of iron-sulfide gangue minerals like pyrite and chalcopyrite in Nilambur is important in evaluating the solution mechanism of gold in this area. Ferrous iron released from iron-sulfide minerals are further oxidised by dissolved oxygen to ferric iron, which in turn is hydrolyzed, a reaction called ferrolysis (Mann, 1984). According to Santosh and Omana (1991) the importance of the ferrolysis reaction in Nilambur area is evidenced by the occurrence of gold particles within iron oxides and the agglutination or coatings of iron oxides. They also found other evidences that suggests gold dissolution by pyrite oxidation, chemical refinement, and subsequent reprecipitation by reduction at the site of iron oxidation in Nilambur is the direct correlation between the mechanism of transportation and fineness levels. In the Yilgarn block of Western Australia, Webster and Mann (1984) noted that gold migration as an $AuCl_4^-$ complex results in high fineness, whereas gold carried as a thiosulfate complex yields low fineness. Based on the presence of exceedingly high fineness values for supergene gold in Nilambur valley and the near absence of silver and copper, Santosh and Omana (1991) suggested dissolution by pyrite oxidation in the weathering profiles and migration in the form of chloride complexes.

In the present study of placer gold particles in the Chaliyar river the microprobe analysis showed minor amounts of Cu (~ 0.2%) especially in core of the grain (Grain 2; Punna puzha), along with Ag and Au which strongly suggests that the lode gold deposits in Wynad Gold Fields are associated with gangue mineral like chalcopyrite. However, the rims of the above particle are almost devoid of Cu and Ag which can be either due to leaching in the fluvial environment and or laterization processes. But because of the similarity of core composition with the primary lodes the former processes can be regarded as the reason for the high purity Au in rims. In addition to this it is interesting to note that the gold particle in Chali puzha (see Appendix 7.2; Chali puzha, Grain 1) has higher Cu (Cu up to 0.87%) than Ag (Ag up to 0.18%).

7.11 Rim formation

Knight and McTaggart (1990), Knight et al. (1999) concluded that the rims on gold particles were formed by the removal of Ag, Hg and Cu from the gold and not by the precipitation of Au. The data in this study (see Table 7.4; Grain 2-Punna puzha and Grain1 - Arikkode; Fig. 7.17 & 7.18) are consistent with this conclusion. The contact between the rim and core is gradational (Fig.'s 7.17 & 7.18), but on sectioning, due to fluvial leaching, the rims are lighter while the core is darker, as seen in backscattered electron images.

It is suggested that the rim of particles from Punna puzha and Arikkode (Fig's. 7.17 & 7.18 respectively) exemplify leaching process. A possible mechanism for Ag and Cu depletion along the rims can be inferred from gold particles from Punna puzha tributary (Fig. 7.17) and sample from Arikkode in the Chaliyar main stem (Fig. 7.18). In both cases the gold particles have pore spaces which acted as probable pathways for the removal of Ag and Cu. The formation of these pore spaces is not clear but Knight et al. (1999) noted that the removal of Cu leaves a porous, pure Au residue in the core. Thus the pore spaces in gold particles in Chaliyar placers could be due to Cu/Ag removal. It is suggested the Arikkode sample (Fig. 7.18), which is compositionaly zoned and porous, similar processes of Ag removal and pore creation is thought to have occurred on its surface to create the outer, Au-rich rim. Thus in addition to the gold refinement due to dissolution, migration and reprecipitation in the weathering zone in Nilambur supergene regime, it is observed that the fluvial placers in Chaliyar also contains gold particles in which the removal (leaching) of Ag, Cu etc. from rims is taking place as a gold enrichment process in the grains. The small tongue like growths at the periphery of the gold particles (Fig. 7.18) suggests Au precipitation is taking place. It is inferred that the rim formation process (Ag, Cu removal) begins as soon as lode gold is exposed to surficial conditions. When the particle enters the fluvial system the rim formation process probably become dynamic where two processes (formation and destruction) compete to form the rims as the particle moves downstream. Particle movement downstream is not continuous; part of the time the gold particles are in the active stream (during which time the rims are probably destroyed); part of the time they are in dormant sediments (during which time the rims are thought to thicken). The dominant rim removal process in the active stage is thought to be abrasion. Hammering is thought to influence rim formation through rim compaction and straining. Groen et al. (1990) have shown that Ag cannot diffuse at a fast enough rate through a single massive crystal of gold to account for the formation of the rims so some other pathways or processes are required, that may be produced by hammering.

Petrovskaya and Fastalovich (1955) have noticed partly collapsed pores along outer rims and suggested that the porosity along the rim will quickly be destroyed by deformation. The figure 7.18 shows that the rim and the core have similar density of pore spaces and they are not destroyed especially in rims suggesting the particle has not undergone significant fluvial transport after the pore creation. Moreover, the significant difference in the pore densities in gold particles (Fig's. 7.19 & 7.20) suggests that the Ag and Cu distribution in them are different which again emphasises that the gold placers in Chaliyar river are derived from multiple sources. In addition to this the gold grain in figure 7.19 (Chali puzha- tributary) shows lower Ag (~ 0.15%) and slightly higher Cu (0.85%) while the gold particle in figure 7.20 (Nilambur- main stem) the Ag content is ~1.7% and Cu ~ 0.08%. This again supports the view that the placers in the Chaliyar river are contributed by multiple sources and the rim formation in some of the particles are in the fluvial environment.

In the present study it is found that the chemical refinement of gold by supergene process and the refinement by fluvial transport cannot be easily distinguished either by morphological or chemical characteristics and it becomes more complicated by contribution of gold particles from multiple sources. Uniformly pure gold (including core) suggests that the particles have remained in weathering zone for a considerable time and they are mainly formed by reprecipitation while particles showing core-rim type relationship might have been formed in the fluvial environment due to leaching of Ag and or reprecipitation of Au. However, the relative proportions of the above two types of gold nuggets in fluvial placers of Chaliyar river is not understood properly and is beyond the scope of the present investigation.

Conclusions

- Gold concentration in bulk sediment samples from upper reaches ranges from 0.09 to 0.53 μg/g (averaging around 0.30 μg/g). In the respective –60 ASTM size fraction it ranges from 0.079 to 0.21 μg/g. The gold particle size ranges between 0.12 to 1.2 mm and averages 0.36 mm. Gold is preferentially accumulated in coarser fractions (medium sand and above) due to high density of gold. The highest gold concentrations are seen in upper reach sediments.
- Gold concentration in TS ranges from 0.004 to 0.009 μg/g while in LCS and LS it ranges from 0.005 to 0.04 μg/g.
- High gold concentration and high percentage of dense minerals (opaques) especially in one of the upper reach samples and moderate positive correlation between mean size and Au concentration point to textural and mineralogical controls in the deposition of gold particles.

- Au and other trace elements like Cr, Ni, V, Co, Cu, Zn and Ti in the four different groups of samples within the basin show a distinct character and their textural and mineralogical identity is also reflected in their distinctive chemistry.
- The interpretations of grain morphology, semi-quantitative and quantitative data like gold particle outline, roundness and flatness indices evolve in the expected lines with distance of transport. They bring forth that gold entrainment and retention have played an important role in addition to primary shape and mass characteristics. Mean Shilo and Corey shape factors range between 2.68 to 5.19 and 0.24 to 0.39 respectively and they fall in the intermediate flatness range.
- Outline shape classes indicate that the complex grains are more dominant in the tributaries and with increasing distance in the main stem, the equant and elongate grains become more dominant. The roundness also shows a shift from angular to sub-rounded in tributaries to sub-rounded to rounded in main stem.
- The maximum flatness index for tributary samples is 18 while it is 22 for main stem samples and the average Cailleux flatness index for gold particles ranges between ~3.6 to 6.5.
- Distance estimation based on the empirical shape classification system does not hold good due to
  (1) involvement of multiple sources with different cycles of gold transport,
  (2) primary gold particle shape (lateritic source) and mass characteristics,
  (3) restricted average flatness (47 to 50) and roundness (45.5 to 57) percentages suggesting that the gold particles have undergone shape unification in weathering zone and are more or less derived from lateritic source, and
  (4) particle entrainment and retention in trunk placers.
- Gold particles from tributary and main stem exemplify leaching processes (either in the fluvial environment or during lateritization processes or both) with outer rims having high purity gold (with 100% Au) while their cores have Ag up to 8% in primary association with Au.

- In gold particles Cu ranges up to 0.8%. The pore spaces in some of the gold particles and the differences in pore densities as seen in polished sections could also be due to Cu/Ag removal in the fluvial environment and possible contributions from multiple sources.
- A preliminary estimate of the amount of gold transport associated with bedload sediments of Chaliyar river annually has been inferred based on the gold concentration in sediments and it is estimated to be around 100 kg (or of the order of a few tens of kg).

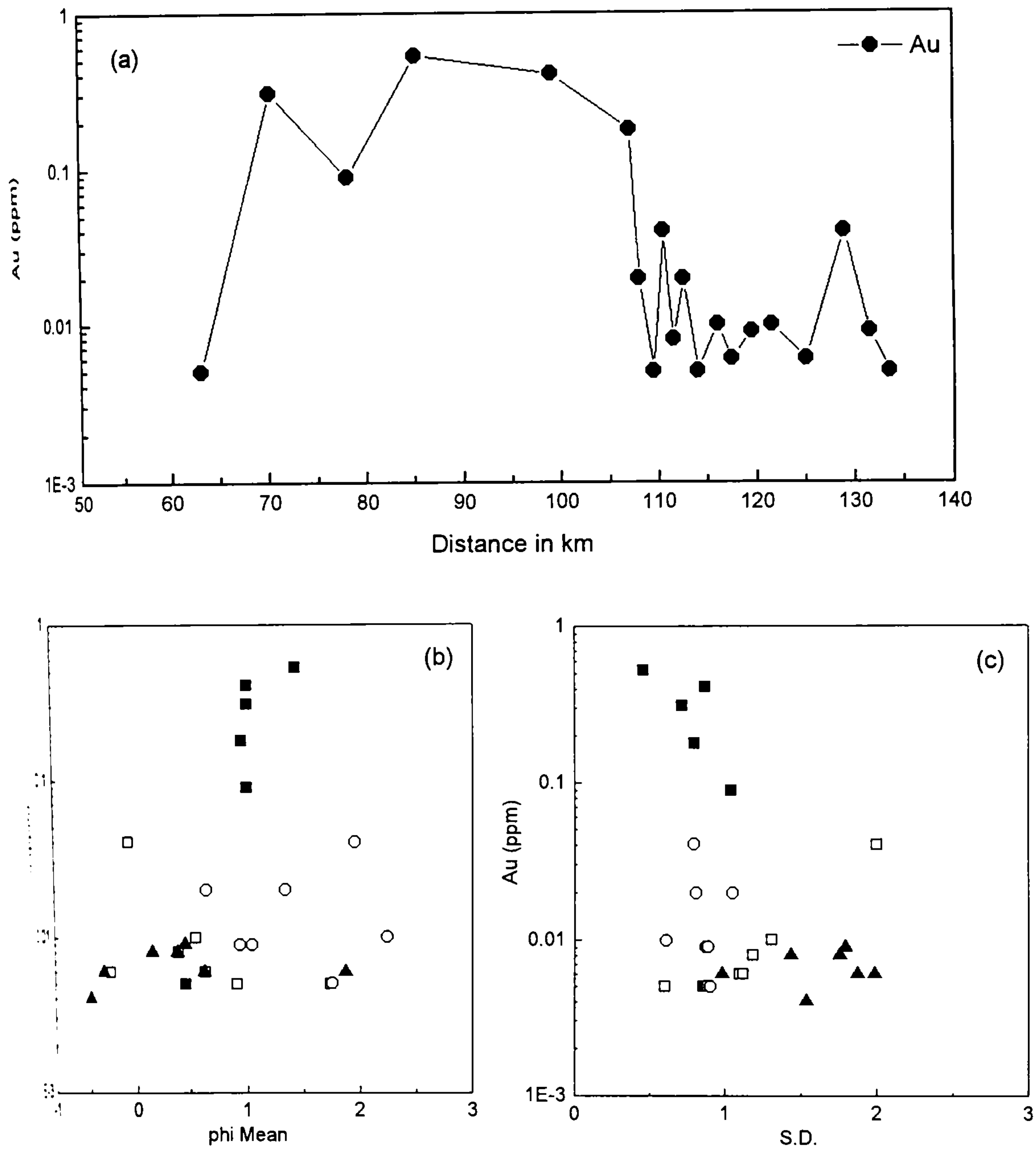


Fig. 7.1 (a) Down stream variation of Au (ppm) in Chaliyar bed load sediments
(b) Au (ppm) vs phi mean; (c) Au (ppm) vs S.D.

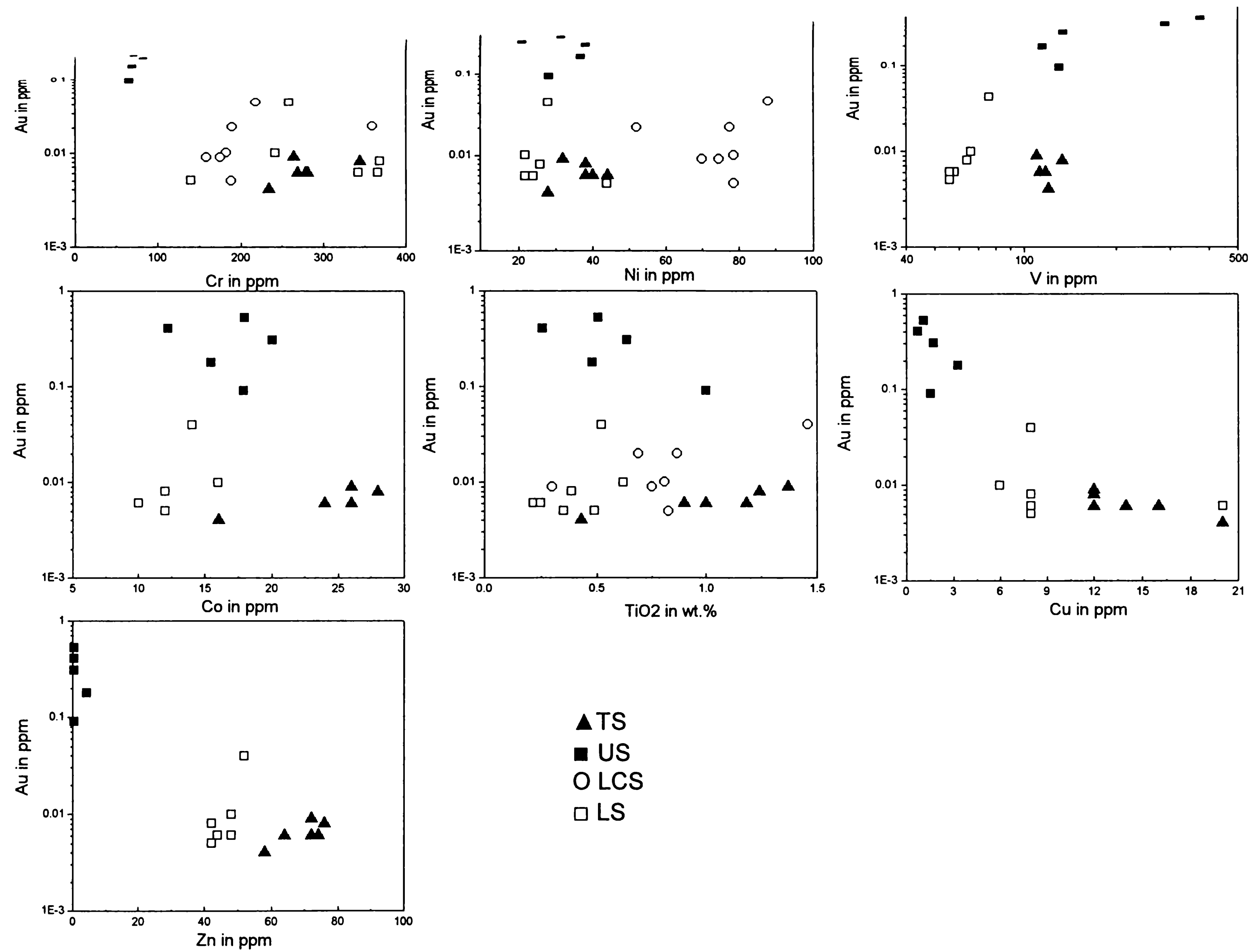


Fig. 7.1d. Au in ppm vs selected trace elements in Chaliyar river sediments

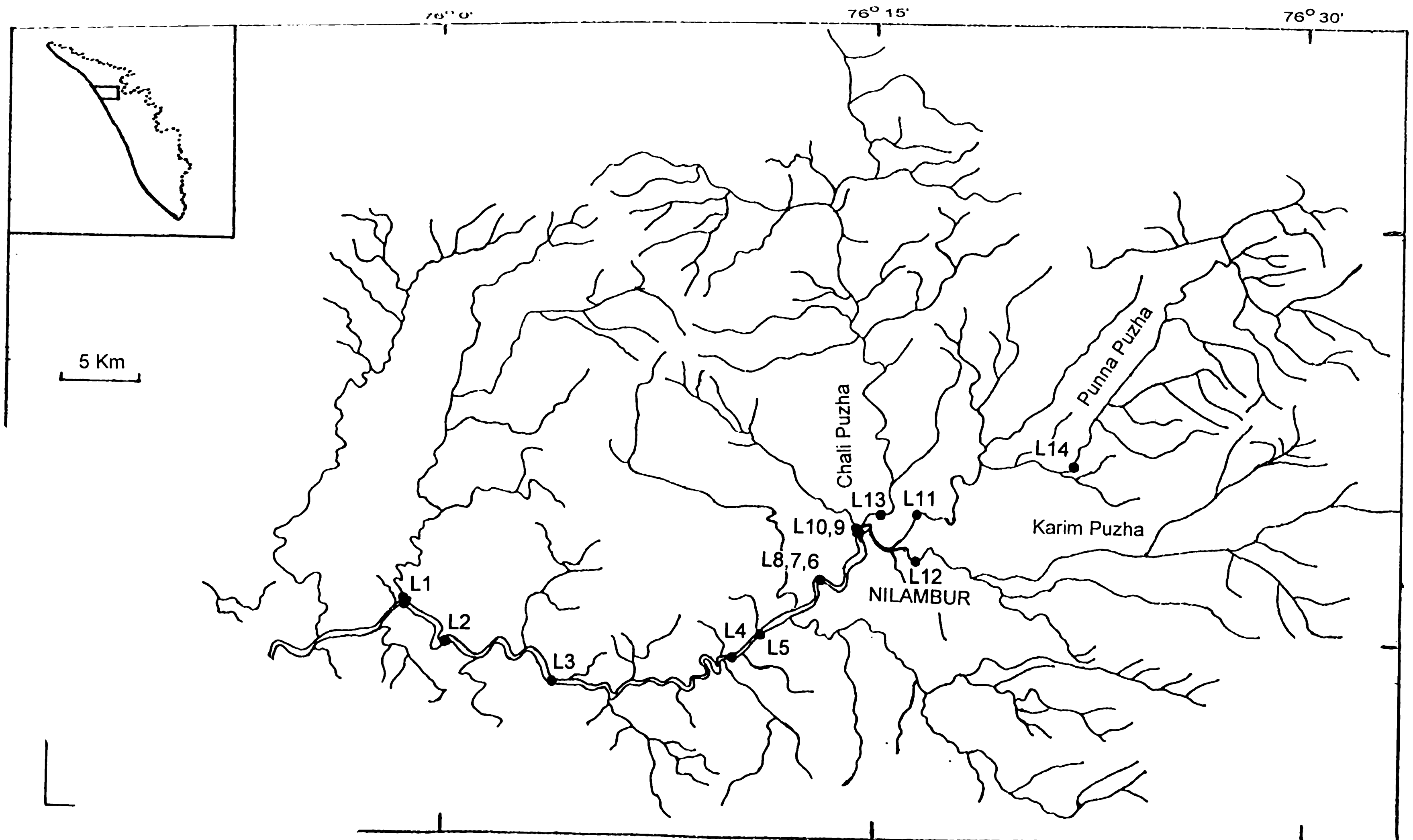


Fig ... amples for quantitative and semi-quantitative study of gold particles
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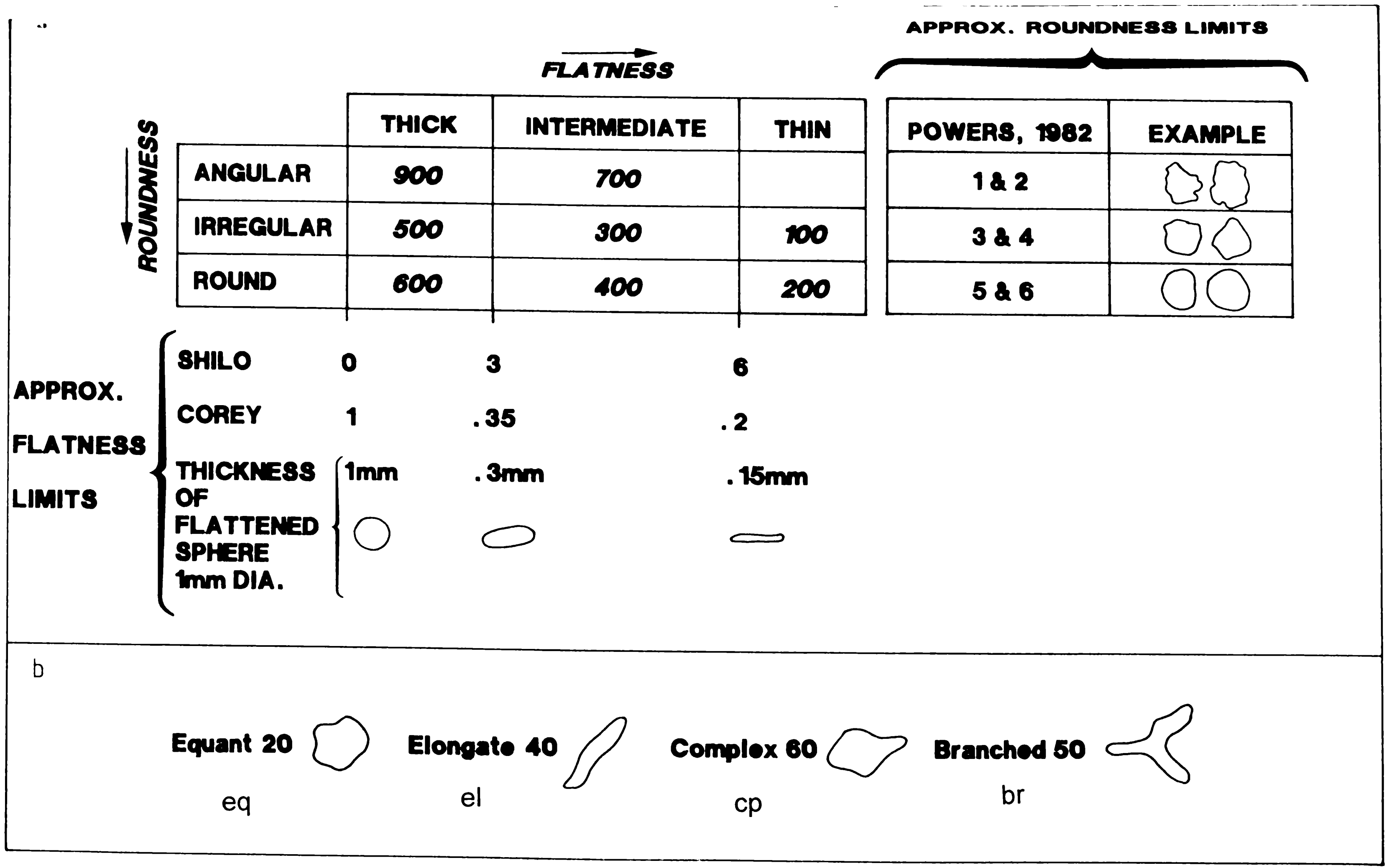


Fig.7.3 Shape classification System : *a) flatness and roundness; b) particle outline as it lies on its preferred side* (after Knight et al., 1999)

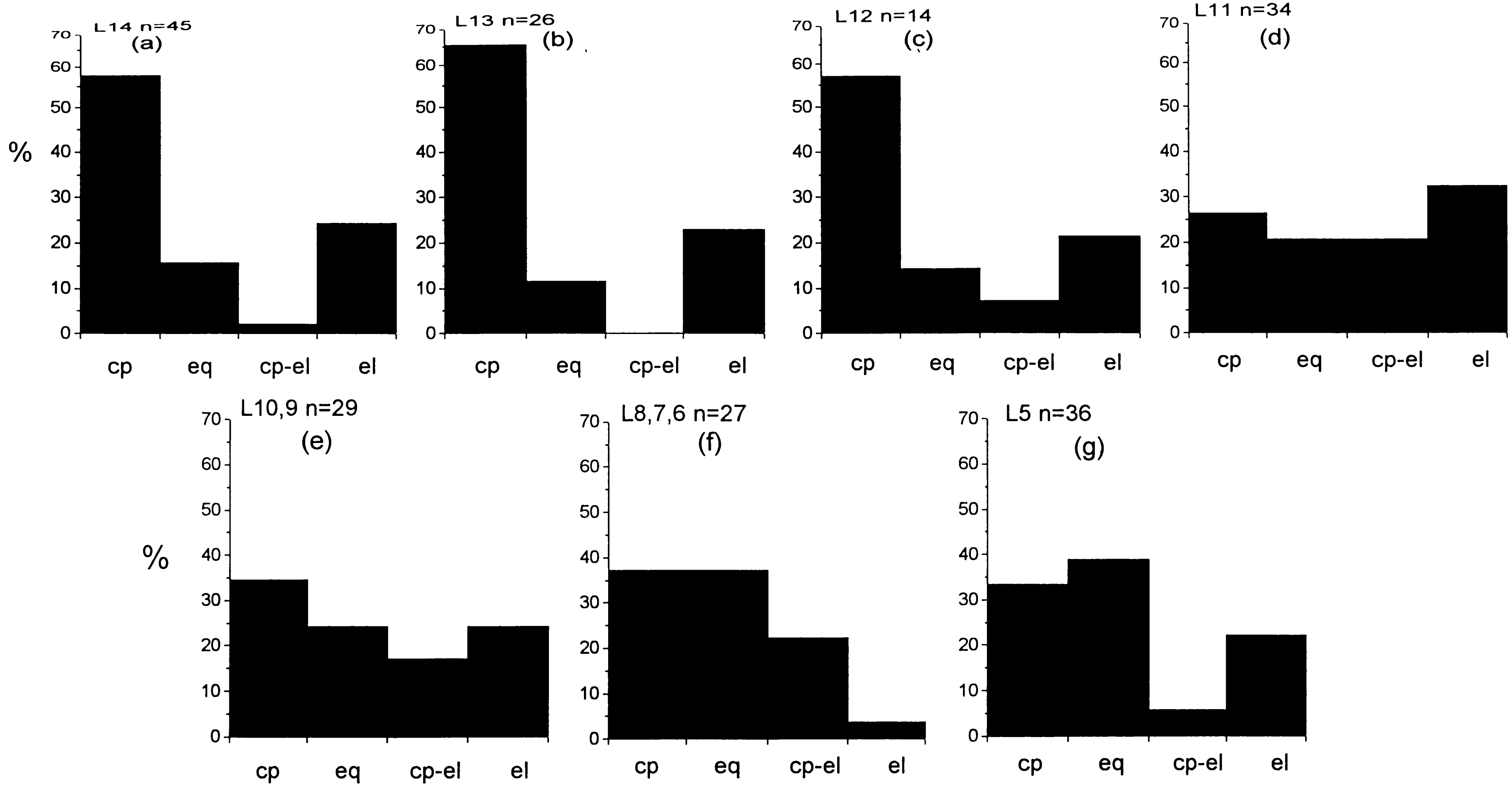


Fig. 7.4 Histograms of outline data for gold particles in major tributaries and Chaliyar main stem sediments

(cp = complex; eq = equant; cp-el = complex-elongate; el = elongate) (n = number of gold grains)

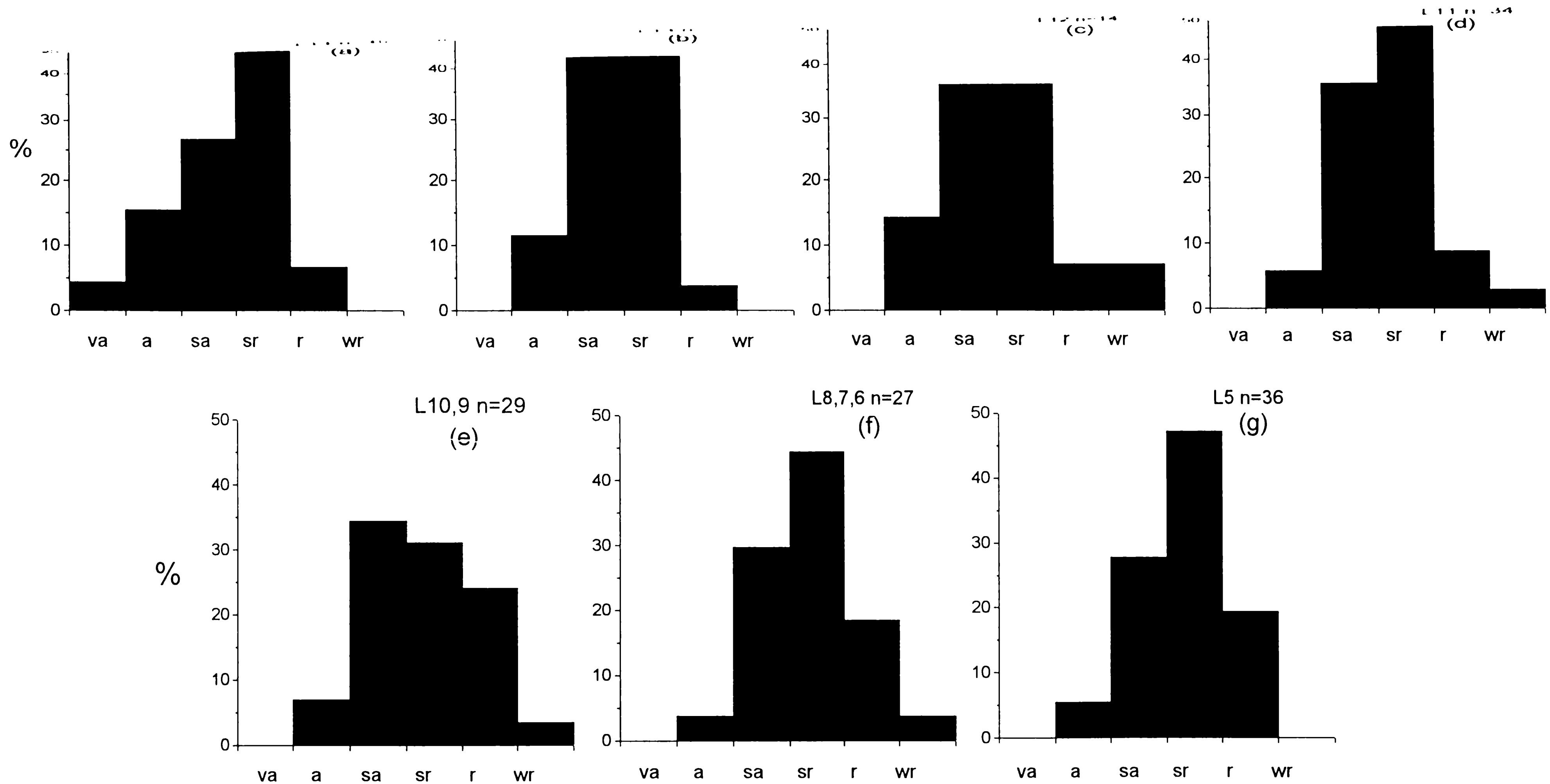
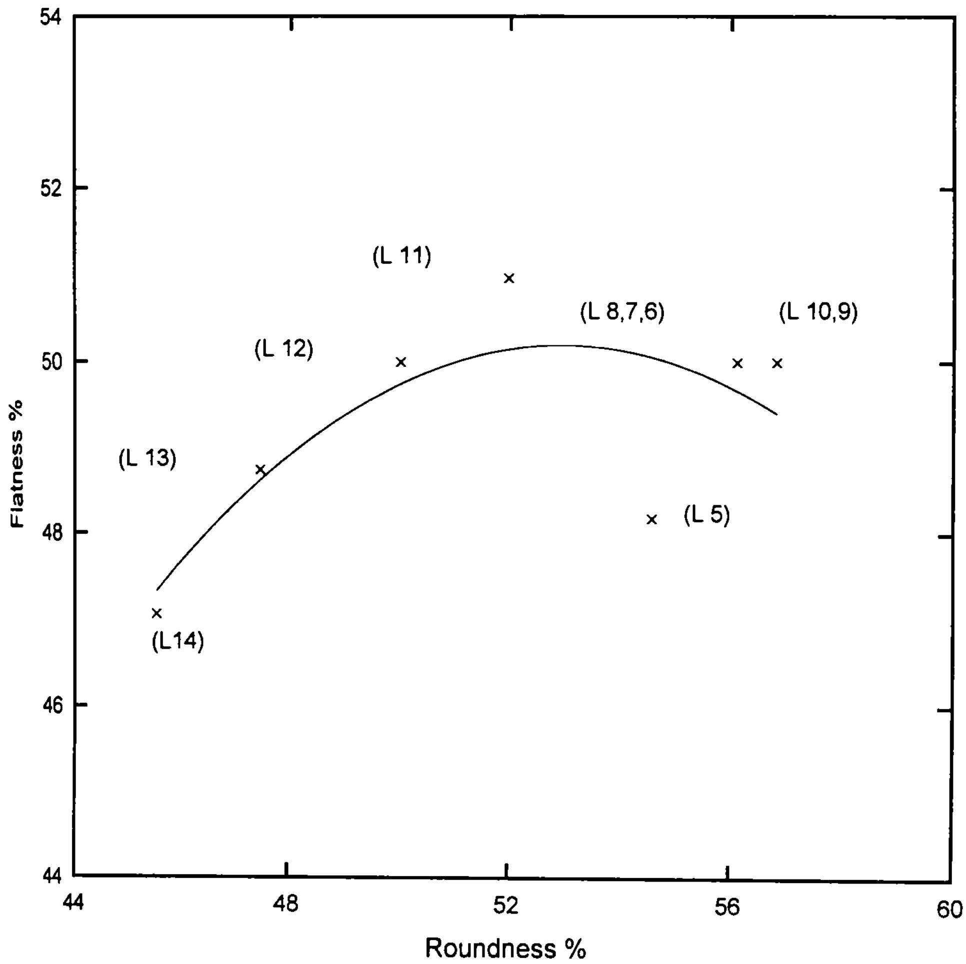


Fig. 7.5 Histograms of roundness data for gold particles in major tributaries and trunk placers of the Chaliyar river

(va = very angular; a = angular; sa = sub-angular; sr = sub-rounded; r = rounded; wr = well rounded) (n = number of gold grains)

Fig. 7.6 Average Flatness vs Average Roundness
for selected samples



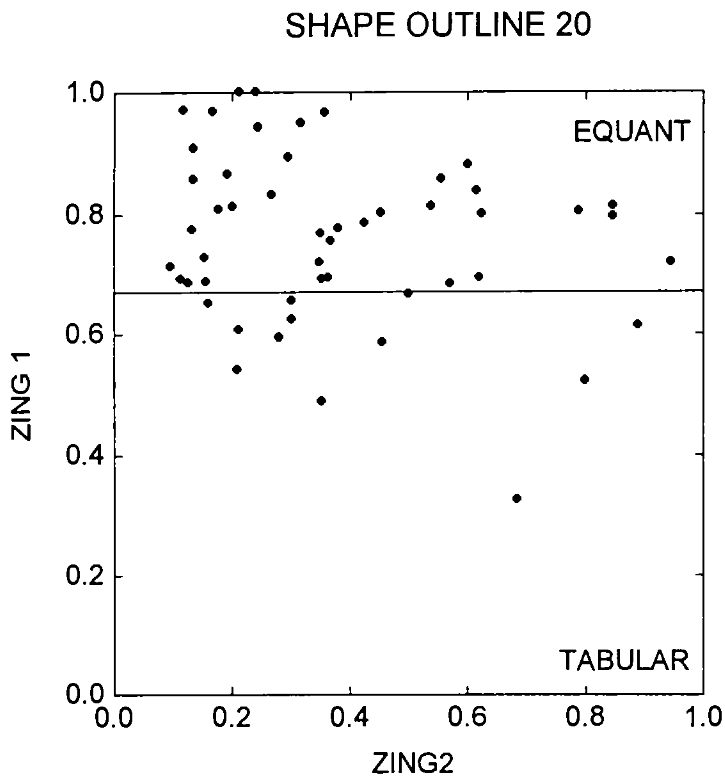


Fig. 7.7a
Plot of Zing1 vs Zing2 for particles with a 20 or Equant Outline. Shapes above the line will have an equant outline.

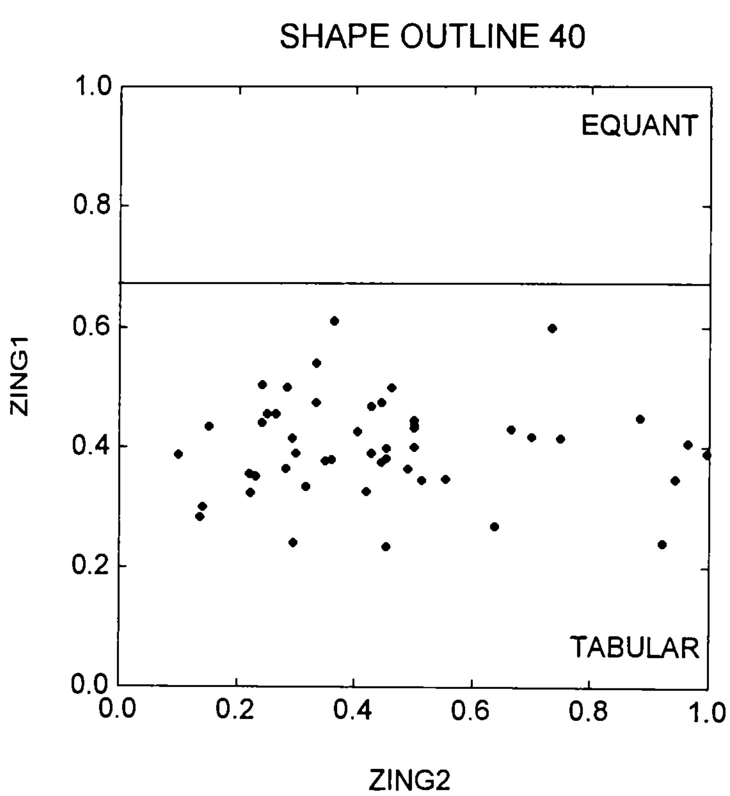


Fig. 7.7b
Plot of Zing1 vs Zing2 for particles with a 40 or Elongate Outline. Shapes below the line will have an elongated outline

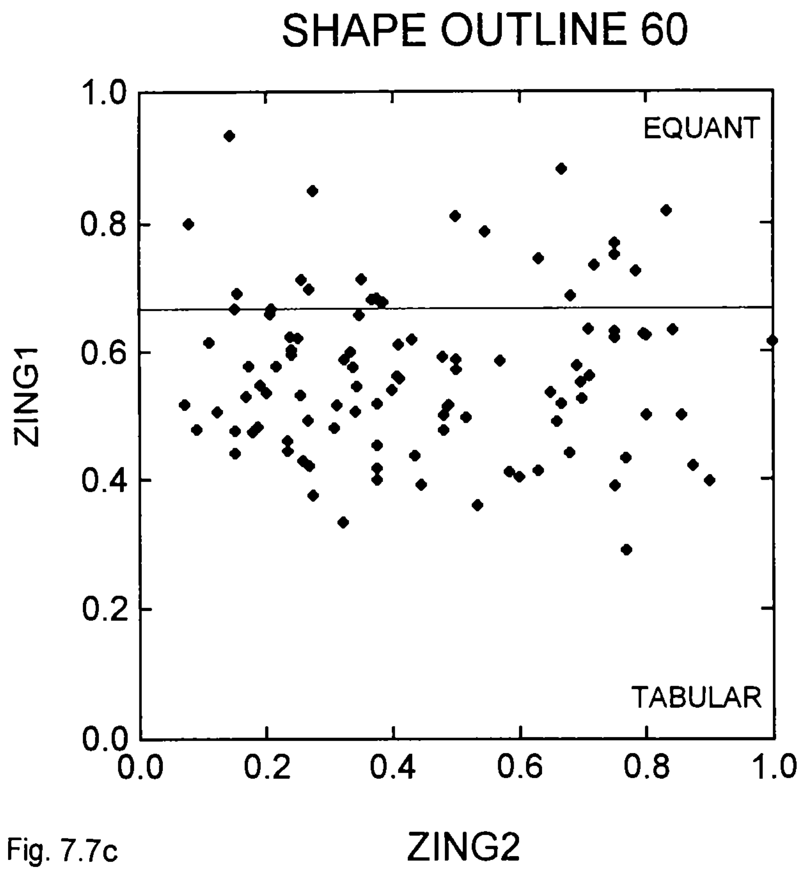


Fig. 7.7c

Plot of Zing1 vs Zing2 for particles with a 60 or Complex Outline. Complex shapes should fall close to the line

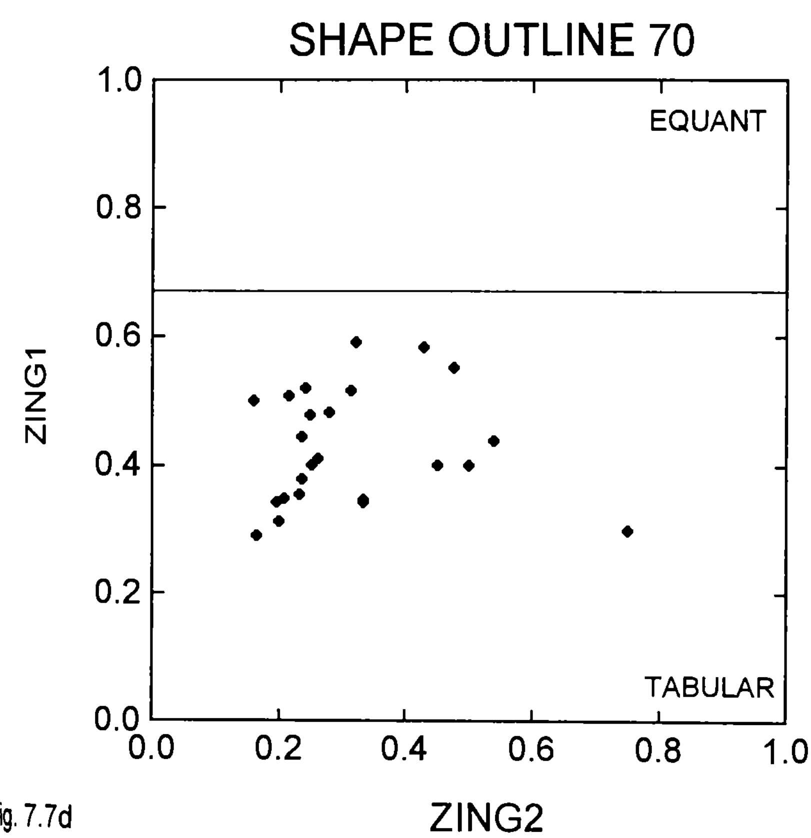


Fig. 7.7d

Plot of Zing1 vs Zing2 for particles with a 70 or Complex-Elongate Outline. Shapes fall below the line similar to Outline 40 or Elongate Outline

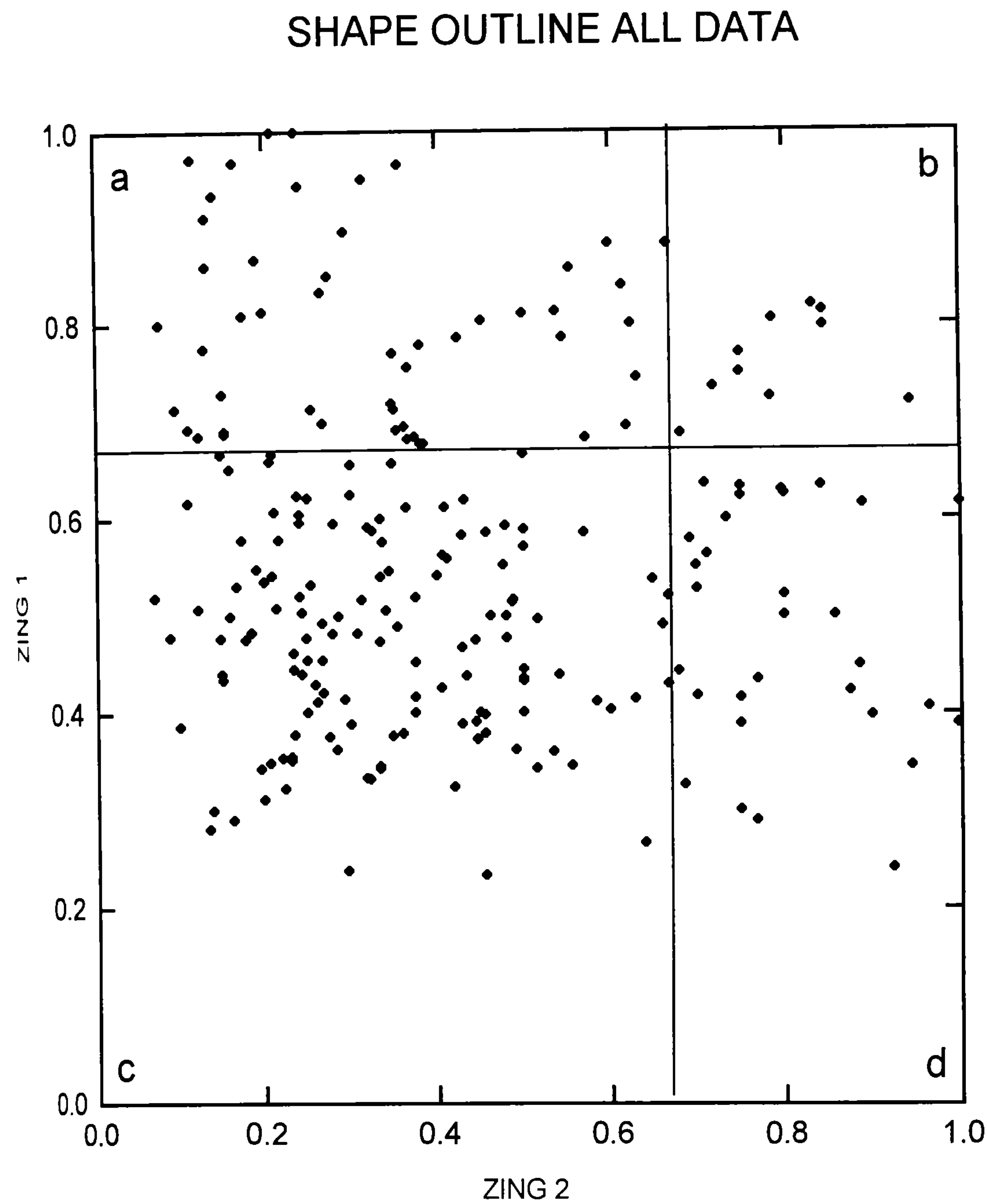


Fig. 7.8 Plot of Zing1 vs. Zing2 for particles from 7 samples for which quantitative measurements were made. For all plots, Zing1=b/a, Zing2=c/b, (a=maximum dimension, b=intermediate dimension and c=minimum dimension). Field a-represents tabular shape, b-represents the equant shape, c-represents the bladed shape and d-represents the prolate shape.

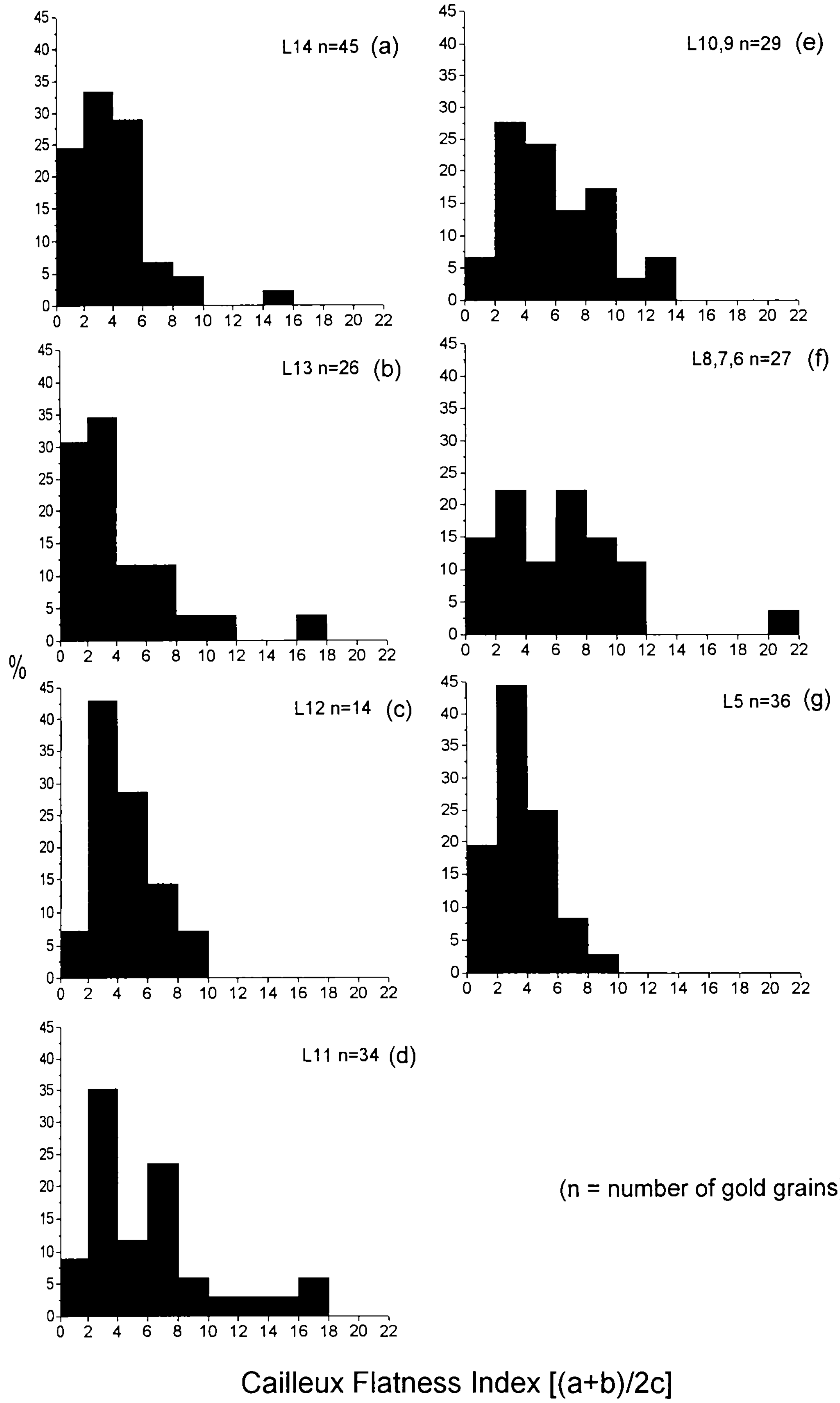


Fig. 7.9 Histograms of percent Cailleux flatness index [(a+b)/2c] for gold particles in major tributaries and Chaliyar main stem

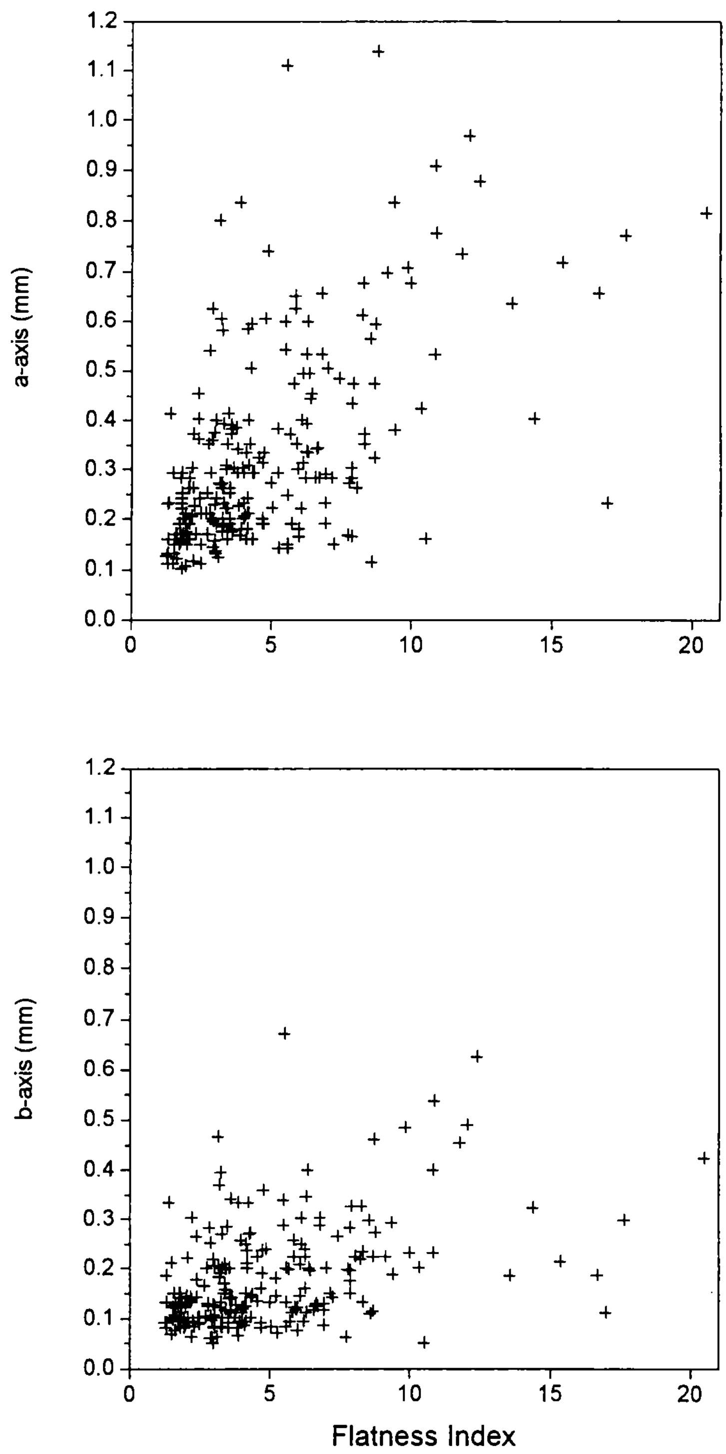


Fig. 7.10 Cailleux flatness index [(a+b)/2c] vs a-axis and b-axis length for all gold particles in Chaliyar river

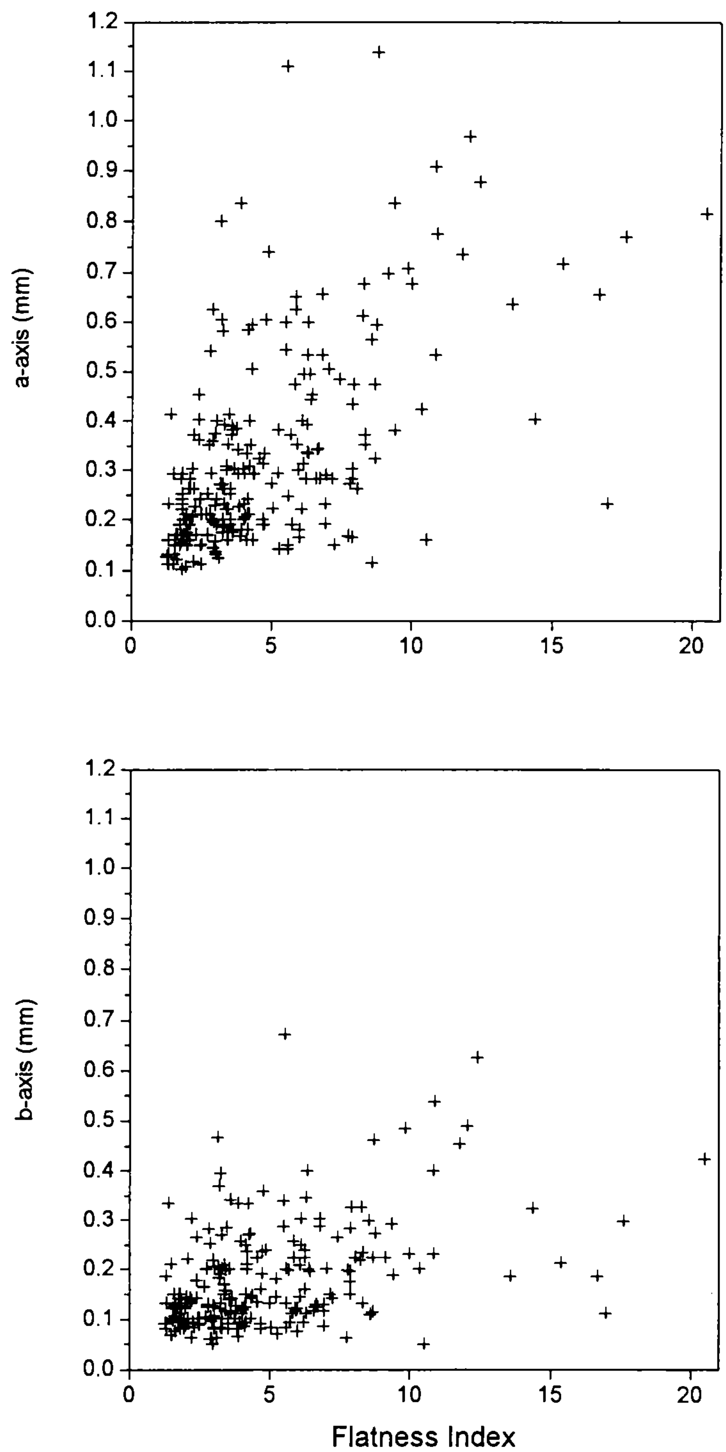


Fig. 7.10 Cailleux flatness index [(a+b)/2c] vs a-axis and b-axis length for all gold particles in Chaliyar river

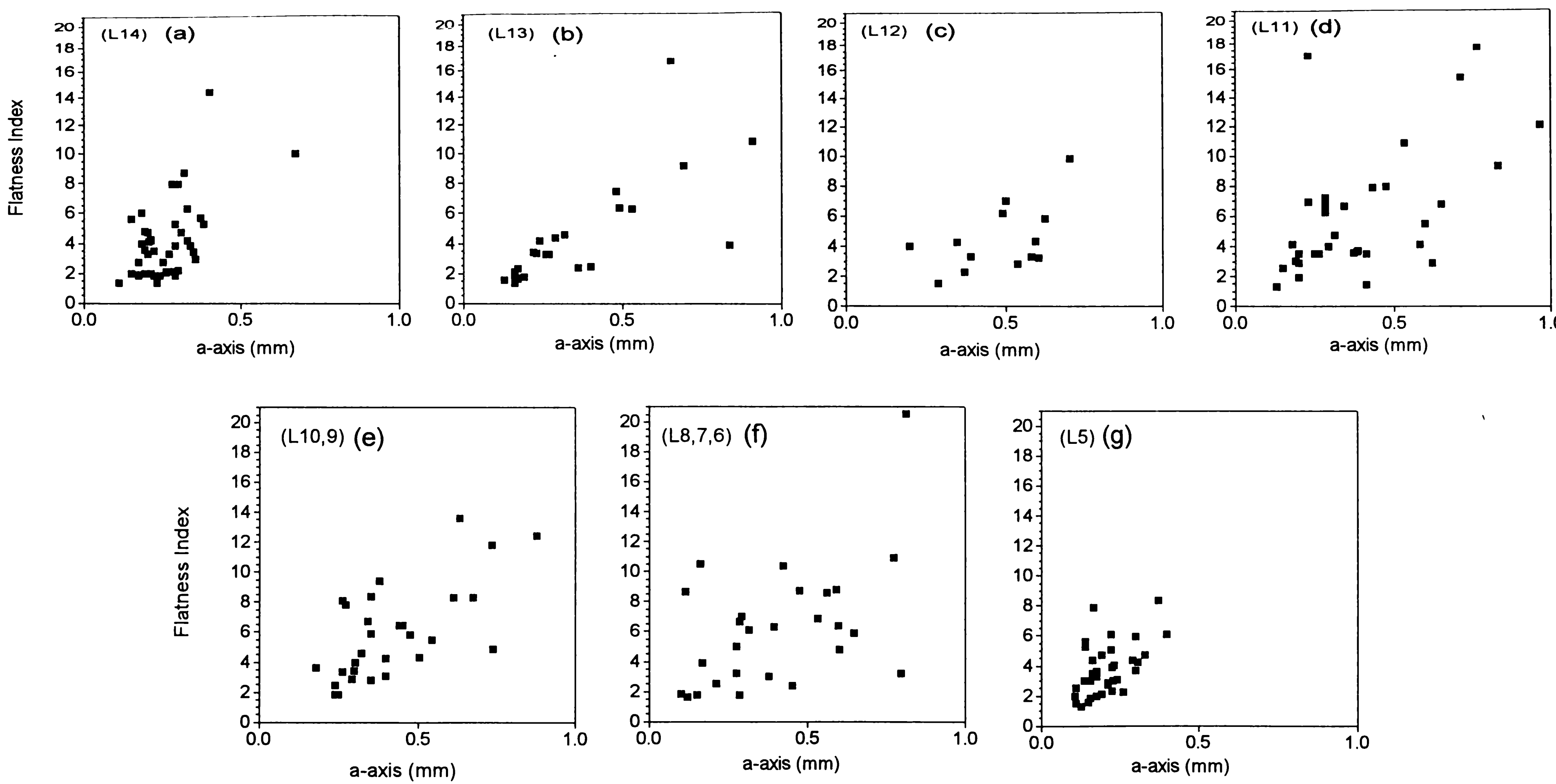


Fig. 7.11 Cailleux flatness index [(a+b)/2c] vs a-axis length for gold particles in tributaries and Chaliyar main stem

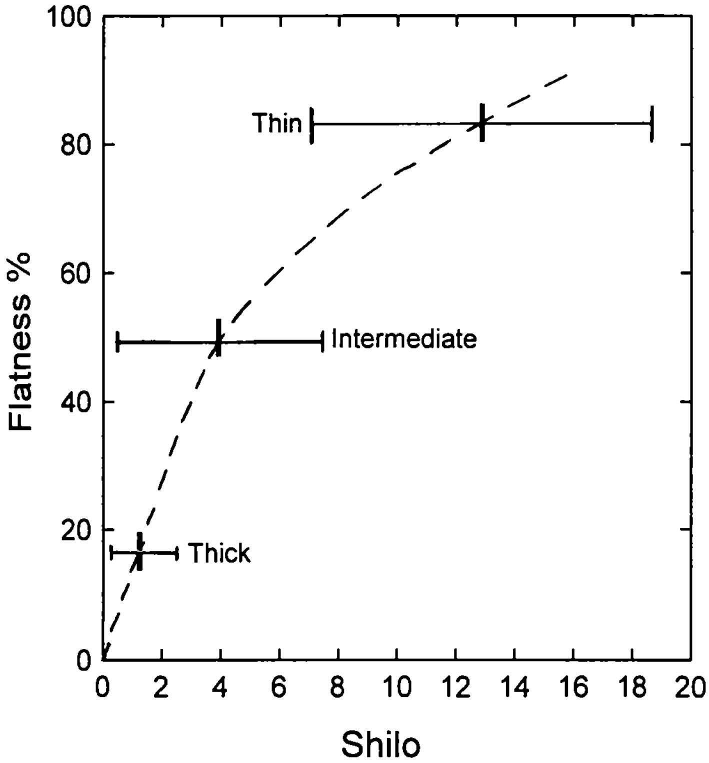


Fig. 7.12a A plot of flatness vs Shilo shape factor for individual particles from samples for which quantitative measurements were made. The horizontal bar represents1 sigma on either side of mean.

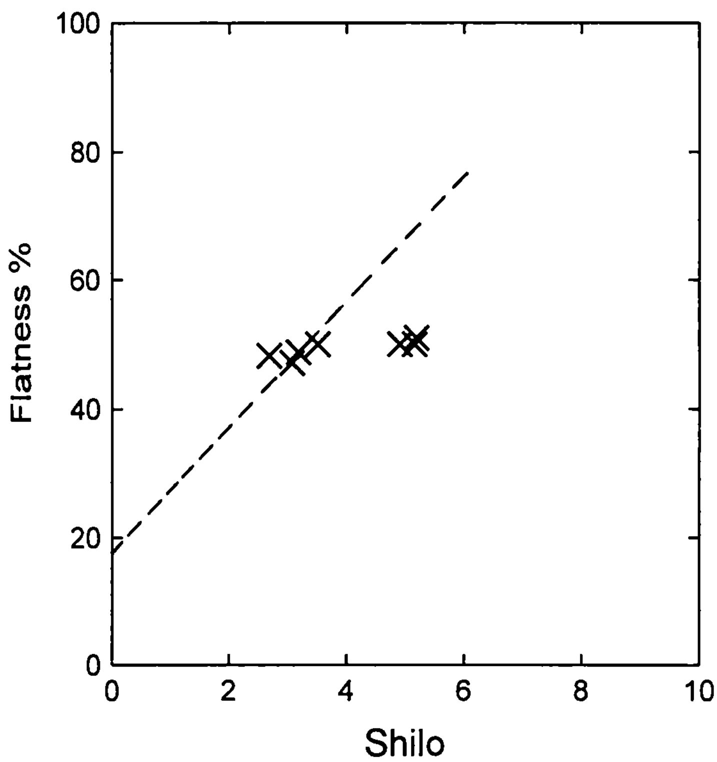


Fig. 7.12b A plot of the average flatness vs the average Shilo factors for 7 samples for which quantitative measurements were made. The curve indicates that the estimated flatness values are likely to err towards a lower flatness.

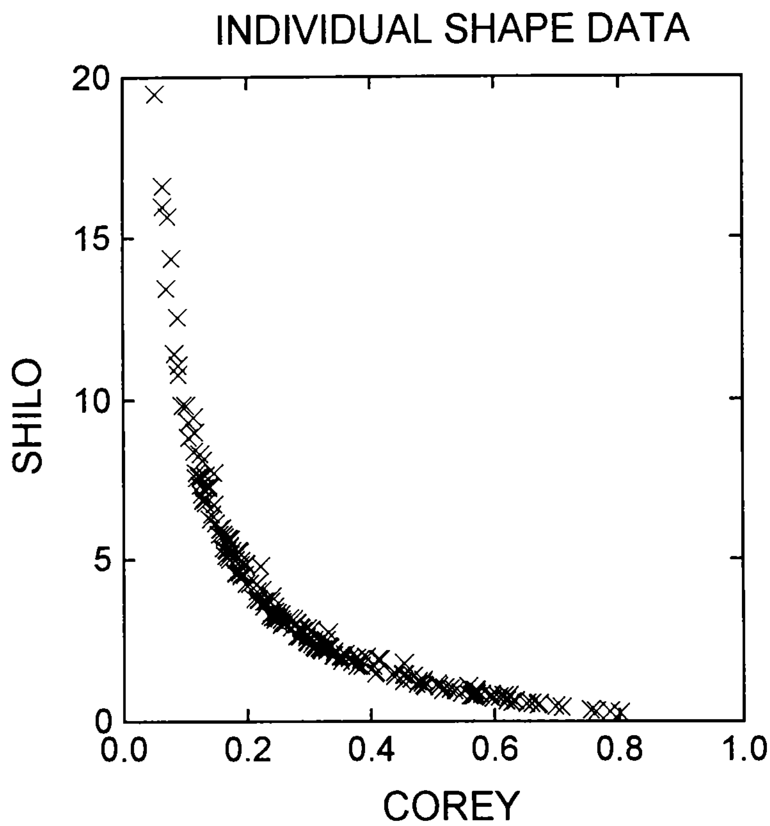


Fig. 7.13 A plot of Shilo vs Corey Shape Factor for individual particles from samples for which quantitative measurements were made

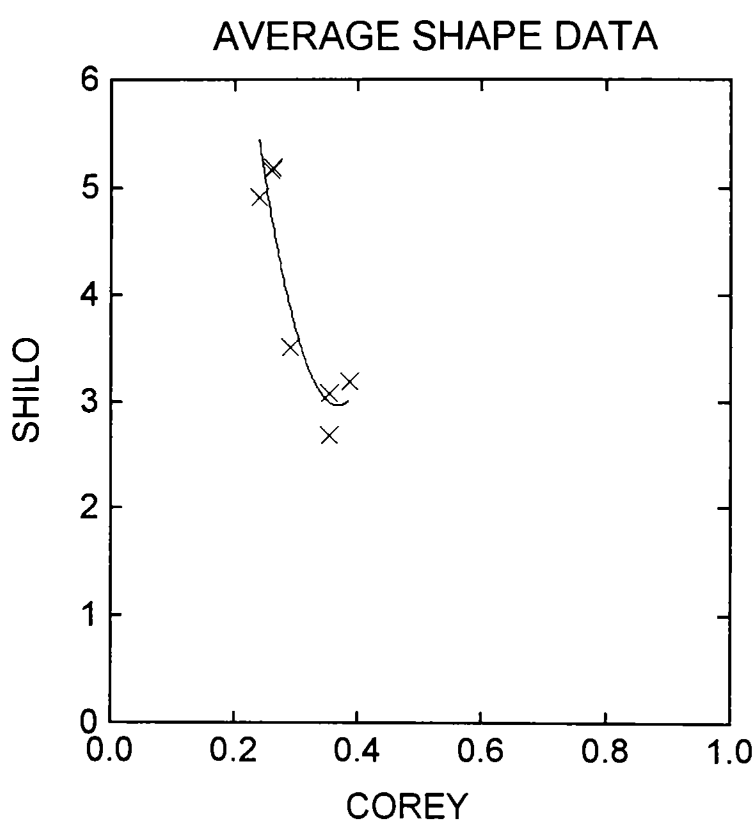


Fig. 7.14 A plot of the average Shilo vs average Corey Factor from 7 samples for which quantitative measurements were made

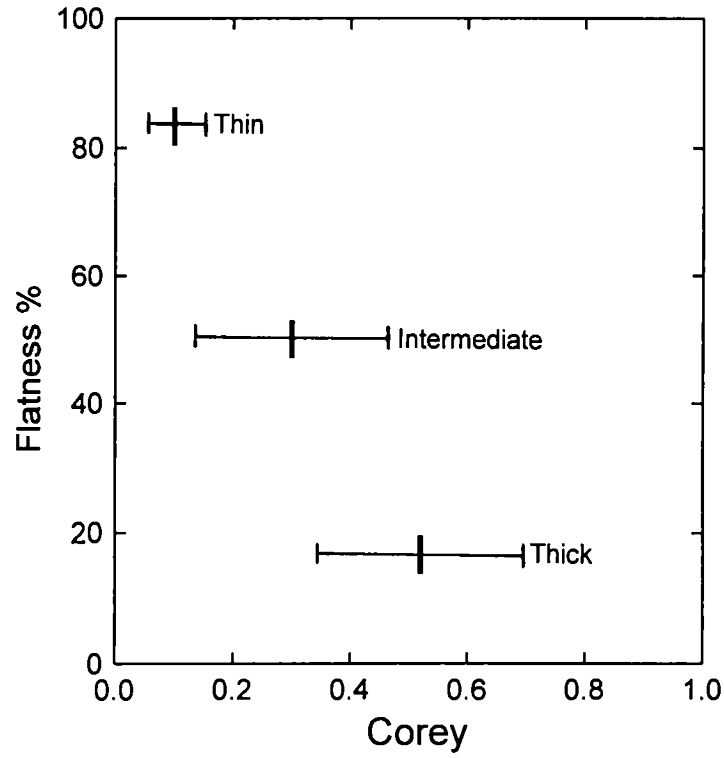


Fig. 7.15a A plot of the flatness vs Corey shape factor for individual particles from samples for which quantitative measurements were made. The horizontal bar represents 1 sigma on either side of the mean.

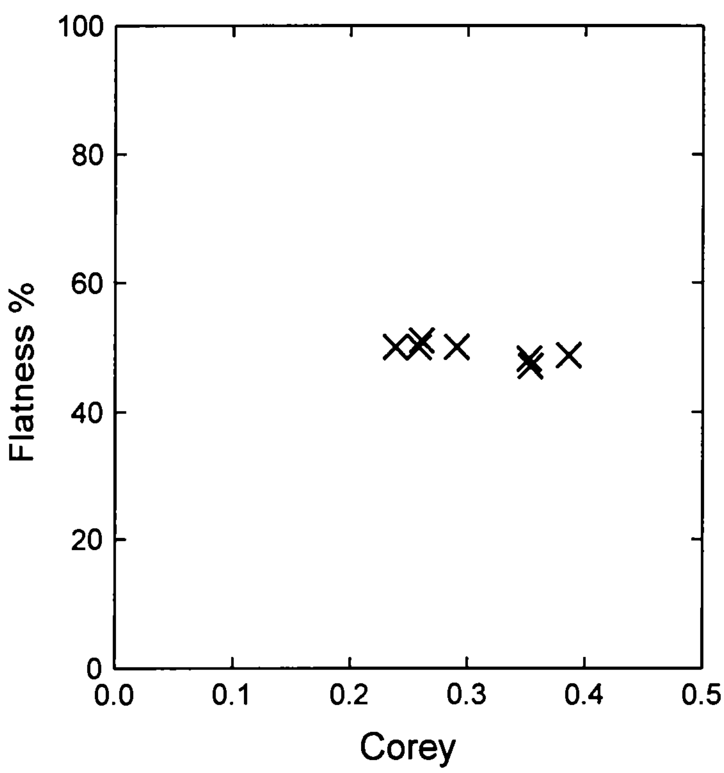


Fig. 7.15b A plot of the average flatness vs the average Corey shape factor for 7 samples for which quantitative measurements were made.

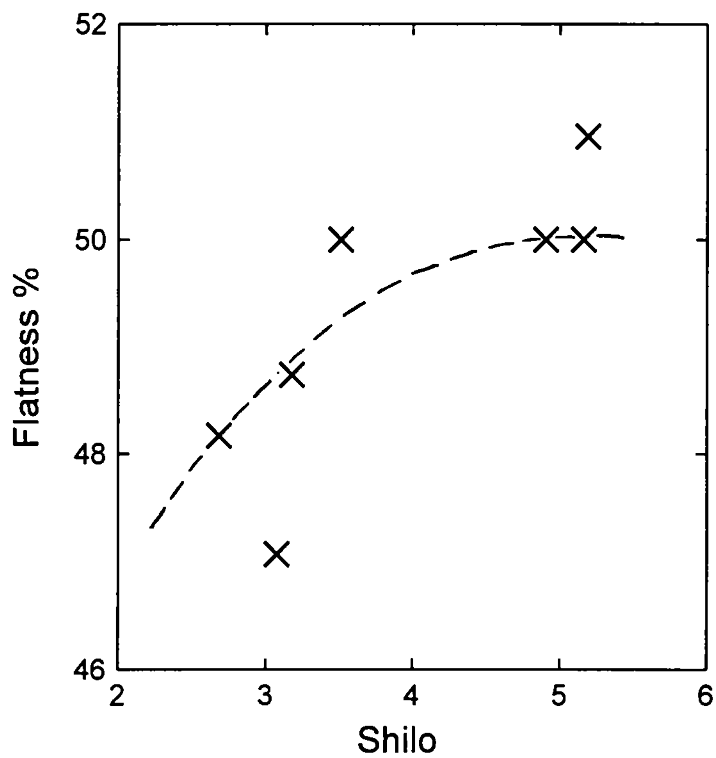


Fig. 7.16a A plot of the average flatness vs the average Shilo shape factor for seven samples for which quantitative measurements were made. The data shows a curvelinear nature.

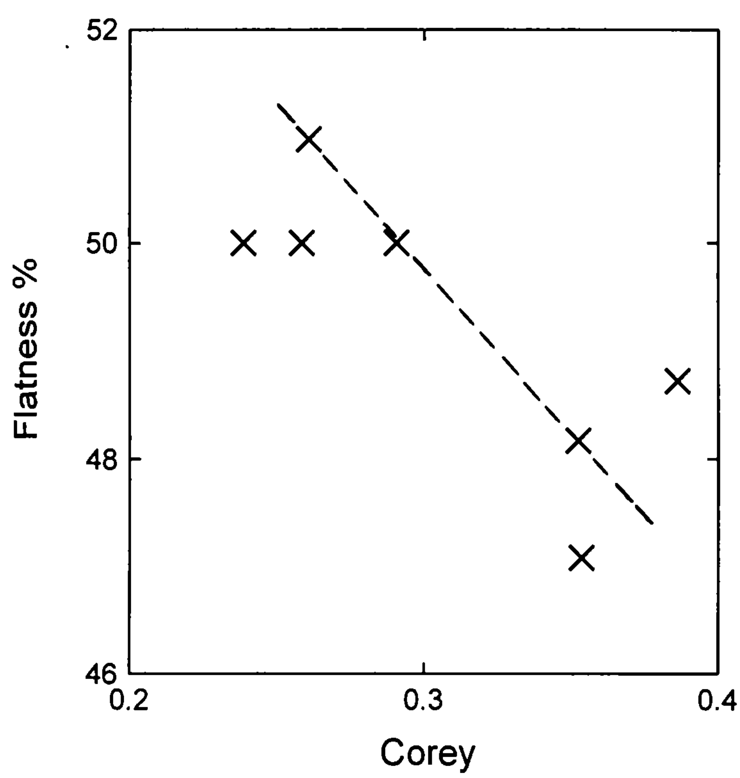


Fig. 7.16b A plot of the average flatness vs the average Corey shape factor for seven samples for which quantitative measurements were made

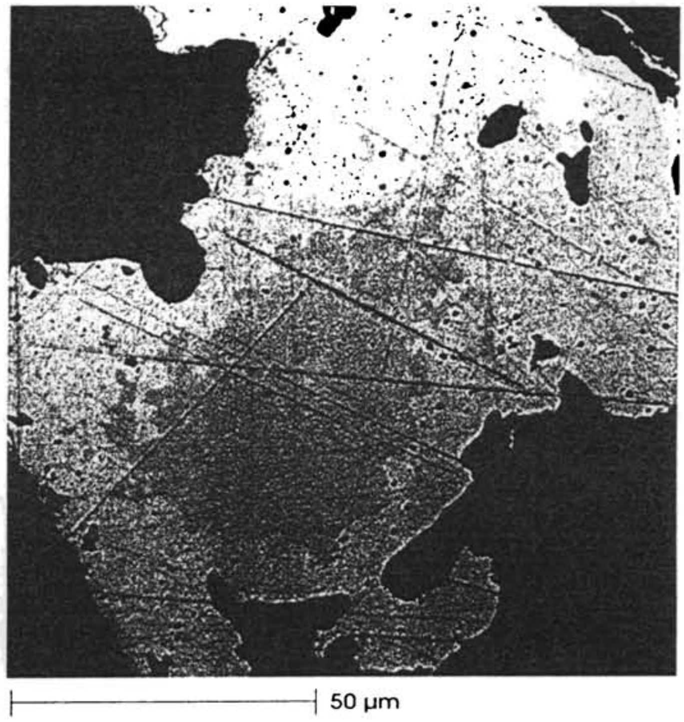


Fig. 7.17 Grains showing rim and core relationship suggesting leaching processes. Note rims are more lighter and show high purity Au while the core is darker and impure. (Grain 2 : Punna puzha).

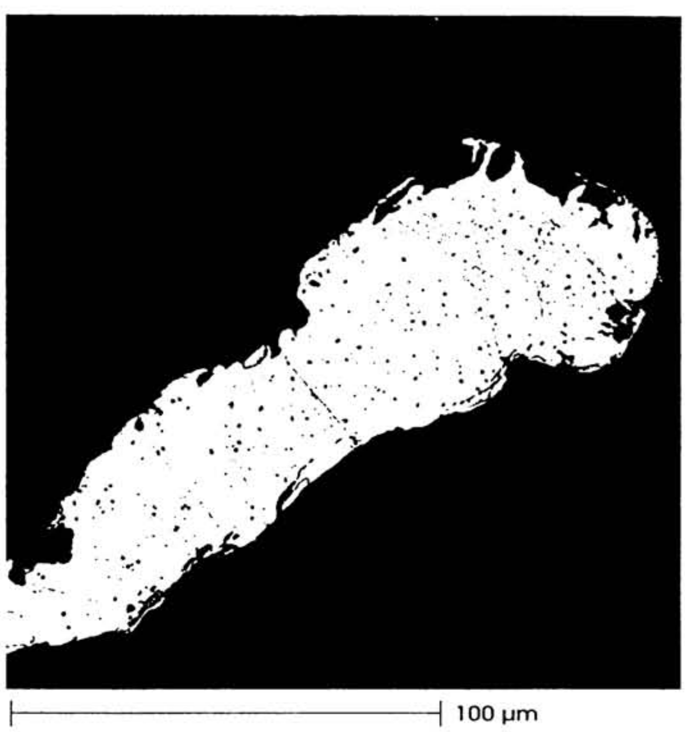


Fig. 7.18 Elongated grain showing tongue like feature at the periphery of the grain (Grain 1 : Arikkode; main stem)

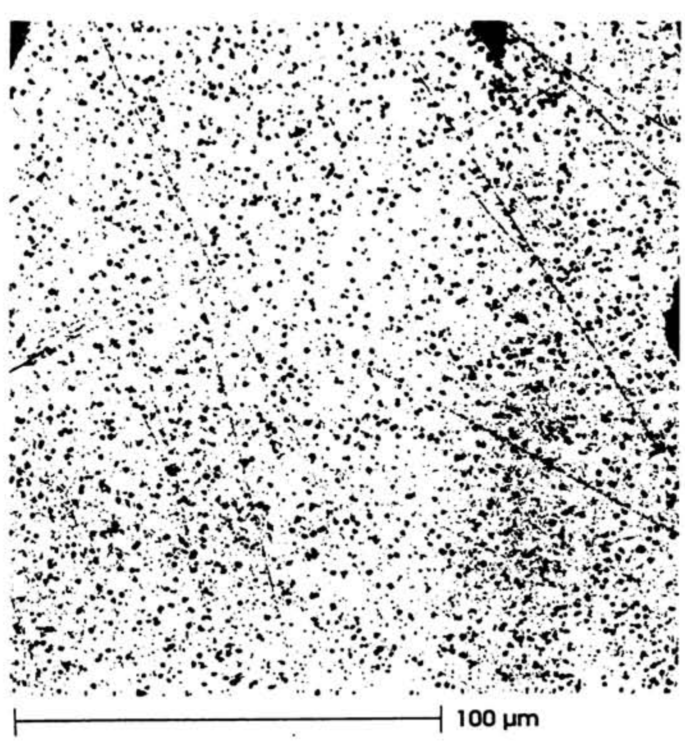


Fig. 7.19 & Fig. 7.20 Polished sections showing differences in the pore densities (Fig. 7.19 Grain 1 : Chali puzha) (Fig.7.20 Grain 1 : Nilambur, main stem sample)

Table 7.1 Gold concentration in the bulk sediment samples of Chaliyar river

Sample No.	Distance	Au (ppm)
H-35	63.0	0.005
H-1	70.0	0.310
H-2	78.0	0.090
H-3	85.0	0.530
H-4	99.0	0.410
H-5	107.0	0.180
H-11	108.0	0.020
H-12	109.5	0.005
H-13	110.5	0.040
H-14	111.5	0.008
H-15	112.5	0.020
H-16	114.0	0.005
H-17	116.0	0.010
H-18	117.5	0.006
H-19	119.5	0.009
H-20	121.5	0.010
H-21	122.5	N.D.
H-22	125.0	0.006
H-23	127.0	N.D.
H-24	129.0	0.040
H-25	131.5	0.009
H-26	133.0	N.D.
H-27	133.5	0.005
H-28 T		0.009
H-29 T		0.006
H-30 T		0.004
H-31 T		0.008
H-32 T		0.006
H-33 TC		0.006
H-34 T		0.008

Table 7.2 Results of analysis for gold in bulk and -60 mesh size fraction in Chaliyar river sediments

Sample number*	Weight (g)	Aliquot used	Amount of gold (ug)	Concentration of gold (ppm)
H-1	0.9996	0ml/25m	0.1250	0.31
H-2	1.0020	"	0.0350	0.09
H-3	1.0009	"	0.2120	0.53
H-4	1.0012	"	0.1650	0.41
H-5	1.0015	"	0.0720	0.18
H-6	1.0086	"	0.0341	0.085
H-7	1.0219	"	0.0324	0.079
H-8	1.0001	"	0.0383	0.096
H-9	1.0175	"	0.0324	0.08
H-10	1.0005	"	0.0840	0.21

*Samples H-6 to H-10 represent the -60 fraction of bulk samples H-1 to H-5 respectively

Table 7.3 Summary of Particle size, Flatness Index, Shape factors and Placer type (individual particle data is given in Appendix 7.5)

Sample number	Placer type	Maximum size (mm)	a-axis range (mm)	b-axis range (mm)	Maximum flatness index	Mean flatness index	Shape Factor Mean Shilo	Shape Factor Mean Corey	Number of particles
L14	Tr; PPP	0.68	0.15-0.68	0.08-0.32	14.40	4.08	3.08	0.35	45
L13	Tr; ChP	0.91	0.13-0.91	0.08-0.40	16.67	4.18	3.18	0.39	26
L12	Tr; KP	1.11	0.20-1.11	0.12-0.67	9.83	4.51	3.51	0.29	14
L11	Tr; DPP	1.14	0.15-1.14	0.06-0.49	17.64	6.19	5.19	0.26	34
L10,9	T; CR	0.88	0.18-0.88	0.10-0.63	13.56	5.91	4.91	0.24	29
L8,7,6	T; CR	0.82	0.10-0.82	0.05-0.54	20.50	6.16	5.16	0.26	27
L5	T; CR	0.40	0.11-0.40	0.05-0.24	8.33	3.68	2.68	0.35	36
L4	T; CR	0.31	0.12-0.31	0.06-0.20	6.00	3.91	2.91	0.31	8
L3,2,1	T; CR	0.39	0.13-0.39	0.06-0.14	7.73	4.99	3.99	0.25	9

Notes: Sample number L4 and L3,2,1 were not used for empirical shape classification like roundness and flatness; other morphological data included in text. Sample locations are shown in Figure 7.2

Abbreviations: Tr = tributary; T = trunk; PPP = proximal Punna puzha; ChP = Chali puzha; KP = Karim puzha; DPP = downstream Punna puzha; CR = Chaliyar river

Flatness Index (a+b)/2c

Shilo shape factor = [(large + intermediate)/(2*small dimension)] - 1

Corey shape factor = thickness/√(length x width)

a =long axes

b = intermediate axes (width)

c = small axes (thickness)

Table 7.4 Results of EPMA of gold grains from Chaliyar river (data as given in appendix 7.2 and 7.3)

Sample location	Au wt.%	Ag wt.%	Au wt.% Light	Ag wt.% Light	Au wt.% Dark	Ag wt.% Dark	Number of points analysed
Punna Puzha (Tr)							
Grain 1 (NGRI)	94.35 - 99.32	1.84 - 2.35					10
Mean	96.46	2.12					
Grain 2 (CSIRO)			99.12-99.62	0.35 - 0.83	93.44-94.46	5.29-6.24	8
Mean			99.39	0.58	93.97	5.75	
Karim Puzha (Tr)							
Grain 1 (NGRI)	97.16 - 99.30	0.63 - 0.99					7
Mean	98.50	0.83					
Grain 2 (CSIRO)	99.94 - 99.93	0.03-0.10					3
Mean	99.85	0.06					
Chali Puzha (Tr)							
Grain 1 (CSIRO)	98.96-99.93	0.03 - 0.18					5
Mean	99.16	0.14					
Nilambur (T)							
Grain 1 (CSIRO)	98.15-98.23	1.68-1.73					6
Mean	98.18	1.71					
Arikkode (T)							
Grain 1 (CSIRO)			98.03-99.68	0.26 - 1.88	91.99-92.45	7.44 - 7.96	15
Mean			99.21	0.73	92.11	7.81	

Abbreviations: Tr = tributary; T = trunk
Note: Appendix 7.1 gives results of other trace elements analysed at CSIRO, Australia

Appendix 7.3 gives results regarding EPMA of gold grains carried out at NGRI, Hyderabad
Appendix 7.4 for EPMA conditions and standards (CSIRO, Australia) used in the present study

Plate 7.1

SEM images of gold grains

SEM images of primary (A, E) and typical fluvial (B, C, D, F, G, H) gold particles from the Punna puzha, Chali puzha, Karim puzha and Chaliyar main stem. Sample locations and sample details are summarised in Figure 7.2 and Table 7.3

(Grain no. and Sample no. are given in parentheses)

A, E : Highly irregular, subhedral-anhedral, and complex primary particles from proximal Punna puzha (282/L14) and Chaliyar main stem (48/L5) respectively.

B, C, D : Highly irregular and complex particles from proximal Punna puzha (281/L14), Chali puzha (228/L13), Chaliyar main stem (116/L10,9) respectively.

F,G, H : Gold nuggets typically derived from weathered zones.

F : Near spherical or ovoidal particles from proximal Punna puzha (283/L14). Note the particle has not undergone significant fluvial transport.

G, H : Rod shaped particles from Karim puzha (197/L12) and downstream Punna puzha (176/L11) respectively.

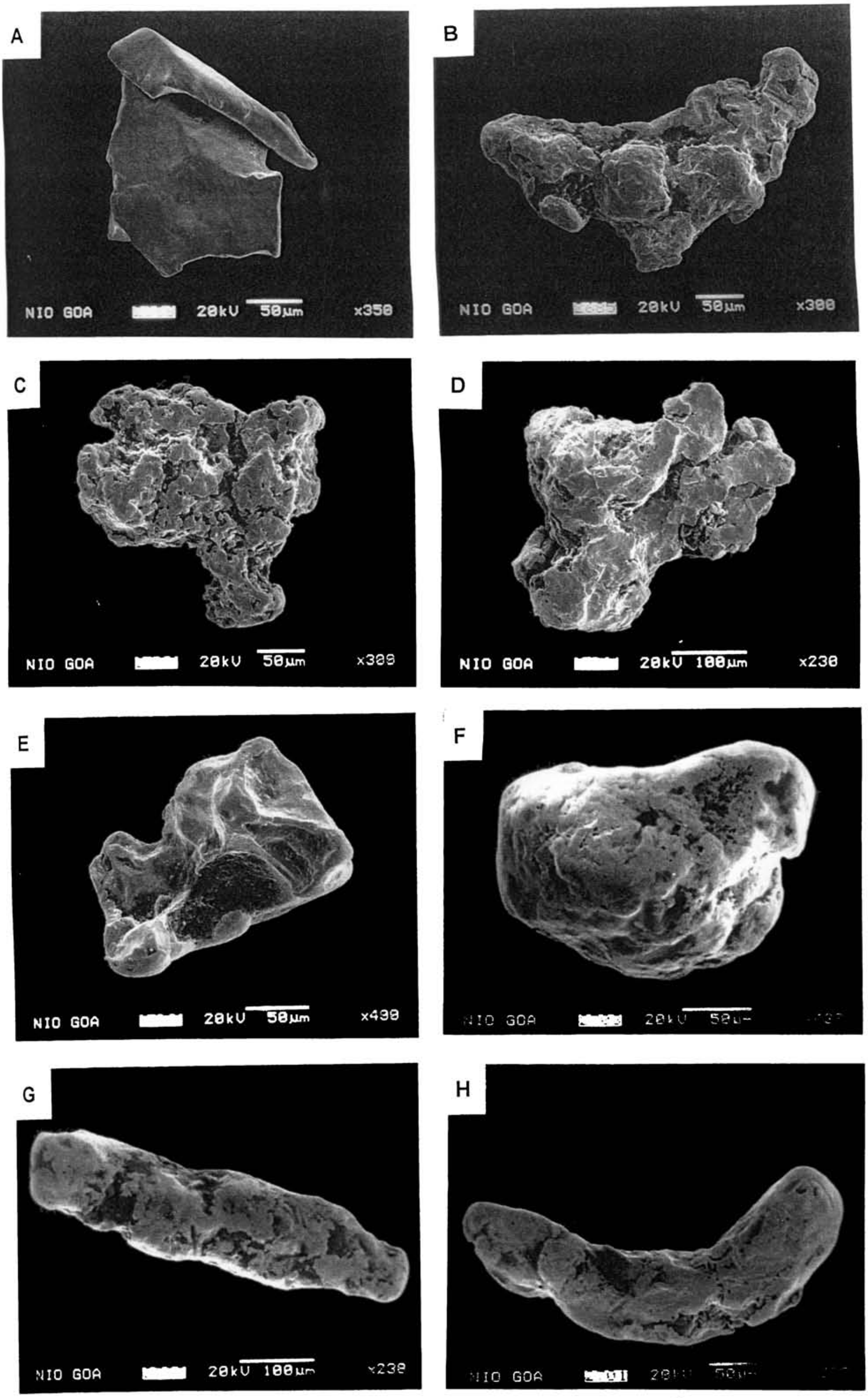

A
NIO GOA 20kV 50µm x350
B
NIO GOA 20kV 50µm x300
C
NIO GOA 20kV 50µm x300
D
NIO GOA 20kV 100µm x230
E
NIO GOA 20kV 50µm x430
F
NIO GOA
G
NIO GOA 20kV 100µm x230
H
NIO GOA

Plate 7.1

Plate 7.2

A, B : Irregular and polygonal grains derived from weathering profiles in the Karim puzha tributary (195/L12) and (196/L12) respectively.

C, D, E : Flattened and folded particles.
C, E from downstream Punna puzha (175/L11), (174/L11); 'C' illustrates how extreme hammering can shear a particle.
D from Chali puzha (229/L13).

F, G, H : Discoid and folded particles from Chaliyar main stem (138/L10,9), (137/L10,9), (136/L10,9).
Note minor infolding and protuberances (D, E, F, H) due to hammering.

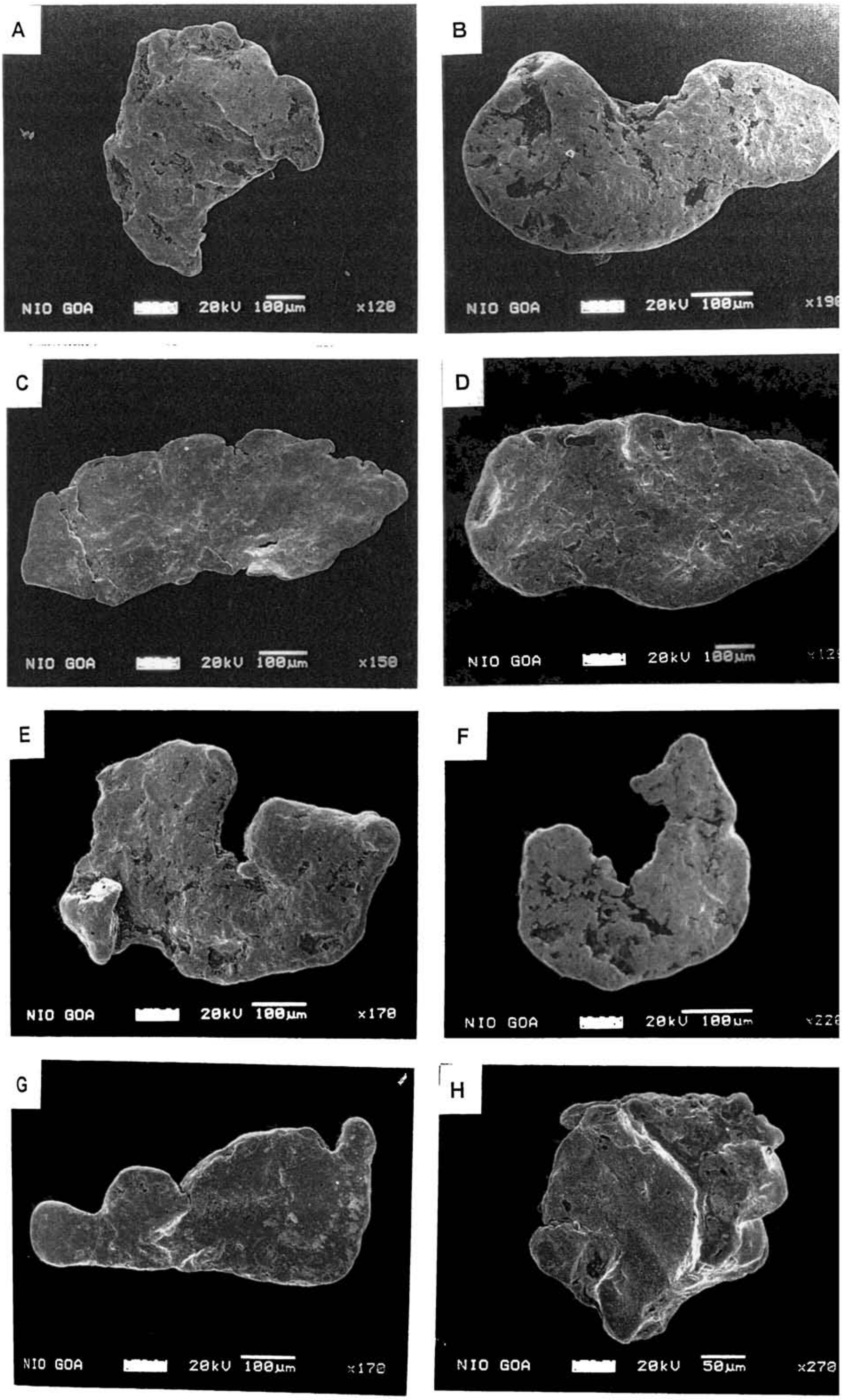

A
NIO GOA 20kV 100µm x120
B
NIO GOA 20kV 100µm
C
NIO GOA 20kV 100µm x150
D
NIO GOA 20kV 100µm
E
NIO GOA 20kV 100µm x170
F
NIO GOA 20kV 100µm
G
NIO GOA 20kV 100µm x170
H
NIO GOA 20kV 50µm x270

Plate 7.2

Plate 7.3

A, B : Discoid and folded particles from main stem with small protuberances due to hammering (114/L10,9), (115/L10,9).

C - H : Highly flattened, folded, irregular particles produced by folding of discoids from Chaliyar mainstem, around Nilambur (77/L8,7,6), (78/L8,7,6), (97/L8,7,6), (98/L8,7,6), (95/L8,7,6), (96/L8,7,6).

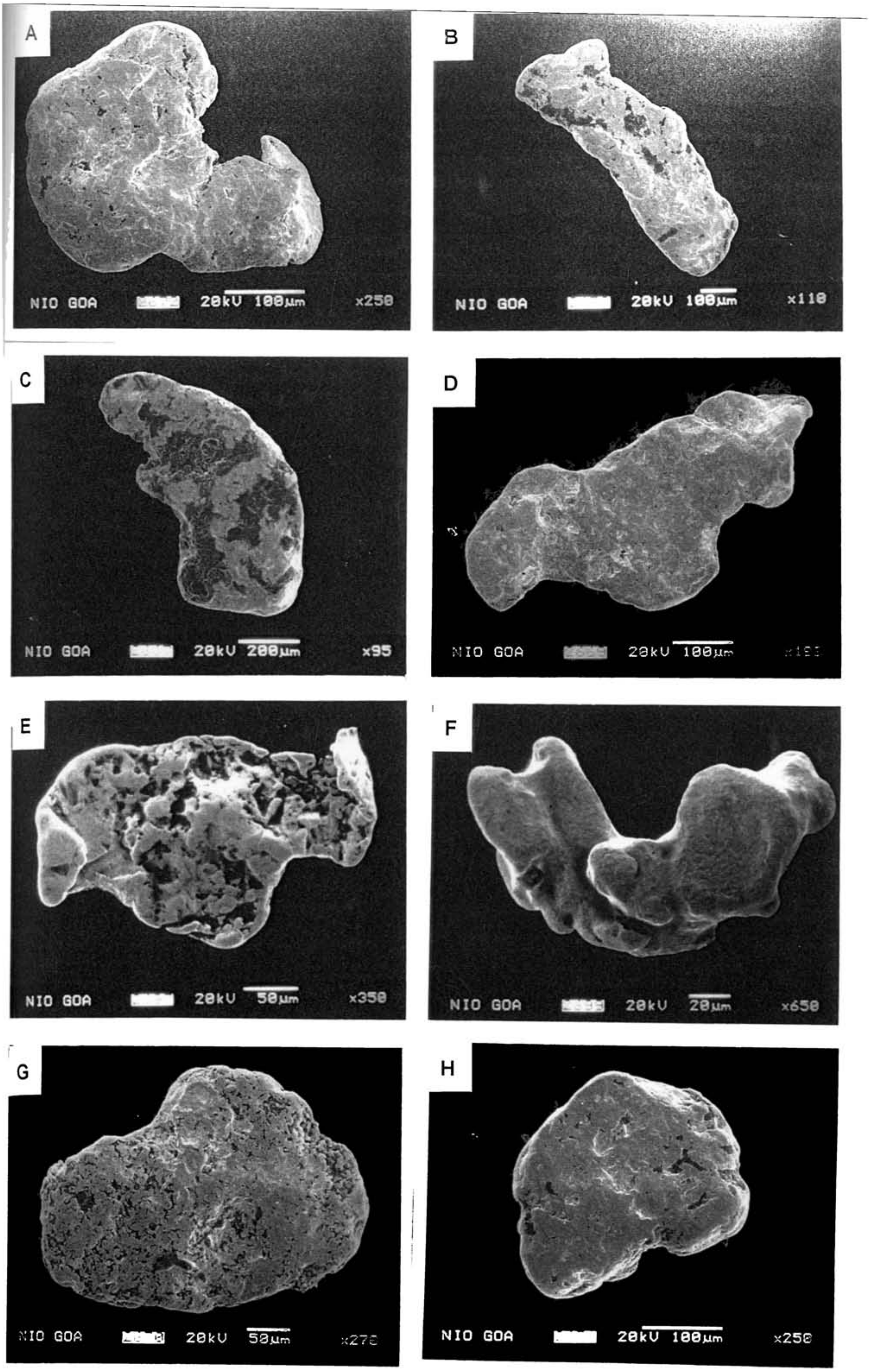

A
NIO GOA 20kV 100µm x250
B
NIO GOA 20kV 100µm x110
C
NIO GOA 20kV 200µm x95
D
NIO GOA 20kV 100µm
E
NIO GOA 20kV 50µm x350
F
NIO GOA 20kV 20µm x650
G
NIO GOA 20kV 50µm
H
NIO GOA 20kV 100µm x250

Plate 7.3

Plate 7.4

A, B : Flattened and irregular particles from main stem showing protuberances formed possibly due to hammering; (68/L8,7,6), (69/L8,7,6).

C, D, F : Gold particle morphology from beyond the downstream limit set for semi-quantitative study.
C and F : flattened grains; (62/L4) and (63/L4) respectively.
D : angular and sub-hedral particle; (64/L4).

E, G : Sub-spherical and rod shaped particles from L5 location (near Vadapuram); (49/L5), (46/L5).
Note the sub-spherical/ovoid shape in G, possibly formed by the flattening, folding and rounding of particles.

H : Highly flattened gold particle from main stem sample (44/L5).

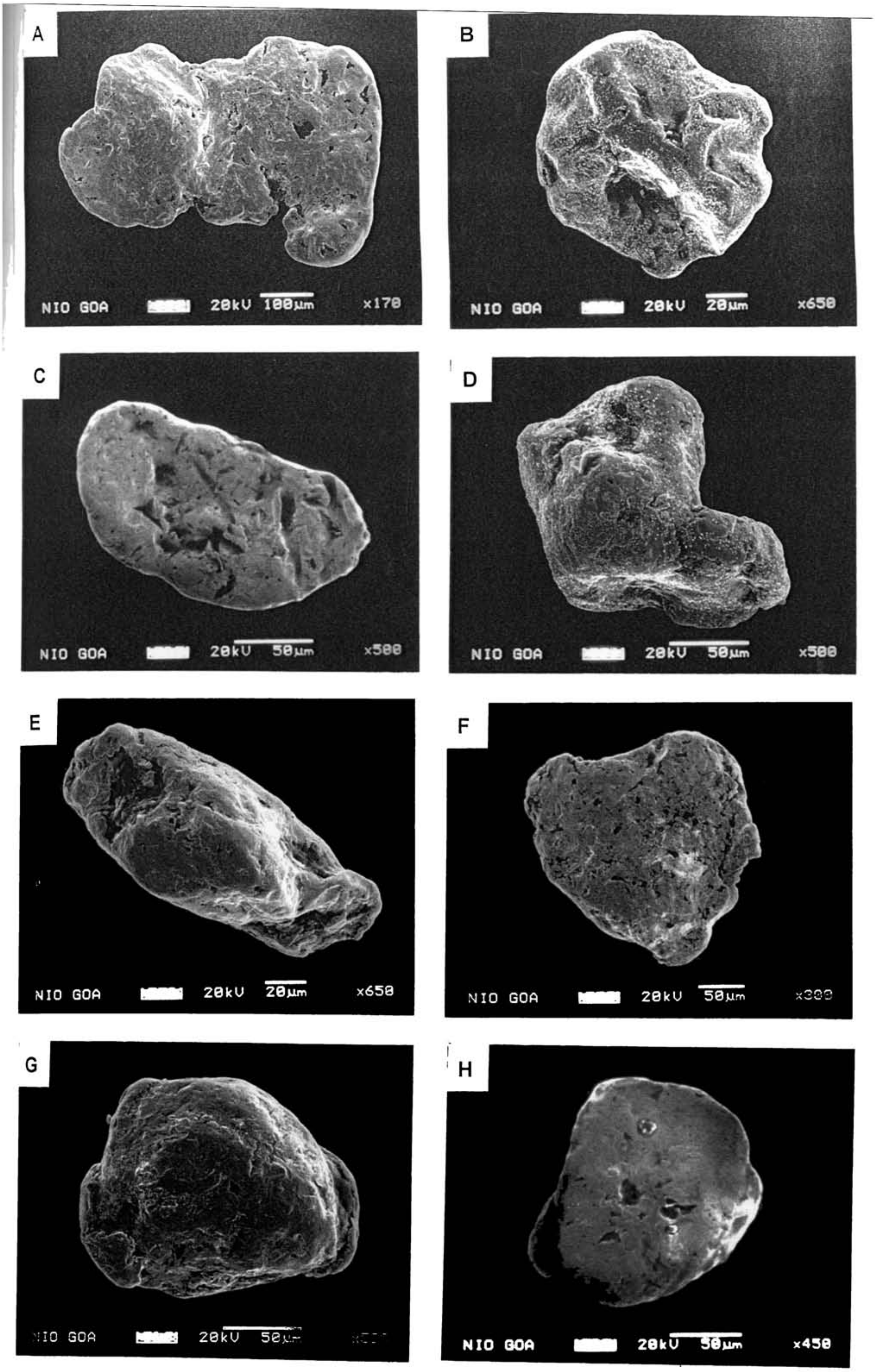

A
NIO GOA 20kV 100µm x170
B
NIO GOA 20kV 20µm x650
C
NIO GOA 20kV 50µm x500
D
NIO GOA 20kV 50µm x500
E
NIO GOA 20kV 20µm x650
F
NIO GOA 20kV 50µm
G
20kV
H
NIO GOA 20kV 50µm x450

Plate 7.4

Plate 7.5

A - E : Morphology of particles from beyond the downstream limit of sampling for the semi-quantitative study; (12/L3), (4/L2), (43/L5), (5/L2), (6/L2).
Note multiply folded particle without flattening occuring between folding events (A, B).
Note sutures annealed by hammering on some grains (E).

F, G : Particle breakage due to extreme flattening and folding; (8/L2), (47/L5).

H : Surface striations seen in gold particle from main stem sample (43/L5).

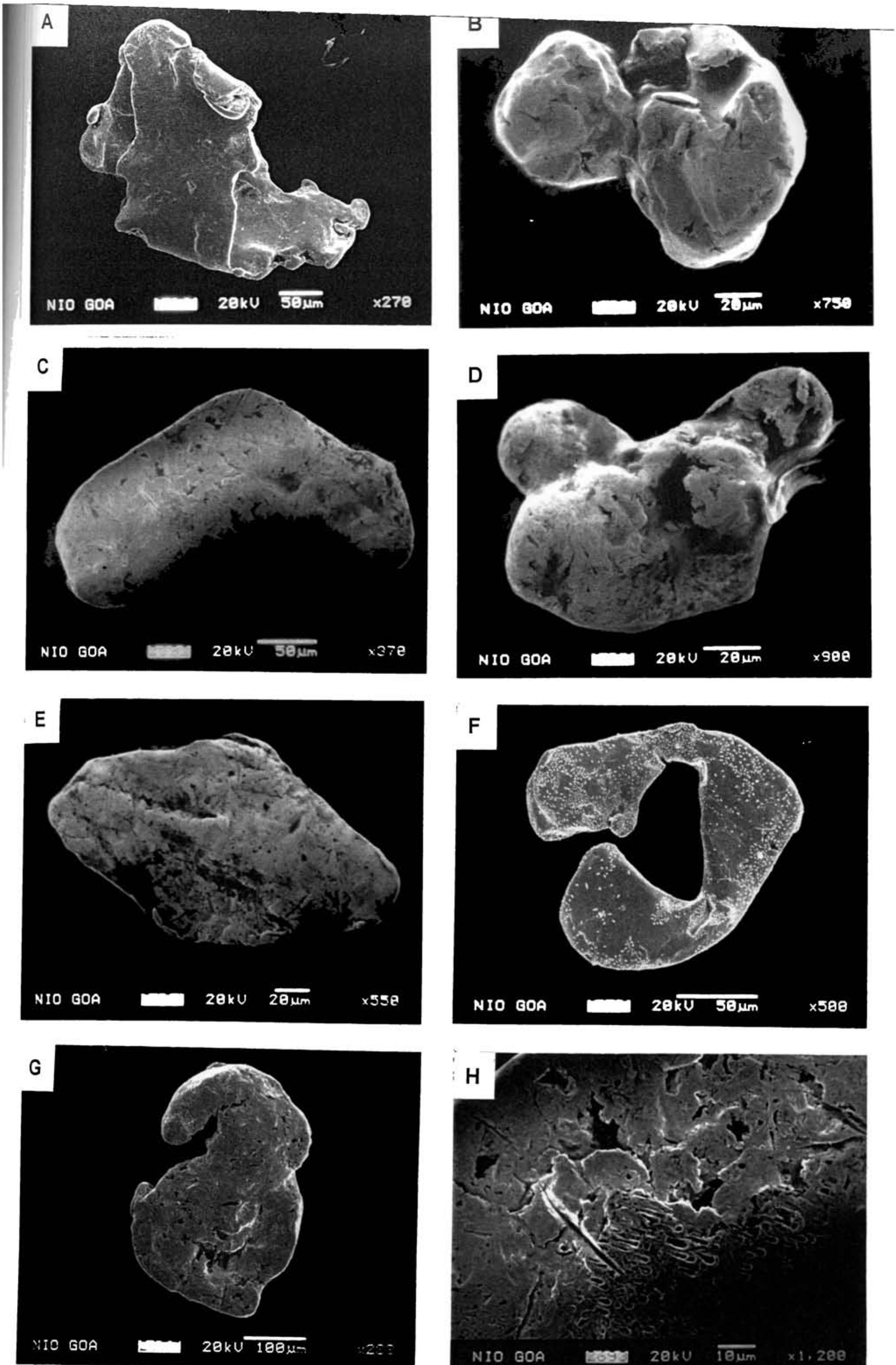

A
NIO GOA 20kV 50µm x270
B
NIO GOA 20kV 20µm x750
C
NIO GOA 20kV 50µm x370
D
NIO GOA 20kV 20µm x900
E
NIO GOA 20kV 20µm x550
F
NIO GOA 20kV 50µm x500
G
NIO GOA 20kV 100µm
H
NIO GOA 20kV 10µm x1,200

Plate 7.5

Plate 7.6

A : Flattened main stem grain showing surface striations (44/L5); note small petal of secondary gold formed in a pit.

B : Primary gold grain showing closely spaced surface striations from proximal Punna puzha; (282/L14).

C : Porous and botryoidal gold nugget from main stem (1/L1).

D : Filaments or dendrites of gold developed on pits/ferruginous oxides (lateritic material) (77/L8,7,6).

E - H : Neo-form gold of spray painted type gold over dull primary grains; (196/L12), (45/L5), (63/L4), (8/L2).

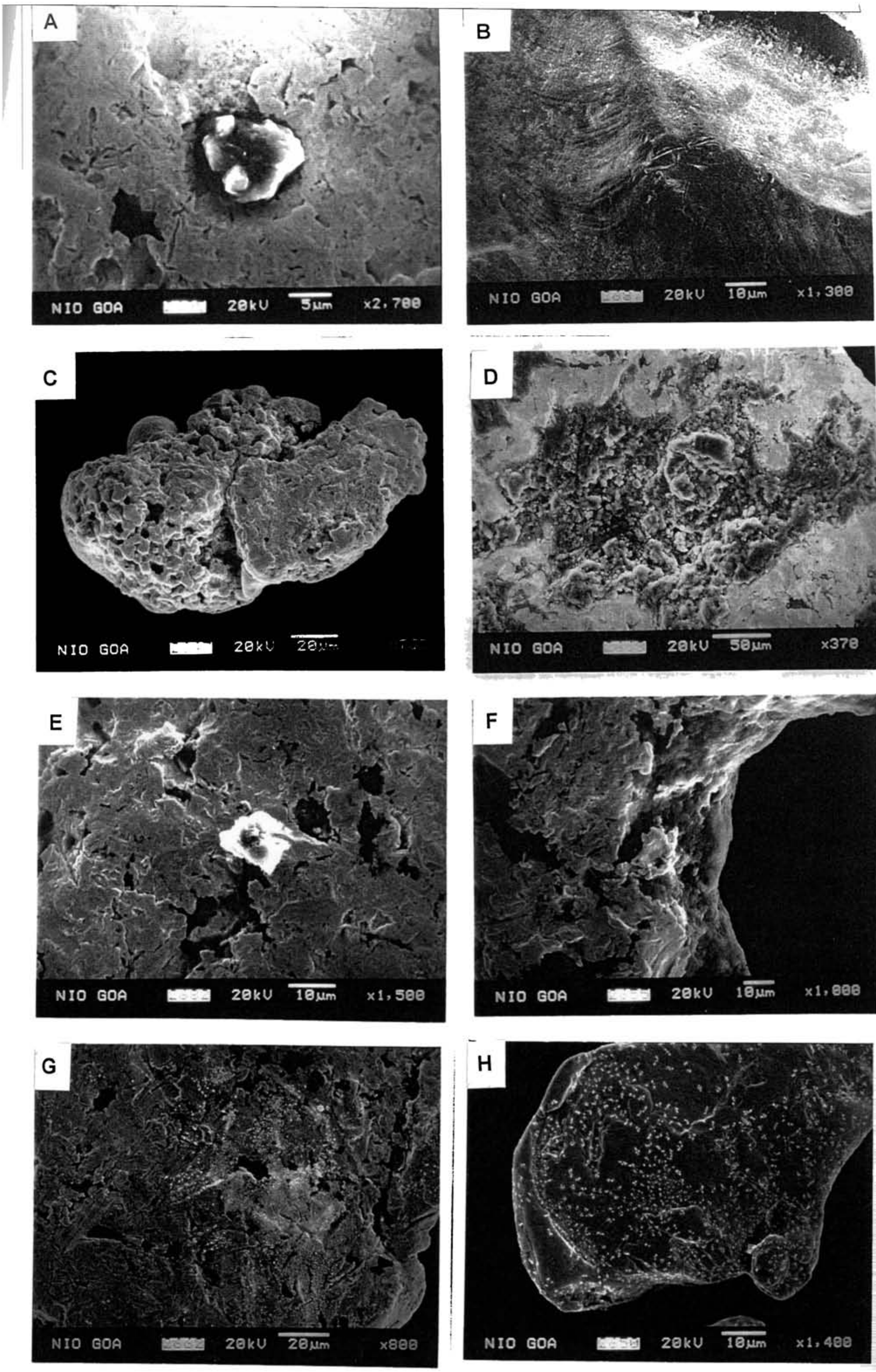

A
NIO GOA 20kV 5µm x2,700
B
NIO GOA 20kV 10µm x1,300
C
NIO GOA 20kV 20µm
D
NIO GOA 20kV 50µm x370
E
NIO GOA 20kV 10µm x1,500
F
NIO GOA 20kV 10µm x1,000
G
NIO GOA 20kV 20µm x800
H
NIO GOA 20kV 10µm x1,400

Plate 7.6

Plate 7.7

A, B, C, D, E : Well rounded gold particles from Karim puzha, downstream Punna puzha and Chaliyar main stem; (187/L12), (168/L11), (126/L10,9), (134/L10,9), (19/L5). Note an oval shaped grain showing secondary material (lateritic ?) within cavities in 'C'.

B : Surface abrasion in well rounded particle from downstream Punna puzha (168/L11).

F : Secondary precipitation seen in cavities of gold grains from Karim puzha tributary (184/L12).

Size in mm : A= 0.35; B= 0.43; C= 0.50; D= 0.29; E= 0.11; F= 1 .0

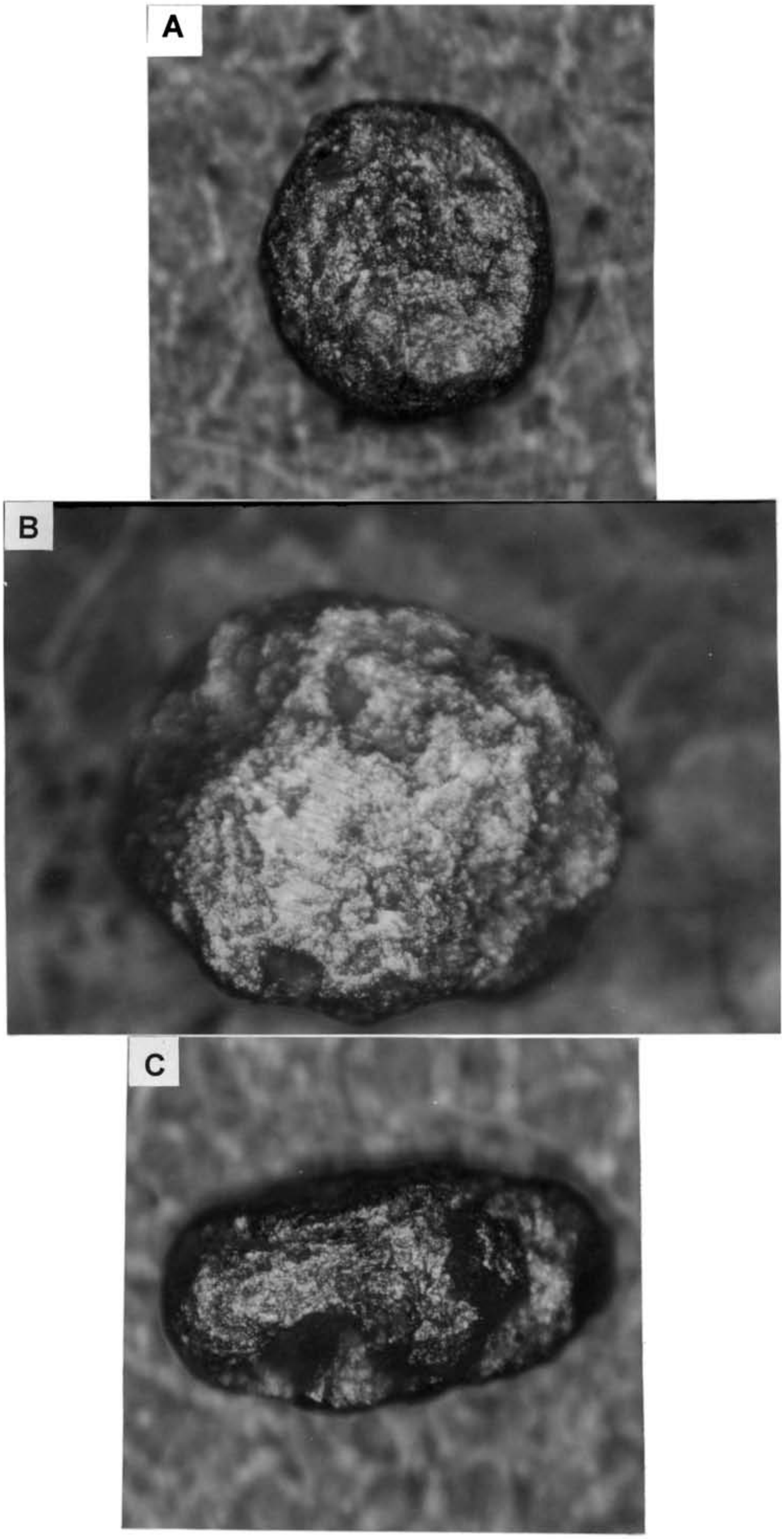


Plate 7.7

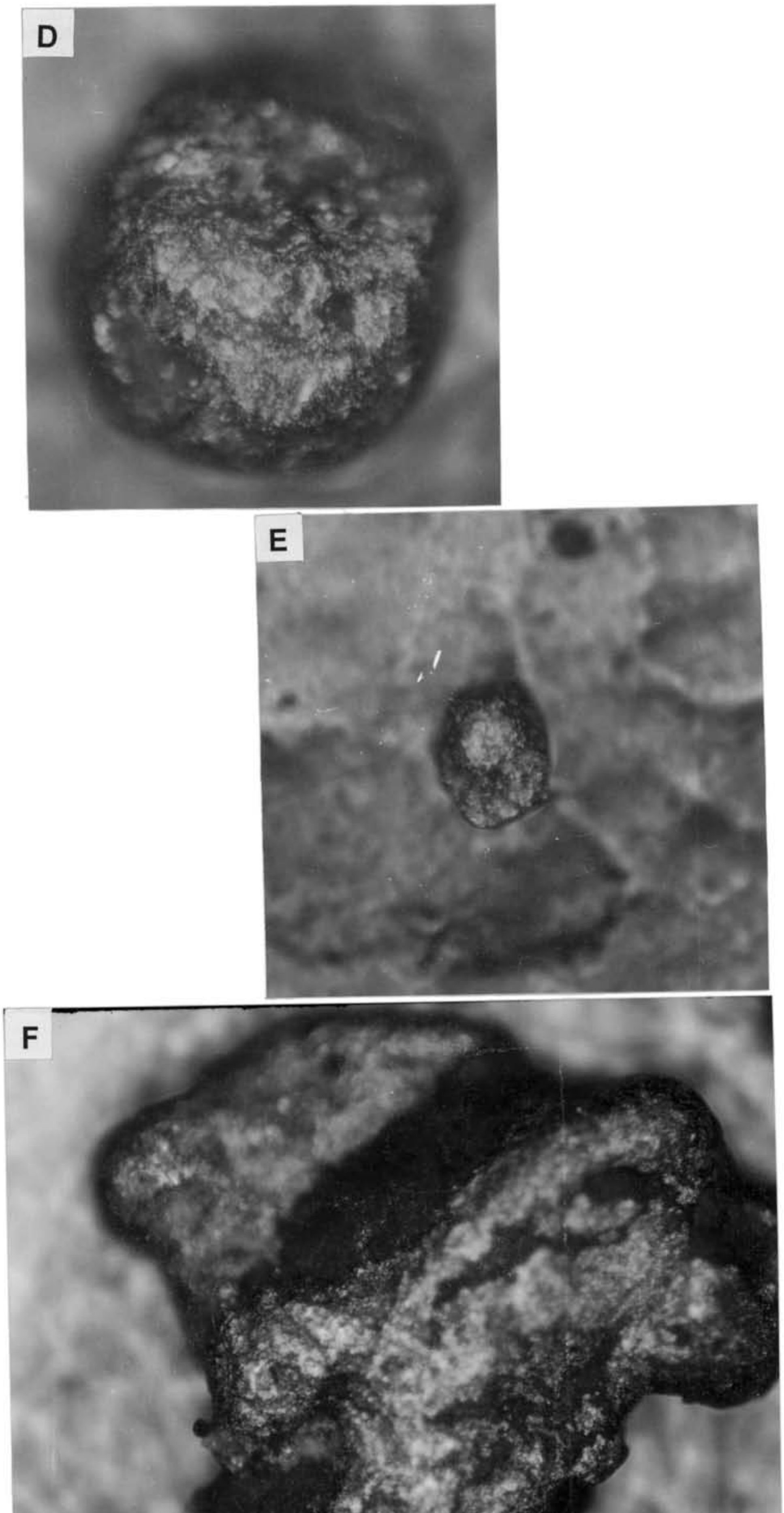


Plate 7.7

SUMMARY

The present work deals with the texture, mineralogy and geochemistry of bedload sediments of the main stream of the Chaliyar basin, a typical small drainage system of the tropics enjoying heavy rain fall and moderate climate, located essentially in the Northern Kerala and flowing over the crystalline rocks (and their laterized duricrust) of the Southern Indian granulite terrain. As the Chaliyar is the major river draining the Wynad Gold Fields and is known for its placer gold occurrences, the thesis gives special emphasize on understanding the nature and distribution of detrital gold in sediments of the basin, while attempting to infer the provenance characteristics and factors involved in the evolution of sediments in general.

The Chaliyar river sediment samples as a whole are gravelly sand (43%), slightly gravelly sand (23%), and slightly gravelly muddy sand (23%) with subordinate amount of sandy gravel (10%). They are moderately to poorly sorted, and in general coarse-skewed and meso to leptokurtic in nature. The mean size of the sediments in the main stem ranges from –0.27 to 2.24 Ø (very coarse to fine sand) while in the tributaries from the headwater region it ranges from –0.5 to 1.86 Ø (very coarse to medium sand). The phi-mean shows moderate fluctuations along the upper reaches of the main stem, between 63 –110 km and fluctuates significantly beyond 107 km from the source. Most of the tributaries have significant amounts of gravel while the lower reaches of the main channel are characterised by the presence of clay. The upper reach sediments are unimodal in nature while those in the lower reaches show alternatively unimodal and polymodal nature along the length of the river. Though many of the sands from the Chaliyar drainage basin are negatively-skewed, the other statistical parameters are similar to those of many of the fluvial sands reported in literature. Their positions in CM pattern indicate that the sediments are transported by mainly rolling and partly by rolling and suspension. The highly variable and complex shape and surface textures of sand-sized quartz grains from the main stem can be directly related to the sedimentary history and transport of the particles. They are indicative of a multi cyclic origin and derivation from mechanical breakdown of

crystalline rocks as well as from the weathering/pedogenic environments where chemical processes dominate.

The observed complexity in sediment distribution and granulometric variation and highly complex textural parameters, especially in the lower reach bedload sediment samples indicate the effects of (i) the temporal heterogeneity of source area; (ii) more than one cycle of sediment genesis, (iii) down stream transport in pulses; and (iv) acceleration of erosion and mobilization of stored sediments mainly in tributaries and in the stable point bars on the main stem.

In general tributary influx is identified as the major cause of natural turbulence in sedimentation.

Mineralogically the Chaliyar basin sands are quartzose. The quartz and feldspar contents in the coarse sand fraction of the basin range from 64 to 86% and 2 to 16% respectively. The Q/F ratio ranges from 4 to 38 with a slight decrease in the lower reaches. Other minerals present include hornblende, pyroxene and heavy minerals like opaques, garnet, rutile, biotite, sphene, silliminite, zircon, apatite and monazite some of which are seen as inclusions in quartz. The sediments are almost devoid of rock fragments and have a sub-arkose affinity. The mineralogical diversities and variation along the profile of the Chaliyar river could be explained mainly by progressive sorting based on densities and shapes of the individual minerals in the upper reaches (63-107 km) while in the lower reaches beyond 107 km they are mainly due to mixing of sands from tributaries having different compositions. The remarkable consistency of mixing patterns as evidenced from rough theoretical or expected average composition of sand (%QF=92,8) for the whole river basin, with that of the actual average composition for the main channel (%QF=92,8) suggests that fluvial sands from major rivers in the basin may indeed retain a traceable signature of their compositional “lineage”. The mineral suites indicate a high grade metamorphic provenance and that the principal control on sand composition in the Chaliyar main stem is the source lithology in the upper and lower reaches of the basin.

The heavy mineral weight percent in the bulk sediments of the main stem varies from 8.9 to 22.0 and from a 4.8 to 27.5 in major headwater tributaries. The mean heavy mineral content in sand is 13.5 wt.% for the whole basin. Plot of sand content against heavy mineral/sand ratio in the lower reaches of the Chaliyar river indicates that samples having low content of sand are enriched in heavies and depleted in light minerals. The near absence of rock fragments, negative correlation between quartz and feldspar and weak positive correlation between phi mean size and total heavy minerals in sand suggest that they form tightly correlated array of textural and mineralogical variables and in turn indicate high degree of sedimentary differentiation in the basin. The clay minerals like kaolinite, gibbsite, goethite and iron-oxides in sediments suggest weathering of feldspar-rich parent rocks and laterization processes in the Chaliyar basin.

The major element composition of Chaliyar bedload sediments in the main channel and the headwater tributaries is seen to be related to the mineralogical and textural characteristics of the sediments, channel morphology and bedrock lithology. The four groups of sediments namely, tributary (TS), upper-reach (US), lower-reach clay-bearing (LCS), and other lower-reach (LS) sediments have chemical characteristics determined by their locations in the basin, bedrock signatures and textural and mineralogical differences. The TS has very high silica (average SiO_2 wt.% 70.9) reflecting the high content of quartz and high FeO(t) and MgO indicating the significant presence of mafics and opaques. In the main channel the SiO_2 and Al_2O_3 contents remain within a small range up to 107 km point but fluctuate highly further beyond due to the variable contents of clay in the lower reaches and inputs of feldspar to the main channel from downstream tributaries.

The SiO_2 and Al_2O_3 variation in relation to the other major oxides reveal linear relationship that reflects the varying contents of quartz, feldspar and clay. The variation, however, is insensitive to the differing bedrock characteristics in the upper and lower reaches of the basin and the larger inflow of quartz-poor sediments from the downstream tributaries that drain dominantly charnockitic terrain. The variations in CaO are influenced by the presence of clay, plagioclase feldspar and mafic minerals like hornblende and garnet in the sediments. FeO(t) and MgO variations with distance show that in the upper and lower reaches of the main stem they are controlled by the bedrock characteristics, hornblende being the main mafic mineral in the upstream derived from the gneissic source rocks and pyroxene in the lower reaches derived from dominantly charnockitic source rocks.

Many of the lower reach samples appear to be immature in terms of their Na_2O content and ratios like Al_2O_3/SiO_2 and Na_2O/K_2O than the upper or middle reach samples due to the addition of plagioclase and K-feldspar by downstream tributaries to the main stem. The high content of CaO and to a certain extent Na_2O but very low K_2O especially in the sands of the lower reaches of Chaliyar main stem point to their derivation from Archean terrain.

The Chaliyar river sediments fall in the greywacke/subarkose chemical space in standard classification diagrams. In terms of their chemical weathering indices like CIA they are comparable with sediments of modern rivers from tropical areas or rivers with extensive flood plain where chemical weathering is predominant. Compared to the Upper Continental Crust (UCC), the average Chaliyar river sediments are enriched in Si and somewhat depleted in Ca, Na, K and Mg. The tectonic settings for the provenance inferred reveal continental margin sediments derived by prolonged chemical weathering of the source areas. The Chaliyar river sediments are depleted with respect to Upper Continental Crust (UCC) in LILE, like Ba, Sr and Rb, which when considered along with the depletion in major elements like K, Ca and Na reflect the LILE depleted nature of the provenance, further modified by weathering. The tributary and upper reach sediments show enrichment of Cr and V suggestive of their enrichment in the soil and weathered products in the source area. From their correlation with TiO_2 and Al_2O_3, it is inferred that V and partially Co are variably concentrated by weathering processes. The Cr, Ni and HFSE contents and ratios among them in the sediments are consistent with an Archean upper crust source. The difference in mafic mineralogy of source regions of the upper and lower parts of the basin is reflected in the contents of several trace elements in samples from the two regions.

The average REE in individual samples from the upper reach bedload sediments are lower (2.7 to 4.68 ppm) when compared to those of the lower reach (5.3 to 12.5 ppm). The upper and lower reach samples are distinguished on plots Eu/Eu* vs La_N/Sm_N and Eu/Eu* vs Gd_N/Yb_N. The Eu/Eu* values range from 0.53 to 0.69 for upper reach samples while the lower reach samples it ranges from 0.8 to 1.03. The lower reach sediment samples have elevated average $LREE_N$ /average $HREE_N$ and La_N/Yb_N ratios when compared to upper reach samples that are attributed to intense weathering in the source area.

The highly fractionated chondrite-normalized REE patterns of the average upper reach as well as lower reach sediments mimic that of the average provenance rocks but for the presence of significant negative Eu anomaly in the upper reach sediments that is suggestive of preferential removal of plagioclase during weathering. However, the lower reach samples have Eu/Eu* values close to unity, consistent with increments in feldspars contributed by tributaries.

The concentration of gold in bulk sediment samples from upper reaches ranges from 0.09 to 0.53 µg/g (averaging around 0.30 µg/g). In the respective –60 ASTM size fraction it ranges from 0.079 to 0.21 µg/g. The gold particle size ranges between 0.12 to 1.2 mm and averages 0.36 mm. Gold is preferentially accumulated in coarser fractions (medium sand and above) due to high density of gold. The highest gold concentrations are seen in upper reach sediments, which are found to be controlled by textural and mineralogical parameters.

The interpretations of grain morphology, semi-quantitative and quantitative data like gold particle outline, roundness and flatness indices evolve in the expected lines with distance of transport. They bring forth that processes of gold entrainment and retention have interacted with such parameters as primary shape and mass characteristics of gold particles in influencing their deposition in riverine morphological sites and the evolution of gold particle shape as it passes downstream through each placer type, such as proximal parts of tributary placers, placers in the first few kilometers downstream from the above and the trunk placers. Mean Shilo and Corey shape factors range between 2.68 to 5.19 and 0.24 to 0.39 respectively and they fall in the intermediate flatness range. Outline shape classes indicate that the complex grains are more dominant in the tributaries and with increasing distance in the main stem, the equant and elongate grains become more dominant. The roundness also shows a shift from angular to sub-rounded in tributaries to sub-rounded to rounded in main stem. The maximum flatness index for tributary samples is 18 while it is 22 for main stem samples and the average Cailleux flatness index for gold particles ranges between ~3.6 to 6.5. Distance estimation based on the empirical shape classification system does not hold good for the gold grain population in the Chaliyar river due to factors like (i) the involvement of multiple sources with different cycles of gold transport, (ii) primary gold particle shape and mass characteristics, (iii) restricted average flatness (47 to 50) and roundness (45.5 to 57) percentages suggesting that the gold particles have undergone shape unification in weathering zone and are more or less derived from lateritic source, and (iv) particle entrainment and retention in trunk placers.

Gold particles from tributary and main stem exemplify leaching processes (either in the fluvial environment or during lateritization processes or both) with outer rims having high purity gold (with 100% Au) while their cores have Ag up to 8% in primary association with Au. In gold grains, Cu ranges up to 0.8%. The pore spaces in some of the gold particles and the differences in pore densities as seen in polished sections could also be due to Cu/Ag removal in the fluvial environment.

As a preliminary estimate it is calculated that around 100 kg (or of the order of a few tens of kilograms) of gold is being transported by the Chaliyar river annually associated with its main channel bedload sediments.

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Appendix - I

THESIS - RELATED PUBLICATIONS

1) Hariharan, G.N. and Nambiar, C.G. (1998). Rare earth element geochemistry of modern detrital sediments from Chaliyar river, Northern Kerala, India. ***Jour. Geol. Soc. Ind.***, v.52, pp.213-217.

2) Hariharan, G.N., Nambiar, C.G., Krishnamoorthy, K.R. and Parthasarathy, R. (1998). Estimation of gold in sediments from the lower reaches of Chaliyar river, Wynad Gold Field, Kerala. ***Indian Minerals***, v.52, pp.107-110.

Appendix 7.1: EPMA data for gold grains analysed at CSIRO, Australia

Sample number	Number of points	Element wt.%									Total	Comment
		As	Fe	Cu	S	Ag	Au	Te	Sb	Pt		
Au standard	1	-0.0115	-0.0269	0.0797	0.0302	0.1991	100.3266	-0.0040	-0.0040	0.0190	100.6082	
Punna	1	-0.0070	0.0071	-0.0015	0.0380	0.8384	100.3327	-0.0031	0.0068	-0.0070	101.2044	Light rim
Puzha (Tr)	2	0.0025	0.0075	0.0035	0.0145	0.3510	100.1005	-0.0022	0.0016	-0.0056	100.4733	"
	3	-0.0036	-0.0181	0.0069	-0.0082	0.5664	99.9864	0.0180	-0.0161	0.0032	100.5349	"
Grain 2	4	0.0121	0.0064	0.1990	-0.0061	5.4546	94.3714	0.0102	-0.0004	-0.0099	100.0373	Dark core
	5	0.0154	-0.0228	0.1846	0.0132	5.2969	94.6646	0.0375	0.0029	-0.0049	100.1874	"
	6	0.0158	-0.0186	0.2671	0.0089	6.1929	92.7966	0.0303	-0.0154	-0.0023	99.2753	"
	7	0.0034	0.0208	0.2606	-0.0007	5.9189	92.8365	0.0478	-0.0071	-0.0220	99.0582	"
	8	-0.0017	-0.0157	0.2342	0.0090	5.7822	93.7216	0.0148	-0.0101	0.0044	99.7387	"
Karim	1	-0.0005	-0.0135	0.2206	-0.0091	0.1025	99.9502	-0.0097	0.0024	-0.0207	100.2222	Light
Puzha (Tr)	2	-0.0097	-0.0227	-0.0016	0.0078	0.0466	100.9812	0.0018	-0.0004	-0.0024	101.0006	"
Grain 2	3	0.0151	-0.0181	0.0069	-0.0041	0.0325	101.1180	0.0173	-0.0336	-0.0009	101.1331	"
Chali	1	0.0096	-0.0058	0.8635	-0.0212	0.1672	100.3029	-0.0095	-0.0092	-0.0191	101.2784	Light
Puzha (Tr)	2	-0.0086	-0.0095	0.0147	0.0259	0.0289	101.6120	-0.0077	-0.0080	-0.0107	101.6370	"
	3	0.0022	-0.0150	0.8625	0.0132	0.1665	99.0075	-0.0047	-0.0163	-0.0156	100.0003	"
Grain 1	4	-0.0088	-0.0151	0.8550	0.0032	0.1789	98.8687	0.0056	-0.0091	-0.0188	99.8596	"
	5	-0.0022	-0.0289	0.8637	-0.0105	0.1515	97.8595	0.0037	-0.0053	-0.0048	98.8267	"
Nilambur (T)	1	-0.0050	-0.0304	0.0777	0.0074	1.7072	97.9819	0.0201	0.0074	-0.0160	99.7503	Light
	2	-0.0051	-0.0075	0.0850	0.0102	1.7319	98.2042	0.0231	-0.0156	-0.0197	100.0065	"
Grain 1	3	-0.0047	0.0057	0.0867	0.0010	1.7316	100.3219	0.0226	0.0009	0.0131	102.1788	"
	4	-0.0079	-0.0172	0.0794	-0.0172	1.6920	99.1077	0.0086	-0.0082	-0.0016	100.8356	"
	5	-0.0135	-0.0203	0.0842	-0.0011	1.7372	99.4906	0.0178	-0.0104	0.0007	101.2852	"
	6	-0.0043	0.0135	0.0893	-0.0097	1.7648	101.5199	0.0225	-0.0074	-0.0259	103.3627	"
Arikkode (T)	1	-0.0016	-0.0135	0.0009	-0.0048	0.4370	101.3177	-0.0032	0.0029	0.0137	101.7491	Light rim
	2	0.0114	-0.0048	0.0052	0.0234	0.2624	101.8671	0.0229	-0.0073	-0.0137	102.1666	"
Grain 1	3	0.0009	-0.0093	-0.0052	0.0084	0.4089	98.4298	0.0160	-0.0059	-0.0120	98.8316	"
	4	0.0066	0.0376	-0.0014	-0.0166	1.8809	98.2577	0.0408	0.0017	0.0055	100.2128	"
	5	0.0035	0.0656	0.0055	0.0085	0.6914	99.0832	-0.0039	-0.0093	-0.0295	99.8150	"
	6	-0.0004	0.0171	0.0036	0.0049	0.7425	100.1480	0.0209	0.0025	0.0079	100.9470	"
	7	0.0065	-0.0027	0.0213	-0.0002	7.9939	92.3631	0.0263	-0.0007	-0.0235	100.3840	Dark core
	8	0.0051	0.0046	0.0172	0.0281	7.3337	91.1296	0.0425	-0.0209	0.0055	98.5454	"
	9	-0.0041	-0.0349	0.0294	0.0127	7.8125	92.1418	0.0583	0.0038	-0.0038	100.0157	"
	10	-0.0112	-0.0379	0.0294	0.0232	7.9227	92.4381	0.0179	-0.0313	0.0005	100.3514	"
	11	0.0003	0.0071	0.0307	0.0115	7.7597	91.8050	0.0207	-0.0204	-0.0301	99.5845	"
	12	-0.0012	-0.0117	0.0259	-0.0015	7.9459	92.8374	0.0254	-0.0129	0.0010	100.8083	"
	13	0.0002	-0.0116	0.0213	-0.0229	7.9524	92.8540	0.0143	-0.0084	-0.0049	100.7944	"
	14	0.0186	0.0059	0.0276	0.0125	7.7505	90.8527	0.0466	-0.0081	-0.0071	98.6992	"
	15	-0.0057	-0.0057	0.0225	0.0178	7.7390	91.1845	0.0576	0.0153	0.0063	99.0316	"

Abbreviations: Tr = tributary; T = trunk

Appendix 7.2: EPMA data for gold grains recalculated to 100% by omitting the negative values in Appendix 7.1

Sample number	Number of points	Element wt.%									Comment
		As	Fe	Cu	S	Ag	Au	Te	Sb	Pt	
Au standard	1	0	0	0.0792	0.0300	0.1978	99.6741	0	0	0.0189	
Punna	1	0	0.0070	0	0.0375	0.8283	99.1205	0	0.0067	0	Light rim
Puzha (Tr)	2	0.0025	0.0075	0.0035	0.0144	0.3493	99.6212	0	0.0016	0	"
	3	0	0	0.0069	0	0.5631	99.4089	0.0179	0	0.0032	"
Grain 2	4	0.0121	0.0064	0.1989	0	5.4517	94.3207	0.0102	0	0	Dark core
	5	0.0154	0	0.1842	0.0132	5.2855	94.4614	0.0374	0.0029	0	"
	6	0.0159	0	0.2690	0.0090	6.2358	93.4398	0.0305	0	0	"
	7	0.0034	0.0210	0.2630	0	5.9734	93.6910	0.0482	0	0	"
	8	0	0	0.2347	0.0090	5.7958	93.9412	0.0148	0	0.0044	"
Karim	1	0	0	0.2200	0	0.1022	99.6754	0	0.0024	0	Light
Puzha (Tr)	2	0	0	0	0.0077	0.0461	99.9444	0.0018	0	0	"
Grain 2	3	0.0149	0	0.0068	0	0.0321	99.9290	0.0171	0	0	"
Chali	1	0.0095	0	0.8521	0	0.1650	98.9735	0	0	0	Light
Puzha (Tr)	2	0	0	0.0145	0.0255	0.0284	99.9316	0	0	0	"
	3	0.0022	0	0.8621	0.0132	0.1664	98.9561	0	0	0	"
Grain 1	4	0	0	0.8558	0.0032	0.1791	98.9564	0.0056	0	0	"
	5	0	0	0.8735	0	0.1532	98.9695	0.0037	0	0	"
Nilambur (T)	1	0	0	0.0779	0.0074	1.7106	98.1766	0.0201	0.0074	0	Light
	2	0	0	0.0850	0.0102	1.7310	98.1508	0.0231	0	0	"
Grain 1	3	0	0.0056	0.0848	0.0010	1.6946	98.1782	0.0221	0.0009	0.0128	"
	4	0	0	0.0787	0	1.6771	98.2357	0.0085	0	0	"
	5	0	0	0.0831	0	1.7144	98.1843	0.0176	0	0.0007	"
	6	0	0.0131	0.0864	0	1.7066	98.1722	0.0218	0	0	"
Arikkode (T)	1	0	0	0.0009	0	0.4294	99.5534	0	0.0028	0.0135	Light rim
	2	0.0112	0	0.0051	0.0229	0.2568	99.6817	0.0224	0	0	"
Grain 1	3	0.0009	0	0	0.0085	0.4136	99.5608	0.0162	0	0	"
	4	0.0066	0.0375	0	0	1.8766	98.0314	0.0407	0.0017	0.0055	"
	5	0.0035	0.0657	0.0055	0.0085	0.6924	99.2244	0	0	0	"
	6	0	0.0169	0.0036	0.0049	0.7355	99.2081	0.0207	0.0025	0.0078	"
	7	0.0065	0	0.0212	0	7.9612	91.9849	0.0262	0	0	Dark core
	8	0.0052	0.0047	0.0175	0.0285	7.4404	92.4551	0.0431	0	0.0056	"
	9	0	0	0.0294	0.0127	7.8079	92.0879	0.0583	0.0038	0	"
	10	0	0	0.0293	0.0231	7.8886	92.0407	0.0178	0	0.0005	"
	11	0.0003	0.0071	0.0308	0.0115	7.7881	92.1413	0.0208	0	0	"
	12	0	0	0.0257	0	7.8801	92.0681	0.0252	0	0.0010	"
	13	0.0002	0	0.0211	0	7.8860	92.0785	0.0142	0	0	"
	14	0.0188	0.0060	0.0280	0.0127	7.8514	92.0359	0.0472	0	0	"
	15	0	0	0.0227	0.0180	7.8138	92.0656	0.0582	0.0154	0.0064	"

Abbreviations: Tr = tributary; T = trunk

Appendix 7.3 EPMA data for gold grains analysed at NGRI, Hyderabad

Sample number	Number of points	Au (wt.%)	Ag (wt.%)	Total
	1	95.45	2.13	97.58
Punna	2	94.98	2.35	97.33
Puzha (Tr)	3	97.14	2.09	99.23
	4	96.09	2.27	98.36
Grain 1	5	96.43	2.20	98.63
	6	96.86	1.96	98.82
	7	94.35	2.23	96.58
	8	96.09	2.16	98.25
	9	97.87	1.84	99.71
	10	99.32	2.01	101.33
	Mean	96.46	2.12	
Karim	1	98.80	0.63	99.43
Puzha (Tr)	2	98.95	0.87	99.82
	3	97.16	0.88	98.04
Grain 1	4	99.30	0.91	100.21
	5	97.73	0.80	98.53
	6	99.26	0.99	100.25
	7	98.32	0.75	99.07
	Mean	98.50	0.83	

Abbreviations: Tr = tributary

Appendix 7.4: EPMA conditions and standards

The following are the analytical conditions used at CSIRO, Australia

Instrument: JEOL 8900R superprobe electron microprobe

Micro analysis conditions:

Accelerating voltage 25kV, beam current 100nA

Element/ line	Counting time	Detection limit	Standards
As; La	40	2 sigma	InAs
211			
Fe; Ka	40	"	FeS_2
569			
Cu; Ka	40	"	$CuFeS_2$
122			
S; Ka	30	"	FeS_2
100			
Ag; La	20	"	Ag
130			
Au; Ma	10	"	Au
1450			
Te; La	40	"	CdTe
200			
Sb; La	40	"	Sb_2S_3
130			
Pt; Ma	40	"	Pt
270			

Above La, Ka, Ma etc. stand for L alpha, K alpha, M alpha lines

Au, Ag, and Pt for metallic standards

Appendix 7.5 showing detailed quantitative data for individual gold particles
(see Table 7.3 for the summary) (mic. = microns)

Grain No.	Location no.	a (mic.)	b (mic.)	c (mic.)	Zing 1	Zing 2	Shilo	Corey	Cailleux
GG 1	L1	145.71	60.00	35.00	0.41	0.58	1.94	0.37	2.94
GG 3	L2	151.20	141.12	20.16	0.93	0.14	6.25	0.14	7.25
GG 4		131.25	81.25	35.00	0.62	0.43	2.04	0.34	3.04
GG 5		125.00	62.50	30.00	0.50	0.48	2.13	0.34	3.13
GG 6		192.00	85.33	20.00	0.44	0.23	5.93	0.16	6.93
GG 7		160.00	87.27	30.00	0.55	0.34	3.12	0.25	4.12
GG 8		168.18	63.64	15.00	0.38	0.24	6.73	0.14	7.73
GG 9		390.63	140.63	75.00	0.36	0.53	2.54	0.32	3.54
GG 12	L3	337.50	161.11	40.00	0.48	0.25	5.23	0.17	6.23
GG 14	L5	161.28	100.80	30.24	0.63	0.30	3.33	0.24	4.33
GG 15		156.24	131.04	80.64	0.84	0.62	0.78	0.56	1.78
GG 16		141.12	70.56	20.16	0.50	0.29	4.25	0.20	5.25
GG 17		231.84	90.72	40.32	0.39	0.44	3.00	0.28	4.00
GG 18		262.08	136.08	90.72	0.52	0.67	1.19	0.48	2.19
GG 19		105.84	90.72	50.40	0.86	0.56	0.95	0.51	1.95
GG 20		211.68	166.32	70.56	0.79	0.42	1.68	0.38	2.68
GG 21		191.52	100.80	70.56	0.53	0.70	1.07	0.51	2.07
GG 22		292.23	142.78	50.40	0.49	0.35	3.32	0.25	4.32
GG 23		226.80	82.30	40.32	0.36	0.49	2.83	0.30	3.83
GG 24		221.76	84.02	30.24	0.38	0.36	4.06	0.22	5.06
GG 25		110.88	68.04	60.48	0.61	0.89	0.48	0.70	1.48
GG 26		136.08	105.84	40.32	0.78	0.38	2.00	0.34	3.00
GG 27		372.96	131.04	30.24	0.35	0.23	7.33	0.14	8.33
GG 28		221.76	146.16	30.24	0.66	0.21	5.08	0.17	6.08
GG 29		307.44	201.60	60.48	0.66	0.30	3.21	0.24	4.21
GG 30		332.64	236.88	60.48	0.71	0.26	3.71	0.22	4.71
GG 31		241.92	124.34	60.48	0.51	0.49	2.03	0.35	3.03
GG 32		302.40	141.12	60.48	0.47	0.43	2.67	0.29	3.67
GG 33		176.40	115.92	40.32	0.66	0.35	2.63	0.28	3.63
GG 34		110.88	89.06	40.32	0.80	0.45	1.48	0.41	2.48
GG 35		226.80	94.10	70.56	0.41	0.75	1.27	0.48	2.27
GG 36		126.00	90.72	85.68	0.72	0.94	0.26	0.80	1.26
GG 37		176.40	84.02	40.32	0.48	0.48	2.23	0.33	3.23
GG 38		191.52	90.72	30.24	0.47	0.33	3.67	0.23	4.67
GG 39		161.28	115.92	40.32	0.72	0.35	2.44	0.29	3.44
GG 40		176.40	99.14	70.56	0.56	0.71	0.95	0.53	1.95
GG 41		151.20	95.76	80.64	0.63	0.84	0.53	0.67	1.53
GG 42		141.12	84.02	20.16	0.60	0.24	4.58	0.19	5.58
GG 43		300.00	116.67	35.00	0.39	0.30	4.95	0.19	5.95
GG 44		165.00	150.00	20.00	0.91	0.13	6.88	0.13	7.88
GG 45		228.57	126.19	60.00	0.55	0.48	1.96	0.35	2.96
GG 46		174.55	121.21	75.00	0.69	0.62	0.97	0.52	1.97
GG 47		400.00	207.84	50.00	0.52	0.24	5.08	0.17	6.08
GG 48		211.77	125.49	60.00	0.59	0.48	1.81	0.37	2.81
GG 49		156.67	51.11	35.00	0.33	0.68	1.97	0.39	2.97
GG 57	L4	206.64	141.12	80.64	0.68	0.57	1.16	0.47	2.16
GG 58		307.44	171.36	70.56	0.56	0.41	2.39	0.31	3.39
GG 59		166.32	75.60	20.16	0.45	0.27	5.00	0.18	6.00
GG 60		115.92	62.14	40.32	0.54	0.65	1.21	0.48	2.21
GG 61		186.48	80.64	40.32	0.43	0.50	2.31	0.33	3.31
GG 62		190.91	93.94	25.00	0.49	0.27	4.70	0.19	5.70
GG 63		246.15	200.00	40.00	0.81	0.20	4.58	0.18	5.58
GG 64		195.46	96.97	50.00	0.50	0.52	1.92	0.36	2.92
GG 66	L8,7,6	604.79	359.55	100.80	0.59	0.28	3.78	0.22	4.78
GG 67		776.15	537.56	60.48	0.69	0.11	9.86	0.09	10.86
GG 68		600.00	346.67	75.00	0.58	0.22	5.31	0.16	6.31
GG 69		113.33	110.00	13.00	0.97	0.12	7.59	0.12	8.59
GG 73		594.71	460.35	60.48	0.77	0.13	7.72	0.12	8.72
GG 74	L8,7,6	473.76	225.08	40.32	0.48	0.18	7.67	0.12	8.67
GG 75		393.12	238.59	50.40	0.61	0.21	5.27	0.16	6.27
GG 76		816.47	423.36	30.24	0.52	0.07	19.50	0.05	20.50
GG 77		800.00	466.67	200.00	0.58	0.43	2.17	0.33	3.17
GG 78		650.00	225.00	75.00	0.35	0.33	4.83	0.20	5.83
GG 82		534.23	288.99	60.48	0.54	0.21	5.81	0.15	6.81
GG 83		272.16	131.04	40.32	0.48	0.31	4.00	0.21	5.00
GG 84		564.47	299.07	50.40	0.53	0.17	7.57	0.12	8.57
GG 85		453.60	265.40	151.20	0.59	0.57	1.38	0.44	2.38
GG 86		282.24	115.92	30.24	0.41	0.26	5.58	0.17	6.58
GG 87		282.24	141.12	120.96	0.50	0.86	0.75	0.61	1.75
GG 88		161.28	50.40	10.08	0.31	0.20	9.50	0.11	10.50
GG 89		423.36	201.60	30.24	0.48	0.15	9.33	0.10	10.33
GG 90		151.20	94.05	70.56	0.62	0.75	0.74	0.59	1.74
GG 91		100.80	80.64	50.40	0.80	0.63	0.80	0.56	1.80
GG 92		120.96	75.60	60.48	0.63	0.80	0.63	0.63	1.63
GG 93		312.48	302.40	50.40	0.97	0.17	5.10	0.16	6.10
GG 94		211.68	90.72	60.48	0.43	0.67	1.50	0.44	2.50
GG 95		375.00	219.44	100.00	0.59	0.46	1.97	0.35	2.97
GG 96		272.73	206.06	75.60	0.76	0.37	2.17	0.32	3.17
GG 97		290.63	129.17	30.24	0.44	0.23	5.94	0.16	6.94
GG 98		166.67	66.67	30.00	0.40	0.45	2.89	0.28	3.89
GG 108	L10,9	735.83	453.60	50.40	0.62	0.11	10.80	0.09	11.80
GG 109		262.08	225.08	30.24	0.86	0.13	7.05	0.12	8.05
GG 110		352.80	120.96	40.32	0.34	0.33	4.88	0.20	5.88
GG 111		302.40	257.04	70.56	0.85	0.27	2.96	0.25	3.96
GG 112		241.92	126.00	100.80	0.52	0.80	0.83	0.58	1.83
GG 113		181.44	110.88	40.32	0.61	0.36	2.63	0.28	3.63
GG 114		400.00	236.36	75.60	0.59	0.32	3.21	0.25	4.21
GG 115		740.00	240.00	100.80	0.32	0.42	3.86	0.24	4.86
GG 116		400.00	206.67	100.80	0.52	0.49	2.01	0.35	3.01
GG 117		342.86	128.57	35.28	0.37	0.27	5.68	0.17	6.68
GG 120		241.92	100.80	70.56	0.42	0.70	1.43	0.45	2.43
GG 121		876.95	624.95	60.48	0.71	0.10	11.42	0.08	12.42
GG 122		453.60	194.84	50.40	0.43	0.26	5.43	0.17	6.43
GG 123		352.80	235.16	35.28	0.67	0.15	7.33	0.12	8.33
GG 124		675.35	325.88	60.48	0.48	0.19	7.28	0.13	8.28
GG 125		443.52	201.60	50.40	0.45	0.25	5.40	0.17	6.40
GG 126		503.99	272.16	90.72	0.54	0.33	3.28	0.24	4.28
GG 127		635.03	184.76	30.24	0.29	0.16	12.55	0.09	13.55
GG 128		252.00	151.20	110.88	0.60	0.73	0.82	0.57	1.82
GG 129		473.76	110.88	50.40	0.23	0.45	4.80	0.22	5.80
GG 130		352.80	201.60	100.80	0.57	0.50	1.75	0.38	2.75
GG 131		322.56	134.37	50.40	0.42	0.38	3.53	0.24	4.53
GG 132		544.31	339.39	80.64	0.62	0.24	4.48	0.19	5.48
GG 133		262.08	201.60	70.56	0.77	0.35	2.29	0.31	3.29
GG 134		292.32	282.24	100.80	0.97	0.36	1.85	0.35	2.85
GG 135		272.16	198.27	30.24	0.73	0.15	6.78	0.13	7.78
GG 136		300.00	208.33	75.60	0.69	0.36	2.36	0.30	3.36
GG 137		613.33	217.78	50.40	0.36	0.23	7.25	0.14	8.25
GG 138		378.95	189.47	30.24	0.50	0.16	8.40	0.11	9.40
GG 143	L11	282.24	151.20	30.24	0.54	0.20	6.17	0.15	7.17
GG 144		201.60	100.80	80.64	0.50	0.80	0.88	0.57	1.88
GG 145		191.52	83.97	45.36	0.44	0.54	2.04	0.36	3.04
GG 146		312.48	161.28	50.40	0.52	0.31	3.70	0.22	4.70
GG 147		151.20	100.80	50.40	0.67	0.50	1.50	0.41	2.50
GG 148		282.24	124.29	30.24	0.44	0.24	5.72	0.16	6.72
GG 149		262.08	90.72	50.40	0.35	0.56	2.50	0.33	3.50
GG 150		231.84	117.63	25.20	0.51	0.21	5.93	0.15	6.93
GG 151		292.32	110.88	50.40	0.38	0.45	3.00	0.28	4.00
GG 152		342.72	124.29	35.28	0.36	0.28	5.62	0.17	6.62

GG 153	L11	282.24	94.05	30.24	0.33	0.32	5.22	0.19	6.22
GG 154		201.60	60.48	45.36	0.30	0.75	1.89	0.41	2.89
GG 155		252.00	100.80	50.40	0.40	0.50	2.50	0.32	3.50
GG 156		231.84	110.88	10.08	0.48	0.09	16.00	0.06	17.00
GG 157		181.44	151.20	40.32	0.83	0.27	3.13	0.24	4.13
GG 158		201.60	80.64	40.32	0.40	0.50	2.50	0.32	3.50
GG 159		413.28	332.64	262.08	0.80	0.79	0.42	0.71	1.42
GG 160		1139.03	272.16	80.64	0.24	0.30	7.75	0.14	8.75
GG 161		655.19	302.40	70.56	0.46	0.23	5.79	0.16	6.79
GG 162		413.28	285.56	100.80	0.69	0.35	2.47	0.29	3.47
GG 163		383.04	342.72	100.80	0.89	0.29	2.60	0.28	3.60
GG 164		473.76	325.88	50.40	0.69	0.15	6.93	0.13	7.93
GG 165		967.67	490.59	60.48	0.51	0.12	11.06	0.09	12.06
GG 166		624.95	252.00	151.20	0.40	0.60	1.90	0.38	2.90
GG 167		836.63	292.32	60.48	0.35	0.21	8.33	0.12	9.33
GG 168		433.44	282.24	45.36	0.65	0.16	6.89	0.13	7.89
GG 169		534.23	231.84	35.28	0.43	0.15	9.86	0.10	10.86
GG 170		584.63	248.67	100.80	0.43	0.41	3.13	0.26	4.13
GG 171		715.67	215.00	30.24	0.30	0.14	14.39	0.08	15.39
GG 172		372.96	201.60	80.64	0.54	0.40	2.56	0.29	3.56
GG 173		131.04	80.64	80.64	0.62	1.00	0.31	0.78	1.31
GG 174		600.00	288.89	80.64	0.48	0.28	4.51	0.19	5.51
GG 175		769.23	297.44	30.24	0.39	0.10	16.64	0.06	17.64
GG 176		384.62	102.56	65.52	0.27	0.64	2.72	0.33	3.72
GG 184	L12	1108.79	670.31	161.28	0.60	0.24	4.52	0.19	5.52
GG 185		292.32	211.68	166.32	0.72	0.79	0.52	0.67	1.52
GG 186		503.99	201.60	50.40	0.40	0.25	6.00	0.16	7.00
GG 187		352.80	332.64	80.64	0.94	0.24	3.25	0.24	4.25
GG 188		705.59	483.83	60.48	0.69	0.13	8.83	0.10	9.83
GG 189		604.79	369.63	151.20	0.61	0.41	2.22	0.32	3.22
GG 190		594.71	268.83	100.80	0.45	0.37	3.28	0.25	4.28
GG 191		372.96	302.40	151.20	0.81	0.50	1.23	0.45	2.23
GG 192		393.12	268.83	100.80	0.68	0.37	2.28	0.31	3.28
GG 193		493.91	248.67	60.48	0.50	0.24	5.14	0.17	6.14
GG 194		201.60	120.96	40.32	0.60	0.33	3.00	0.26	4.00
GG 195		581.82	393.94	150.00	0.68	0.38	2.25	0.31	3.25
GG 196		625.00	258.33	75.60	0.41	0.29	4.84	0.19	5.84
GG 197		540.00	130.00	120.00	0.24	0.92	1.79	0.45	2.79
GG 204	L13	655.19	184.76	25.20	0.28	0.14	15.67	0.07	16.67
GG 205		534.23	225.08	60.48	0.42	0.27	5.28	0.17	6.28
GG 206		695.51	225.08	50.40	0.32	0.22	8.13	0.13	9.13
GG 207		403.20	178.11	120.96	0.44	0.68	1.40	0.45	2.40
GG 208		836.63	332.64	151.20	0.40	0.45	2.87	0.29	3.87
GG 209		483.83	265.40	50.40	0.55	0.19	6.43	0.14	7.43
GG 210		493.91	399.87	70.56	0.81	0.18	5.33	0.16	6.33
GG 211		191.52	120.96	90.72	0.63	0.75	0.72	0.60	1.72
GG 212		161.28	110.88	75.60	0.69	0.68	0.80	0.57	1.80
GG 213		171.36	151.20	100.80	0.88	0.67	0.60	0.63	1.60
GG 214		362.88	141.12	105.84	0.39	0.75	1.38	0.47	2.38
GG 215		171.36	126.00	90.72	0.74	0.72	0.64	0.62	1.64
GG 216		322.56	225.08	60.48	0.70	0.27	3.53	0.22	4.53
GG 217		262.08	131.04	60.48	0.50	0.46	2.25	0.33	3.25
GG 218		292.32	147.87	50.40	0.51	0.34	3.37	0.24	4.37
GG 219		241.92	94.05	40.32	0.39	0.43	3.17	0.27	4.17
GG 220		171.36	83.97	55.44	0.49	0.66	1.30	0.46	2.30
GG 221		161.28	131.04	110.88	0.81	0.85	0.32	0.76	1.32
GG 222		231.84	100.80	50.40	0.43	0.50	2.30	0.33	3.30
GG 223		161.28	131.04	70.56	0.81	0.54	1.07	0.49	2.07
GG 224		171.36	107.55	85.68	0.63	0.80	0.63	0.63	1.63
GG 225		221.76	151.20	55.44	0.68	0.37	2.36	0.30	3.36
GG 226		131.04	100.80	75.60	0.77	0.75	0.53	0.66	1.53

GG 227	L13	161.28	120.96	90.72	0.75	0.75	0.56	0.65	1.56
GG 228		270.83	183.33	70.56	0.68	0.38	2.22	0.32	3.22
GG 229		909.09	400.00	60.48	0.44	0.15	9.82	0.10	10.82
GG 237	L14	332.64	110.88	35.28	0.33	0.32	5.29	0.18	6.29
GG 238		332.64	124.29	55.44	0.37	0.45	3.12	0.27	4.12
GG 239		262.08	90.72	85.68	0.35	0.94	1.06	0.56	2.06
GG 240		302.40	131.04	100.80	0.43	0.77	1.15	0.51	2.15
GG 241		403.20	322.56	25.20	0.80	0.08	13.40	0.07	14.40
GG 242		252.00	104.13	65.52	0.41	0.63	1.72	0.40	2.72
GG 243		201.60	80.64	30.24	0.40	0.38	3.67	0.24	4.67
GG 244		110.88	90.72	75.60	0.82	0.83	0.33	0.75	1.33
GG 245		312.48	161.28	50.40	0.52	0.31	3.70	0.22	4.70
GG 246		372.96	198.27	50.40	0.53	0.25	4.67	0.19	5.67
GG 247		282.24	194.84	30.24	0.69	0.16	6.89	0.13	7.89
GG 248		342.72	117.63	60.48	0.34	0.51	2.81	0.30	3.81
GG 249		171.36	151.20	90.72	0.88	0.60	0.78	0.56	1.78
GG 250		181.44	120.96	25.20	0.67	0.21	5.00	0.17	6.00
GG 251		383.04	144.45	50.40	0.38	0.35	4.23	0.21	5.23
GG 254		211.68	83.97	75.60	0.40	0.90	0.96	0.57	1.96
GG 255		241.92	94.05	93.74	0.39	1.00	0.79	0.62	1.79
GG 256		201.60	191.52	60.48	0.95	0.32	2.25	0.31	3.25
GG 257		292.32	127.71	55.44	0.44	0.43	2.79	0.29	3.79
GG 258		191.52	191.52	40.32	1.00	0.21	3.75	0.21	4.75
GG 259		211.68	211.68	50.40	1.00	0.24	3.20	0.24	4.20
GG 260		282.24	221.76	120.96	0.79	0.55	1.08	0.48	2.08
GG 261		352.80	198.27	80.64	0.56	0.41	2.42	0.30	3.42
GG 262		302.40	174.68	30.24	0.58	0.17	6.89	0.13	7.89
GG 263		322.56	114.21	25.20	0.35	0.22	7.67	0.13	8.67
GG 264		292.32	131.04	115.92	0.45	0.88	0.83	0.59	1.83
GG 265		262.08	144.45	100.80	0.55	0.70	1.02	0.52	2.02
GG 266		181.44	94.05	35.28	0.52	0.38	2.90	0.27	3.90
GG 267		231.84	94.05	90.72	0.41	0.96	0.80	0.61	1.80
GG 268		292.32	181.44	45.36	0.62	0.25	4.22	0.20	5.22
GG 269		675.35	231.84	45.36	0.34	0.20	9.00	0.11	10.00
GG 270		221.76	157.95	55.44	0.71	0.35	2.42	0.30	3.42
GG 271		151.20	131.04	25.20	0.87	0.19	4.60	0.18	5.60
GG 272		211.68	124.29	40.32	0.59	0.32	3.17	0.25	4.17
GG 273		191.15	80.64	70.56	0.42	0.88	0.93	0.57	1.93
GG 274		151.20	131.04	25.20	0.87	0.19	4.60	0.18	5.60
GG 275		151.20	87.39	60.48	0.58	0.69	0.97	0.53	1.97
GG 276		191.15	90.72	40.32	0.47	0.44	2.50	0.31	3.50
GG 277		171.36	127.71	80.64	0.75	0.63	0.85	0.55	1.85
GG 278		231.84	184.76	156.24	0.80	0.85	0.33	0.75	1.33
GG 279		272.16	120.96	60.48	0.44	0.50	2.25	0.33	3.25
GG 280		171.36	100.80	50.40	0.59	0.50	1.70	0.38	2.70
GG 281		359.38	104.17	80.00	0.29	0.77	1.90	0.41	2.90
GG 282		206.25	118.75	40.00	0.58	0.34	3.06	0.26	4.06
GG 283		221.05	140.35	99.50	0.63	0.71	0.82	0.56	1.82

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