# STUDIES ON ILMENITE OF CHAVARA AND MANAVALAKURICHI DEPOSITS, SOUTHWEST COAST OF INDIA

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# CERTIFICATE

I certify that this thesis entitled **"Studies on ilmenite of Chavara and Manavalakurichi deposits, southwest coast of India"** has been prepared by Shri. Ajith G. Nair 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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# CHAPTER 1

# PLACER GEOLOGY AND INDIAN DEPOSITS

## 1.1 INTRODUCTION

Placers are mineral deposits that have been formed by the mechanical concentration of mineral particles from weathered debris. They occur in beaches, rivers, dunes and offshore areas. The minerals that constitute the placer deposits are resistant to chemical breakdown and have high density and durability. For any placer deposit to form the conditions to be satisfied are the following:

1) a primary source for the mineral placers, which are usually crystalline rocks.
2) a suitable weathering environment, which is required to liberate the minerals from the source rocks and
3) agents of transportation like running water, wind etc. which move the placer-forming minerals to the zones of concentration where they are deposited.

The placer deposits encompass a wide range of minerals having varying specific gravity. For the sake of convenience, they have been classified (Emery and Noakes, 1968) as (1) heavy heavy minerals with specific gravity between 6.8 and 21. eg: native gold, cassiterite etc., (2) light heavy minerals with specific gravity between 4.2 and 5.3. eg: ilmenite, rutile, monazite, zircon, and (3) those with densities falling between 2.9 -4.1. eg: garnet, sillimanite, hypersthene etc. Folk (1974) divided the heavy minerals into four groups, based on their physical and chemical nature namely, opaques, micas, ultra-stables and meta-stables.

Placers are classified into (1) eluvial, (2) alluvial or fluvial, (3) eolian, (4) beach placers, and (5) fossil placers based on their mode of transportation and site of deposition

1. Eluvial placers: These are formed upon the release of minerals from the rock matrix. This is the embryonic stage in the development of placers. The noted Indian examples are the cassiterite, columbite and tantalite placer deposits of Bastar district, Bihar.

2. Alluvial placers: They represent the next stage in the placer formation. The heavy minerals are introduced into the fluvial system by the action of runoff, gravity or by the erosion process of streams themselves. The most famous examples are the deposits of the Colorado river which caused the famous California Gold Rush in the 19h century. In India, xenotime deposits in the Singhbhum shear zone are fluvial in origin.

3. Eolian deposits: wind is the agent of concentration of these deposits. They occur in arid/semi arid regions, where the influence of wind is strong and sufficient vegetation does not exist to cover the soil. Wind action progressively concentrates the heavy minerals by blowing away the associated light minerals, and over a period of time give rise to the deposits eg: Australian gold deposits. Teri deposits of Tamil Nadu are also of eolian origin.

4. Beach placers: Such placers are formed by the interacton of the terrestrial processes with the coastal hydrodynamics. The heavy minerals among the sediments, that are contributed to the sea by various processes of transportation are selectively panned and sorted and then deposited at suitable locations, by the action of waves and currents. The factors controlling the formation of beach placers are geomorphology of the area, climate, drainage pattern, coastal processes, neotectonics etc.

The heavy minerals are concentrated by a combination of these processes in the upper part of the beach, where the action of the wind may erode them and form heavy mineral rich coastal dune deposits (Kudrass, 2000). Most of the important deposits of ilmenite, rutile, zircon, monazite and garnet are found in form of beach placers. India has some of the largest placer deposits along its coast.

5. Fossil placers: Placers formed in the geologic past, which were removed from the sub aerial environment by factors like changes in climate and/or epirogenic movements and eustasy are called fossil placers or submerged placers. Along the coast of India considerable reserves of fossil placers are known to occur, which are formed during the previous low stands of sea level. The fossil placers may form the source of recent deposits.

## 1.2 FACTORS CONTROLLING THE FORMATION OF PLACER DEPOSITS

Climate: Climate influences the weathering processes, which ultimately decomposes the rock matrix and liberate the minerals. Tropical to subtropical climate promotes chemical weathering, which has given rise to a decomposed stage of crystalline rocks called laterites. This could be considered as a pre-concentration process of the placer minerals. Most of the rich placer deposits of the world are in tropical regions.

Drainage Pattern: The fluvial processes act as a conduit of sediment transport from the source rock to the zone of concentration. In their youthful stages, the erosive power of rivers is strong and they release heavy minerals from the parent rock and transport them down stream. In Kerala, the west flowing rivers with their steep gradient was the major agent of erosion and transportation of sediments to the Arabian Sea, which gave rise to the placers along the southwest coast.

Coastal processes: The beach deposits are essentially a result of the coastal hydrodynamics of rivers and currents. The waves sort out the heavy minerals and transport them onshore based on their size and specific gravity. The direction and strength of the coastal currents and the geomorphology of the coast determine the location of the deposit.

## 1.3 PLACER DEPOSITS OF INDIA

The history of placer deposits as a source of economic minerals began with the discovery of monazite in the beach sands of Manavalakurichi (Tipper, 1909). This was first worked in 1911 and rapidly developed with the establishment of $TiO_2$ (titania) pigment industry in Europe and America. In early 1930's, India accounted for 80% of the total ilmenite production in the world.

However, by the 1950's the ilmenite production marked a sudden decrease in the country. This owes, in part to the discoveries of new deposits in Australia and Canada and the presence of undesirable impurity like chromium and ferric iron in Indian ilmenite. However, after the nationalization of all the major deposits, the national production of ilmenite and rutile has increased over the years. The current production rate is of the order of 140,000 tons for ilmenite and 6000 tons for rutile. Governmental concerns like the Indian Rare Earths Ltd. and Kerala Minerals and Metals Ltd. are involved in the production and marketing of the placer minerals.

Over the last few decades new deposits have been discovered in placers like Chattarpur in Orissa, Visakapatnam in Andhra Pradesh in the east coast and Ratnagiri in Maharashtra in the west coast of the country. Along the coastal stretches of Tamil Nadu, deposits of heavy minerals occur in the inland areas in the form of Teri sands. The current reserves of the placer minerals in India, are as follows; 278 million tonnes (MT) of ilmenite 13.49 MT of rutile, 18 MT of zircon, 7 MT of monazite, 84 MT of sillimanite and 86 MT of garnet (AMD, 2000). The major placer concentrations of India are located along the east and west coasts (Fig. 1.1).

### 1.3.1 Ratnagiri Deposits

High concentrations of placer minerals occur along Jaigarh and Vijaydurg in Maharastra particularly in the bays of Kalbadevi, Mirya and Ratnagiri bays. Heavy minerals range from 1-91% with 1-52% of ilmenite. Ilmenite assays about 50-52% $TiO_2$. The placers in Bhatya, Purangad and Goankhede contain high content of magnetite (40-60%) and limonite/haematite (25-35%) with relatively low ilmenite (5-25%). The total reserves of the heavy minerals are estimated to be around 3.45 MT. The break up of the reserves of the constituent minerals in million tonnes is as follows: 1.67 of ilmenite, 0.08 of leucoxene, 0.009 of zircon, 0.53 of magnetite (Ali et al, 1998).

The provenance of the heavy minerals is attributed mainly to the Deccan Trap provinces. The Kaladgis consist of both granitic and metamorphic rocks and the gneissic basement of south Konkan forms a secondary source of heavy minerals. Extensive areas of Deccan Traps are overlain by laterites.

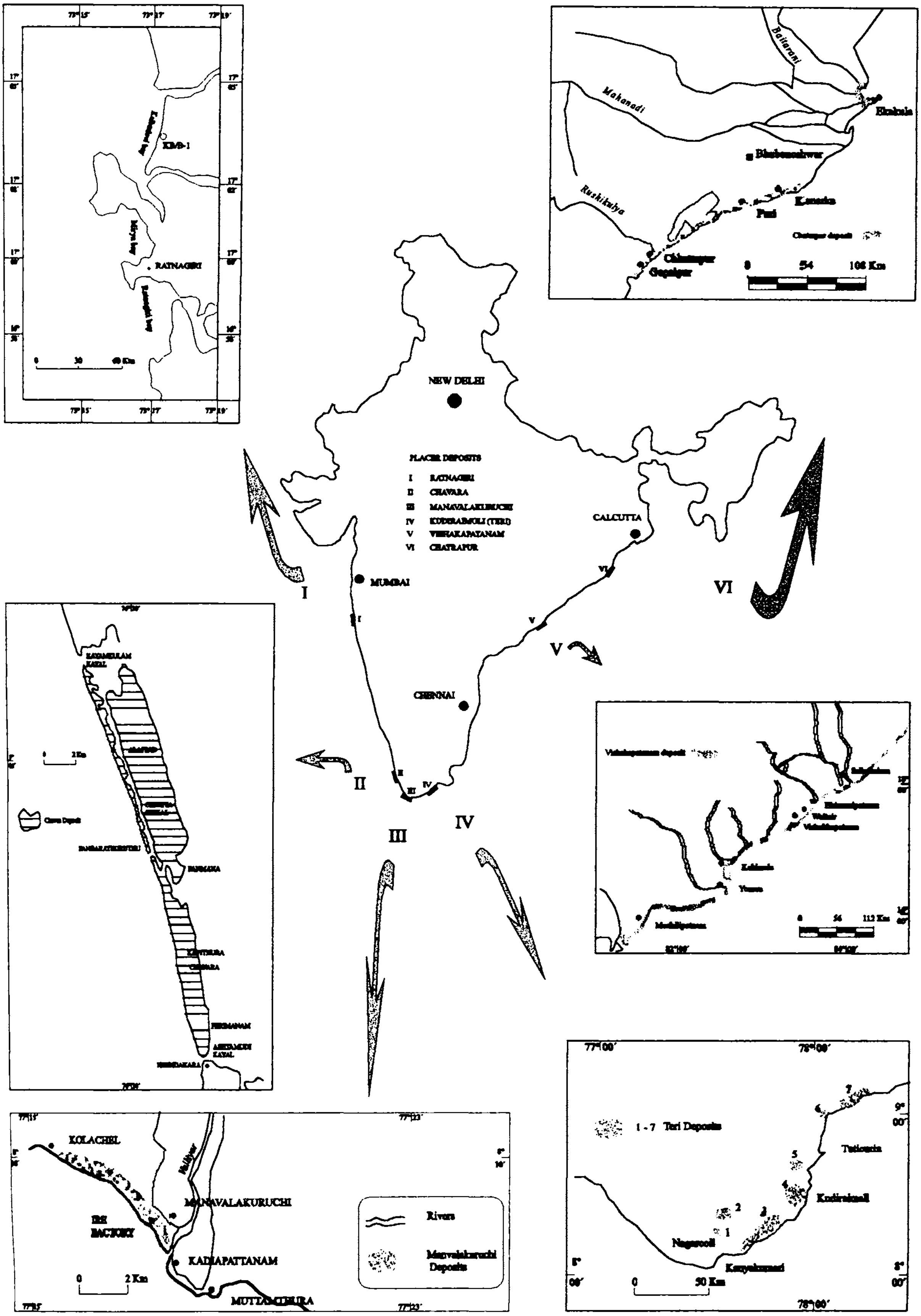


Fig. 1.1 Major placer deposits of India

### 1.3.2 Chavara Deposit

This deposit, popularly known as Quilon deposit is one of the largest and richest in the world. It extends to about 22 km with a width of around 500m. It stretches as a barrier beach between Neendakara, at the mouth of Ashtamudi estuary and Kayamkulam. The deposit has a maximum depth of 15m and is estimated to contain about 12.7 MT of ilmenite, 1 MT of rutile, 1.9 MT of zircon and 0.41 MT of monazite and 6 MT of sillimanite (Fig. 1.2).

The heavy mineral content of the beach is about 50% with a maximum of about 80% in some places. Of these, ilmenite accounts for the bulk of the heavy minerals consisting of about 68%. The content of other minerals are as follows: leucoxene 2%, rutile 7%, zircon 6% monazite 1%, sillimanite 14% etc. The garnet content is rather low compared to other deposits (0.35%). However, the ilmenite of Chavara has a high content of chromium (0.12% $Cr_2O_3$) and ferric iron (24.18% $Fe_2O_3$), which render it undesirable for pigment manufacture, in spite of high $TiO_2$ content of 60% (Ali et al, 1998).

The dunes behind the beach are rich in heavy minerals constituting about 40-50% of sediment. The estuarine systems adjacent to the Chavara deposits, namely, Ashtamudi and Kayamkulam contain about 3 to 7.5 % of heavy minerals. Investigations by Atomic Minerals Division and Geological Survey of India have revealed that off Kayamkulam-Anjengo sector, the heavy minerals occur as discontinuous patches with concentration ranging from 5-20%. The total reserves in lakes and seabed are estimated to be about 57,860, 151 tonnes (Soman, 1997).

The placer deposits are located in the southwest margin of the Indian Shield, where the Archean lower crust metamorphosed to granulite grade

Fig.1.2 Beach placer sands of the Chavara deposits

Fig.1.3 Beach placer sands of the Manavalakurichi deposits

as represented by the charnockite-khondalite rocks and migmatite gneisses (Refer Fig. 3.1). The khondalite suite comprises a series of inter layered metapelite rocks like garnet sillimanite gneiss ± graphite, garnet biotite gneisses and garnet quartz feldspar and their migmatised equivalents. Locally bands of biotite rich gneisses and calc silicates also occur. At many places khondalites are intercalated with bands of charnockites and pyroxene granulites. Progressive transformation of khondalite to charnockites and retrogressive of charnockites to garnet biotite are observed.

The charnockite suite consists of hypersthene and/or diopside bearing granulite, their retrograded equivalents, hornblende granulites and hornblende biotite gneisses. The Achankovil lineament forms the general boundary of the khondalite migmatite complex from the northern charnockite terrain. Along this zone, discontinuous patches of cordierite bearing gneisses occur within an 8-10 km wide zone. The rocks of the area show evidences of polyphase deformation and they are intruded by dolerite dykes and pegmatites.

The western fringe of the area is covered by the tertiary formations of the Malabar Super Group with a maximum thickness of 628m consisting of varigeated sand stone, clays and lignite belonging to Warkkalai beds and fossiliferous limestone, sandy and calcareous clays and sands of Quilon beds. The crystalline rocks and Tertiary sequence are overlain by laterites at many localities. They are the products of three phases of lateritisation.

The hinterland of the Chavara deposit is drained by nine rivers from Neyyar in the south to Periyar in the north and is bordered on the coast by the estuarine system the evolution of which is inextricably linked to the evolution of the deposit.

### 1.3.3 Manavalakurichi Deposit

It is located in the Kanyakumari district of Tamil Nadu. It is one of the oldest known deposits, which was first worked for its monazite. The deposit extends to a length of about 6 km, from the north of Muttom promontory to Kolachel, with an average width of 45m (Fig. 1.3).

The total average content of heavy minerals is around 39%. Of these, ilmenite forms the major constituent (24%), with rutile (1.8%), leucoxene (0.9%), zircon (2%), monazite (1%), sillimanite (3.5%) and garnet (5.5%). Ilmenite contains about 56% $TiO_2$. The monazite has a total of 58% REE oxides and 8% $ThO_2$. The total reserves of heavy minerals in the Manavalakurichi-Kolachel stretch are estimated to be about 1.6MT. Ilmenite amounts to about 1 MT. The reserves of other minerals estimated are as follows): 0.075 MT of rutile, 0.035 MT of leucoxene, 0.082 MT of zircon, 0.043 MT of monazite, 0.23 MT of garnet, 0.14 MT of sillimanite and about 6850 tonnes of kyanite. The area north of Kolachel to Midalam has been found to contain workable deposits of heavy minerals estimated to about 0.5 MT. The reserves of ilmenite and rutile are worked out to be around 0.31 MT and 15,300 tonnes respectively (Chandrasekharan et al, 1988).

The hinterland consists of khondalite suite of Archean age composed of quartzite of arenaceous facies, calc silicates with pockets of crystalline limestone representing calcareous facies and quartz garnet sillimanite graphite schists and gneisses or argillaceous facies. Charnockite intrudes into khondalites in some places.

Muttom and adjacent areas are characteristised by extensive occurrence of fine sandy loam known as Teris. Their genetic prqperties are disputed, though generally an aeolian origin is ascribed to them. The vegetation is of semi arid type and the topography is similar to Bad Lands of the United States.

### 1.3.4 Teri sands of Tamil Nadu

These inland deposits occur along parts of south eastern coast of Tamil Nadu in the form of Teris in parts of Tirunelveli, Chidambranagar, Ramanathapuram districts. They standout prominently in the area, at elevations of 30-60 m. They occur as widely separated isolated patches with dimensions ranging from a few hectares to about 6000 hectares. They are found about 0.1-10 km inland from the beach placers in a semi arid setting. Seven such deposits with an aggregate area of 144 $km^2$ have been identified (Krishnan et al, 1994). They are Navaladi-Periathalai, Kudiraimoli, Sattankulam, Kuttampuli, Surangudi, Kilakarai and Kulathur with heavy mineral concentration ranging from 6-17%. The average mineral grade is about 10% with reserves of 123 MT (AMD, 2000). The split up of the total reserves are as follows, 77.2 MT of ilmenite, 4.03 MT of rutile, 3.9 MT of leucoxene, 7.07 MT of zircon, 1.2 MT of monazite, 12MT of garnet and 17 MT of sillimanite.

The Sattankulam and Kudiraimoli deposits have reserves of about 22 and 13 MT of total heavy minerals respectively. While Sattankulam area contains about 14.3 MT of ilmenite, 1.4 MT of rutile, 1.1 MT of leucoxene, 0.96 MT of zircon, 0.21 MT of monazite and 4.3 MT of sillimanite, the Kudiraimoli deposit contain estimated reserves of minerals as follows: 9.3 MT of ilmenite , 0.63 MT of rutile, 0.38 MT of leucoxene, 0.46 MT of zircon, 0.11 MT of garnet and 1.9 MT of sillimanite (Ali et al, 1998).

The Teris are believed to be formed due to aeolian action in an arid-semi arid climate. The sediments owe their origin to the Eastern and Western Ghats, tertiary sandstones and limestones and Cuddalore beds.

### 1.3.5 Visakapatnam Deposit

Black sand deposits occur in the Visakapatnam-Bhimunipatanam coastal stretch of Andhra Pradesh for a length of 37 km with a width ranging from 150m to 1 km. The average heavy mineral concentration is about 20% with ilmenite (9%), rutile (0.6%), monazite (0.09%), zircon (0.3%), garnet (4%) and sillimanite (4%). The total reserves are worked out to be between 6.18-2.88 MT of ilmenite. The split up of the reserves of the different minerals encompass 5.8 MT of ilmenite, 0.03 MT of magnetite and 0.005 MT of garnet (Anon, 1983). The assay of this mineral is about 49% $TiO_2$. The coastal stretch between Kakinada and Tandava river contain a total heavy mineral content of about 70 MT with a grade of about 12%. The reserves of ilmenite are about 30 MT (AMD, 2000).

The lithology of the area consists of charnockite and khondalite group of rocks of the Eastern Ghats Province. Granites and granitic gneisses also exist in the rock assemblages. A part of the sediment for the deposit formation may have been brought by large drainage systems like Krishna and Godavari, which flow through a range of lithologic successions like Deccan Traps, Cuddapah sedimentary formations and tertiaries of Rajamundry sequence.

### 1.3.6 Chatarpur Deposit

This deposit falls in the Ganjam district of Orissa near Gopalpur. It extends to a length of 22 km with an average width of 1.54 km. The average grade of the heavy mineral is about 20% with ilmenite (8.80%), rutile (0.38%), monazite (0.27%), garnet (6.70%), zircon (0.31%) and sillimanite (3.40%). The total reserves are estimated to be 46.61 MT with a grade of about 20.22% (Ali et al, 1998). Of these, ilmenite constitutes about 20.3 MT. The assay of $TiO_2$ in ilmenite is around 50%.

The heavy minerals are essentially derived from the Eastern Ghats province, which consists of khondalites, charnockites with their migmatised equivalents. Frequent exposures of anorthosites have been reported.

## 1.4 BACKGROUND AND OBJECTIVES

Among the minerals present in various placer occurrences, ilmenite deserves an important stress due to its industrial implications and its high concentration. An indepth study on the this mineral is essential on its mode of concentration, temporal relation between placer formation and geomorphic cycles, quality differentiation of ilmenite in various locations, influence of lateritisation and other exogenic processes on the mineral, mineralogical and geochemical factors capable of distinguishing spatially different ilmenite deposits to gain an understanding on the origin and nature of the present placer ilmenite.

Systematic studies are lacking on the chemical hetrogenity within individual deposits. Trace element distribution is important as they too determine the quality of the ilmenite ore. Nowadays, the titanium pigment production has become so specialized that the absence or presence of a particular trace element determine the suitability of the ore to be manufactured to pigments for definite end use. In addition, they serve as geochemical signatures of the various weathering processes and provenance characteristics. Such investigations are lacking for the Indian deposits, in spite of our abundant reserves of ilmenite. Since the ilmenite ore in a deposit is a composite of differently weathered fractions, the mineral phases, which form subsequent to alteration is an indicator on the quality of the deposit and point to the structural and chemical changes accompanying alteration. Physical properties like magnetism and specific gravity are dependent on the ferrous-ferric ratios in the mineral and thus are direct functions of alteration patterns of the mineral. The occurrence of intergrowths of other mineral phases with ilmenite holds a definite clue on their genesis and the accompanying temperature and pressure conditions. They also influence the ore quality and the beneficiation techniques to be adopted in the mineral processing. Investigations tracing the physical and chemical changes of ilmenite, since their release from the country rocks to being deposited as constituent of placer deposits in the beach, through the progressive weathering environments of laterite, sedimentary rocks, rivers and estuarine systems have not, so far been attempted. Studies as above mentioned are not only useful to unravel the different physical and chemical changes accompanying ilmenite alteration, but also, given the economic significance of ilmenite, would have industrial implications. Only a multifarious approach encompassing the above aspects can give a broad and clear picture of the different physcio-chemical characteristics of ilmenite under different geologic set ups and its associated alteration phases. The present investigation is taken up in this backdrop with the following objectives

- Determination of associated minerals/phases associated with the alteration of ilmenite using XRD, TGA and Mössbauer methods
- Characterization of ilmenite concentrates from Chavara and Manavalakurichi deposits as regards the variation of physical properties like magnetism with compositional change
- Sequence of tropical alteration stages in ilmenite grains from the latertisation process to placer concentration in the beach
- A comparison of the Chavara and Manavalakurichi beach placer deposits from the aforesaid perspectives

# CHAPTER 2

# ILMENITE RESEARCH- A REVIEW

Although research on ilmenite started only at the turn of the century, it has now emerged as an important topic of discussion among scientists due to its relevance as the common ore of titanium, the metal of the 21st century. Of particular interest to mineralogists and metallurgists is the alteration of ilmenite, since the $TiO_2$ content is progressively enriched along with the change in iron ions and trace elements.

## 2.1 TRENDS OF RESEARCH ON ILMENITE

A pioneering attempt in this direction was made when Palmer (1909) termed the alteration product arizonite, which is high in ferric content. Later Creitz & Mcvay (1949) and Spencer (1948) suggested that occurrences of leucoxene might be actually a product of the weathering of ilmenite. Cannon (1949) correlated the variation of titania content with the degree of alteration of the mineral. Gillson (1950) stated that arizonite is not a weathered product of ilmenite, questioning the view proposed by Overholt et al (1950). Later on it was established that alteration is accompanied by removal of ferrous ions from the mineral structure (Lynd et al, 1954) and the crystal lattice undergoes progressive break down (Bailey and Cameron, 1957).

Further, the composition of the alteration product of ilmenite has been attempted by many workers. According to Flinter (1959), ilmenite undergoes alteration to form a mixture of ilmenite and 'diffuse' rutile. Kharkanavala and Momin (1959), from studies on Chavara leucoxene concluded that it contained rutile, pseudo brookite, anatase and haematite; while Buddington & Lindsley (1964) suggested a mixture of haematite, rutile, anatase and ilmenite. Temple (1966) & Teufer and Temple (1966) described the alteration product of ilmenite as pseudorutile, since it has a pseudo hexagonal structure and similar properties of rutile and described its chemical composition. Dyadchenko & Khatutseva (1960) assigned a variable composition for this mineral. Gevorkyan and Tanavayev (1964) described this alteration phase as a mixture of titanium and iron oxides, while Grey et al (1983) specified pseudorutile as a mixture of goethite rutile intergrowths. Haggerty (1976) and Rumble (1976) are of the view that ilmenite alters essentially to rutile *and haematite. The geochemical significance of ferrous to ferric* conversion during alteration has been studied in detail (Shirane et al, 1962; Ronov & Taroshovsky, 1971; Carranza & Cox, 1979; White, 1990).

Bailey et al (1956) first formulated the delineation and identification of the stages of alteration of ilmenite on the basis of microscopic observations and X-ray studies. By progressive alteration, ilmenite evolves into 1) patchy ilmenite 2) amorphous Fe-Ti oxides and ultimately 3) leucoxene. Braksdale (1966) argued that rutile is the final end product of ilmenite alteration before passing through an amorphous stage. Grey & Reid (1975) and Dimanche & Bartholme (1976) explained the alteration of ilmenite as a two-stage mechanism in which ilmenite forms pseudorutile in groundwater environment, followed by a process of rutile formation by a dissolution precipitation process (Grey & Reid, 1975; Pakharykov et al, 1979; Frost et al, 1983). The question of alteration of ilmenite to rutile being a continuos process or not has had been hotly debated (Chaudhuri et al, 1988,1989). Mucke and Chaudhuri (1991) is of the opinion that it is a continuous process and they have named yet another alteration phase between ilmenite and pseudorutile. However, Chaudhuri & Newsley (1990) and Hugo & Cornell (1991) opined that the end product of leucoxene can form directly from ilmenite, without the formation of intermediate phases. The terminology for the various stages of alteration as proposed by Frost et al (1983), namely, ferric ilmenite, hydrated ilmenite, pseudorutile and leucoxene is now commonly accepted.

The important changes in physical properties during weathering include considerable variation in magnetic susceptibility and density (Bailey et al, 1956; Flinter, 1959 and Braksdale, 1966). Comprehensive studies in this direction were further taken up by Hoffman (1975) and Wort and Jones (1980). Frost et al (1986), Garanin et al (1989) and Braksdale (1966) studied the porous nature of altered crystals and its effect on density.

An increasing application of chemical studies of ilmenite, is for the delineation of provenance and age of sediments. Though Hutton (1950) & Buddington & Lindsley (1964) had mentioned the compositional variation of the mineral, according to heterogeneity of source rocks, the potential of this mineral for provenance research were first established by Blatt (1967) and Force (1976). Darby (1984) used this method to differentiate the origin of various deposits of coastal Virginia and the variation among the drainage basins with the aid of statistical methods. Similar techniques were used to determine the major fluvial contributor of the US Atlantic shelf (Darby, 1990) and quaternary beach sediments (Darby and Evans, 1992). Morad & Aldahan (1982; 1986) argued that diagenesis could alter the chemical fingerprints in a sedimentary unit. The viability of this method was stressed by Basu and Molinaroli (1989). Anand & Gilkes (1985) investigated the weathering of ilmenite along the weathering profiles of laterites. Morad & Aldahan (1986) studied the alteration of ilmenite under various chemical environments and their trace element variation. Grigsby (1992) established the threshold limits of certain trace elements in ilmenite depending on the petrogenesis of the source.

Gibb et al (1969) carried out the Mössbauer analysis of natural ilmenite samples from throughout the world and suggested this method as a quick and simple method of determining the weathering undergone by the mineral samples. The efficiency of this relatively new technique is described by Ahmed et al (1992), who determined the exsolution mineral phases of ilmenite of Cox's Bazar beach, Bangladesh.

Sinha (1979) argued that the solubility of ilmenite concentrates varies depending on the degree of alteration undergone by the ilmenite grains. Hoselmann (1987) and Välimaa (1993) pointed out that the fine-grained nature of the alteration products of ilmenite could cause problems during the titania production process. Hayes (1985) and Chernet (1999) used microscopic observations of the textural relationships of the different alteration phases in ilmenite grains, complemented by chemistry to highlight the importance of these analyses on understanding the suitability of the ilmenite ore to different processing techniques.

The microscopic examination and interpretation of the mineral and the delineation of the weathering environments involved were undertaken by several authors (Ramdohr, 1959; Morad & Aldahan, 1986; Frost et al, 1983; Darby, 1984, Darby et al 1985; Hugo & Cornell, 1991; Mucke and Chaudhuri, 1991; Grigsby, 1992).

## 2.2 ILMENITE RESEARCH IN INDIA

The provenance of the southwest placer deposits has been a matter of dispute since the earliest attempts of investigations in this direction. Gillson (1959), who did a pioneering study of these deposits, suggested basic rocks as the likely source of the deposits. However, subsequent authors (Krishnan, 1968; Subrahmanyam and Rao, 1980), based on the geographical location of the deposits and the lithology of the hinterland pointed to the rocks of the khondalite-charnockite suite as the source. Soman (1985) attributed the khondalite migmatite complex of southern

India as the source rocks of the south west coast placer deposits, and from petrographical observations linked the origin of ilmenite to the action of alumina rich solutions on biotite, which was related to the migmatitisation phase of the region. Bhattacharyya et al, (1997), based on the low Mn/Mg (1.32-2.92) ratios for the ilmenite of these deposits suggested a more basic parentage.

Except for some isolated attempts, a critical and systematic analysis of this important mineral, ilmenite, is yet to be brought out in a comprehensive manner in India. Viswanathan (1957) reported on the black sand deposits of southwest coast and outlined the variation of properties like magnetism of ilmenite. Rao and Rao (1965) and Mallik (1986) carried out a detailed study of ilmenite of Kerala including microscopic evaluation. Mallik (1986) identified the different micromorphological features and explained their formation to solution activity, chemical reaction and mechanical impact during transportation. Ilmenite alteration and the study of its associated intermediate phases were carried out by Subrahmanyan et al (1982) using X ray and Mössbauer analyses. They identified a two-stage model of weathering for ilmenite of Manavalakurichi deposit and observed that magnetism of the mineral increases during alteration and then decreases after reaching the pseudorutile stage. Suresh Babu et al (1992; 1994) under took the varietal studies of ilmenite, including chemistry, magnetism and specific gravity. They investigated the chemical variation of the different magnetic fractions of ilmenite and concluded that the alteration has succeeded in altering low magnetic fractions of ilmenite to the pseudorutile stage in Manavalakurichi placers.

However, the Manavalakurichi ilmenite, as a whole could be labelled as belonging to the hydrated ilmenite stage (Nair et al, 1995). In Chavara deposit, on the other hand, weathering has reached a more advanced phase of the pseudorutile stage (Ramakrishnan et al, 1997). The alteration patterns of ilmenite may be along, either 1) continuous, with the formation of intermediate phases before the ultimate formation of rutile; or 2) the discontinuous series, whereby the ilmenite alters directly to rutile, or both simultaneously (Chaudhuri & Newsley, 1990). In the southwest placer ilmenite, intergrowths of mineral phases could not be noted, unlike in the case of Vishakapatnam and Gopalpur ilmenite. This was further confirmed by the application of Mössbauer techniques in the study of the mineral (Suresh Babu et al, 1994). The ilmenite of Ratnagiri deposit was analysed for its chemistry by Sukumaran and Nambiar (1994) in relation to the other ilmenite occurrences of India. They argued that, given its similarities with the ilmenite of the southwest coastal placers, the Ratnagiri ilmenite could be considered a good quality raw mineral for industrial processing.

## 2.3 ILMENITE BASED INDUSTRY

The economic and industrial significance of ilmenite lies in its role as the most common ore of titanium. The increasing significance of titanium and titanium based products in the industrial spectrum in recent years, from the manufacture of pigments and paints to its use in aerospace/defence industries, underscores the importance of the mineral and the intense research currently on in the industrial world for the characterization of the ore and updating of the processing technology.

### 2.3.1 Industrial forms of titanium minerals

2.3.1.1 Natural ilmenite: Ilmenite and its product leucoxene are used widely in the welding rod industry as slag formers and modifiers in flux formulations. The low ferric oxide content is the main criterion, which finds use in the industry. Recently a form of reduced ilmenite called "ferutil" is being used in the welding electrode industry. Ilmenite is also used in sand blasting operation and as a weighing agent in oil industry.

2.3.1.2 Titanium metal: About 4% of the annual production of titanium minerals are used in the production of the metal. In India, this capability is very limited though the Nuclear Fuel Complex is producing sponge titanium in a small scale. There are three stages in the initial production of titanium metal. The initial stage is the production of $TiCl_4$ by the reduction and chlorination of rutile or synthetic rutile (upgraded ilmenite). The second stage is the reduction of $TiCl_4$ in the presence of Mg (Kroll process) or Na (Hunter) process. The impure sponge titanium thus formed is treated to acid leaching or vaccum distillation. The extraction of metal titanium involves special techniques such as double ore melting or electrolysis.

The aerospace industry accounts for 45% of the total metal consumption where it is used for the manufacture of air frame structural parts and in jet engine components. The high strength/weight ratio and ability to maintain its mechanical properties at elevated temperatures are the properties, which move it suitable for the above uses.

Because of its high corrosion resistant properties and non toxic nature, titanium finds extensive use in chemical industry and desalination plants, marine machinery and fittings, deep water research, storage tanks, heat exchange units, electricity generating plants, prosthetic devices such as heart pace makers and in oil and gas industry. It is an important alloying element and a effective deoxidizer and cleaning agent in metallurgy. Ferro titanium (15-45% Ti) is a widely used alloy. In ceramic industry Ti is used for producing colored glasses and enamels.

2.3.1.3 Manufactured Titanium dioxide: At the beginning of this century $TiO_2$ was almost exclusively used for the manufacture of pigments and paints. Now the manufacture and production of $TiO_2$ has become very specialised in that different grades of titania are used for specific products. This includes plastics, paper, cosmetics, rubber and pharmaceutical industry, to name a few.

The Titanium dioxide was manufactured commercially only in1916, but the total consumption now exceeds 2 million tons/year. The properties which make this product so important in industry are its high refractive index, which imparts high opacity, high reflectivity, which gives a high degree of brightness and brilliance, chemical inertness, which gives rise to high colour retention capability, thermal stability over a wide range of temperature, non toxicity, non fibrogenic nature etc.

Two types of manufactured $TiO_2$ are available in the market -'anatase' and 'rutile' grade. The applications in the industry are different, depending on the end products required. The 'rutile' grade is suited to products like paints, printing inks, plastics, cosmetics etc. Anatase grade finds application in paper industry, latex, rubber, pharmaceutical products and soap industry. About 62% of the total $TiO_2$ produced go into the paint industry. Plastic and paper manufacture consumes almost the rest of the pigment produced. $TiO_2$ are used to produce gemstones synthetically.

### 2.3.2 Upgradation of raw ilmenite

Three processes are generally used for synthetic rutile manufacture from raw ilmenite.

2.3.2.1 Thermal reduction (Smelting): This essentially involves the high temperature oxidation of ilmenite to form pseudorutile structure. The pseudobrookite is treated to solid-state reduction using carbon. Finally, the aqueous oxidation of metalllc iron forms hydrated oxide and the upgraded ilmenite is separated out. This process is used by a number of companies like Richards Bay Minerals of Australia and Nissho Inai Corporation of New Zealand.

2.3.2.2 Reduction/oxidation/leaching/Rusting (Becher process): These processes involve a series of oxidation and reduction reactions, which break down ilmenite to $TiO_2$ and iron fractions. The titanium oxide is separated out by the leaching away of iron. This process yields almost pure $TiO_2$. Various variants of this process were developed by different agencies like CSIRO, Australia, Benilite Corp, Ishihara Sangayo, Japan.

2.3.2.3 Reduction/Chlorination: The ilmenite is reduced and subsequently chlorinated to produce a very high grade synthetic rutile (95-98% $TiO_2$). The iron chlorides are removed and oxidised to produce chlorine. Various agencies like Mistibishi Minerals, Japan and Iron Chemicals, Canada use this process for ilmenite upgradation.

Though endowed with some of the largest and high quality deposits in the world, India still imports part of the titanium pigment for domestic consumption. Moreover, India still has a long way to go before it can join the select group of countries with the capability to produce sponge titanium. A limited sponge production is being carried out in Nuclear Fuel complex, but till now it is not viable in the commercial scenario. Although the commercial production of Ti is only a few decades old, the application of the metal range from the manufacture of chemical to the aerospace/defence sector. In the developed world, the manufacture of pigment has become very product specific, ie., different grades of the $TiO_2$

is manufactured suited to various end products. The production of value added products of ilmenite could yield valuable foreign exchange for the country. At present the bulk of the ilmenite that is produced is being exported at a rate of Rs.2700 per tonne, while we import the finished products, straining the economy.

This calls for the characterisation and grading of the ilmenite ore, which could be used to produce different grades of pigment, based on the impurities present and the iron content. The extractive techniques in the country need to be updated depending on the physical and chemical characteristics of each deposit.

### 2.3.3 Manufacture of titania pigment

The $TiO_2$ pigment is manufactured by the following processes.

2.3.3.1. Sulphate process: was developed at the beginning of this century. This involves the leaching of ilmenite or titanic slag with con $H_2SO_4$ and heating by steam. The resultant soluble sulphates of Ti and Fe are dissolved and passed over scarp Fe to convert ferric sulphate to the ferrous form. The resultant solution is clarified and precipitated out as 'Copperas'. The titanyl sulphate containing liquid is hydrolised by injection of steam and an anatase grade or rutile grade Ti pigment is produced. The recovery range is about 85% $TiO_2$ depending on the titanium content of the feed material. This process has the disadvantage of the high consumption of $H_2SO_4$ and the problems of disposal of the large amounts of the work products formed like sulphuric acid and iron sulphates. This process is being phased out in developed nations. The Travancore Titanium Products uses this technology for the pigment manufacture.

2.3.3.2. The chloride process: was developed in 1956 by Dupont. The feedstock consists of rutile or synthetic rutile since using ilmenite cause problems in the disposal of the large amounts of iron chloride formed. The feedstock is chlorinated at 950°C in the presence of oxygen and a carbon source forming Ti and iron chlorides. The $TiCl_4$ formed is separated, purified and then oxidised.The recovery is about 90% $TiO_2$.

The production of a large amount of waste product during the processing of ilmenite to $TiO_2$ pigment posed problems in waste disposal and pollution hazards. So high $TiO_2$ containing substances like rutile or upgraded ilmenite is generally preferred as raw material for the pigment manufacture. The scarcity of rutile, has led to the usage of synthetic rutile and titanic slag as the feedstock in pigment production.

### 2.3.4 Titanium based industrial concerns in India

Indian Rare Earths: The Indian Rare Earths Ltd. has plants in Quilon (Kerala), Manavalakurichi (Tamil Nadu) and Chatrapur (Orissa), in addition to a Rare Earth plant at Alwaye. The current capacity of the Quilon plant is 13,00,00 tons of ilmenite/year. Though the Chatrapur plant was commissioned with a planned capacity of 220,000 tons/year, due to certain technical problems involved in the processing of the Orissa ilmenite, the production at present is not up to the expected levels, though synthetic rutile is produced at a rate of 25,000 m. tons/year (AMD, 2000).

Kerala Minerals & Metals Ltd. (KMML): In the 1980's the KMML was established with a Benilite type plant for the manufacture of synthetic rutile. The expected capacity was 30,000 tons/year. The company isalso producing $TiO_2$ pigment using the chloride process at a rate of about 22,000 tons/year. This plant owned by Kerala government is now preparing schemes for expanding its activities both for ilmenite mining and beneficiation.

Travancore Titanium products (TTP): This is a concern of Govt. of Kerala, which started functioning in 1950. The initial capacity was 1800 tons/year, which have been expanded to the present capacity of 30,000 tons/year subsequently. The company uses the sulphate process for the production of pigment and the wastes are discharged to the Arabian Sea.

Dharangadhara Chemical Works Ltd: This company is situated at Sahupuram near Tirunelveli. It was commissioned in 1970 and is the first one in the world to produce synthetic rutile. The plant uses the Benilite process. The present capacity is about 12,000 MT/year. The synthetic rutile produced contains about 90% $TiO_2$.

Cochin Minerals & Rutile Ltd.: This concern has started producing synthetic rutile with a moderate capacity, from 1990. The company makes use of Benilite technology for the upgradation of Chavara ilmenite to synthetic rutile. The products in this plant are earmarked exclusively for export.

# CHAPTER 3

# MATERIALS AND METHODS

The present work attempts to trace the variation in the physical and chemical behaviour of ilmenite, since its release from country rocks and subsequent transportation to the coast through the progressive weathering environments of laterite, sedimentary rocks, rivers and estuarine systems. Since the hinterland of the study area consists of crystalline and sedimentary rocks and their weathered forms (laterites), the contribution of each lithological system to the beach placer is attempted. Though the main emphasis of the study is on the characterization and grading of the ore along the coast, particularly in the placer deposits, such work as mentioned above would go a long way in unraveling the genesis of the placers, which have not been completely resolved so far.

## 3.1 SAMPLE COLLECTION AND PRE-TREATMENT

### 3.1.1 Sampling

Representative samples were collected from various environments of mineral occurrence like primary rocks, laterites, rivers, estuary and beaches (Fig. 3.1). Rock samples up to 20 kg were crushed for possible separation of ilmenite and huge quantities of rock powder from the crushing units were subjected to wet panning. The collection of ilmenite was attempted from crystalline rock samples, but the mineral grains were always found associated with minerals like pyroboles, rendering the physical separation of ilmenite grains difficult. Laterites and sand stone samples were collected from road cuttings and quarries and crushed at the location itself before insitu panning. The alluvial samples were

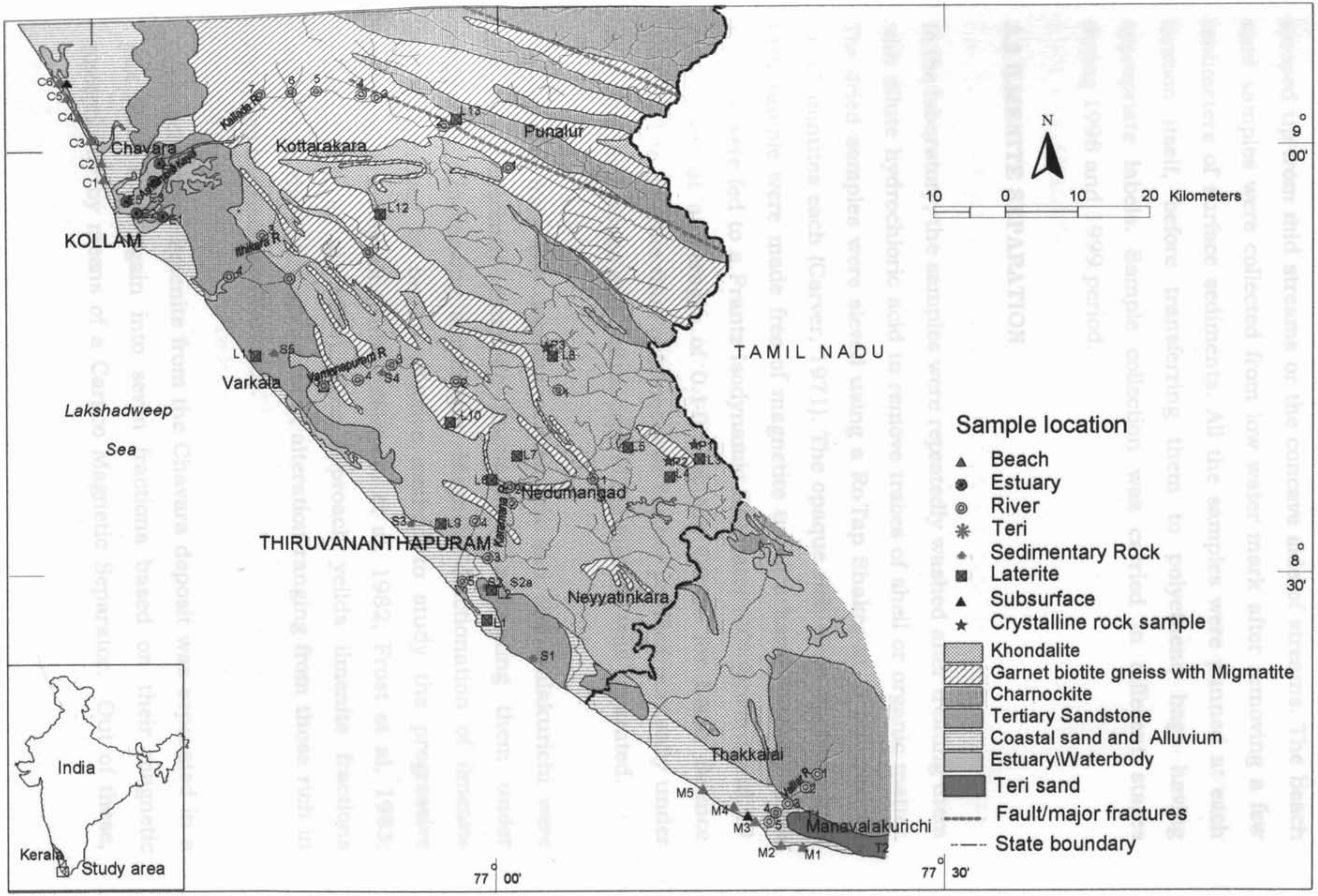


Fig. 3.1 Map of the study area showing sampling locations

scooped up from mid streams or the concave side of streams. The beach sand samples were collected from low water mark after removing a few centimeters of surface sediments. All the samples were panned at each location itself, before transferring them to polyethene bags having appropriate labels. Sample collection was carried in different stages during 1998 and 1999 period.

## 3.2 ILMENITE SEPARATION

In the laboratory, the samples were repeatedly washed after treating them with dilute hydrochloric acid to remove traces of shell or organic matter. The dried samples were sieved using a Ro-Tap Shaker at ½ phi interval for 15 minutes each (Carver, 1971). The opaque rich sieve fractions from each sample were made free of magnetite using a hand magnet. These samples were fed to a Frantz Isodynamic Separator (20$^0$ forward and 15$^0$ side slopes) at amperages of 0.1-0.3 at the Centre for Earth Science Studies. The ilmenite thus obtained was further purified manually under an optical microscope and a pure crop of the mineral was separated.

The ilmenite from the deposits of Chavara and Manavalakurichi were split into differently magnetic fractions by separating them under progressively increasing amperages. Magnetic fractionation of ilmenite has had proved to be an effective method to study the progressive alteration in a deposit (Subrahmanyam et al, 1982; Frost et al, 1983; Suresh Babu et al, 1994). This approach yeilds ilmenite fractions belonging to the entire spectrum of alteration ranging from those rich in iron to the leucoxenised varieties.

Commercial grade ilmenite from the Chavara deposit was separated in a pilot plant scale again into seven fractions based on their magnetic susceptibility by means of a Carpco Magnetic Separator. Out of these, IRE1 represents ilmenite grade, IRE2-4 rutile grade, while the last three fractions correspond to leucoxene. This was carried out to study the differently altered fractions of ilmenite from an industrial point of view. Such studies will complement the efforts to produce homogenous ore grades and also in adopting suitable processing techniques.

## 3.3 X RAY ANALYSIS

The X-ray diffraction analysis is used in the identification of different mineralogical phases present in a mineral sample and their crystal structure. Variation of the lattice parameters and changes in crystallinity can be determined by this method.

Selected samples collected from different environment were finely powdered in an agate mortar. The samples so powdered were on a mounted Phillips Diffractometer with CuK$\alpha$ target and Ni filter, keeping $2\theta$ values in the range of $20^0$-$60^0$. The reflections caused to the X-rays were recorded in the form of peaks of different heights on the recording strip chart. The heights of the peaks are proportional to the intensity of reflection. The individual peaks characteristic of each mineral phase were identified by comparing the 'd' values with standard JCPDS files. Based on the XRD data the following analyses were carried.

### 3.3.1 Semiquantitative determination

The semi quantitative measurement of the mineral phases was carried out by measuring the area of each identified peak using a planimeter. The area thus determined is proportional to the quantity of the phases available (Ramakrishnan et al, 1997).

### 3.3.2. Measurement of lattice parameters

The unit cell lattice parameters like the 'a'. 'c' and 'v' values were calculated from the XRD data (Cullity, 1978). Such studies reveal the influence of weathering on the structure of the mineral..

### 3.3.3 Crystallinity index

This factor indicates the degree of crystallinity of the mineral grains. As the well crystalline ilmenite undergoes alteration to secondary products like pseudorutile or rutile, the crystalline nature is changed and less defined. The crystallinity index = $A+B/A_t$ where A and B are the peak heights of two nearby reflections of the same phase from the bottom of peaks and $A_t$ is the peak height from the back ground. These indices were calculated for certain samples, particularly when grains of the same size grade or of the same separating amperage.

## 3.4 STUDIES ON MAGNETISM OF ILMENITE

The magnetism of ilmenite is studied since it has implications of weathering on the mineral and the consequent compositional changes. In addition, the magnetic properties of the mineral would be relevant in the adoption and upgradation of the industrial processing of ilmenite.

### 3.4.1 Magnetic fractionation in Isodynamic Separator

The different magnetic fractions of ilmenite samples were separated out using Frantz Isodynamic Separator, by varying the amperage of the instrument. Samples of different size grades were fed to the machine to understand the dependence of magnetism on the textural characters. The mass magnetic susceptibility was calculated using the empirical formula of Flinter (1959)

$$K_m = \frac{20\sin\theta * 10^{-6}}{I^2}, \text{ where}$$

$K_m$ =mass magnetic susceptibility

$\theta$ =angle of the side slope and

I = current in amperes

### 3.4.2 Magnetic analysis using Bartington Magnetic Susceptibility Meter

The accurate measurement of selected samples was carried out using Bartington Magnetic Susceptibility Meter. This is one of the most sensitive instruments available for the determination of magnetism (Dearing, 1999).

A calibration sample is provided which contains a mixture of 1% magnetite and alumina tightly packed together. The sensor of the susceptibility meter is calibrated for a sample mass of 10 g. The ilmenite samples to be analyzed are packed into standard sample pots using polythene bags. The analysis by the instrument was carried out in the mode of 0.1 range of measurement. The susceptibility meter was first allowed to thermally equilibrate with the room temperature. Blank measurements were carried out before and after the sample measurements to eliminate the small variations of instrumental drift between the readings. The measurements were repeated for each sample and the mean value is taken.

The mass specific magnetic susceptibility is measured by the formula,

Mass specific magnetic
susceptibility, x = (measurement reading x calibration mass)/ mass of the sample

## 3.5 MÖSSBAUER SPECTROSCOPY

The different stages of alteration and their chemical composition cannot be completely estimated by XRD analysis, because of the diffused nature of the XRD curves of these phases. Another useful parameter for this sort of study is the determination of the degree of isomorphous lattice replacement and quadrupole shifting of ferrous and ferric ions (Gibb et al, 1969; Kopcewicz, 1994). Such analysis using Mössbauer techniques would give an idea about the phase changes in ilmenite alteration.

Mössbauer measurements were made with a standard PC-based Shimadzu model operating at the constant acceleration mode. The radioactive source was a 5mCi$^{57}$Co in Rh matrix 25 cm away from the proportional gas counter. Absorbers were made by pressing (at 0.5KN/cm$^2$) circular discs and land 1 cm diameter, containing 100 mg of boron nitride into which 30 mg of sample was finely mixed. The spectrometer was calibrated using 25 cm thick natural iron foil. The measurements were carried out in transmission geometry at room temperature. The data obtained were fitted using a least squares fitting program assuming Lorentzian line shape.

## 3.6 THERMOGRAVIMETRIC STUDIES

Selected samples from different weathering environments were finely powdered using an agate mortar. About 20-50 mg. of each sample were subjected to thermogravimetric analysis in a Shimadzu TGA 50H at a heating rate of 10°C/minute to a maximum temperature of 1000°C. The data obtained in the form of curves indicate the weight change suffered by the mineral under increasing temperatures. This would depend on the structural changes associated with weathering like the alteration phases formed and the resultant inclusion of water in the mineral structure (Suresh Babu et al, 1994; Ramakrishnan et al, 1997). Different magnetic fractions of selected samples were analyzed by this method to understand the behaviour of ilmenite during varying alteration stages under high temperatures.

## 3.7 CHEMICAL ANALYSIS

The chemical analyses include those of the major elements (iron and titanium) and the minor and trace elements Al, Si, V, Cr, Mn, Mg, Zn, Ni, & Cu. The trace elements were selected on the basis of their relevance as indicators of provenance, alteration, chemical changes and economic importance.

### 3.7.1 Major elements

Wet chemical methods were followed to determine the major elements Fe and Ti based on Vogel (1961). Ferrous iron in the mineral is determined to understand the effect of alteration on the oxidiation state of the mineral.

About 0.5 gm of finely powdered sample was fused with 10-15 gm of the sulphate after melting and cooling the salt first. The fusion was conducted initially at low temperature. The temperature was gradually increased to maximum. The crucible was kept at this temperature (900°C)) for 20-30 minutes. The crucible was cooled and placed inside a beaker containing 20% $H_2SO_4$ and heated till the dissolution is complete. The solution was cooled and made up to 250 ml.

i) Estimation of total iron: 25ml of the sample solution was pipetted out into a conical flask and 5ml of con. HCl added and heated to 80°C. Freshly prepared stannous chloride solution was added to reduce the iron in solution, until the yellow colour of the solution disappears. The solution was rapidly cooled to 20°C. The excess stannous chloride was removed by adding 10ml. of saturated $HgCl_2$ A silky white precipitate of mercurous chloride results. About 5ml. Con. $H_2SO_4$ and 10 drops of N-phenyl anthranilic acid indicator are added after 4-5 minutes. This is titrated against standard potassium dichromate solution. The end point is the appearance of a permanent pink colour.

The percentage of total iron is calculated as

$$\text{Total Iron (\%)} = \frac{\text{volume } K_2Cr_2O_7 \text{Xnormality X55.85x100}}{\text{solution pipettedx4xweight of the sample}}$$

ii) Estimation of ferrous iron: About 0.3 gm of the sample is weighed out to a 100 ml conical flask fitted with two curved glass tubes using a cork. 10 ml of 80% concentrated sulphuric acid and 5ml of HF are added. The apparatus is closed and $CO_2$ is passed. The flask is heated on a hot plate. The flask is cooled and 15% boric acid is added. 5ml of phosphoric acid is added followed by 10ml. Of 1:1 sulphuric acid. The solution is titrated against standard dichromate with diphenyl sulphonate as indicator. The end point is the appearance of purple colour.

$$\text{Ferrous iron (\%)} = \frac{\text{Volume of } K_2Cr_2O_7 \text{ X factor X 100}}{\text{Weight of the sample}}$$

$$\text{Factor} = \frac{55.84 \text{ X Normality of } K_2Cr_2O_7}{1000}$$

iii) Estimation of titanium dioxide: This method is carried out in an apparatus, which consists of a 500ml Erlenmeyer flask and a two holed stopper. A pointed glass rod is placed in one hole and the other one holds the short end of a delivery tube.

About 10 ml of the fused solution is taken in the flask and added 15ml con. $H_2SO_4$ some distilled water is added. The solution is boiled. 2gm of Al foil is attached to the glass rod of the apparatus. The flask is immediately closed with the rubber stopper and the free end of the delivery tube is placed inside a beaker of sodium bicarbonate solution. When all the aluminum is dissolved, the solution is gently boiled.

The flask is suddenly cooled. The carbonate solution is drawn to the flask and gives the necessary $CO_2$ Atmosphere. The flask is cooled and the stopper removed. The solution is titrated against standard ferric ammonium sulphate solution with 24% ammonium thiocynate indicator.

$$TiO_2\ (\%) = \frac{\text{volume of titrant x factor x250x 100}}{\text{weight of the sample x volume of solution pipetted}}$$

$$\text{Factor of ferric alum} = \frac{\text{volume of alum pipetted out x wt. of standard } TiO_2 \text{ x assay of } TiO_2}{\text{250 x volume of titrant x 100}}$$

### 3.7.2 Minor and Trace element analysis

The samples were fused with potassium bisulphate as described above and dissolved in 20% nitric acid (Darby and Tsang, 1987). The standard solutions of various concentrations were prepared. They were fed to Sartorius model Atomic Absorption Spectrophotometer. The absorbance values were plotted against concentration. The absorbance of the sample solution was noted from the graph and its concentration determined. The instrument was set in characteristic wavelengths depending on the trace elements to be detected while the readings were taken.

## 3.8 MICROSCOPIC STUDIES

Scanning electron microscopy has become an essential tool in the micromorphological investigation of the mineral and its alteration features. Such studies are important to delineate the environment of weathering and transportation and the subsequent alteration (Krinsely & Doomkamp, 1973).

The samples were boiled with con. hydrochloric acid for ten minutes and washed with distilled water. They were then treated with stannous chloride solution for twenty minutes to remove iron oxide coatings. About 15-20 grains were selected randomly for each sample. The grains were arranged in rows over the SEM stubs using a double sided stick tape. A thin layer of conducting silver paint was applied to the bottom of the grains for better conduction. The specimen was coated with gold palladium alloy in a vacuum evaporator. The sample was then scanned using stereoscan. The shape, relief, orientation and density of distribution of various features in the different grains were studied and suitably filmed.

Observation of ilmenite grains under ore microscope was carried out to study the alteration patterns as well as the intergrowths. Selected grains were mounted on a polymer resin. It was then polished initially by carborandum paper. The grains were further polished on a velvet cloth using alumina solution. This was done till the grains became scratchless and reflecting.

## CHAPTER 4

# MINERALOGICAL STUDIES

## Part 4.1. MICROSCOPIC STUDIES

### 4.1.1 Introduction

The microscopic observations provide a direct insight into the grain and its natural characters like morphology and alteration features. Since a mineral like ilmenite passes through a series of changes as a result of the leaching of iron and hydroxylization, these changes are manifested in the variation of these phases which are readily identified under the microscope due the variation of the optical properties with progressive leaching (Temple, 1966; Hugo and Cornell, 1991; Mucke and Chaudhuri, 1991).

Unlike the chemical and thermal investigations, the observations under microscope are easily reproducible and non destructive. Mucke and Chaudhuri (1991) have demonstrated the importance of microscopy in the delineation of alteration phases of ilmenite. They argue that the phase identification is better conducted using the microscopic techniques rather than XRD and other mineralogical methods. In addition, the non-stochiometric occurrence of the intermediate alteration products is more easily identified and fixed using these techniques while chemical and XRD data are more ambiguous and less discernible with regard to the mineral phase identification and comparison. The transformation of ilmenite to leucoxene happens either through a series of intermediate products or directly, depending on the mode of alteration mechanism taking place (Hugo and Cornell, 1991; Mucke and Chaudhuri, 1991). The micro morphology of the surface of the grains in the form of features like pits, solution cavities and growths etc. reveal the environment of transportation and depositional regimes suffered by the mineral (Mallik, 1986).

The microscopic methods have been found to be useful in the quality of alteration, no matter whether it is a consequence of the action of magmatic fluids or the normal low temperature weathering process. Post depositional weathering of ilmenite in sedimentary formations and laterites leads to the occurrence of secondary minerals like clays, which are identified only by the application of microscopy (Anand and Gilkes, 1984; Morad and Aldahan, 1986). These aspects are difficult to interpret from the chemical and XRD data.

In this study, the ilmenite samples from beaches and those from the geological environments of the hinterland were observed under ore and scanning electron microscopes. An attempt has been made to correlate the microscopic data with the chemical and XRD results. Various authors have proposed different nomenclature for the alteration phases of ilmenite (Bailey et al, 1956; Temple, 1966; Frost et al, 1983; Chaudhuri and Newsley, 1990; Mucke and Chaudhuri, 1991, Chernet, 1999). These classifications are essentially similar for the major phases like pseudorutile and leucoxene. The transitional and metastable phases between these major products from ilmenite have non-stoichiometric compositions depending on the leaching of the iron content. This is manifested in the difference in optical properties exhibited by these intermediate phases, which some authors have attempted to define and classify.

## Terminology applied for ilmenite and its alteration phases in microscopy

In this work, the terminology proposed by Chernet (1999) was adopted to describe the phases in ilmenite alteration. However, similar phases with different nomenclature coined by other authors also have been referred to, wherever required.

Ilmenite: This mineral purplish grey in colour, anisotropic with good reflectivity under reflected light. (Plate 1)

Leached ilmenite: It refers to the intermediate phase having compositions between ilmenite and pseudorutile. The optical properties are similar to those of ilmenite but are distinguished from the former by their grey bluish colour and weaker anisotropism. Reflection pleochroism has been observed in this phase. The term 'hydrated ilmenite' used by various authors (Frost et al, 1983; Hugo and Cornell, 1991) apparently corresponds to leached ilmenite stage. This phase is generally seen along crystallographic directions or along the regions of weakness on the grains intergrown with ilmenite (Plates 2&3).

Pseudorutile: This mineral phase is distinguished by its greyish blue colour when compared to ilmenite. The reflectance of this phase is in general at a higher range than shown by ilmenite. Frequently, this phase is observed to be isotropic with decrease in iron content. The optical properties show variation with the difference in its range of composition. Generally, pseudorutile develops along crystallographic directions and along the boundaries of grains and fractures. Micro fractures may be observed due to reduction of cell volume with leaching. This phase could be distinguished from the neighbouring ilmenite/leached ilmenite stages by the weaker aniostropism of the latter (Plates 4,5 & 6).

Leached pseudorutile: Internal reflections of brown to reddish brown are observed, which is dependent on the content of iron present. Microfractures are very common in this stage of alteration. This phase is markedly metastable and breaks down to form rutile (Plate 7).

Leucoxene: The mineral is characterised by sugary internal reflections ranging from brownish through reddish brown, reddish orange, yellow and whitish yellow to white, with depletion of the iron content. Shrinkage cracks are a common characteristic of this phase. This phase has been identified as essentially microcrystalline rutile (Temple, 1966; Frost et al, 1983; Mucke and Chaudhuri, 1991). Leucoxene replaces pseudorutile and sometimes ilmenite/leached ilmenite either from the rim of grains, along cleavage lines or as patches within the grains (8,9&10). The leucoxenization is also observed in the grains, in the form of pits or even from the core. The presence of leucoxene with ilmenite separated by sharp boundaries, or the occurrence of fingerprint like textures are also noted (Plates 11&12). Such features have been explained as resulting from recrystallization of these phases.

In this work, ilmenite samples collected from the beach deposits of Chavara and Manavalakurichi and the different geological environments of the hinterland are discussed

### 4.1.2 Ilmenite from beach

Alteration starts along the periphery of the grains or along lines of weakness like cleavages. Since alteration is a progressive phenomenon in ilmenite, most of the grains consist of more than one phase. In some grains, the alteration has reached an advanced state that, only relict islands of unaltered ilmenite remains in a sea of the alteration products (Plates 5, 13).

The transformation of ilmenite into the hydrated ilmenite phase could be seen in the polished sections (Plates 2&3). The leaching appears to have taken place along cleavage lines or along planes of weakness within the grain (Plate 14) in the form of patchy occurrences. In most of the grains, the boundaries of the phases are diffused indicating a gradual, continuous alteration. In such grains, the transformation of ilmenite to leucoxene through the stages of hydrated ilmenite and pseudorutile could be clearly made out, indicating that the alteration of ilmenite is continuous (Plate 13). Such observations have been recorded in the previous works as the evidence of the continuous alteration of ilmenite to leucoxene (Temple, 1966; Grey and Reid, 1975; Frost et al, 1986; Mucke and Chaudhuri, 1991).

The alteration of ilmenite has been reported to occur in two stages (Grey and Reid, 1975). The first stage is the oxidation of ferrous ions to ferric state together with the diffusion of one third of the ferric ions out of the mineral structure. Such a leaching out of the ferric ions is necessary to maintain the lattice structure. This stage is assumed to take place in acidic and oxidizing environments at ground water conditions (Grey and Reid, 1975).

$$\underset{\text{(ilmenite)}}{3FeTiO_3} + 2H + 1/2O_2 \longrightarrow \underset{\text{(pseudorutile)}}{Fe_2Ti_3O_9} + Fe^{2+} + H_2O$$

Further leaching of the remaining iron from the mineral leads to the formation of leucoxene. This is the second stage of alteration and involves the disruption of the anionic lattice as both iron and oxygen are removed. This stage takes place through a dissolution and reprecipitation phenomenon in near surface soil conditions in a reducing and acidic environment (Grey and Reid, 1975; Frost et al, 1983).

$$\underset{\text{(pseudorutile)}}{Fe_2Ti_3O_9} + 4H^+ \longrightarrow \underset{\text{(rutile)}}{3TiO_2} + 2Fe^{2+} + 1/2O_2 + H_2O$$

However, Mucke and Chaudhuri (1991) suggest that the alteration beyond the pseudorutile stage is a process of leaching and hydrolization taking place, in general, in an acidic or slightly acidic environment. According to these authors the alteration of ilmenite is a continuous process, with the formation of intermediate alteration products.

Hugo and Cornell (1991) have argued that, since evidence of ilmenite transforming directly to rutile or leucoxene could be found in nature, the weathering of ilmenite may not always be continuous (Plates 11, 15). Such a route of alteration is characterized by sharp boundaries between leucoxene and the ilmenite/leached ilmenite, with no gradual change in the phases as in the type of alteration described previously. The leucoxene may be found as isolated patches in the ilmenite, intergrown with the ilmenite or leucoxenization occurs along lines of weakness (Plate 16). The boundary between the ilmenite and leucoxene could be abrupt and sharp (Plates 15, 16, 17, 18) or a transitionary zone consisting of porous area of microcrystalline leucoxene (Plate 11). Such observations are in agreement with those of Hugo and Cornell (1991). They suggested that the intermediate zone as mentioned above indicates isovolumetric replacement of ilmenite by leucoxene.

The altered portions of the grains like the cavities are often observed to contain flaky and plate like structures associated with altered products of ilmenite and suspected to be clay minerals (Plates 19,20,21). This has been explained as due to the result of dissolution and reprecipitation mechanism and/or of the leucoxene (Frost et al, 1983; Anand and Gilkes, 1984).

Frost et al (1983) have explained the existence of ilmenite cores with leucoxene rims as a result of a single step dissolution and reprecipitation process. Thus intermediate stages like the formation of pseudorutile or leached pseudorutile are bypassed.

$$FeTiO_3 + 2H^+ \longrightarrow TiO_2 + Fe^{2+} + H_2O$$

Such direct leaching of ilmenite to form leucoxene usually takes place in near surface regions or pedogenic zones, acted upon by soil acids.

However, Mucke and Chaudhuri (1991) explained the apparent occurrence of leucoxene and ilmenite without the existence of intermediate phases as observed in Plates 15 & 18 due recrystallization. They argued that even such apparently discontinuous type of alteration is chemically found to belonging to continuous alteration series. In the present work, grains exhibiting other patterns of direct leucoxenization are found as observed in Plates 11 and 17 discussed earlier. The grains with fingerprint features are also attributed to the recrystallization of leucoxene during alteration by Mucke and Chaudhuri (1991).

The alteration of ilmenite has been suggested to be mainly post depositional (Bailey et al, 1956; Temple, 1966; Hugo and Cornell, 1991). The evidences stated in favour of this phenomenon by these authors are generally in concurrence with observations in this work. Alteration of rounded grains indicates that the alteration occurred after the rounding of grains by transportation. However, it is also observed in many grains that the boundaries between the alteration phases are truncated by grain surface, indicating that alteration occurred in a larger grain, which was subsequently disintegrated into smaller pieces (Plates 5,11). Hugo and Cornell (1991) opined that such features are indicative of reworking undergone by the grains. Temple (1966) suggested that the older deposits generally contain more altered ilmenite, since most of the alteration suffered is post depositional. Thus the Chavara deposit is considered to be older than the Manavalakurichi deposit on the strength of the higher degree of alteration (Plates 8, 22) suffered by most of the ilmenite grains when compared to that of the Manavalakurichi ilmenite (Plates 23, 24). This lends credence to the observations made by earlier authors and the mineralogical and chemical investigations of the present work.

### 4.1.3 Ilmenite from laterite

It is observed that ilmenite grains from this environment show only a marginal degree of alteration (Plate 25). Still, a few grains exhibiting a complete spectrum of alteration phases within a single grain could be seen. The limited studies on ilmenite in laterite bodies indicate advanced state of alteration in the mineral grains (Anand and Gilkes, 1984). Cracks and pits could be seen on the surface of the grains, which form loci of alteration (Plates 26, 27, 28). The pits present porous intergrowths of leucoxene and clay like bodies (Plates 29, 30). Such features are products of the series of alteration stages dealt with previously. Detrital fragments of the grain with alteration products are also observed. Clays are reported from the ilmenite in this environment, as a consequence of the precipitation of leucoxene (Frost et al, 1983; Anand and Gilkes, 1984).

The discontinuous type of alteration or the Type 2 of alteration of Hugo and Cornell (1991) could also be seen in a few number of the grains of this geological set up (Plate 28). The pattern of occurrence of ilmenite and leucoxene suggests the mechanism of recrystallization of leucoxene as suggested by Mucke and Chaudhuri (1991). Such alteration has been documented during lateritisation and bauxitisation (Hartman, 1959; Frost et al, 1983). During these processes, iron titanates undergo incongruent dissolution. Subsequently, iron stays in solution while titanium reprecipitates back to the original grains (Frost et al, 1983; Hugo and Cornell, 1991).

Unlike in the studies by Anand and Gilkes (1984), where anatase is found to be the final product of alteration, it has been confirmed from XRD results that, in this work the product of weathering of ilmenite is rutile. Rutile is the common end phase of ilmenite in beaches reported (Teufer and Temple, 1966; Grey and Reid, 1975). The presence of anatase in latertic soil ilmenite has been argued as due to the ability of the structure of this mineral to accommodate structural distortions due to the incorporation of foreign ions during the dissolution precipitation mechanism. Since the presence of ions is much enhanced in the pallid zone weathering conditions, due to the disintegration of primary minerals, the formation of anatase is prevalent in laterite regime, than beaches where concentration of such ions are scarcer. The only explanation for the absence of anatase in the lateritic ilmenite of present study could be due to the relative young age (Miocene) of the lateritization processes in southwest India. That the lateritization process is not advanced is indicated by the relatively fresh appearance of ilmenite grains themselves.

The sample from the lateritised corderite gneiss shows intergrowths with a good number of grains. Different patterns of intergrowths are seen. The prominent patterns are identified as seriate (Plates 31, 32) and emulsion patterns (Plate 33), as reported by Ahmed et al (1992). The interlocking patterns of the ilmenite and haematite phases are rarely seen (Plate 34).

### 4.1.4 Ilmenite from the Tertiary sandstone

The ilmenite samples from the Tertiary formations of Kerala, exhibit a wide spectrum of alteration depending on the location of the samples. It could be seen from the mineralogical and chemical analysis, that while in certain locations, ilmenite shows relatively a marginal degree of weathering, comparable to lateritic ilmenite (Plate 35), other locations like those from samples S1 or S2 (Refer Fig.3.1; Table 5.1.6) present a more advanced state of alteration (Plate 36). The microscopic studies, too are compatible with the results of the various analysis. Magnetite is found in large quantities in the bulk mineral samples too.

Features like lenticular pits (Plate 37) and cracks (Plate 38) are frequently seen on the grains. The pits appear deep and spindle shaped on plan view. Such features are reported to arise due to the effect of dissolution of activity consequent to diagenesis (Morad and Aldahan, 1986). Such structures are suggested as a result of reducing conditions in sand stones. Detrital mass of ilmenite with leucoxene are found inside the pits and cracks (Plates 38, 39). The surfaces of some grains are mottled with fine pits (Plate 40). Etching of the grain surface along the crystallographic directions is also observed (Plate 41). The leaching of ilmenite gives rise to a diffuse body of the alteration products in the loci of alteration (Plates 38, 42). Dissolution activity has succeeded in replacing ilmenite with leucoxene in many pits and microfractures. Shrinkage cracks are seen on the grains with advanced alteration (Plates 44, 43). The flaky nature of the grain surfaces and maintenance of the outline of the grains suggest that alteration is in situ and mainly post depositional (Plates 44, 45).

It is also observed that the leucoxene is formed in grains having sharp boundaries with the adjacent ilmenite phase (Plate 46). Such grains are noted and discussed in laterites and beaches and are attributed to recrystallization (Mucke and Chaudhuri, 1991). It is possible that under favourable conditions, the in situ alteration of ilmenite is favourable to recrystallization effects. The highly porous phase of pseudorutile and/or leucoxene is seen commonly found in the pits and fractures which form the loci of alteration (Plates 39, 47). This favours further alteration due to the enhanced permeability to circulating solution and ground water action.

Brookite is reported to be the common end product of ilmenite alteration in sandstones (Morad and Aldahan, 1986). But XRD investigations of the present work provide evidence of rutile in the grains. Presence of anatase peaks are sometimes rarely observed. The existence of brookite might be due to the diagenetic changes in the sandstones, which may create favourable environment for the genesis of this mineral. The formation of anatase as a product of ilmenite alteration in laterite pallid zone was explained by Anand and Gilkes (1984). Similar conditions may apply for the formation of brookite consequent to the diagenetic processes in sedimentary formations. It has to be investigated further whether the absence of brookite or anatase in this study could be related to the younger age of the sandstones (Tertiary), when compared to the Visingso Group in Sweden, where the prevalence of brookite has been reported in weathering of ilmenite.

### 4.1.5 Ilmenite from the Teri deposits

The Teri samples show less altered grains than in the adjoining Manavalakurichi beach. Intergrowths of haematite are seen in a few grains. The leaching patterns of ilmenite grains depend on the environment of deposition. Grains with intergrowths of haematite are found with either alteration of the ilmenite phase or the leaching away of the haematite part. According to Dimanche and Batholome (1976) the patterns of alteration is dependent on the Eh-pH conditions of the deposit. Thus under reducing and acidic environments, haematite is unstable than ilmenite (Plate 48). At oxidizing conditions, ilmenite is relatively prone to alteration (Plate 49). Such variation in weathering environments point to the alteration under different conditions as described above.

### 4.1.6 Ilmenite from the Ashtamudi estuary

Ilmenite grains from this set up show evidences of transportation in the grain morphological features like pits and impact marks (Plate 50). Some of the grains are angular indicating the fast rate of transportation by rivers and/or the result of relatively short course of rivers in south Kerala. However, the large areal extent of the estuary and presence of large bodies of creeks ensure that this environment, by and large (except for the zones near the river and estuarine mouths), represent a comparably 'undisturbed locality'.

The presence of clay like bodies in pits and cracks on the surface of the grains are ascribed to this sedentary condition. Dissolution voids are frequently observed indicating insitu alteration akin to post-depositional changes of the rock units (Plate 51). The coexistence of leucoxene and clay minerals indicate the porous nature of the leucoxene phase, which aided by water lead to the precipitation of clays (Plates 52, 53). They occur as a rich aggregate mass with microcrystalline leucoxene and clayey units. Detrital powder like grains of early alteration phases including ilmenite are scattered in this mass. The association of clay like minerals along with leucoxene lends credence to the idea of dissolution-precipitation suggested by some authors (Frost et al, 1983; Anand and Gilkes, 1984; Hugo and Cornell, 1991).

Another significant observation noted is the presence of association of ilmenite/leached ilmenite and leucoxene separated by sharp boundaries (Plate 54). The various theories suggested for such growths have been dealt with in the previous section of the chapter. Mucke and Chaudhuri (1991) have argued that since alteration of ilmenite is a continuous process, such features are caused due to recrystallization of leucoxene and supersession of early phases of weathering. On the other hand, many authors suggest that direct alteration of ilmenite to leucoxene is possible in nature and both continuous and discontinuous types of leaching takes place (Hartman, 1959; Frost et al, 1983; Hugo and Cornell, 1991). In this work, it has been observed that, grains suggesting both continuous and discontinuous types of alteration are seen, along with grains that seem to indicate recrystallization effects as suggested by Mucke and Chaudhuri (1991). The occurrence of the latter type of grains, most in laterites and sandstones, as well in creeks of estuary, point to the undisturbed nature of environment in their genesis. However, comprehensive investigations are needed before such assumptions are ascertained.

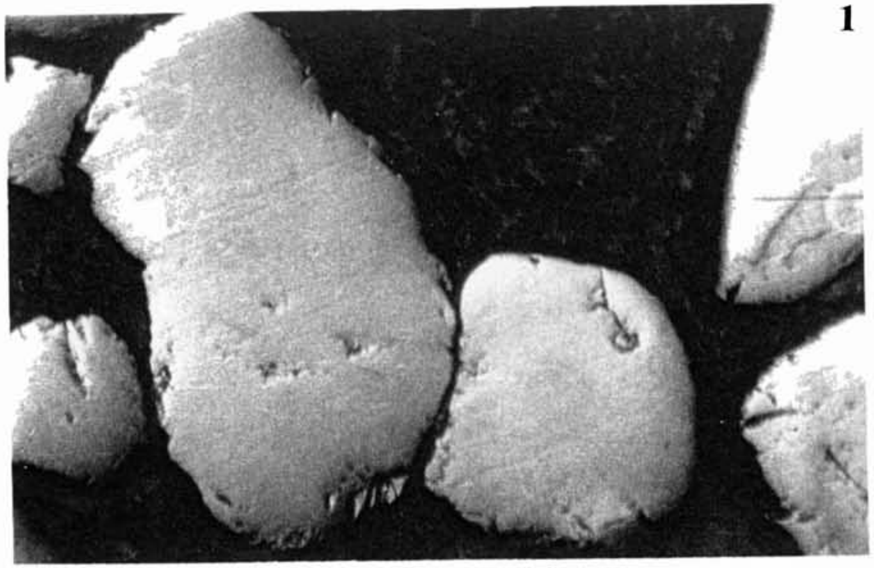
Plate 1. Ilmenite grains under reflected light. Note the slight alteration along the pits and cracks. (Laterite) (x100)

Plate 2. Alteration of ilmenite (i) into leached ilmenite (l), which occurs in patches. (Chavara beach)

Plate 3. A more advanced state of alteration showing the dominance of leached ilmenite (l) over ilmenite (i). (Chavara beach)

Plate 4. Grain showing alteration of leached ilmenite (l) to pseudorutile (p) along fractures. (Manavalakurichi beach) (x100)

1



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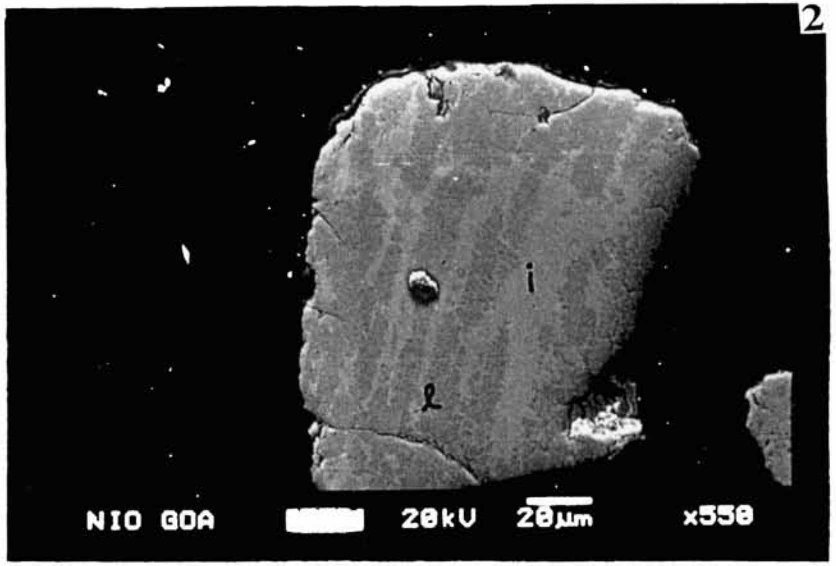

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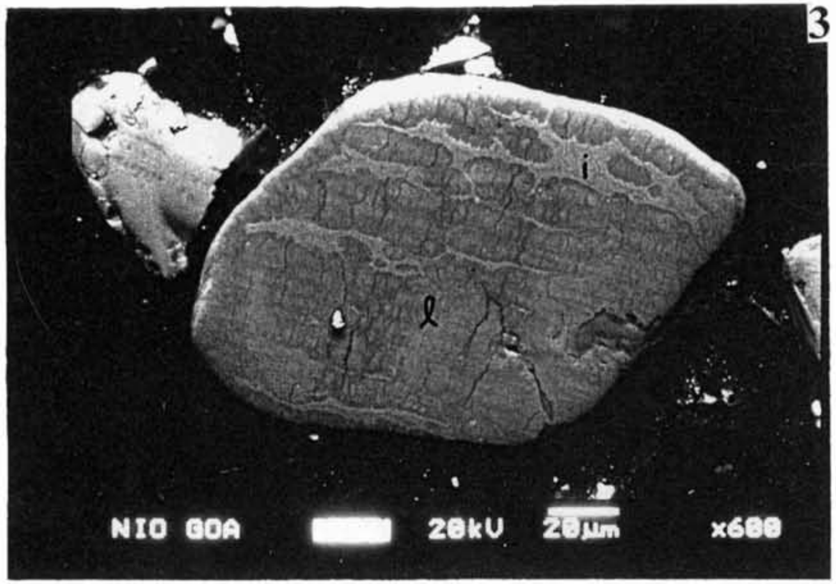

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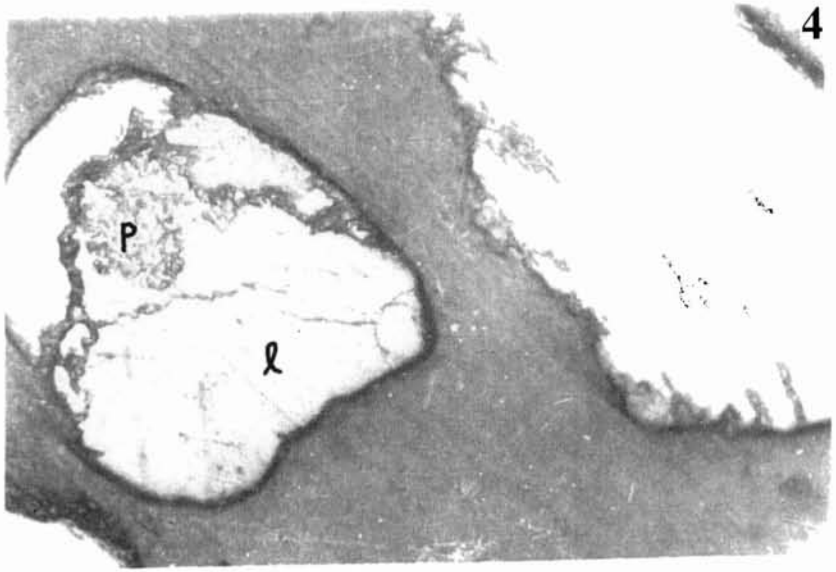
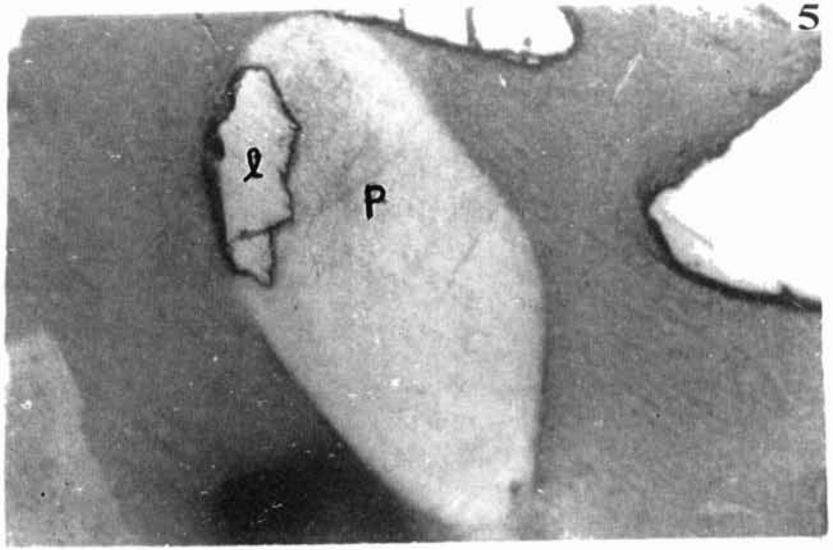


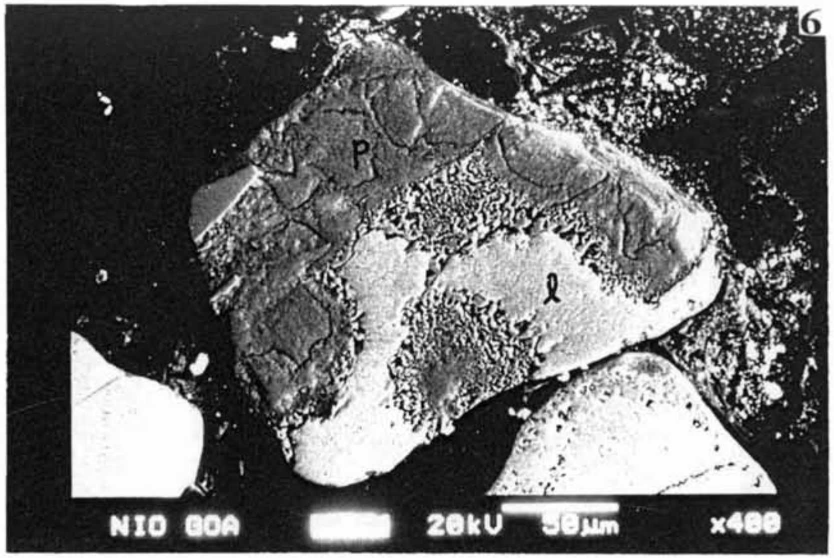
Plate 5. Alteration of leached ilmenite (l) to pseudorutile (p). Note the relict nature of the ilmenite phases and the truncation of the boundary between the phases at the grain surface. (Chavara beach) (x100)

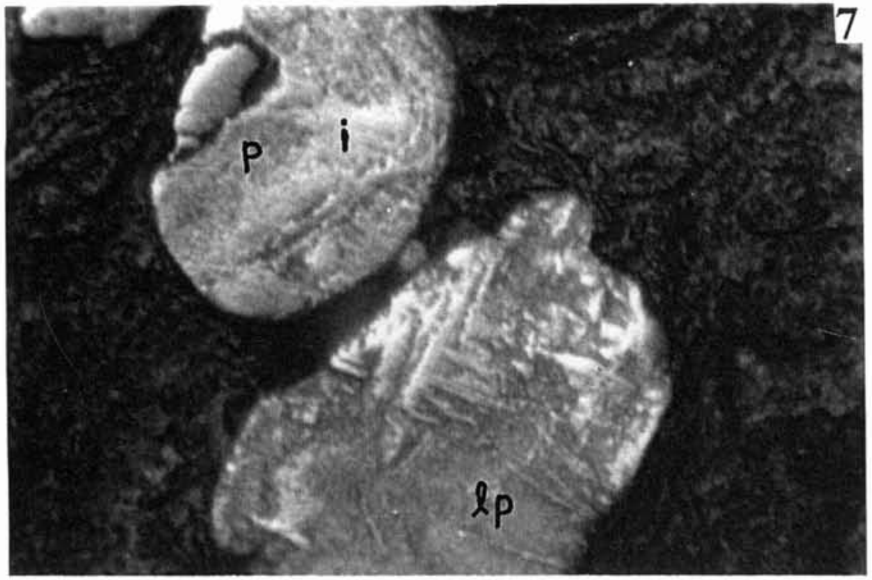
Plate 6. Replacement of leached ilmenite (l) by pseudorutile (p). Note the patchy of occurrence of ilmenite (Manavalakurichi beach)

Plate 7. Grain showing phases of leached ilmenite (l), pseudorutile (p) and leached pseudorutile (lp). Note the shrinkage cracks. (Chavara beach) (x100)

Plate 8. Grain showing alteration of ilmenite (i) into leucoxene (lx). Relatively unaltered grains are also seen. (Chavara beach) (x50)


5
l
P


6
P
l
NIO GOA
20kV
50μm
x400


7
P
i
lp

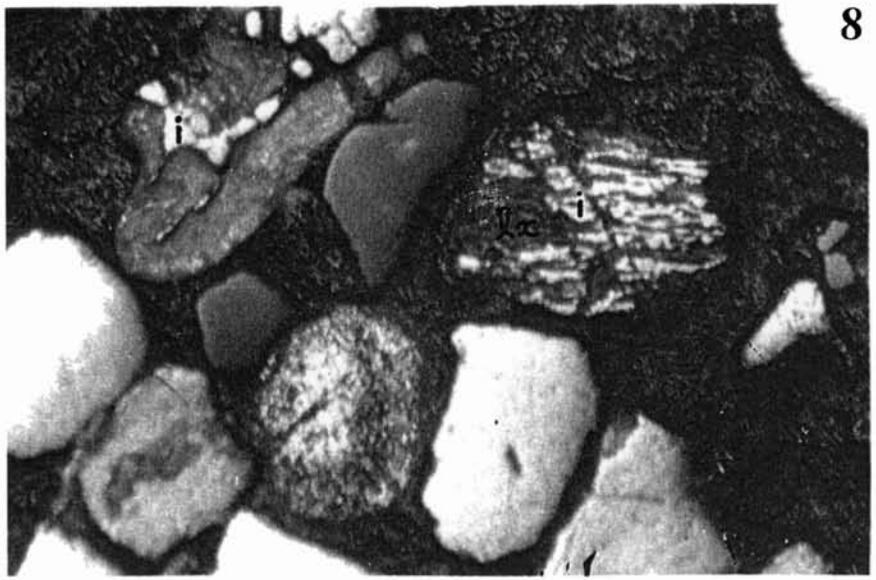
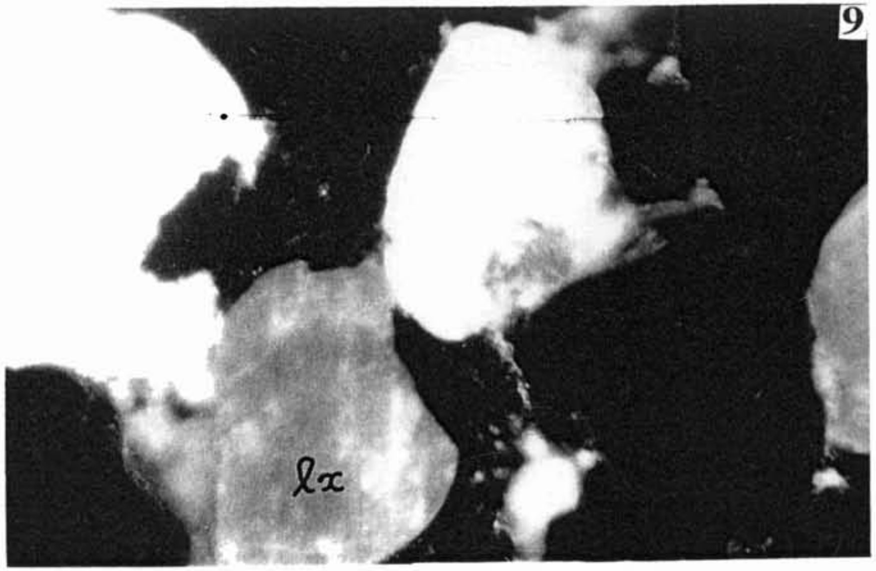

8
i
lx
i

Plate 9. Leucoxene grain (lx) showing internal reflections. (Chavara beach) (x50)

Plate 10. Replacement of pseudorutile (p) by leucoxene (lx). Note the internal reflection in the leucoxene phase. (Chavara beach) (x100)

Plate 11. Grain showing leucoxene (lx) replacing leached ilmenite (l). Note the porous nature of the leucoxene at the boundary between the phases and the truncation of the boundary between the phases at the grain surface. (Chavara beach)

Plate 12. Leucoxene (lx) formation showing fingerprint like structures. An ilmenite relict (i) is also seen. (Chavara beach)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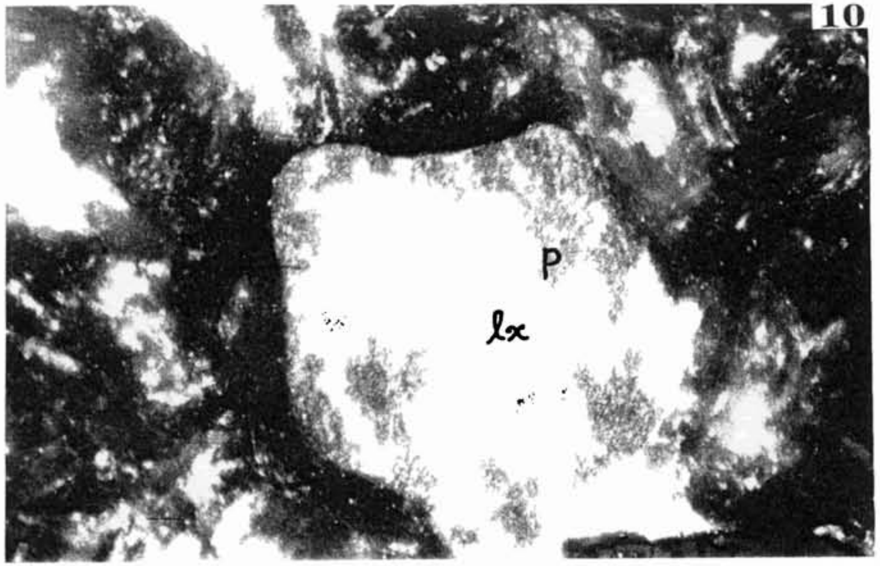
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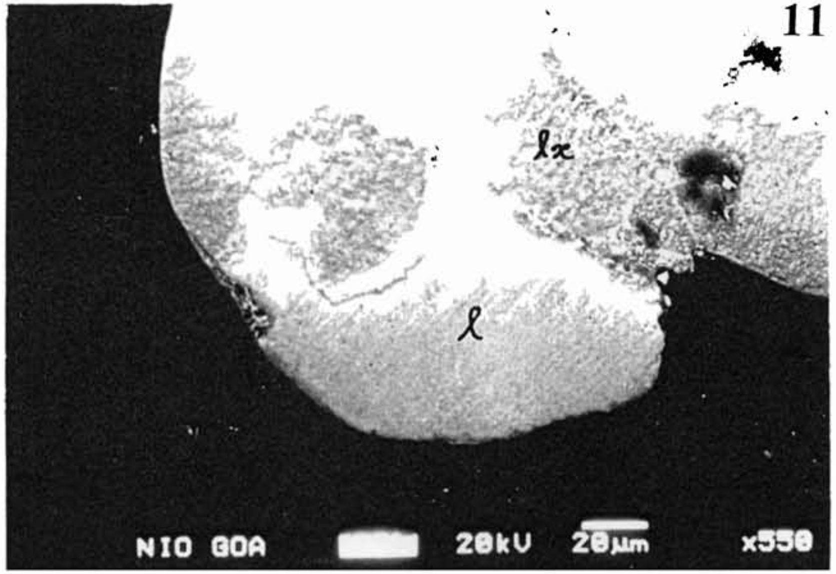
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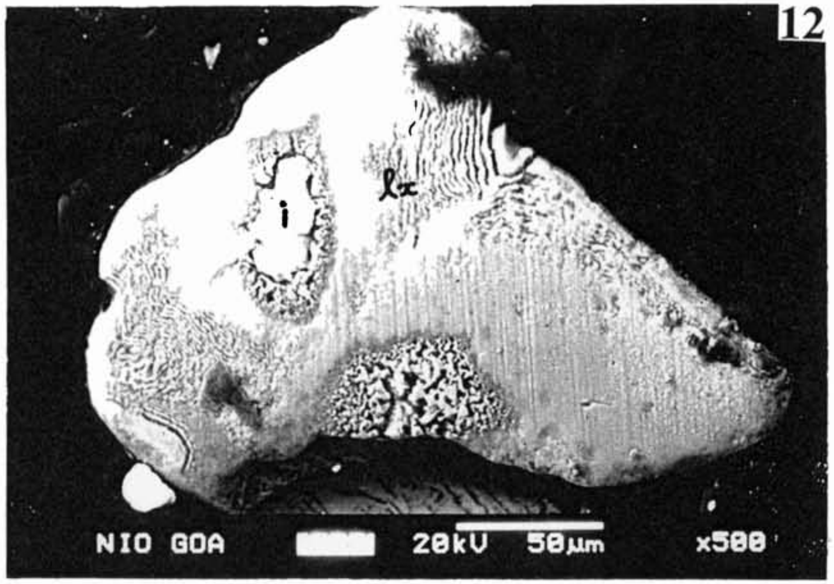
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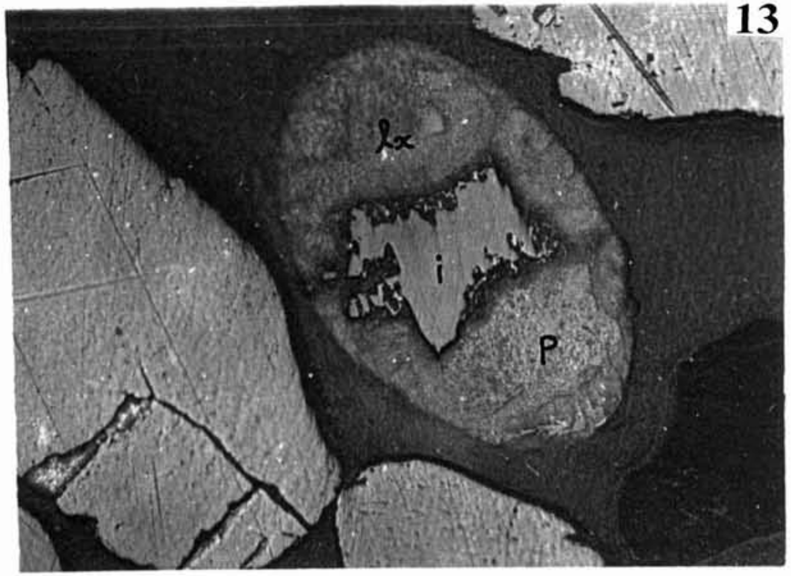
Plate 13. Ilmenite relict (i) in a sea of altered phases, pseudorutile (p) and leucoxene (lx). (Manavalakurichi beach)

Plate 14. Alteration along cleavage lines in the ilmenite grain. (Chavara beach)

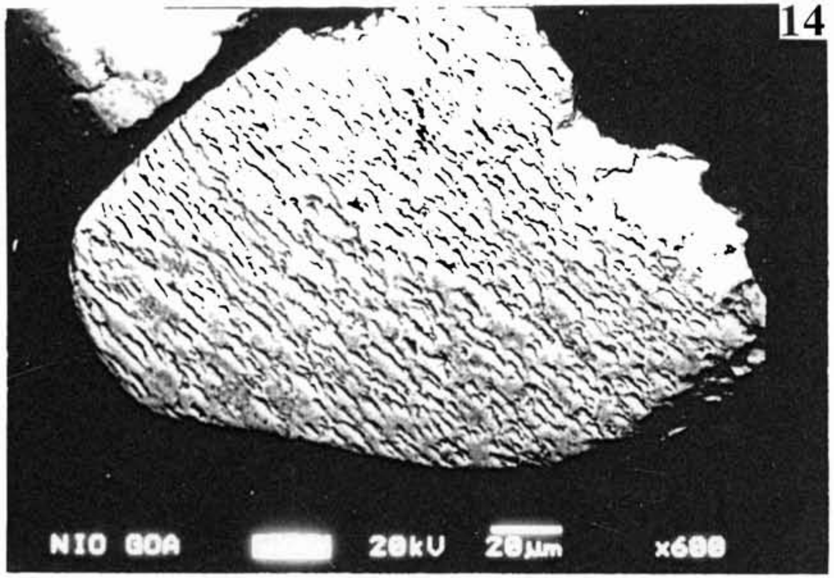
Plate 15. Discontinuous transformation of ilmenite (i)/ leached ilmenite (l) into leucoxene (lx). (Chavara beach)

Plate 16. Alteration of ilmenite (i)/leached ilmenite (l) in to leucoxene (lx), showing sharp boundaries between the phases. (Chavara beach)

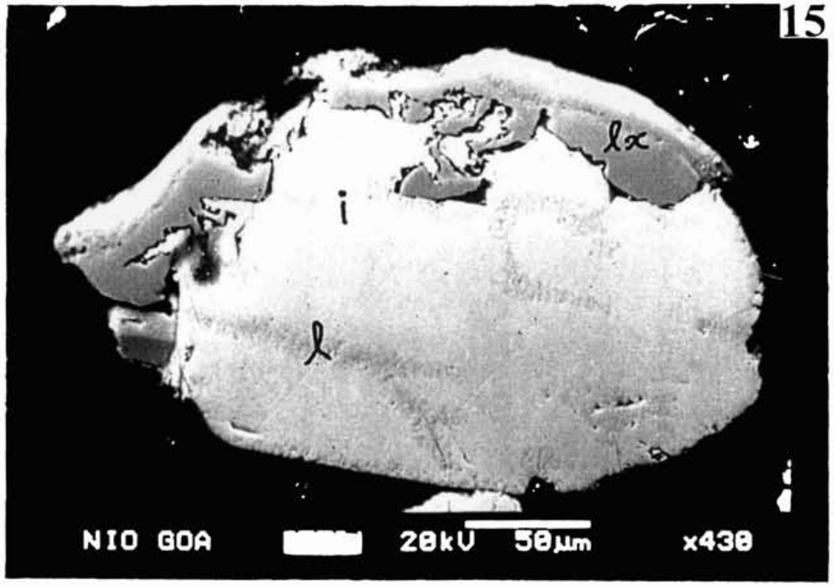
13


lx
i
P

14


NIO GOA
20kV
20µm
x600

15


lx
i
l
NIO GOA
20kV
50µm
x430

16

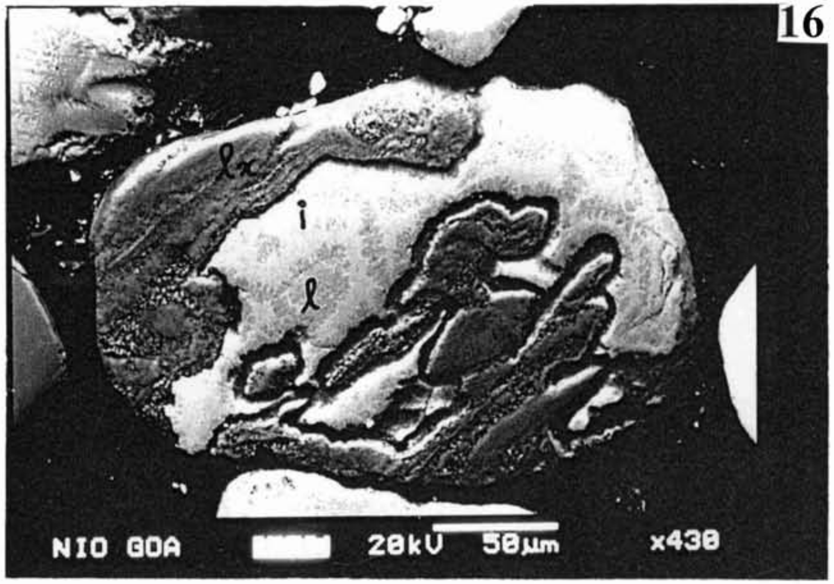

lx
i
l
NIO GOA
20kV
50µm
x430

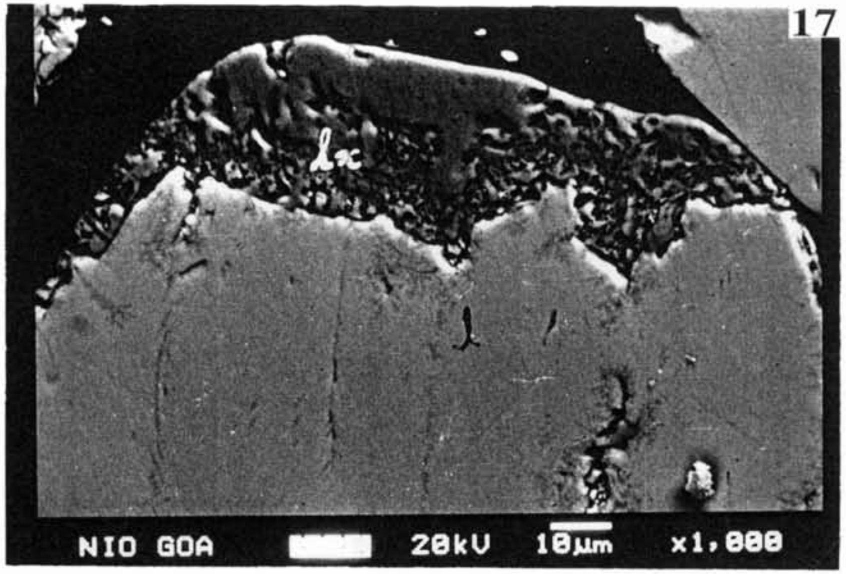
Plate 17. Alteration along the grain boundary showing leucoxene (lx) replacing leached ilmenite (l). (Manavalakurichi beach)

Plate 18. Discontinuous transition of ilmenite (i)/leached ilmenite to leucoxene (lx). Note the replacement of ilmenite by leached ilmenite along cleavage lines. (Chavara beach)

Plate 19. Altered phases of ilmenite in a crack on the grain surface. Fine clay like bodies (a) are seen in association with the altered phases. (Chavara beach)

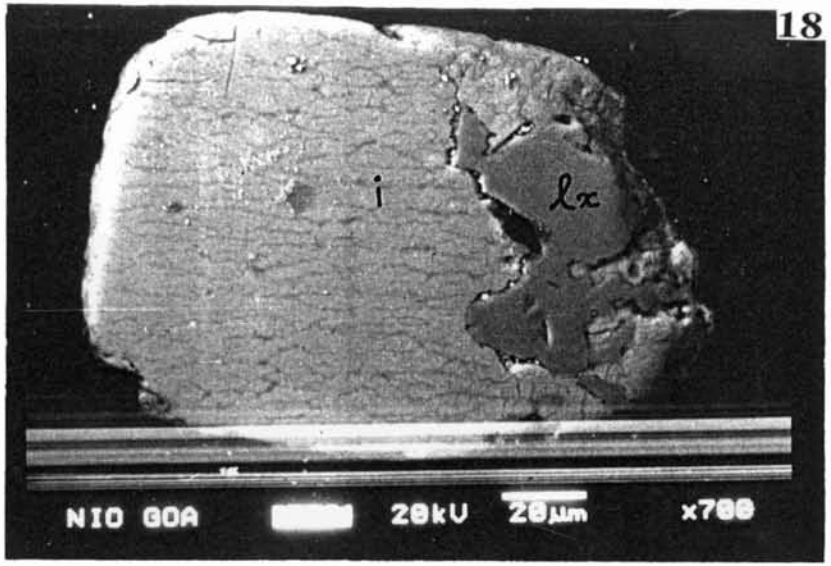
Plate 20, Crack on the grain surface showing detrital altered phases of ilmenite. (Manavalakurichi beach)

17



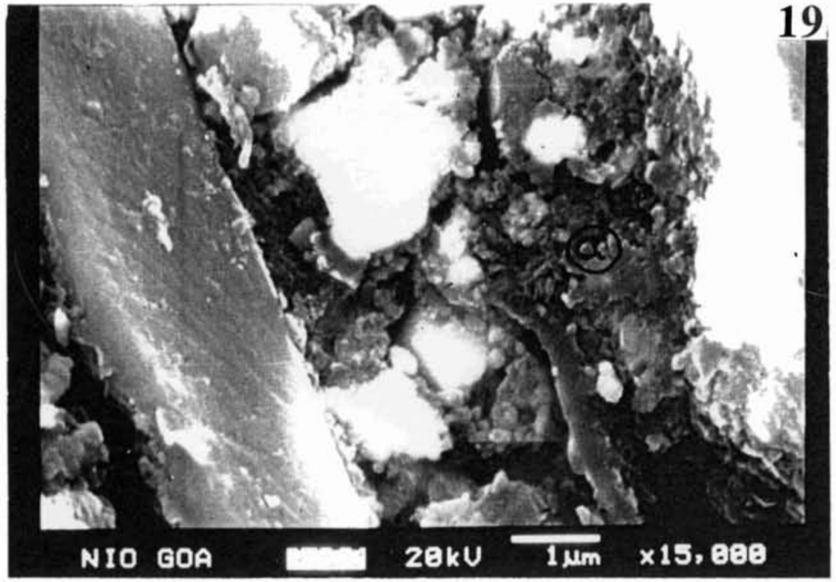
lx
l
NIO GOA
20kV
10µm
x1,000

18



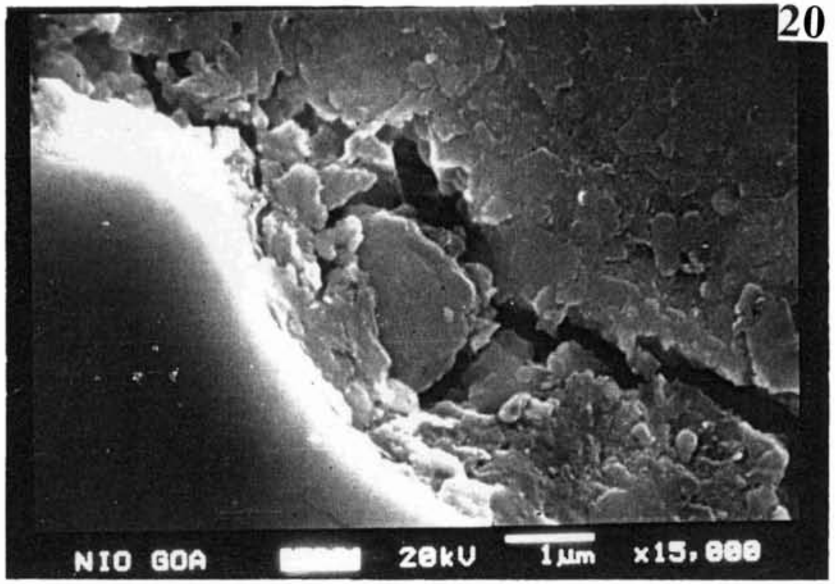
i
lx
NIO GOA
20kV
20µm
x700

19



NIO GOA
20kV
1µm
x15,000

20



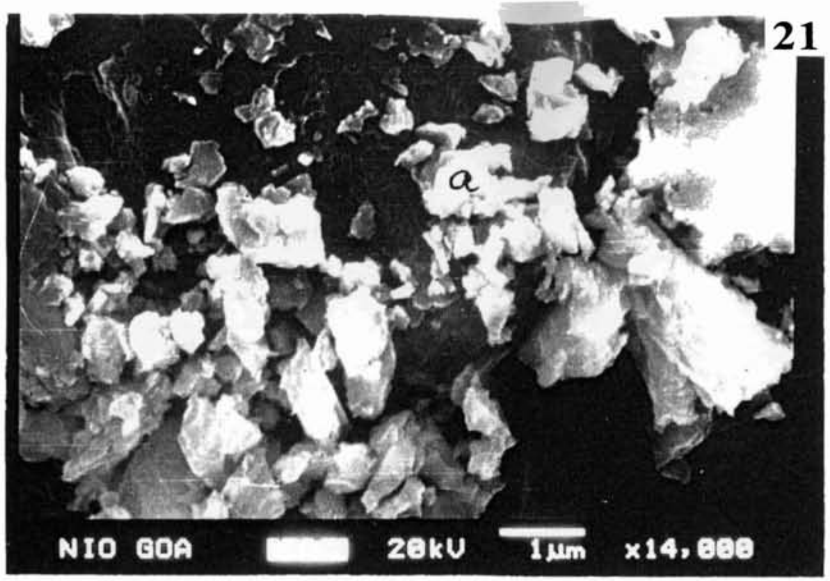
NIO GOA
20kV
1µm
x15,000

Plate 21. Clay like bodies (a) inside a fracture on the grain surface. (Chavara beach)

Plate 22. Ilmenite grains from Chavara deposit showing advanced alteration. (x50)

Plate 23 & 24. Ilmenite grains from Manavalakurichi showing limited scale of alteration. (x10)

21



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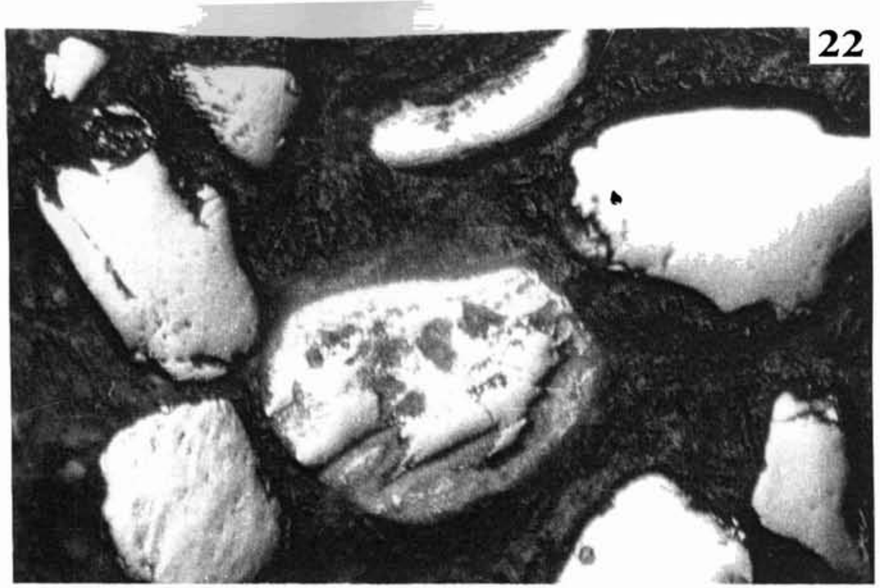

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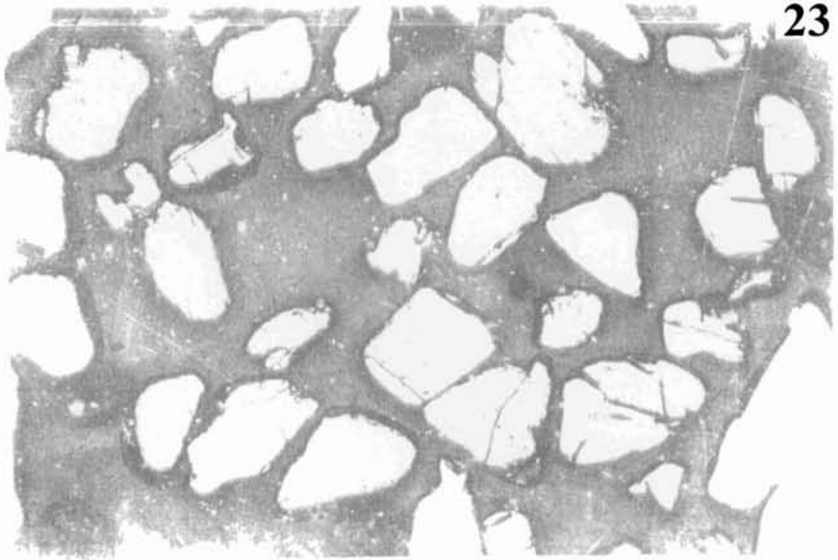

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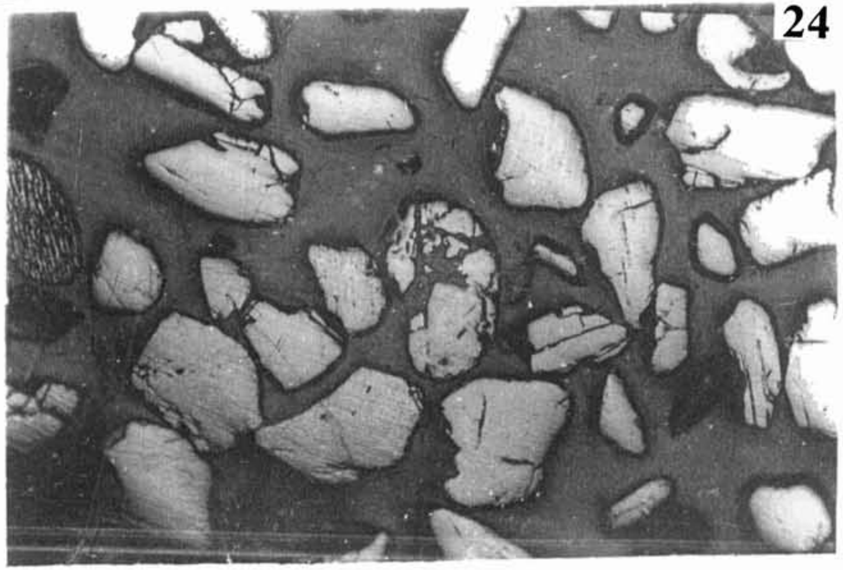
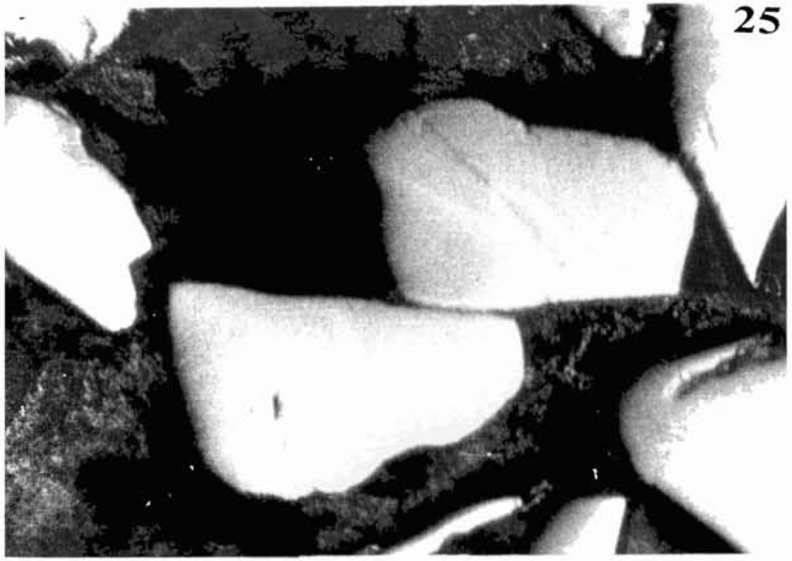


Plate 25. Relatively 'fresh' ilmenite grains from laterite, showing angular grains (x100)

Plate 26 & 27. Limited alteration along fractures on the grain surfaces (laterite) (x50)

Plate 28. Grain showing discontinuous alteration to leucoxene (lx) along fractures. (laterite)

25



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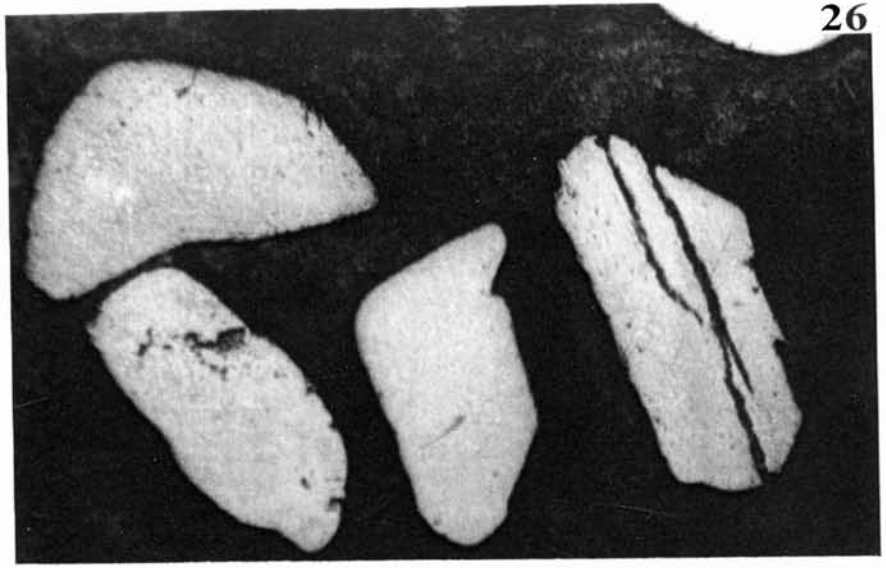

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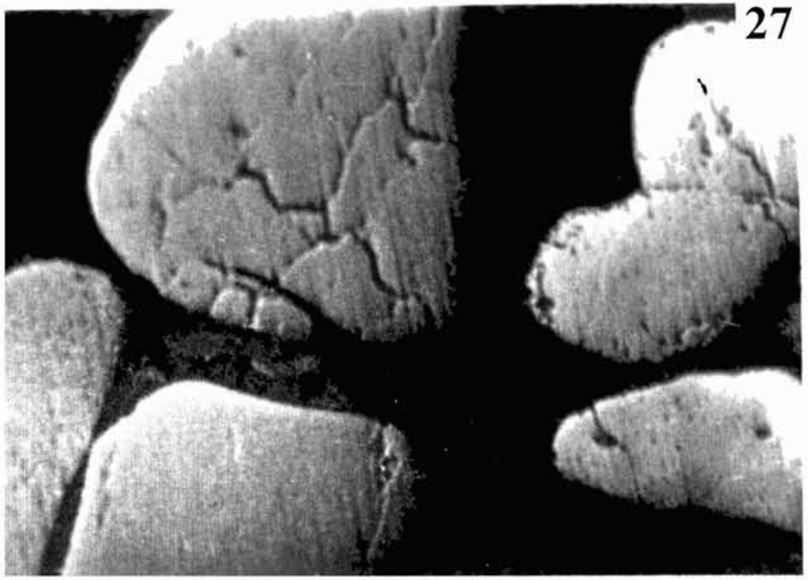

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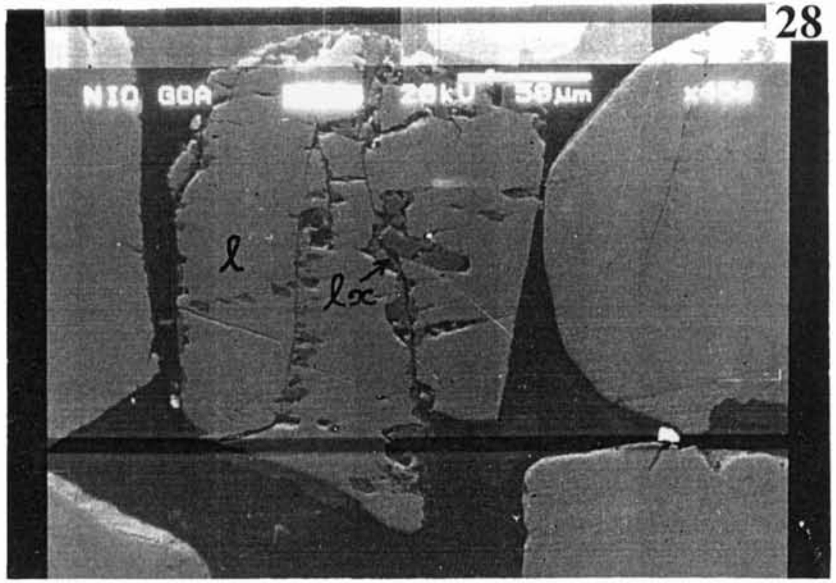
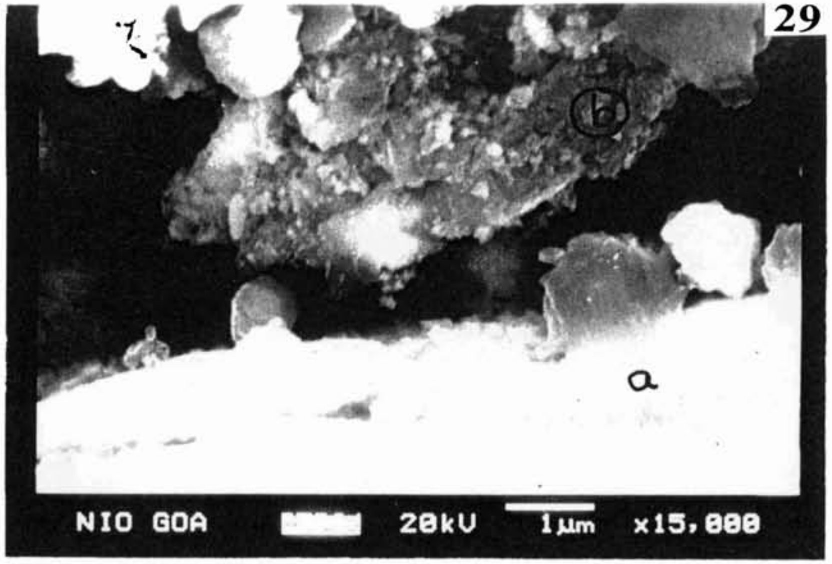


Plate 29 & 30. Alteration in pits on the grain surface showing association of the altered phases (a) and clay like masses (b). (laterite)

Plate 31 & 32. Grain showing seriate texture with alternating lamellae of ilmenite (dark grey) and haematite (light grey). (laterite-cordierite gneiss)



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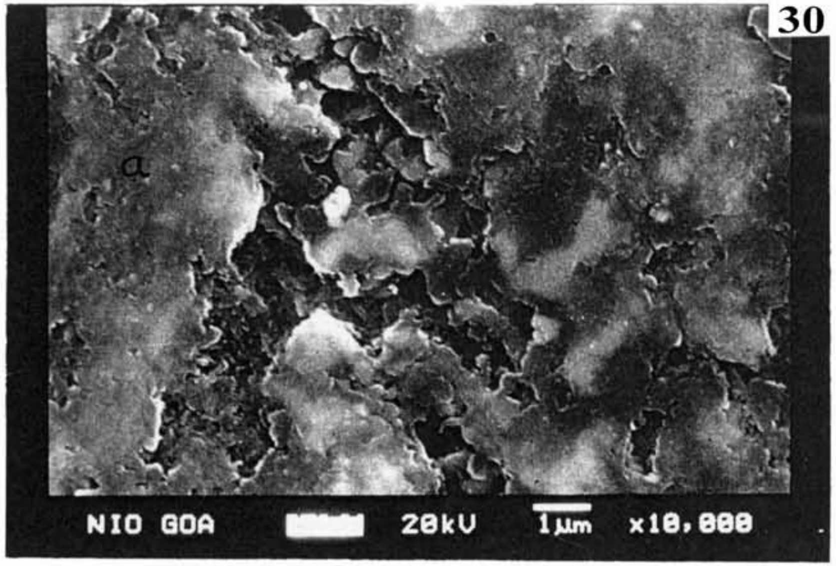

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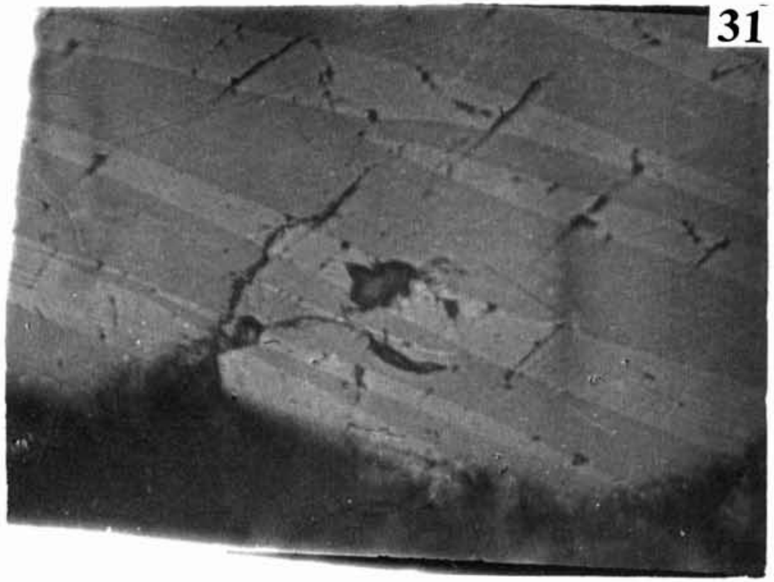

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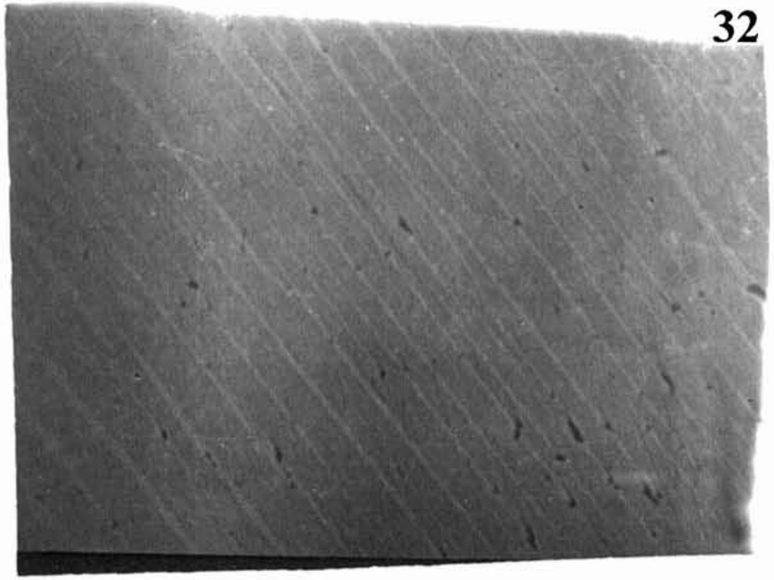


32

Plate 33. Blebs and patches of magnetite (light grey) in ilmenite (dark grey) host forming emulsion texture.

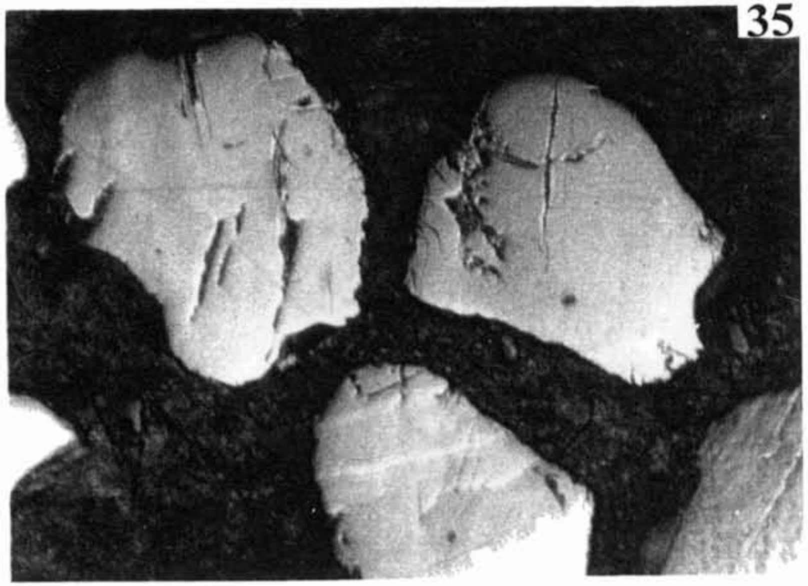
Plate 34. Grain exhibiting interlocking relationship of ilmenite (dark grey) and magnetite (light grey)

Plate 35. Marginal alteration in ilmenite grain from Tertiary sandstone (S4), showing pseudorutile (p) and leucoxene (lx) phases. (x100)

Plate 36. Ilmenite grains in advanced state of alteration in sandstone (S1) (x100)


33


34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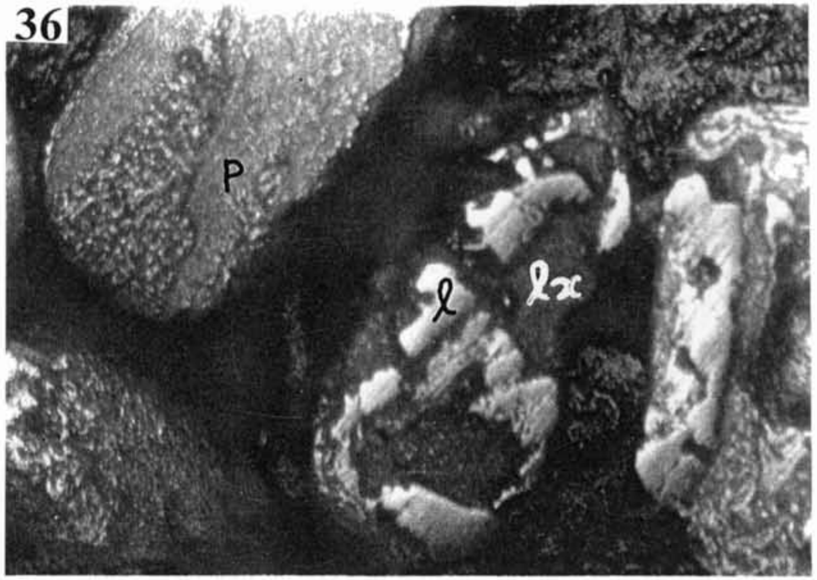

36

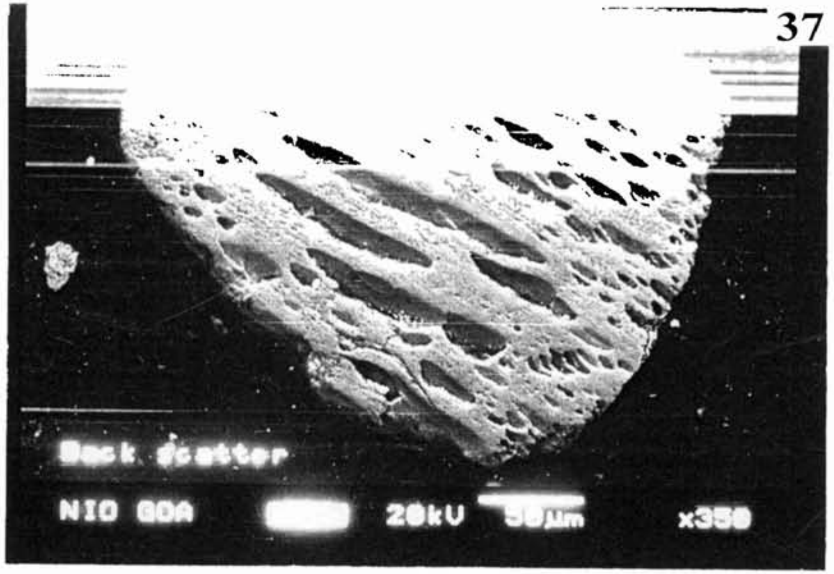
Plate 37. Lenticular pits formed due to dissolution activity in sandstone

Plate 38. Pit on the grain surface containing highly leucoxenised portions (lx) with relict patches of leached ilmenite (l). (sandstone)

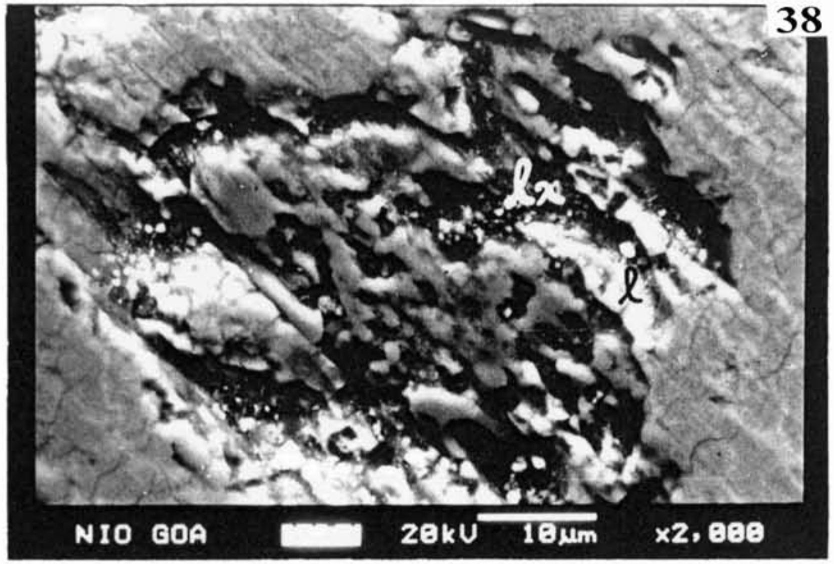
Plate 39. Magnified view of a pit on the grain surface showing association of highly altered (a) phases with ilmenite

Plate 40. Highly pitted surface of an altered grain (sandstone)

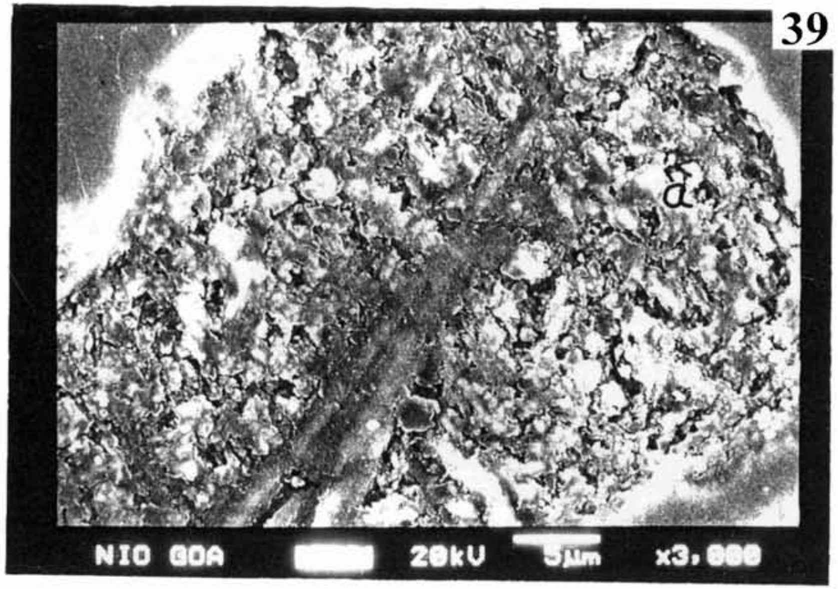
37


Back scatter
NIO GOA
20kV
50µm
x350

38


lx
l
NIO GOA
20kV
10µm
x2,000

39


a
NIO GOA
20kV
5µm
x3,000

40

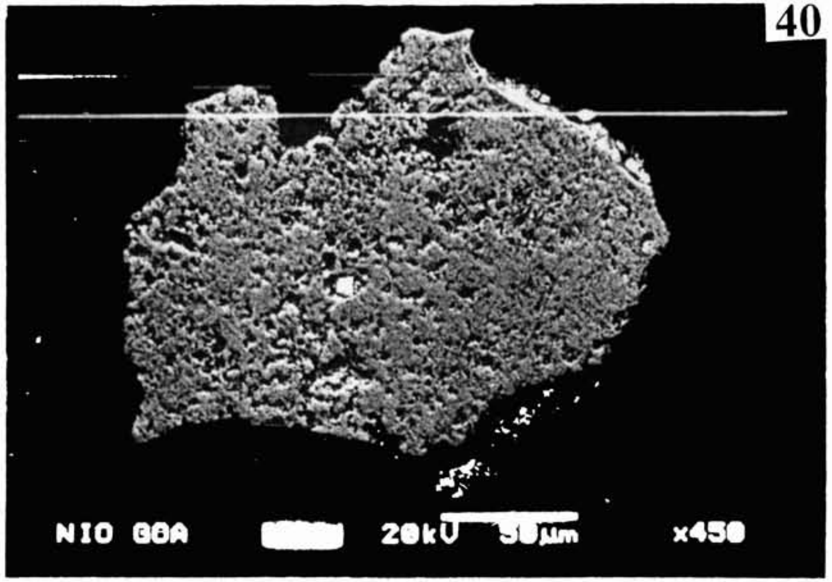
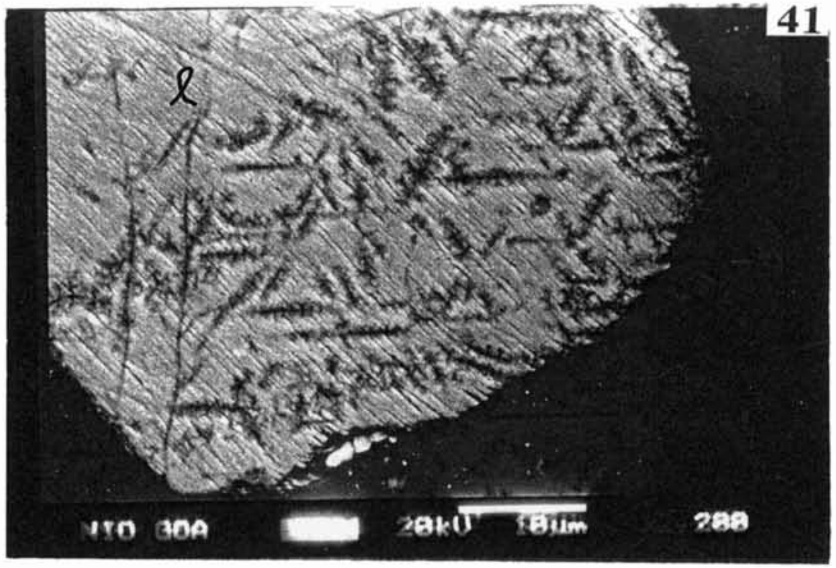

NIO GOA
20kV
50µm
x450

Plate.41. Alteration of ilmenite resulting in etch-like marks along the crystallographic directions

Plate 42 & 43. Grains in advanced state of alteration into pseudorutile (p) /leucoxene. Note the shrinkage cracks (a) formed. (sandstone)

Plate 44. Flaky nature of the grain surfaces due to insitu alteration. (sandstone)

41


l
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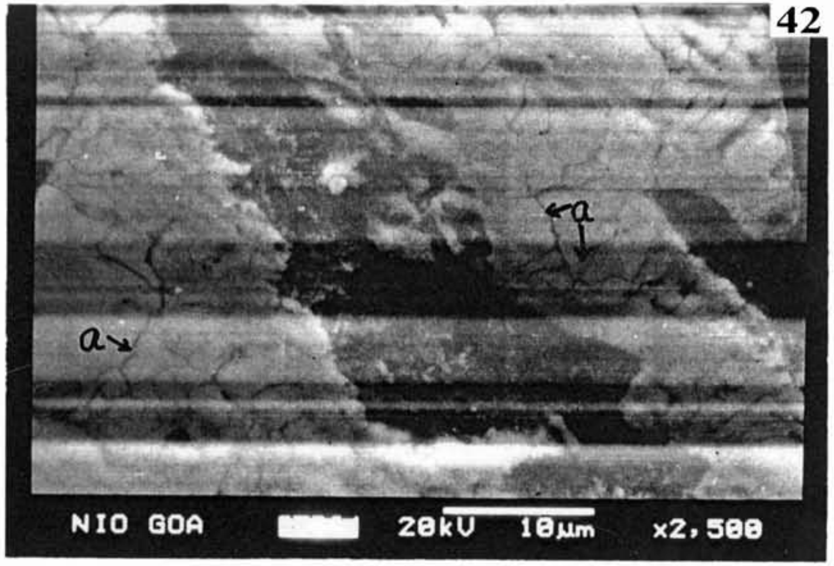
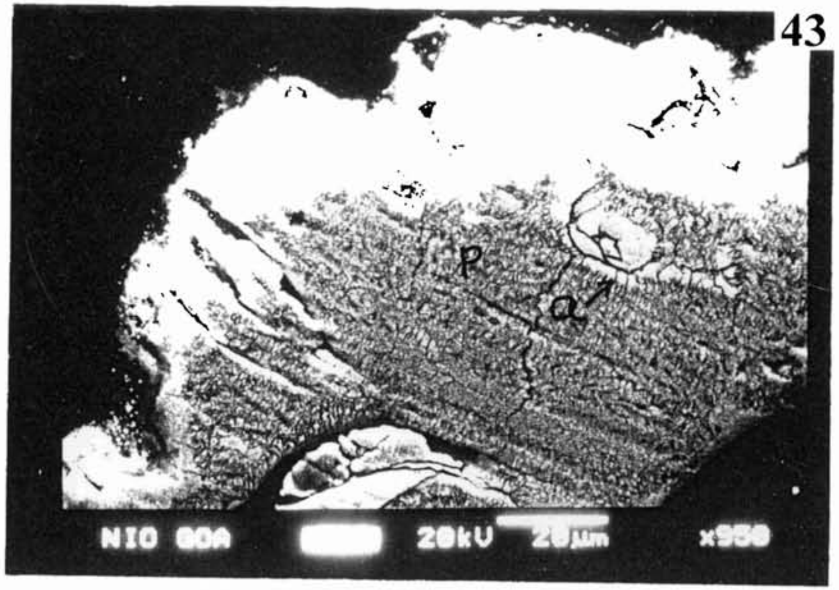
20kV
10µm
200

42


a
a
NIO GOA
20kV
10µm
x2,500

43


P
a
NIO GOA
20kV
20µm
x950

44

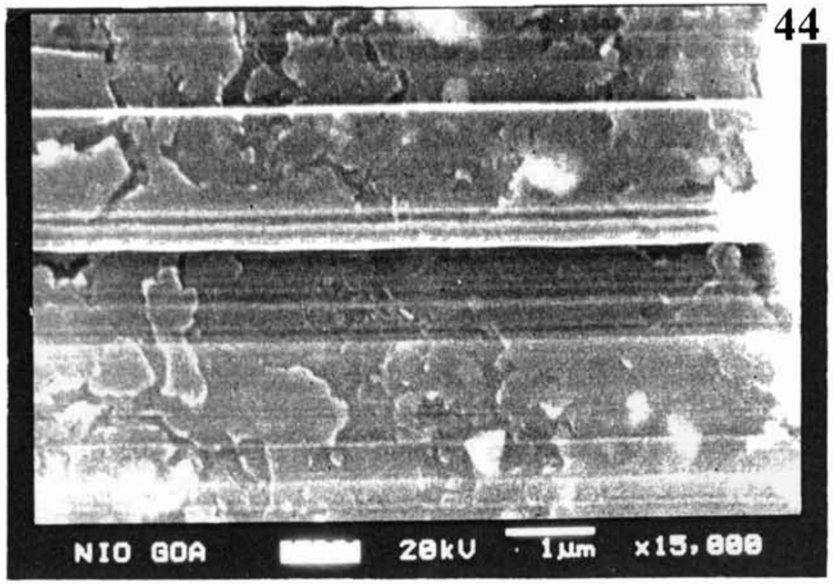

NIO GOA
20kV
1µm
x15,000

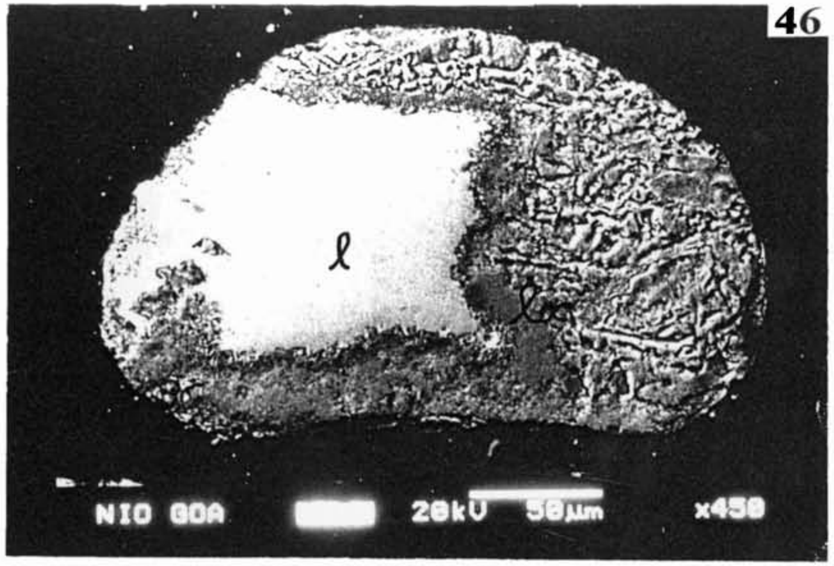
Plate 45. Grain (left hand side of the plate) showing alteration advancing from the rim of the grain. Note that the outline of the grain (a) could be seen despite alteration. (sandstone) (x100)

Plate 46. Alteration of leached ilmenite (l) to leucoxene (lx). Note the sharp boundary between the phases. (Sandstone)

Plate 47. Highly porous advanced altered phases of ilmenite with in a pit on the grain surface. (sandstone)

45

46



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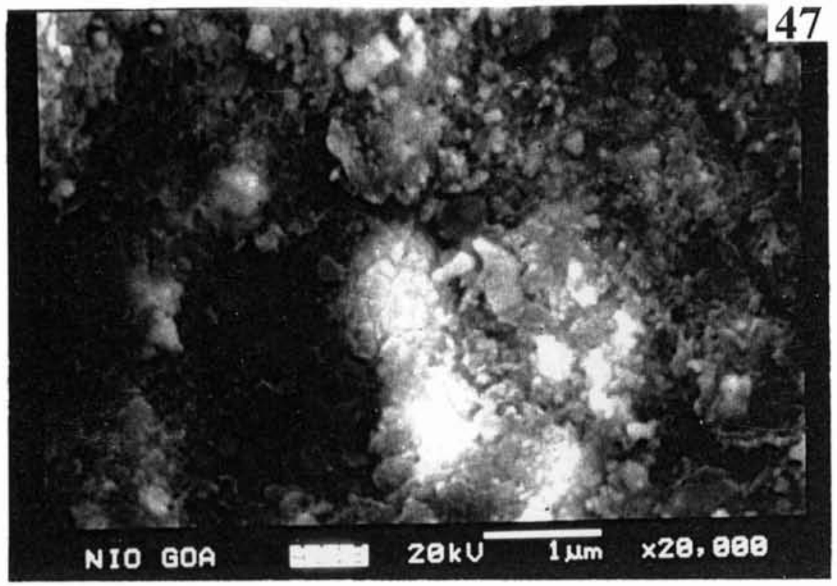


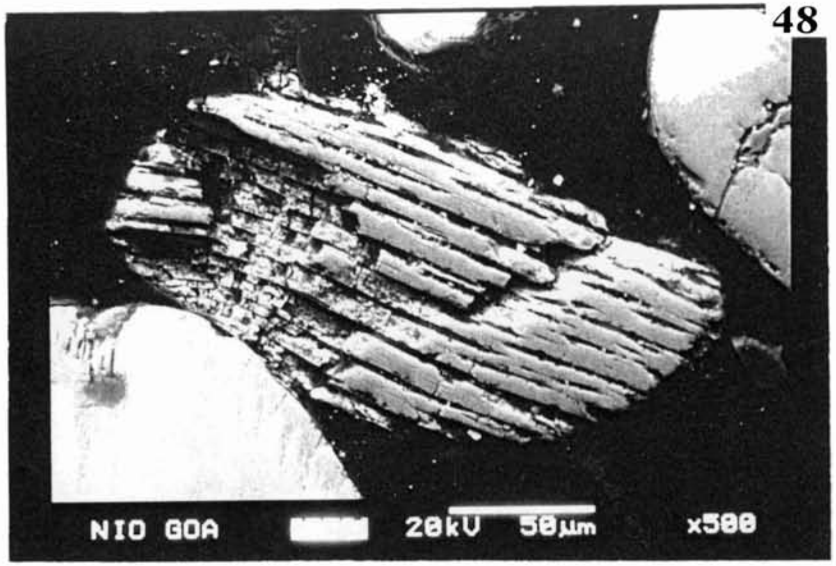
Plate 48. Alteration along cleavage lines in the grain. The fractures are likely to be caused by the dissolution of haematite. (Teri)

Plate 49. Grain showing intergrowth of ilmenite (dark grey) in a haematite (light grey) host. (Teri)

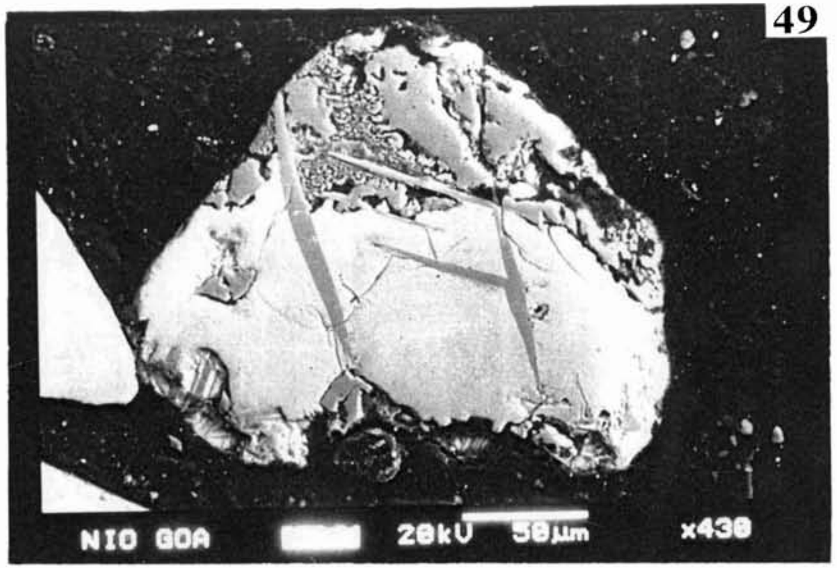
Plate 50. A fracture on the ilmenite grain surface showing detrital ilmenite with altered phases (b). (Estuary)

Plate 51. Pits formed by dissolution activity containing altered phases. (Estuary)

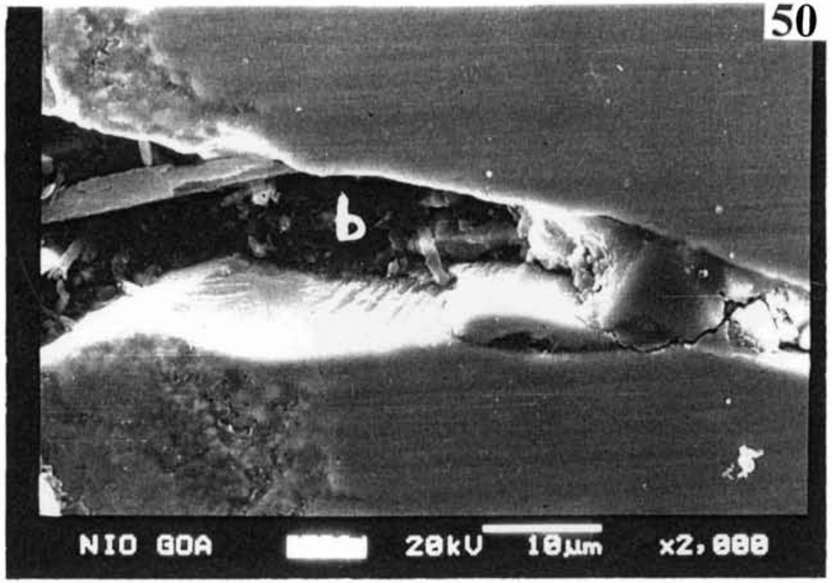
48


NIO GOA
20kV
50µm
x500

49


NIO GOA
20kV
50µm
x430

50


b
NIO GOA
20kV
10µm
x2,000

51

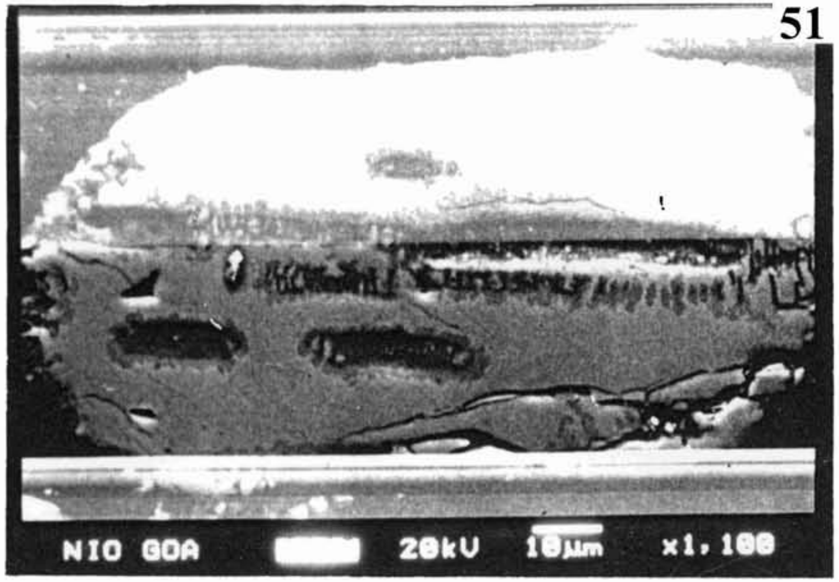
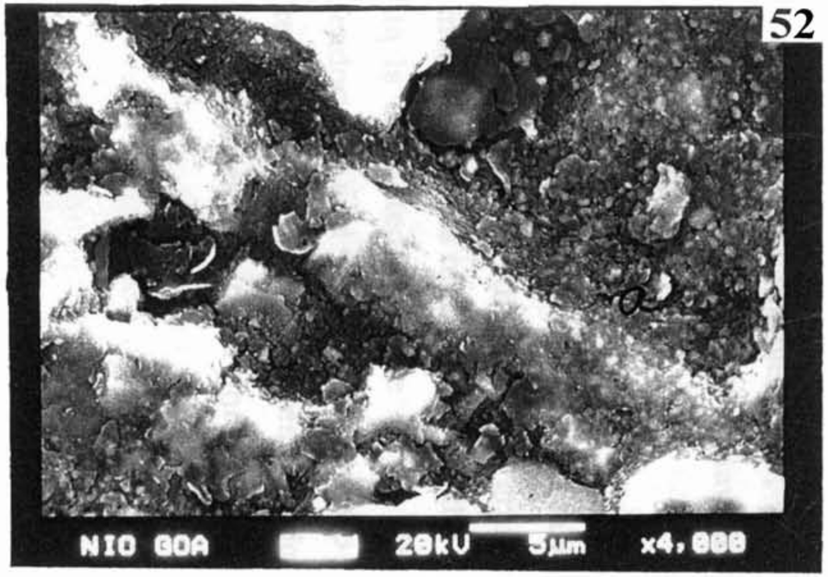

NIO GOA
20kV
10µm
x1,100

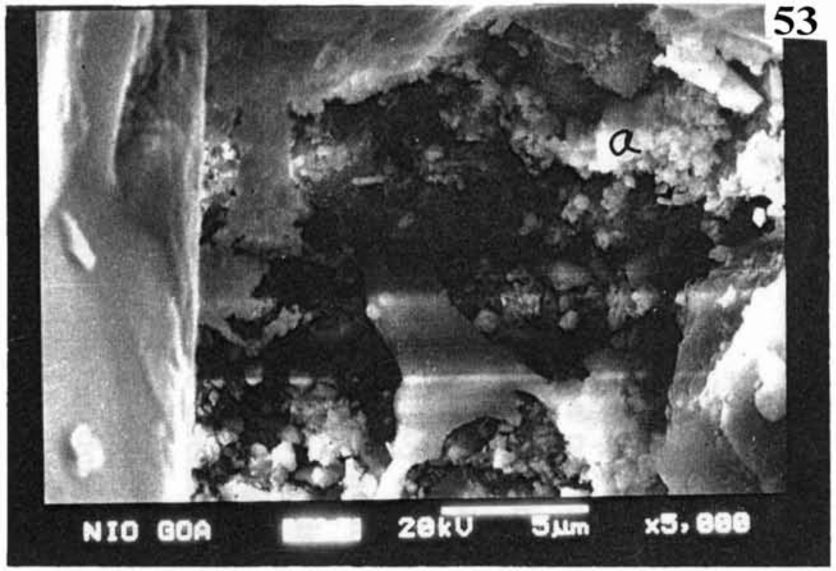
Plate 52 & 53. Leucoxene and other altered phases associated with clay like mass (a) in cracks on the grains. (Estuary)

Plate 54. Association of ilmenite (i) and leucoxene (lx) forming sharp boundary between the phases. (Estuary)

52


a
NIO GOA
20kV
5µm
x4,000

53


a
NIO GOA
20kV
5µm
x5,000

54


i
lx
NIO GOA
20kV
50µm
x350

## Part 4.2. X -RAY DIFFRACTION STUDIES

### 4.2.1 Introduction

X Ray diffraction has been a powerful tool in mineralogical studies, from the early decades of the 20th century. The versatility of the various X ray methods are useful that they could be used both in quantitative and qualitative modes of analyses in mineralogical and chemical investigations. While the phenomenon of X ray diffraction is used in the mineralogical identification and estimation of mineral phases present in geological samples, its spectral properties are used in various instruments for qualitative chemical analysis. XRD studies on geological samples throw light on the mineralogical changes consequent to weathering, but also aid the determination of structural changes on the unit cell lattice of the mineral. The details regarding the methodology followed and the instrument used are described in Chapter 3. The XRD data of ilmenite and its alteration phases have been described earlier (Bailey et al, 1956; Temple, 1966; Wort and Jones, 1980; Subrahmanyam et al, 1982, frost et al, 1986; Chaudhuri and Newesely, 1990; Mucke and Chaudhuri, 1991).

Samples were subjected to XRD analysis so as to understand the mineral phases present in the ilmenite grains. The quantitative amount of the mineral phases is measured from the respective peaks (Fig. 4.2.2) and the data is tabulated in Table 4.2.1. Since many of the diffracion lines of pseudorutile and rutile often overlap and are diffused, the peaks of the intermediate alteration phases pseudorutile and rutile are taken together and accounted as altered phases in this work.

### 4.2.2 Phase identification

The XRD patterns reveal that the important diffractions lines are those of ilmenite, rutile and pseudorutile. While the ilmenite concentrates from the laterite samples in general are dominated by ilmenite peaks, the beach and other hinterland samples contain a significant proportion of the weathered phases. As would be seen in the following sections, the weathering may be so advanced as to render the dominance of the pseudorutile/rutile over ilmenite in some samples. Ilmenite peaks are commonly observed to be narrow and sharp, pointing to the well-formed crystalline structure of the phase. The peaks of pseudorutile and leucoxene/rutile are broader and diffused, indicating the poor crystallinity of the mineral structure. The crystallinity of these phases points to their probable secondary origin, which confirm that the rutile in the samples of this study does not owe its genesis to the high temperature reactions in the parent rocks during magmatic crystallization. The occurrence of primary rutile has been reported in ilmenite grains (Haggerty, 1976; Frost et al, 1986; Hugo and Cornell, 1991). Thus the mineral, formed as a result of the leaching out of iron from the mineral structure is microcrystalline rutile, as per the present investigations and not anatase or brookite as reported elsewhere (Anand and Gilkes, 1984; Morad and Aldahan, 1986).

The most intense diffraction line of ilmenite phase is due to the crystallographic face (104) with d values of 2.74 $A^0$. The other principal peaks are formed by the crystallographic faces (116), (204), (110), (108) and (113). The rutile (leucoxene) peaks are characterized by the following diffraction lines of the faces (211), (101), (111) and (210). The intermediate phase of pseudorutile is characterized by the diffraction lines of (102), (100) and (101). The diffraction lines of rutile and pseudorutile overlap, as a result of the similarity in the d values and hence the weathered products are marked together for both the phases as R/PR.

In the present work, the quantitative estimation of the mineral phases in the samples is carried out by the semiquantitative methods as reported in Ramakrishnan et al (1997). The results are presented in Table 4.2.1.

### 4.2.2.1 Ilmenite from beach

Six samples were selected from the Chavara deposit. The formation of pseudorutile/rutile is significant in all the samples (Fig. 4.2.1; Table 4.2.1). The altered phases constitute near to about half or more of the samples. These phases range from about 27% (C1) to a maximum of 55% in C4. The XRD patterns for the Chavara ilmenite as published by Ramakrishnan et al (1997) are compared with those of samples from Manavalakurichi deposit. The Chavara samples, in general shows more content of the alteration phases than those of the Manavalakurichi deposit, the most important beach placer deposit in the southwest coast after the Chavara deposit. The ilmenite phase ranges from about 45% to a maximum of around 72%. The maximum value is shown by the ilmenite from the southernmost sample of the Chavara deposit. This echoes the chemical results, which would be dealt later in the work. The plausible reason for the significant lower degree of alteration of this sample when compared to the other samples from the Chavara deposit is the accumulation of fresh material to the southern extremity, by the dominant northern currents and the refraction of the waves due to the change in attitude of the Neendakara headland. In the Manavalakurichi deposit, the samples contain ilmenite phases around 84%, which point to the limited grade of alteration suffered (Fig. 4.2.2). The sample, M3 is found to be the maximum altered sample, where the ilmenite content seems to be about 77% in the mineral grains. The chemical analysis too

Table 4.2.1 Distribution of ilmenite and altered phases in the ilmenite samples from Chavara and Manavalakurichi beaches

| Deposit | *Sample No. | Ilmenite Phase (*I) % | Altered Phases (*R/PR) % |
|---|---|---|---|
| Chavara | C1 | 72.63 | 27.37 |
| | C2 | 52.9 | 47.1 |
| | C3 | 45.84 | 54.16 |
| | C4 | 44.71 | 55.29 |
| | C5 | 47.94 | 52.6 |
| | C6 | 69.3 | 30.7 |
| Manavalakurichi | M1 | 83 | 17 |
| | M2 | 84 | 16 |
| | M3 | 77 | 23 |
| | M5 | 84 | 16 |

*I -Ilmenite *R/PR -Rutile/Pseudorutile

*See Fig. 3.1 for sample locations

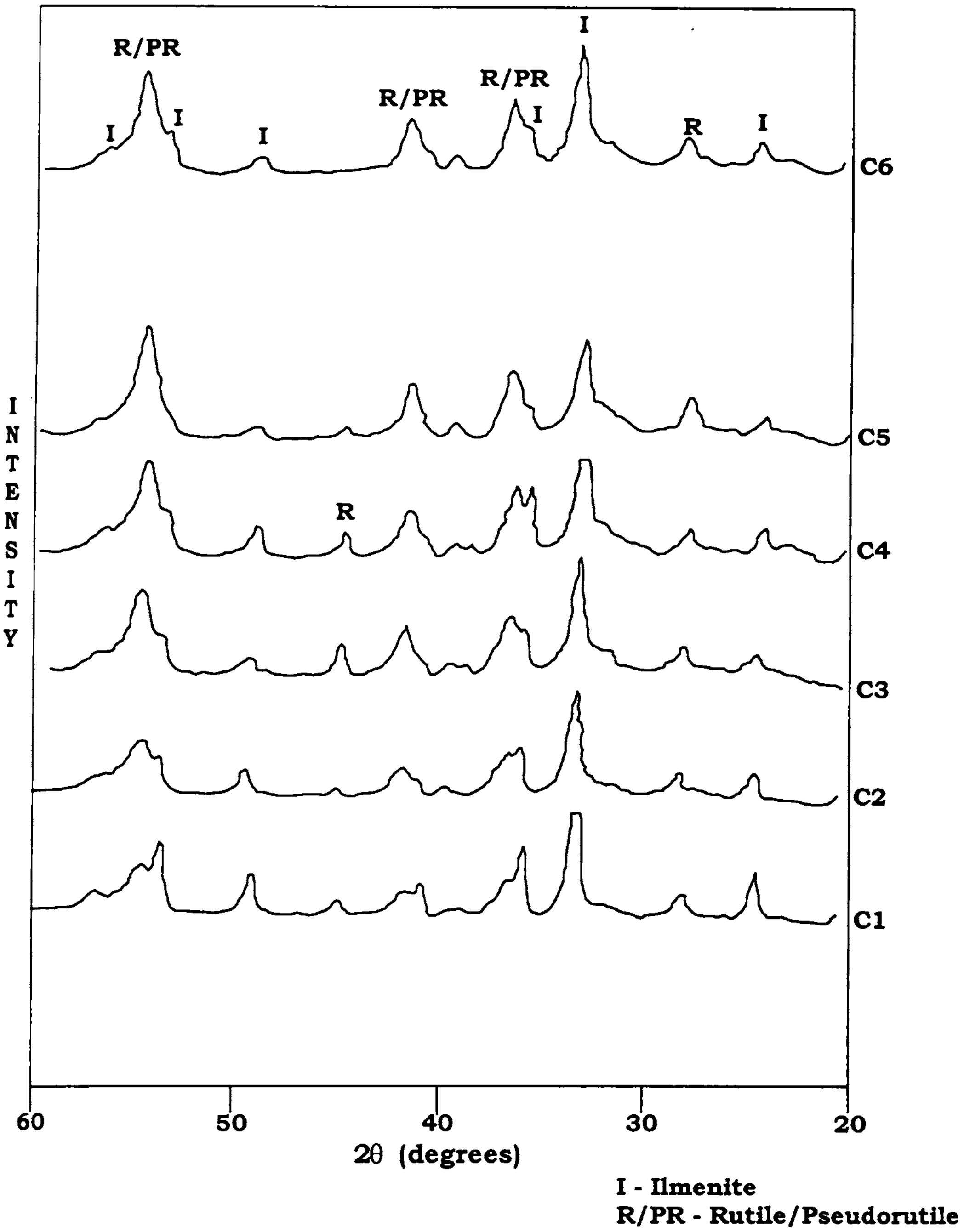


Fig. 4.2.1. XRD patterns of ilmenite samples from Chavara beach

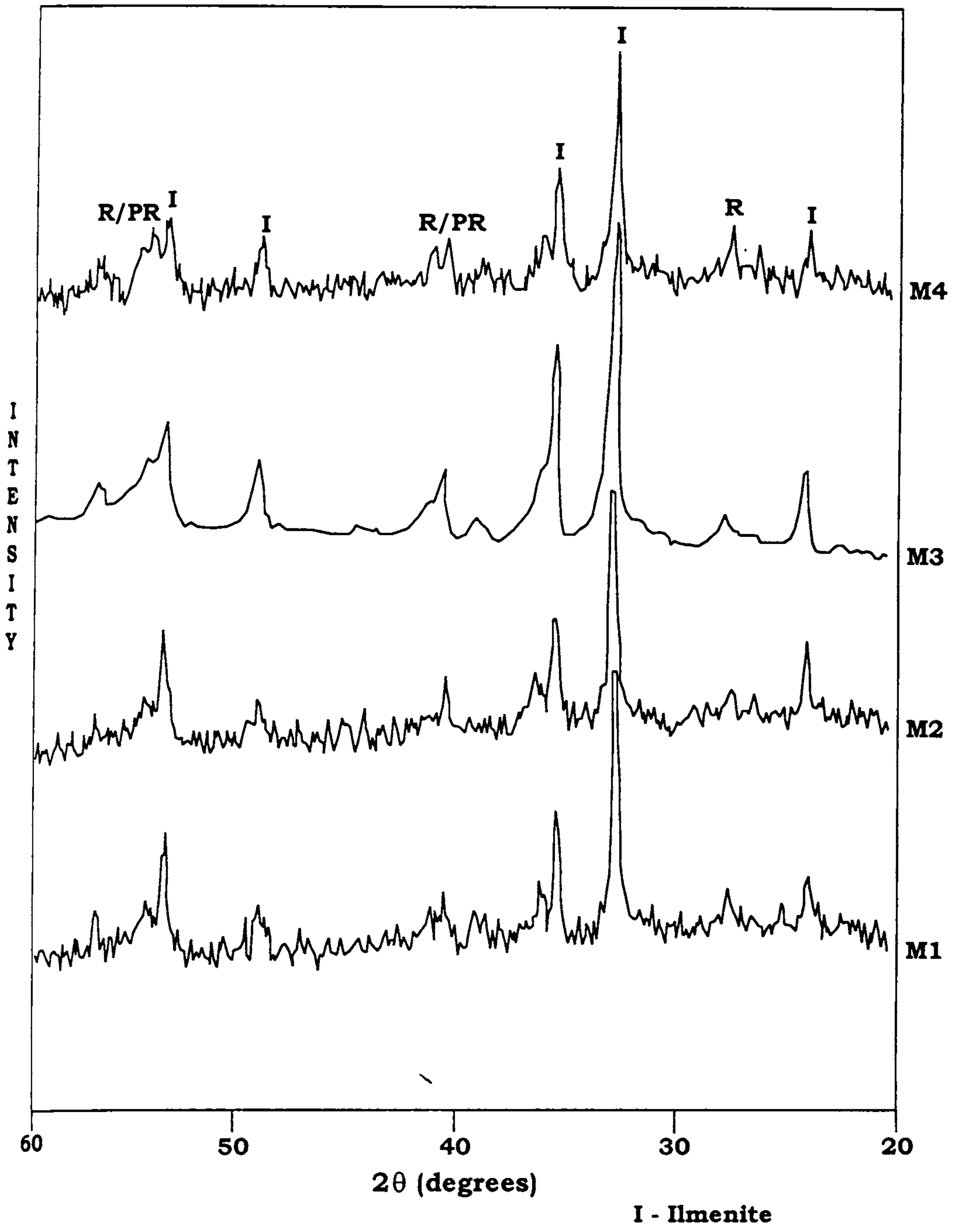


Fig. 4.2.2. XRD patterns of ilmenite samples from Manavalakurichi beach

supports the higher weathered nature of ilmenite from this location. The XRD patterns indicate a relatively lower alteration in the northern part of the Manavalakurichi deposit.

When compared to the Manavalakurichi deposit, the alteration undergone by the Chavara ilmenite is very obvious. In Manavalakurichi, the content of the altered phases hover around 16 to 23% and the ilmenite peaks are sharp and well defined than the Chavara samples.

The XRD studies on ilmenite reveals that, in the hinterland, the ilmenite varies from the relatively unaltered mineral in the laterites to those like some of the estuarine and sand stone samples which are weathered to a high degree which is comparable to the ilmenite samples from the beach. These differently weathered ilmenite samples are transported to the coastal zone as a part of the influx of the sediment load from the hinterland, where they are sorted and deposited in favourable locations by the coastal processes like waves and currents to form the heavy mineral assemblages.

4.2.2.1.1 Magnetic fractions of bulk ilmenite: Factory grade ilmenite was undertaken for magnetic fractionation under amperages applied at uniform increasing intervals using Isodynamic separation. Such studies have been attempted to a limited extent and have been found useful in the delineation of alteration trends and the chemical variation in beach ilmenite (Subrahmanyam et al, 1982; Frost et al, 1986; Suresh Babu et al, 1994). Since magnetism is a function of the total iron content and the ferrous-ferric ratio, the weathering processes which control these elemental contents exert considerable influence on the magnetism of the mineral.

The XRD patterns of the Chavara and Manavalakurichi fractions are given in Figs. 4.2. 3 and 4. The Manavalakurichi samples show well defined and pronounced ilmenite peaks when compared to those of Chavara. This pattern is reflected in the distribution of ilmenite and the altered phases (Fig. 4.2.5). In the Chavara sample, the last four fractions (CH6-CH8) have a dominance of altered phases of about or more than 64% (Table 4.2.2). The first four fractions represent, on the contrary, very well developed ilmenite peaks, pointing to the limited alteration suffered by these fractions. In Manavalakurichi too the first four fractions represent the least altered fractions. But all the Chavara magnetic fractions are highly altered than the corresponding magnetic fractions of Manavalakurichi, indicating the advanced weathering undergone by the Chavara deposit.

Among the Chavara magnetic samples, the ilmenite content range from 64% (CH4) to a minimum of 13% in CH8. In Manavalakurichi, these values are higher ranging from 92% (MK3) to about 20% in MK7.

Though magnetic susceptibility has been described as being inversely related to the degree of alteration undergone (Temple, 1966), the highest magnetic fractions need not be the least altered (Wort and Jones, 1980). In Chavara samples, the XRD patterns and the distribution of mineral phases reveal that CH3 and CH4 are the most altered (Table 4.2.2; Fig. 4.2.3), when compared to the first two fractions. In Manavalakurichi, MK7 can easily observed to be the least altered. But in the less magnetic samples from CH5-CH8 and in the case of Manavalakurichi, the magnetic susceptibility is directly related to the alteration by weathering. Subrahmanyam et al (1982) investigated the alteration of the Manavalakurichi magnetic fractions of ilmenite and has explained the apparent discrepancy shown by the highly magnetic fractions as due to the increase of $Fe^{3+}$ ions with weathering. Magnetic property is a direct

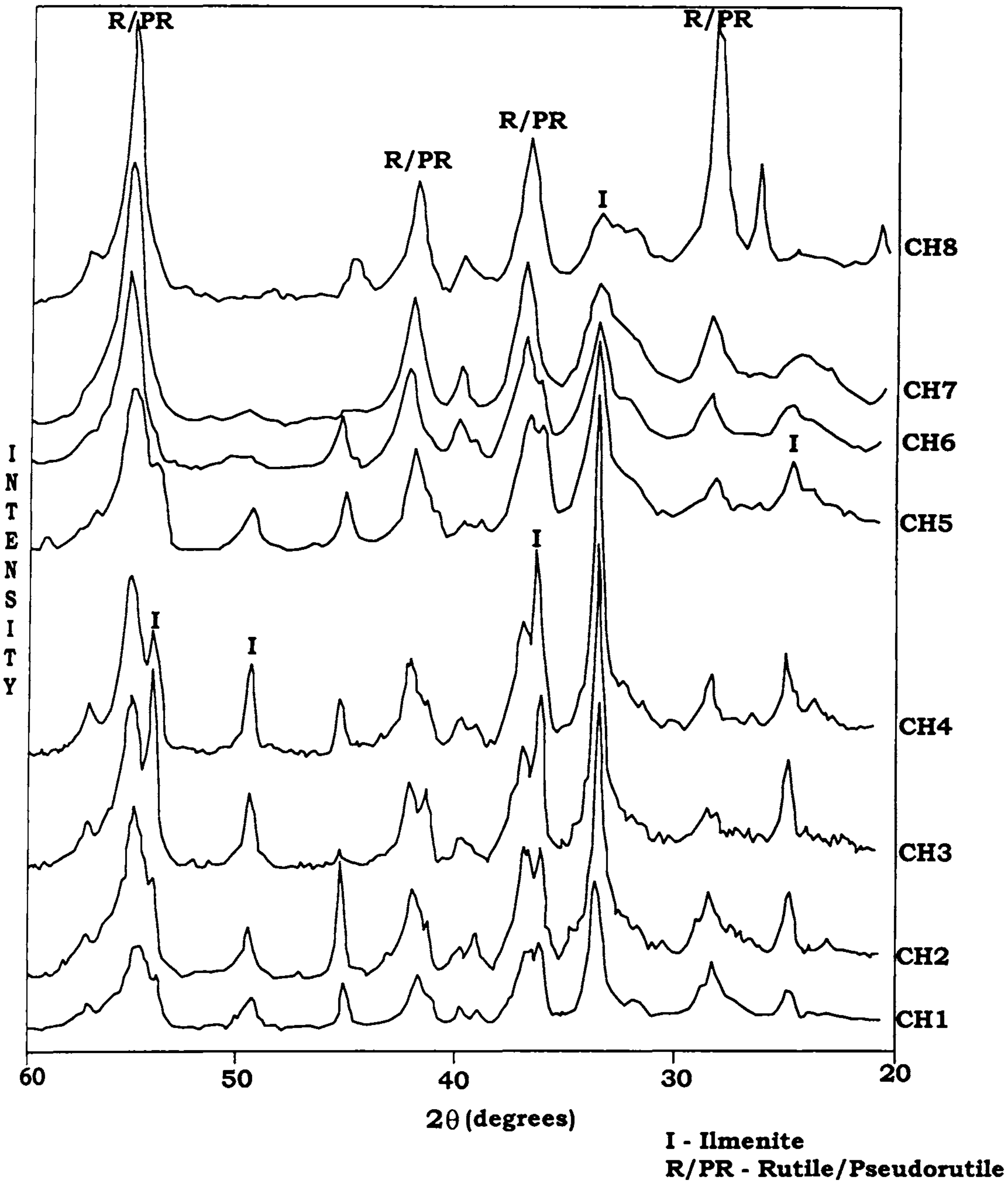


Fig. 4.2.3. XRD patterns of magentic fractions of ilmenite from Chavara deposit.

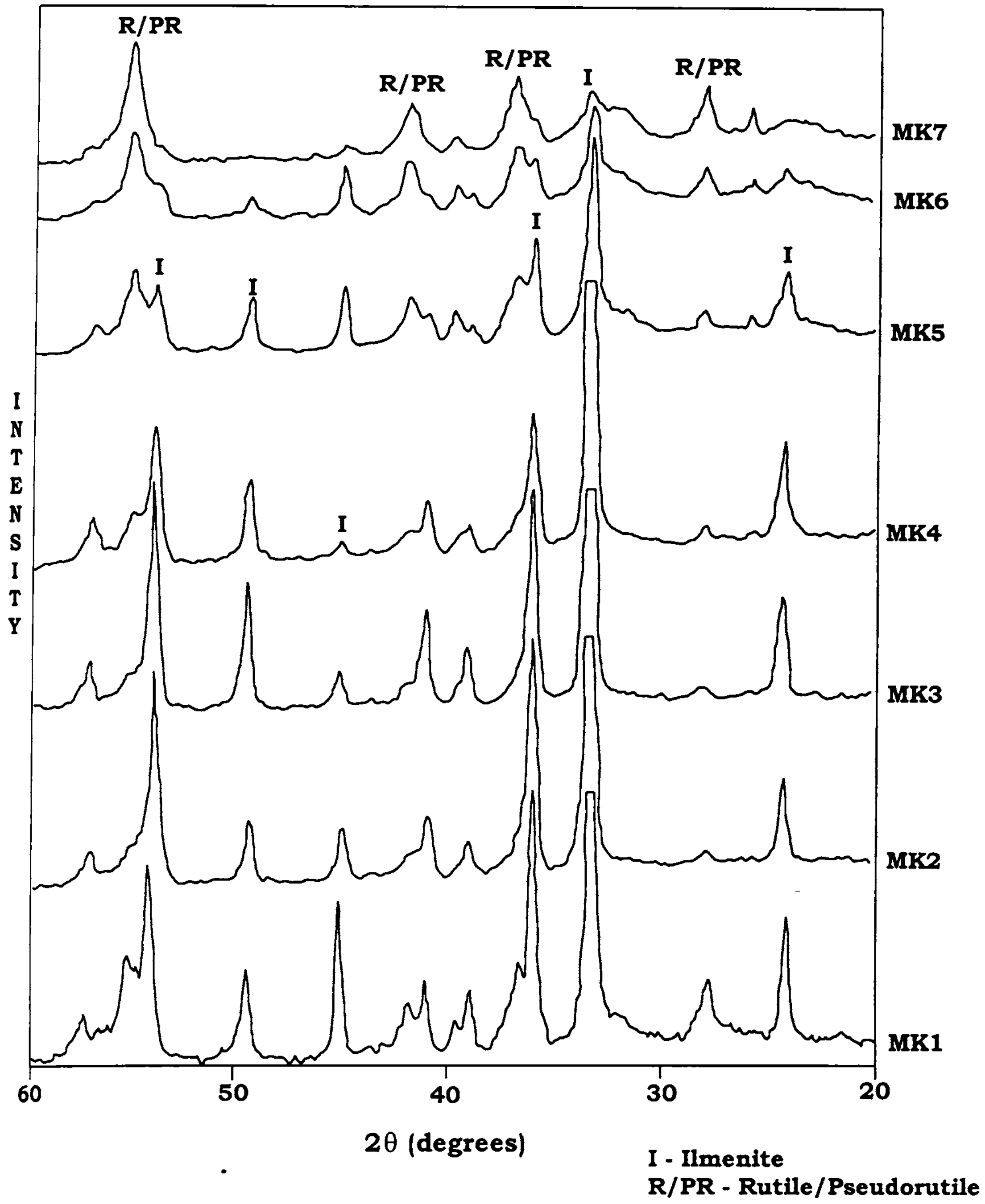
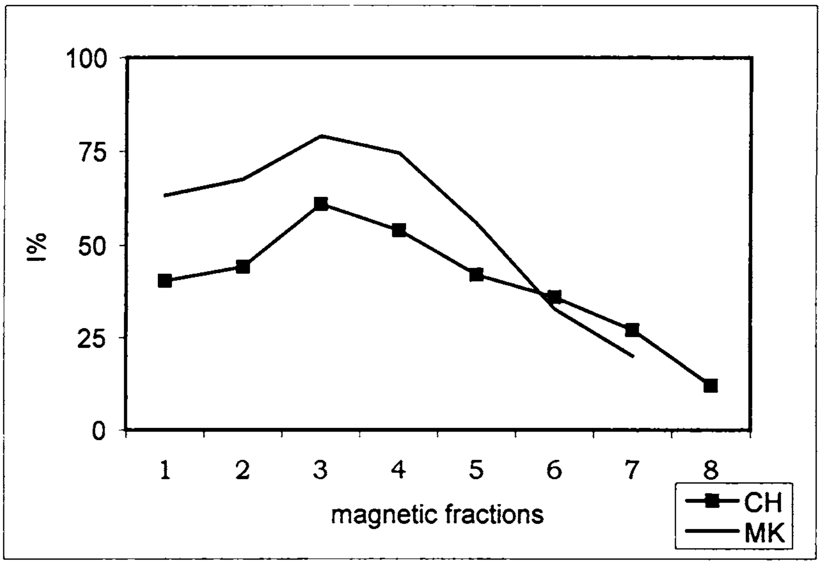


Fig. 4.2.4. XRD patterns of the magentic fractions of ilmenite from Manavalakurichi deposit

Table 4.2.2 Distribution of altered phases in the magnetic fractions of Chavara (CH) and Manavalakurichi (MK) ilmenite

| Sample | Amperage (A) | Ilmenite Phase (I) % | Altered Phases (R/PR) % |
|---|---|---|---|
| CH1 | 0.15 | 40.32 | 59.68 |
| CH2 | 0.20 | 44.12 | 55.88 |
| CH3 | 0.25 | 56.11 | 43.89 |
| CH4 | 0.30 | 64.13 | 35.87 |
| CH5 | 0.35 | 42.17 | 57.83 |
| CH6 | 0.40 | 35.58 | 64.42 |
| CH7 | 0.45 | 27.59 | 72.41 |
| CH8 | >0.45 | 12.51 | 87.49 |
| MK1 | 0.15 | 63.39 | 36.61 |
| MK2 | 0.20 | 67.60 | 32.40 |
| MK3 | 0.25 | 92.46 | 7.54 |
| MK4 | 0.30 | 86.31 | 13.69 |
| MK5 | 0.35 | 55.89 | 44.11 |
| MK6 | 0.40 | 32.67 | 67.33 |
| MK7 | >0.40 | 19.95 | 80.05 |

*I -Ilmenite *R/PR -Rutile/Pseudorutile



I- Ilmenite

Fig. 4.2.5 Contents of ilmenite phase in the magnetic fractions of bulk ilmenite from Chavara and Manavalakurichi deposits function of the unpaired electrons present in the sample. These increase with the ferrous-ferric conversion since due to the high spin of the ferric ions. Hence the most magnetic samples may not show the least alteration.

When at a high degree of alteration takes place, excess $Fe^{3+}$ ions are leached out, related to the pseudorutile formation and consequently for low magnetic samples, the susceptibility is influenced directly by the alteration of the mineral.

Samples of varying magnetic susceptibility and grain size of the Chavara and Manavalakurichi deposit were subjected to XRD analysis to delineate the influence of grain size and magnetism on the alteration of the mineral and to study the qualitative contrast between ilmenite of the two deposits. As the susceptibility values decrease, the peaks become shorter and broader and the content of rutile/pseudorutile phases increase proportionately (Fig 4.2.6; Table 4.2.3). The Chavara samples show a low ilmenite phase (14%) in the fractions separated at 0.4 A. A maximum of 54% is noted in the sample CH2, which was separated at 0.2 A. In the Manavalakurichi, these values assume 17 and 92 % respectively for 0.7 and 0.2 A fractions. The samples separated at low currents give sharply defined peaks. Among the various size grades studied, the 2.75 Φ (+100 mesh) fraction is found to be the most altered, judging by the high rutile/pseudorutile content and the crystallinity indices. The MK 2 sample is an exception to the above trend, where the 2.75 Φ size grade exhibit a high ilmenite content (92%), than the 2 and 3.35 Φ grades (78 and 86 % respectively).

4.2.2.1.2 <u>IRE factory graded samples of ilmenite</u> The Ilmenite product is very similar to the magnetic fractions separated at 0.2 and 0.25A and is compositionally close to the beach sample C3 (Fig. 4.2.7). The d values of

Table 4.2.3 Mineralogical phases in the magnetic fractions of various size grades

| Sample | Size (ϕ) | Current (A) | Area (%) - I | Area (%) – PR/R | Crystallinity Index (CI) |
|---|---|---|---|---|---|
| CH | 2 | 0.2 | 53.94 | 46.06 | 0.95 |
| | 2.75 | 0.2 | 45.36 | 54.64 | 0.71 |
| | 3.25 | 0.2 | 50.45 | 49.55 | 0.81 |
| | 2.75 | 0.2 | 45.36 | 54.64 | 0.71 |
| | 2.75 | 0.5 | 22.98 | 77.02 | 0.31 |
| | 2.75 | 0.7 | 14.40 | 85.6 | 0.18 |
| | 3.25 | 0.2 | 50.45 | 49.55 | 0.81 |
| | 3.25 | 0.5 | 32.10 | 67.9 | 0.34 |
| | 3.25 | 0.7 | 19.49 | 80.51 | 0.23 |
| MK | 2 | 0.2 | 78.14 | 21.86 | 1.11 |
| | 2.75 | 0.2 | 91.94 | 8.06 | 1.13 |
| | 3.25 | 0.2 | 85.87 | 14.13 | 1.15 |
| | 2.75 | 0.2 | 91.94 | 8.06 | 1.13 |
| | 2.75 | 0.5 | 48.10 | 51.90 | 0.91 |
| | 2.75 | 0.7 | 16.82 | 83.18 | ---- |
| | 3.25 | 0.2 | 67.40 | 32.60 | 1.15 |
| | 3.25 | 0.5 | 19.03 | 80.97 | 0.68 |

*I - Ilmenite *R/PR - Rutile/ Psuedorutile

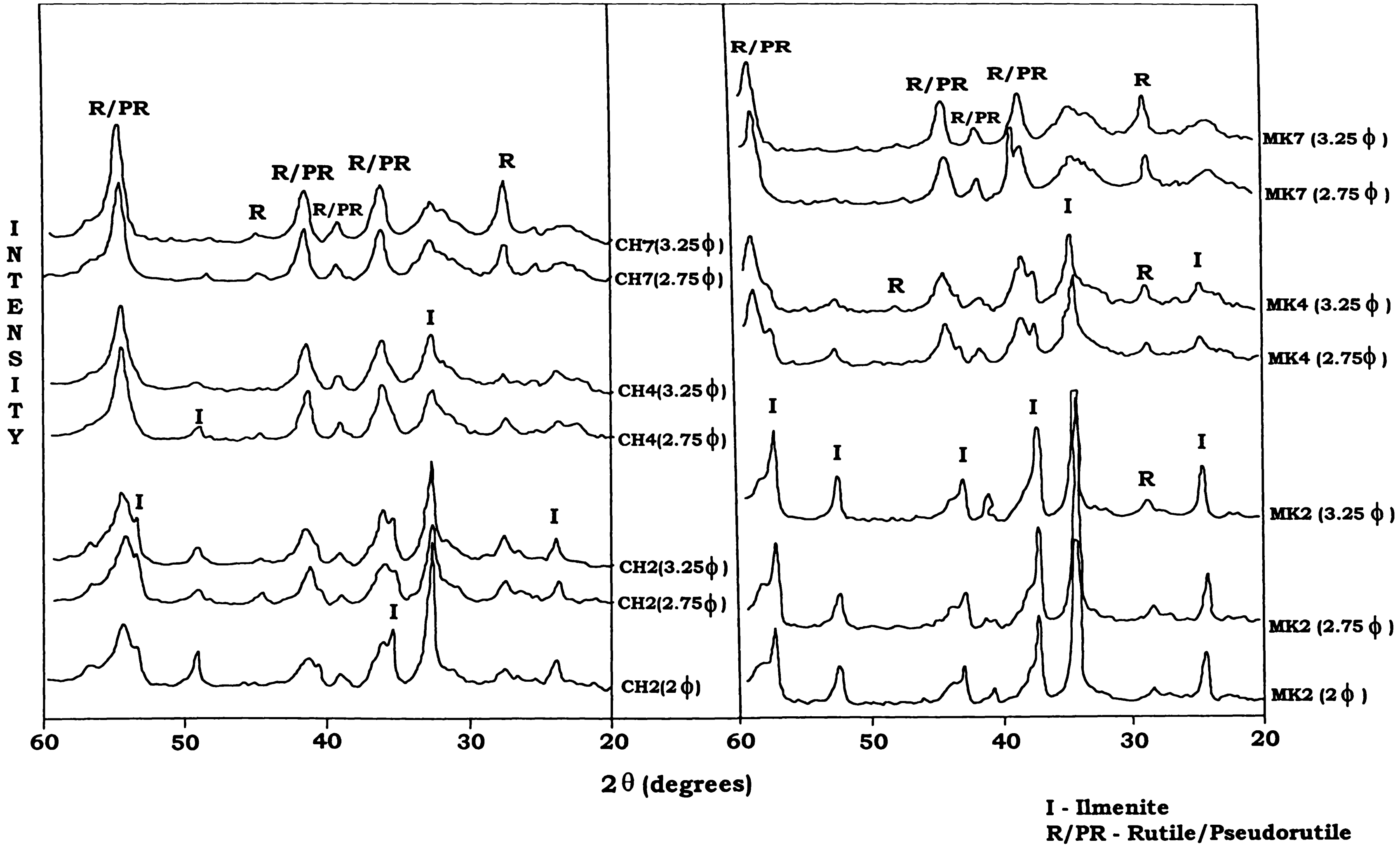


Fig. 4.2.6. XRD patterns of magentic fractions of bulk ilmenite belong to different size grades from Chavara and Manavalakurichi deposites

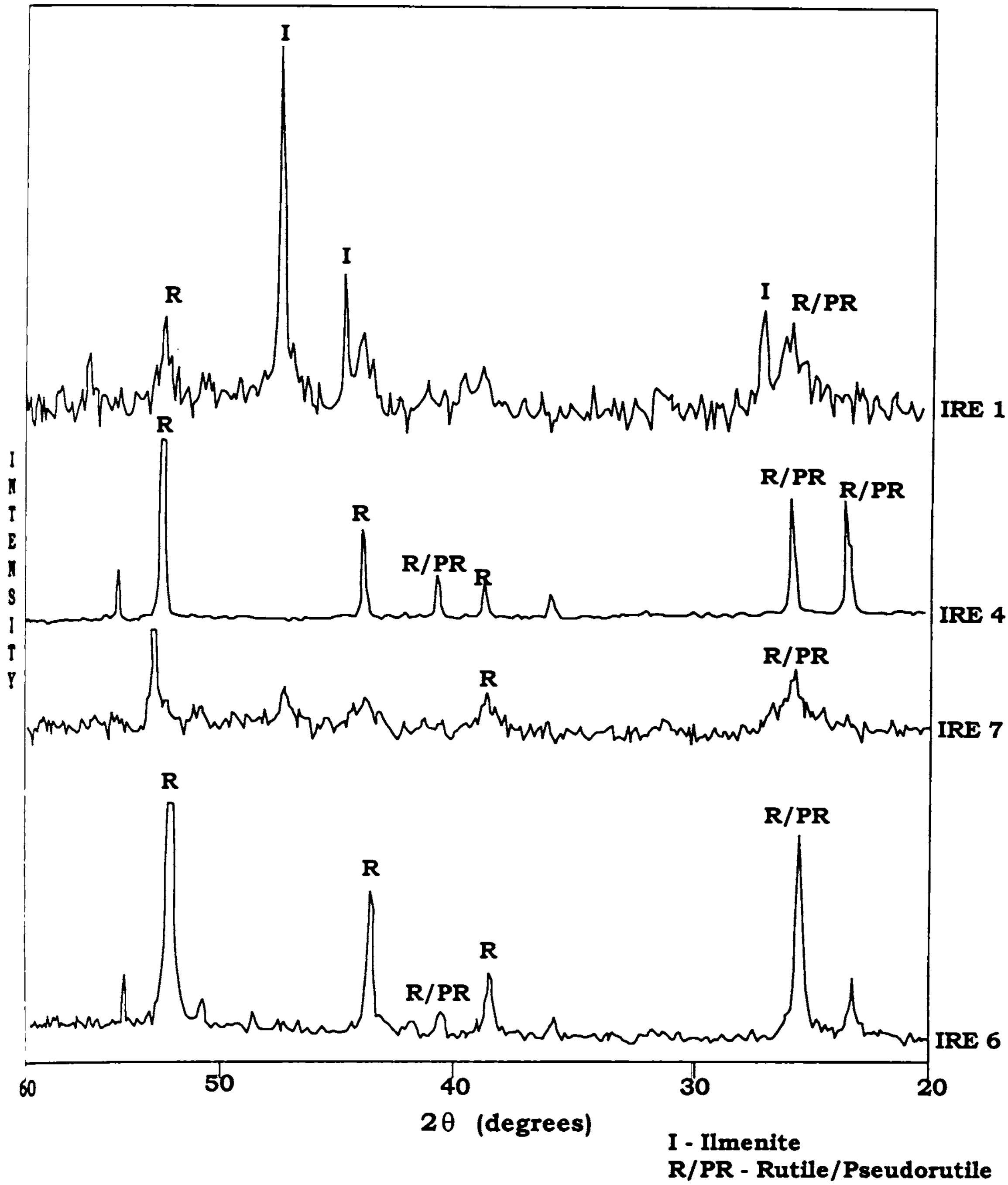


Fig. 4.2.7. XRD patterns of IRE factory grade samples of ilmenite.

the prominent diffraction lines in the XRD pattern of rutile, are identical to that reported for rutile/leucoxene, namely 3.25, 2.49 and 2.19 A$^0$. Ilmenite peaks are not found in any considerable amount, as noted from the d values of the diffraction peaks. The relatively sharp and well-defined peaks of the sample, indicates its well-formed crystallinity. This coupled with the absence of the mineral phases associated with alteration of ilmenite, could indicate the prominence of primary rutile in this product. The XRD data for the Leucoxene sample IRE 6 is in contrast with the above observations. The prominent peaks report to those for rutile in the XRD file. A slight broadening of the principal peaks, when compared to that for Rutile, indicates the overlapping of diffraction lines of similar d values. But minor peaks, which are diffused and broad, indicates the association of other mineral phases. This could be silicates present as impurities or low contents of pseudorutile and ilmenite. This sample is the most iron deficient with around 3% of iron content.

Another grade of Leucoxene IRE 7 exhibits significantly different d value (2.31 A$^0$) for the most principal diffraction peak. This grade is quite similar to the Brown leucoxene (d value of 2.32 A$^0$), identified by Bailey et al (1956). The value obtained falls between that of the theoretical value reported and that observed by Mucke and Chaudhuri (1991), for recrystallized leucoxene. This sample may represent an intermediate phase, with characteristics of both the pseudorutile-leucoxene transition and the practically iron-free White leucoxene. The subdued occurrence of other diffraction lines might be due to the presence of impurities.

### 4.2.2.2 Ilmenite from the crystalline country rocks

In general, the samples separated from crystalline rocks show peaks corresponding to ilmenite with sharp and narrow patterns, indicating a high degree of crystallinity (Fig. 4.2.8; Table 4.2.4). In certain samples a

Table 4.2.4 Distribution of ilmenite and altered phases in the samples from the hinterland

| Sampling Environment | Sample No. | Ilmenite Phase (*I) % | Altered Phases (*R/PR) % |
|---|---|---|---|
| Crystalline Rock | P1 | ~100 | _ |
| | P2 | ~100 | _ |
| | P3 | ~100 | _ |
| Laterite | L3 | 95 | 5 |
| | L 6 | 89 | 11 |
| | L7 | 85 | 15 |
| | L13 | 99 | 1 |
| Sandstone | S2 | 47 | 53 |
| | S3 | 82 | 18 |
| | S4 | 73 | 27 |
| Rivers | Kallada | | |
| | 1 | 92.1 | 7.9 |
| | 2 | 90.12 | 9.88 |
| | Valliyar | | |
| | 1 | 96.50 | 4.50 |
| | 2 | 94.77 | 5.27 |
| | 3 | 93.49 | 6.51 |
| | 4 | 85.91 | 14.09 |
| | 5 | 85.25 | 14.75 |
| Estuary | E1 | 41 | 59 |
| | E2 | 36 | 64 |
| | E3 | 36 | 64 |
| | E4 | 83 | 17 |

* I -Ilmenite *R/PR –Rutile/Pseudorutile

* See Fig. 3.1 for sample locations

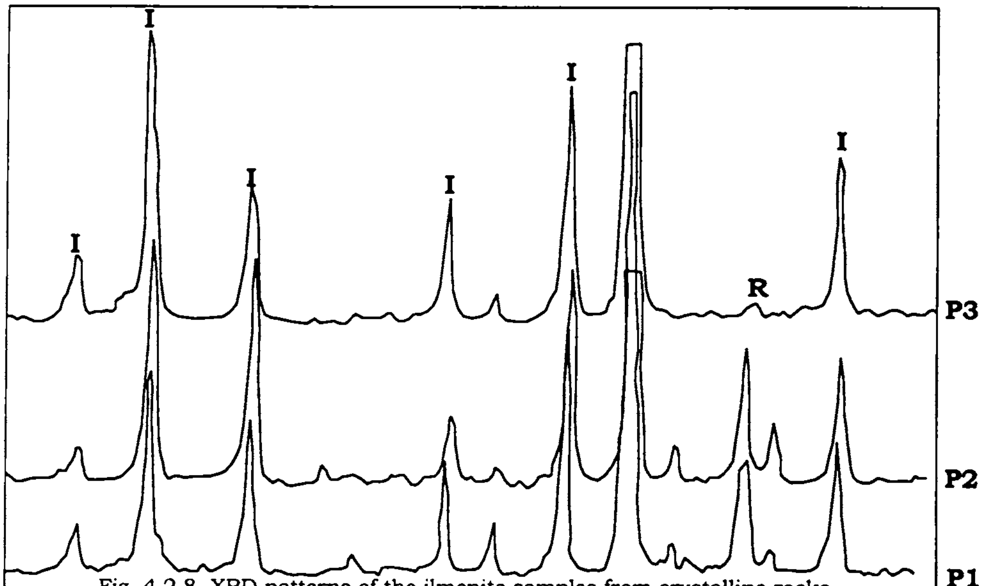


Fig. 4.2.8. XRD patterns of the ilmenite samples from crystalline rocks.

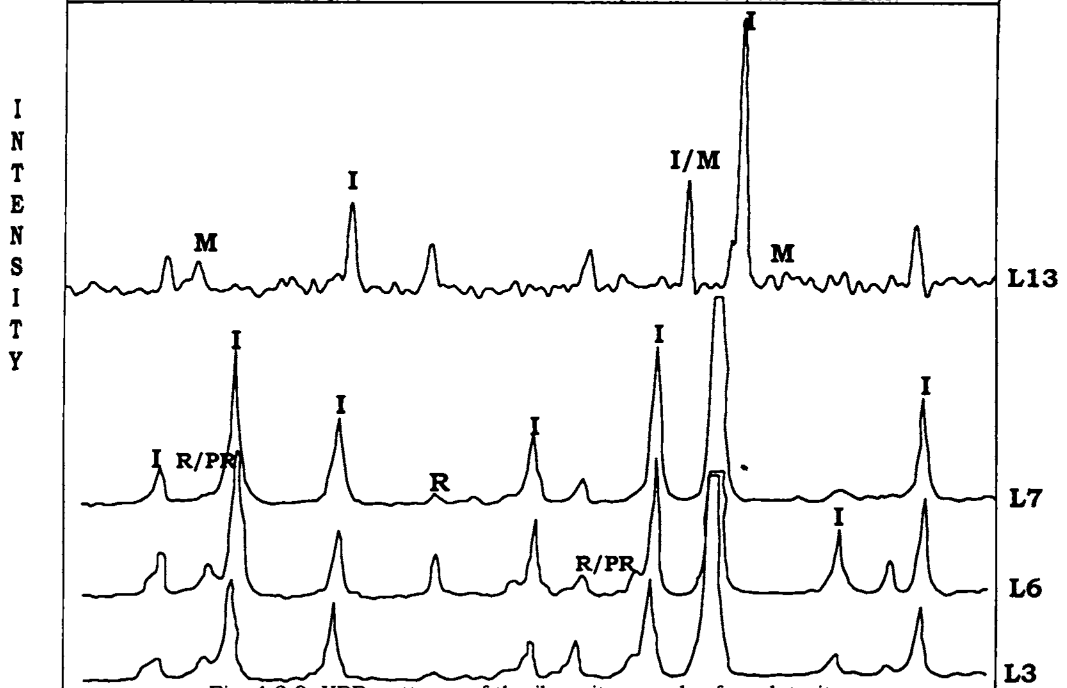


Fig. 4.2.9. XRD patterns of the ilmenite samples from laterite.

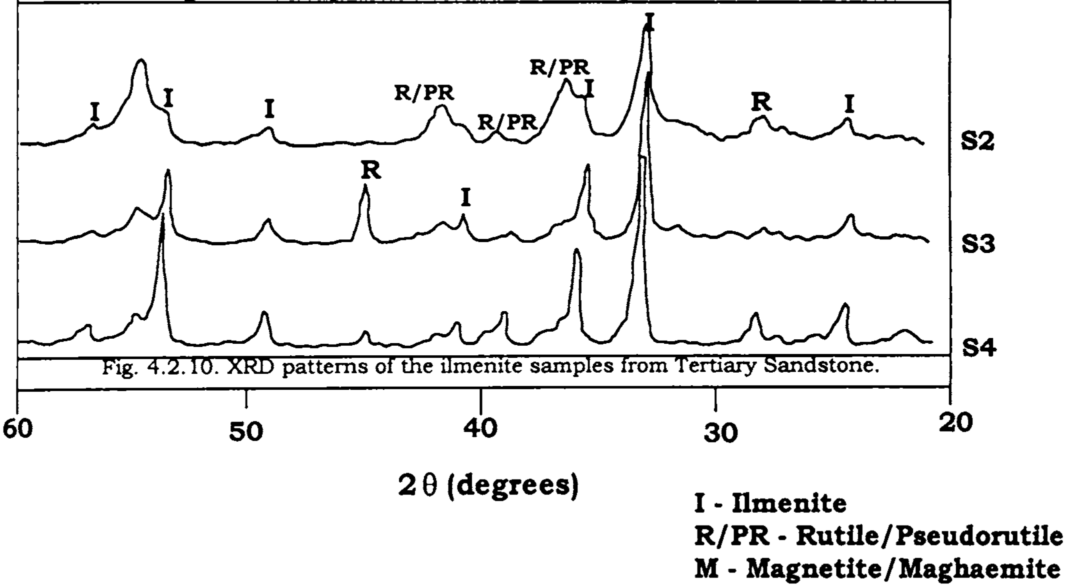


Fig. 4.2.10. XRD patterns of the ilmenite samples from Tertiary Sandstone.

by the JCPDS files. Suspected anatase peaks are found in some samples, but their presence is too meager to be considered. Therefore the results under consideration in this work show a trend different from that of Anand and Gilkes (1984). They have suggested that the alteration of ilmenite to rutile in beaches takes place because the concentrations of foreign ions in soil solutions is relatively low in beaches due to the paucity of easily weathered minerals unlike in lateritic environment. The significant content of rutile found in the laterite ilmenite in the present work and the marked anatase presence in the lateritic ilmenite as described by the above authors, could be due to the difference in the weathering environment in the lateritisation zones in the two areas. In this work, it is very obvious that the lateritisation has not altered ilmenite significantly, as seen from the XRD patterns. Other analysis too supports the XRD data which will be discussed in thecourse of the work.

### 4.2.2.4 Ilmenite from the Tertiary sedimentary rock

Ilmenite samples from the Tertiary sandstones show more subdued ilmenite peaks (Fig. 4.2.10; Table 4.2.4). Extensive occurrence of associated mineral phases especially pseudorutile, is indicated by the presence of broad and short diffraction patterns, corresponding to their poor crystalline nature. The highly weathered sample, S2 shows an assemblage of three minerals namely ilmenite, pseudorutile and rutile, where alteration has left the ilmenite content to about 47%. In the S4, ilmenite and pseudorutile occurs at levels of about 73 and 27% respectively. The highest content of ilmenite is shown by the sample S3 (82%).

Though all the samples belong to the Tertiary formation of Kerala, it could be seen that the alteration under gone by the ilmenite is different in different samples. This difference is reflected in the nature of the sand stone at the different sampling locations. At the various locations, the Tertiary formations exhibit wide variation in texture, colour and mineralogy. Though the Warkallais are thought to be deposited in a lacustrine and near shelf environment (Soman, 1997), the local environment of deposition and/or the post depositional weathering set ups may vary from to place. This is indicated by the high alteration state of S2, which has been weathered to an extent that the sample is predominantly constituted by the altered phases. On the other hand, S4 presents a different picture, with sharp and prominent ilmenite peaks and low content of the altered phases.

Morad and Aldahan (1986) studied in detail, the alteration patterns of Fe Ti oxides and found out that, among the final alteration product of $TiO_2$, most of the grains exist as anatase or more prominently brookite. The present investigation presents different results. Irrespective of the degree of alteration undergone by the ilmenite samples, all the samples undertaken for the XRD analysis show only rutile peaks, along with that of the intermediate mineral phase of pseudorutile. It could be seen from the previous studies that, where diagenetic changes dominate the weathering process, the alteration results in the formation of anatase (in laterites) or brookite and anatase (sand stones) with low contents of rutile. The secondary rutile formed under diagenetic conditions is reported to be unstable and transforms to other forms of $TiO_2$ like anatase (Morad and Aldahan, 1986). The results are different in this work and could be related to the difference and nature of the prevailing weathering processes.

4.2.2.5 Ilmenite from the rivers

The Valliyar is the only river in the vicinity of the MK deposit. In the upper reaches of the river, the grains contain almost pure ilmenite (about

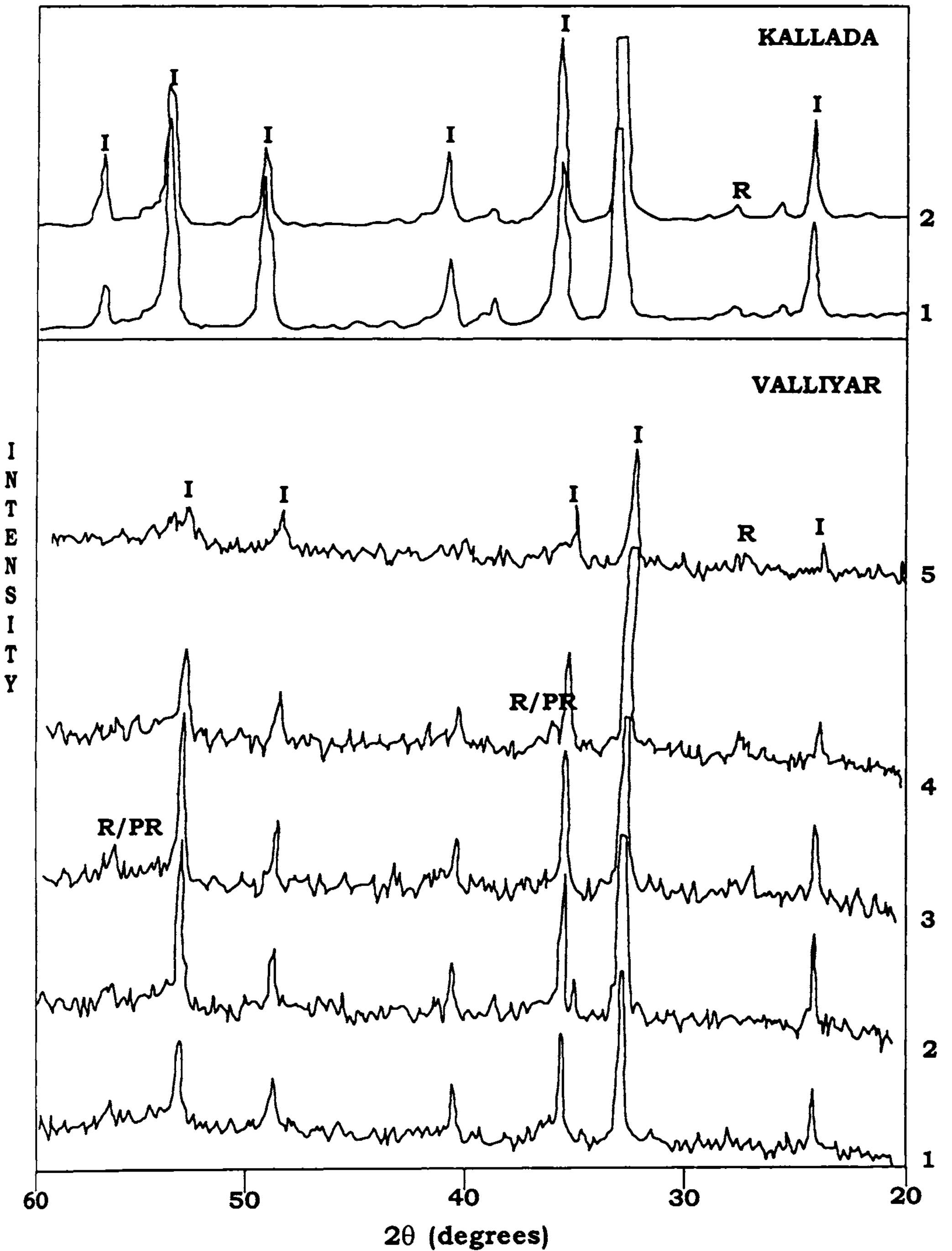


Fig. 4.2.11. XRD patterns of ilmenite samples from the rivers of the hinterland.

95%) as seen in Fig. 4.2.11 and Table 4.2.4. However, in the lower reaches, the weathering succeeds in lowering the ilmenite phase to as much as about 85%, which is the general value of this phase in the beach ilmenite grains. The Valliar is relatively a short river, with a length of about 20 km. Significant weathering process cannot be expected in the sediments in this river. In the samples from the rivers in the hinterland of the Chavara deposit, high contents of ilmenite phase are observed. The altered phases are not observed to be more than 13%. The samples were taken from the midcourse of the rivers and still, alteration is not noticed to the expected levels. The rivers of South Kerala have relatively shorter durations, when compared to the drainage system in the rest of the peninsula. The high gradients in their upper course coupled with their short duration, ensures a youthful stage for the fluvial systems through most of their length. The sediments are carried in large quantities by stream action and dumped into the sea without undergoing much erosion activity. This is evident in the angular nature of the sediment grains, even in the river stretches on the coastal plain. This may explain the relatively unweathered nature of ilmenite in the fluvial systems in the study area. The other mineralogical and chemical analyses bear out this observation.

### 4.2.2.6 Ilmenite from the Ashtamudi estuary

In the Ashtamudi estuary, the samples from E1 and E2, the total ilmenite phase accounts for less than the alteration products with levels of 41 and 36% respectively (Fig. 4.2.12; Table 4.2.4). In sample E1 the leucoxenisation seems to be high, with about 19.5% rutile, while in Mutathumala, it is about 10%. The lowest degree of alteration is shown by the sample from Ashtamudi area with a high ilmenite content (83%) followed by ilmenite of E3 (~64%).

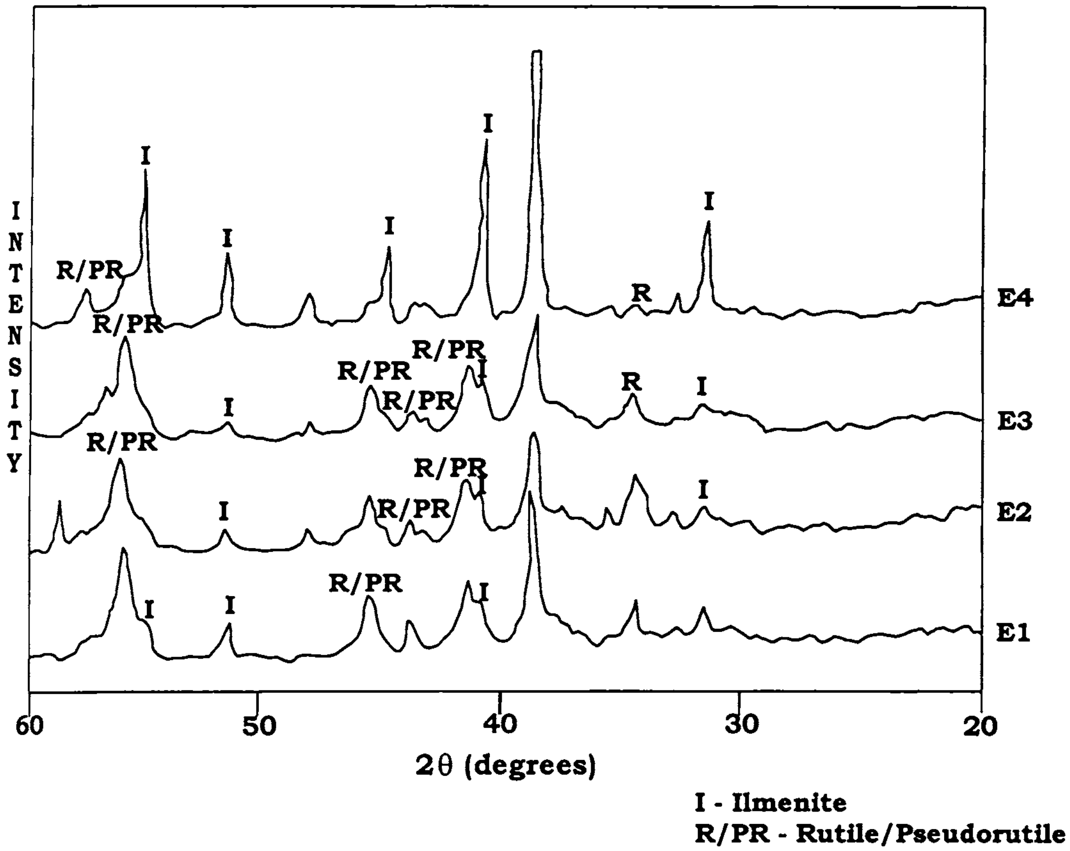


Fig. 4.2.12. XRD patterns of ilmenite samples from the Ashtamudi estuary.

The estuary represents an intermediate zone between the riverine environment and the marine system, where the geologic processes are influenced by the fluvial marine interaction. The ilmenite samples fom this geologic setup represent a spectrum of alteration stages from more or less fresh samples to significantly altered ones. Thus, E2 and E3, which are sampled from the inlets of the estuary, show a highly altered state. In the inlets, because of their sheltered and undisturbed nature, alteration progresses without hindrance. E1 is from the main body of the estuary, which is more dynamic and the supply of material from the marine and fluvial processes is prominent. Thus, in this sample, the depletion of ilmenite phase (45%) is less than the earlier samples. The sample location of E4 is situated near the point of debouching of Kallada river into the estuary, where the supply of fresh sediments from the hinterland is continuous. This could be the reason for its relatively unaltered state with ilmenite phase forming about 83% of the sample.

### 4.2.3 Unit cell parameters

The unit cell parameters are calculated from the XRD patterns. These values of a. b, and 'c' and the lattice volume, 'V' defines the basic structure of any substance. The studies of the patterns of variation of these values is useful in deciphering the weathering of minerals (Chaudhuri and Newesely, 1990; Suresh Babu et al, 1994), since the mineralogical and chemical changes consequent to alteration directly reflect on the unit cell values. Chaudhuri and Newesely (1990) have tabulated the different mineral alteration products in the alteration of ilmenite and the structural changes defined by the change in the lattice cell parameters. The results of the calculation of lattice values for ilmenite from the beach environments of Chavara and Manavalakurichi are given in Table 4.2.5.

### 4.2.3.1 Ilmenite from beach

The ilmenite from the Chavara beach exhibit a range of values for the lattice parameters from 5.05 to around 5.06 A$^{O}$ for the length of 'a' axis, 14.01 to 14.08 A$^{O}$ for 'c' axis and the cell volume ranges from 305 to about 315 A$^{O}$ (Table 4.2.5). The theoretical values of the unit cell parameters are reported as, 5.09 A$^{O}$ for 'a', 14.06 A$^{O}$ for 'c' and the cell volume amounts to 315.83 A$^{O}$ (Roberts et al, 1974). But the natural ilmenite samples are found to vary significantly from these values, depending on the intensity of alteration undergone and the presence of the foreign ions (Chaudhuri and Newesley, 1990; Suresh Babu et al, 1994). The C1 sample is found to be the least weathered sample from the Chavara deposit, as discussed in the sections concerning phase identification. The lattice volume of the sample shows the maximum value among the Chavara fractions at 313 A$^{O}$. The 'a' values generally follow the trend of the variation of lattice volumes, while the 'c' values follow a reverse pattern. The cell volume is generally found to decrease with increasing alteration, due to the contraction of the lattice structure consequent to the oxidation and leaching of ferric iron from the mineral structure (Chaudhuri and Newesely, 1990; Mucke and Chaudhuri, 1991). The Chavara ilmenite generally seems to follow this observation. The C2 and C3 samples exhibit the minimum volume for the unit cell at 306 and 307 A$^{O}$, echoing their altered status shown in the XRD patterns.

In Manavalakurichi deposit the cell volume ranges from 313.58 to about 317.50 A$^{O}$. The lengths of the axes,'a' and 'c' ranges from 5.07 to 5.1 A$^{O}$ and 14.08 to 14.11 A$^{O}$ (Table 4.2.5). M3 is found to be the most altered sample from the relatively lower content of ilmenite phase in the XRD patterns. This sample M3 is found to have the least lattice volume in the deposit due to the shrinkage resulting under weathering. This sample is from the deposit proper. The northernmost sample M5 is the least

Table 4.2.5 Lattice parameters of the ilmenite from the Chavara and Manavalakurichi beaches

| Deposit | Sample | 'a' A$^{o}$ | 'c' A$^{o}$ | 'V' A$^{o}$ |
|---|---|---|---|---|
| Chavara | C1 | 5.06 | 14.01 | 310 |
| | C2 | 5.02 | 14.05 | 306 |
| | C3 | 5.01 | 14.08 | 306.5 |
| | C4 | 5 | 14.08 | 306 |
| | C5 | 5.06 | 14.03 | 313 |
| Manavalakurichi | M1 | 5.09 | 14.11 | 316.9 |
| | M2 | 5.1 | 14.1 | 317.5 |
| | M3 | 5.07 | 14.08 | 313.58 |
| | M4 | 5.1 | 14.1 | 317.5 |

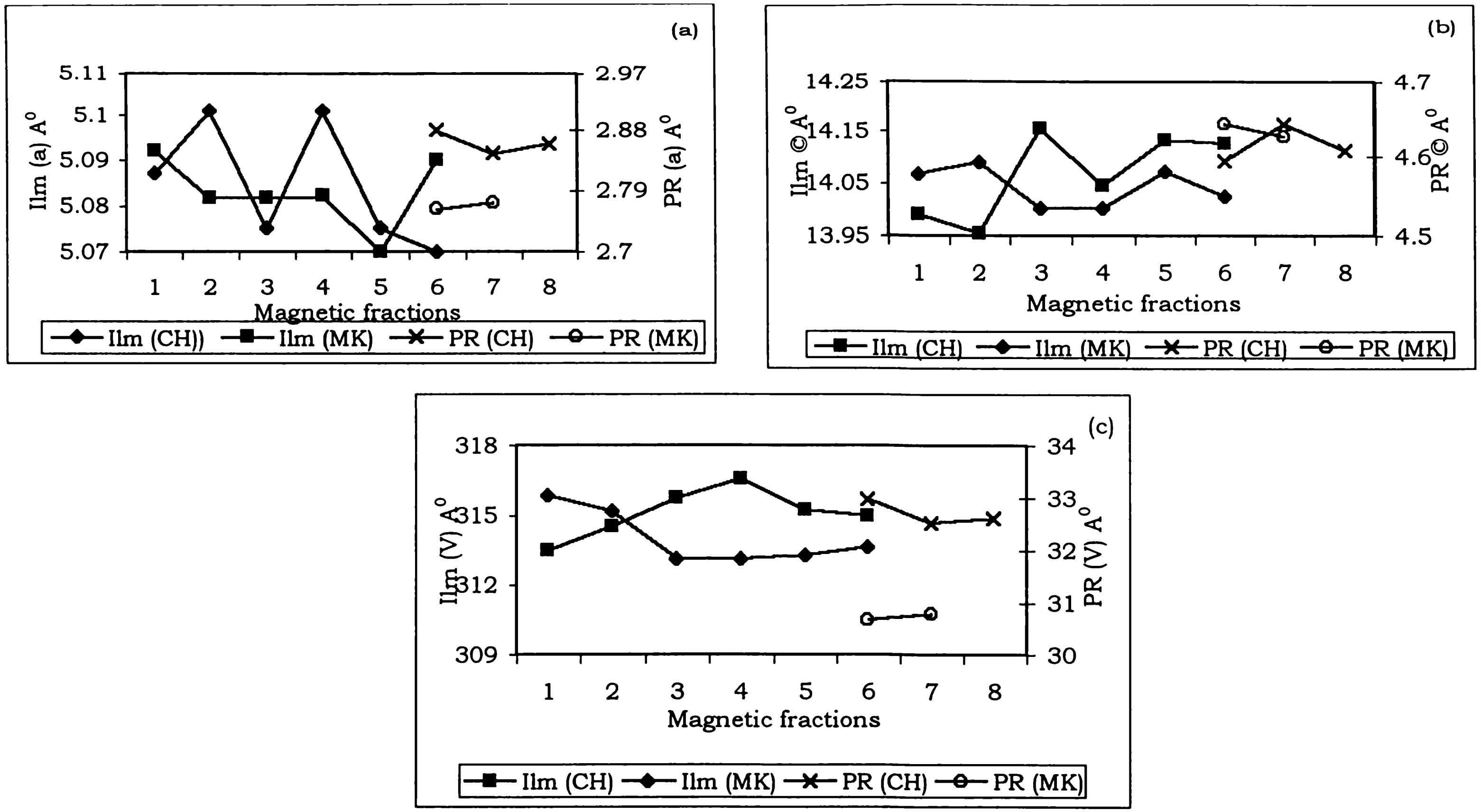
Table 4.2.6 Variation of lattice parameters of the different magnetic fractions of bulk ilmenite of Chavara (CH) and Manavalakurichi (MK). The lattice parameters of pseudorutile phase are given in parantheses

| Amperage (A) | 'a' A$^{o}$ | | 'c' A$^{o}$ | | 'V' A$^{o}$ | |
|---|---|---|---|---|---|---|
| | CH | MK | CH | MK | CH | MK |
| 0.15 | 5.087 | 5.092 | 13.990 | 14.068 | 313.463 | 315.875 |
| 0.20 | 5.101 | 5.082 | 13.956 | 14.089 | 314.532 | 315.171 |
| 0.25 | 5.075 | 5.082 | 14.156 | 14.002 | 315.753 | 313.124 |
| 0.30 | 5.101 | 5.082 | 14.046 | 14.003 | 316.560 | 313.146 |
| 0.35 | 5.075 | 5.070 | 14.133 | 14.072 | 315.240 | 313.274 |
| 0.40 | 2.879 | 5.090<br>(2.762) | 4.595 | 14.024<br>(2.762) | 32.975 | 314.632<br>(30.663) |
| 0.45 | (2.844) | (2.772) | (4.642) | (2.772) | (32.524) | (30.787) |
| >0.45 | (2.859) | -- | (4.608) | -- | (32.622) | -- |

weathered as observed from the higher proportion of the ilmenite phase in it. The ilmenite here also possesses the maximum cell volume. The cell volume of ilmenite in Manavalakurichi beach decreases with weathering, following the reported trend of reduction of cell volume with progressive alteration. Since the alteration in this deposit is not advanced as in the case of Chavara, the expansion of the lattice structure of ilmenite, as seen in the more advanced state of leaching is not observed here. Thus, in general, it could be noted that in Manavalakurichi ilmenite, the cell volume is markedly greater than that of Chavara, pointing to the lesser alteration suffered by the former.

4.2.3.1.1 <u>Magnetic fractions of bulk ilmenite</u>: The varying magnetic fractions of ilmenite from Chavara and Manavalakurichi factory grade samples were calculated to determine their lattice parameters. The results are given in Table 4.2.6. It may be noted from the determination of phase contents, that the fractions separated at progressively varying amperages represent the complete spectrum of fractions of ilmenite which have undergone varying degrees of weathering. Thus the magnetic crops could be used to investigate the patterns of variation of mineralogical and chemical characters in ilmenite of a deposit. Here, the change of lattice parameters with progressive alteration is attempted, to understand the effect of weathering on the mineral structure.

The cell volumes of the magnetic crops of Chavara ilmenite range from 313 to 317$^{0}$A (Fig 4.2.13a-c). The length of c axis ranges from about 14 to 14.15$^{0}$A, while the shorter 'a' axis present values from 5.08 to a maximum of 5.1$^{0}$A. In general, 'a' and 'V' decrease for Manavalakurichi fractions separated at increasing amperages. The 'a' values fall from 5.1 to 5.07 $^{0}$A and the cell volume shows a corresponding decrease (313 to 316$^{0}$A). The 'c' axes increase from 14.1 to 14.7$^{0}$A for the fraction separated at 0.35 A.



Ilm - Ilmenite , PR - Pseudorutile

Fig 4.2.13.(a-c). Variation in the lattice parameters, a) 'a' b) 'c' and c) unit cell volume 'v' in the magnetic fractions of bulk ilmenite from Chavara and Manavalakurichi deposit.

Among Chavara samples, the most unaltered sample is the CH4, as indicated by the phase measurements. This represents the sample with the maximum lattice volume (316.56 A9. According to several authors, the cell volume of ilmenite decreases with weathering, as indicated by the shrinkage cracks in altered grains (Temple, 1966; Chaudhuri and Newesely, 1990) due to the oxidation and leaching of ferric ions from the mineral structure. The 'a' and 'c' values fall between the lattice values for these parameters proposed by Chaudhuri and Newesely (1990). The samples from CH6 contain predominantly pseudorutile. CH5 represents the mixed phase where considerable quantities of both these phases occur. The lattice parameters obtained in the present work for pseudorutile are similar to those suggested by the above mentioned authors for pseudorutile. Among Manavalaurichi ilmenite samples, MK1, is most similar to pure ilmenite in the dimensions of the lattice parameters, though it is not the most unaltered. Similar observations have been noted elsewhere (Suresh Babu, 1994). The 'a' and 'c' values fall within a narrower range than the Chavara magnetic fractions and that too does not show the trend expected. This might be due to the less state of weathering of MK magnetic crops and the similar composition of the Manavalakurichi fractions.

The cell lattice parameters of the magnetic fractions of Chavara and Manavalakurichi are plotted against increasing ferrous content, the depletion of which is taken as the index of progressive alteration (Fig. 4.2.14, a-c). An effective decrease is presented for the 'a' and 'V' values, while the 'c' values trace a reducing trend. An increase is marked when the pseudorutile phase becomes prominent. The ilmenite structure is observed to expand to facilitate the leaching of ferric ions to form pseudorutile (Suresh Babu et al, 1994). The Chavara ilmenite is at an advanced state of alteration and therefore, the lattice parameters exhibit

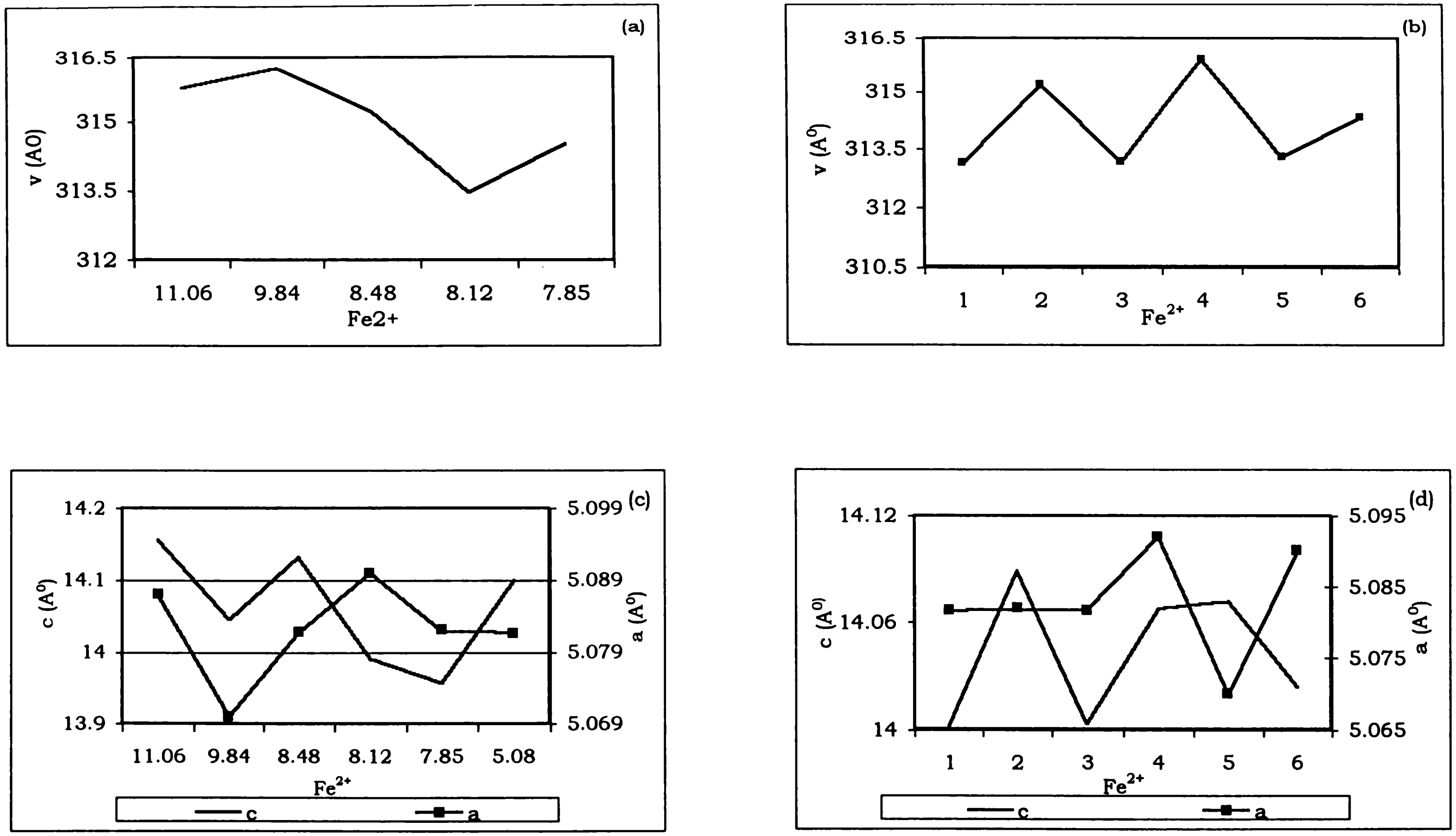


Fig 4.2.14(a-d). Variation of the lattice parameters, (a-b) and (c-d) 'a' and 'c' axes with alteration (indicated by decreasing ferrous contents, in the magnetic fractions of Chavara and Manavalakurichi deposits.

the expected variation patterns. In the magnetic fraction of Manavalakurichi ilmenite, the variation of lattice parameters do not show any notable trend. However, the mixed phase registers an increase in volume as noted in the CH fractions. It would be seen that a clearer pattern is noted in the MK samples, when the progressive magnetism (as denoted by the separating amperage) of the grains are considered (Fig 4.2.13c). The cell volume strikes a general decrease with lowering of magnetic susceptibility.

The difference in behaviour of the ilmenite from the two deposits might be explained by the varying stage of alteration suffered by them. As would be discussed in the sections dealing with the chemistry, the Chavara deposit has so advanced in the alteration that the low magnetic fractions have almost reached the state of 'Leucoxene', while ilmenite from Manavalakurichi has just managed to complete the 'Hydrated Ilmenite' stage. The studies in the interrelationship and leaching of the major elements based on statistical analysis reveal that, theoxidation of ferrous state of iron to the ferric state is the significant chemical reaction in Manavalakurichi, while the correlation between them is much less significant in Chavara ilmenite. In the latter deposit, the leaching of iron from the mineral structure and the enrichment of titanium is the more significant trend. The cell contraction due to weathering and leaching of iron in ilmenite is much more prominent in the final stages of alteration rather than in the initial stages of alteration (Mucke and Chaudhuri, 1991). Thus, in Manavalakurichi ilmenite, the variations in cell parameters are more noticeable when progressive magnetism of the samples is taken into consideration, where the ferrous-ferric transformation is the controlling factor.

### 4.2.3.2 Ilmenite from laterite

The lattice parameters are close to the theoretical values for those given for pure ilmenite (Table 4.2.7). Apparently, this could be accounted for by taking into consideration their nearly unweathered occurrence. L6 is more close to the values for cell axes and volume suggested by Chaudhuri and Newesley (1990) for ilmenite-pseudoilmenite transition. L13 show the 'a', 'c' and volume values of 5.05, 14.07 and 311.72 A$^o$ respectively. These are generally associated with significantly altered ilmenite samples, and the values could be the result of the considerable intergrowths of magnetite/maghaemite observed under the microscope.

### 4.2.3.3 Ilmenite from the Tertiary sedimentary rocks

The ilmenite samples present a wide variation in the cell volumes (Table 4.2.7). While, the samples, S3 and S4 present the axes lengths, which are close to the ideal amounts, the more altered S2 shows a reduction in the lattice volume at 311.50 A$^o$. Microscopic observations and chemical results and XRD patterns indicate that the first of the mentioned samples are relatively less weathered and iron rich, while the latter contains alteration mineral phases, as indicated by the reduction in cell volume. The wide variation in alteration states of the samples from locations of the same formation which are geographically close to each other, point to the difference in the leaching process that had taken place either during the transportation of the sediments that later constituted this sedimentary formation or the post depositional diagenetic changes in the formation. Microscopic observations reveal features generally associated with diagenetic changes.

Table 4.2.7 Unit cell parameters from the ilmenite samples of the hinterland

| Sampling Environment | Sample | ‘a’ A$^{o}$ | ‘c’ A$^{o}$ | ‘V’ A$^{o}$ |
|---|---|---|---|---|
| Laterite | L6 | 5.0574 | 13.9013 | 307.9129 |
| | L7 | 5.0764 | 14.0366 | 313.2486 |
| | L3 | 5.0792 | 14.0487 | 313.8662 |
| | L13 | 5.0700 | 14.0137 | 312.1235 |
| Sand stone | 2 | 5.0695 | 14.0146 | 311.9045 |
| | 3 | 5.0382 | 13.9348 | 306.3158 |
| | 4 | 5.0846 | 14.0726 | 315.0691 |
| River | Kallada | | | |
| | 1 | 5.0574 | 13.8758 | 307.3480 |
| | 2 | 5.0438 | 13.8715 | 305.6026 |
| | Valliyar | | | |
| | 1 | 5.1 | 14.1 | 317.5 |
| | 2 | 5.09 | 14.06 | 314.77 |
| | 3 | 5.09 | 13.92 | 311.7 |
| | 4 | 5.1 | 14.1 | 317.51 |
| | 5 | 5.07 | 14.1 | 312.07 |
| Ashtamudi Estuary | E1 | 5.0300 | 13.8822 | 304.1672 |
| | E2 | 5.0438 | 13.9929 | 308.2765 |
| | E3 | 5.0574 | 13.9500 | 308.9916 |
| | E4 | 5.0680 | 14.0170 | 311.7831 |
| *Ilmenite (theoretical) | | 5.093 | 14.06 | 315.838 |

* Roberts et al (1974)

### 4.2.3.4 Ilmenite from the rivers

Two samples from the river in the vicinity of the Chavara deposit were taken for the XRD analysis (Table 4.2.7). The iron rich state of the upper and middle course of the rivers have been dealt in the section concerning phase identification. The lower values of the lattice parameters than expected for slightly altered ilmenite could be due to the lithology of the drainage basin of this river. This portion of the study area has occurrence of rocks like calc granulite, corderite gneiss, pyroxene granulite etc. The ilmenite from the corderite gneiss has been noted to contain suspected exsolved phases of magnetite. As mentioned in the previous section, this ilmenite sample has lower lattice values than expected. In Manavalakurichi area, the ilmenite samples from Valliyar show a decreasing trend for cell volumes down steam. Such a pattern, in this small stream could be explained as a result of alteration suffered.

### 4.2.3.5 Ilmenite from the Ashtamudi estuary:

The values for lattice parameters from this environment are along expected lines. Low lengths for the ‘a’ (5.05) axis and the cell volume (310A) are shown by the sample E2. The sheltered nature of the sampling location gives rise to undisturbed process of weathering which leads to the presence of high amounts of intermediate phases. The sample E4 is from the zone of the river mouth of the Kallada River into the estuary, and consequently, the sample is found to be relatively less altered. The lattice values are close to those for pure ilmenite (‘a’=5.08A, ‘c’=14.05A and ‘V’=313.65A). The lattice volume for this sample is the largest among the estuarine samples. The ilmenite from the estuarine mouth shows an affinity with the beach ilmenite in the unit cell axes and volume. In general, the lattice parameters for the samples from this geologic setup are found to be generally lower, due to advanced alteration undergone.

## Part 4.3. MAGNETISM OF ILMENITE

### 4.3.1 Introduction

Iron form the pre-eminent seat of magnetism in natural minerals and iron compounds are among the most ubiquitous components of natural materials, forming about 2% of the earth's crust (Thompson and Oldfield, 1986). The carriers of magnetic properties of rocks are oxides of iron such as magnetite, titanomagnetite, haematite and maghaemite and to a lesser extent by minerals like ilmenite, goethite etc.

Magnetic fields arise from the orbital motion of electrons around the nucleus and the spin motion of the electrons about their axes in an atom. These grossed up effects of magnetic relationships at the atomic scale are a major influence on the magnetic properties of substances in bulk. Magnetic iron-titanium oxides under which the ilmenite falls are ionic compounds in which the iron ions ($Fe^{2+}$, $Fe^{3+}$) carry net magnetisation (spin moments) proportional to the number of unpaired electron spins on each iron (Stacey and Banerjee, 1974). Though transition metal elements of the 3d series like Fe, Mn, Ni, Co etc. are all main magnetic carriers in Fe-Ti oxides, iron forms the chief source of magnetism. Ilmenite is defined to be paramagnetic based on its magnetic behaviour (Dearing, 1999). For paramagnetic substances, the magnetisation is possible when an external field is applied. The magnetisation thus produced is caused due to the alignment of magnetic dipoles parallel with the direction of the field. The incompletely filled inner electron shells of Mn, $Fe^{2+}$ and $Fe^{3+}$ are generally responsible for the paramagnetic behaviour, as they have unpaired electrons with free spin magnetic moments (Thompson and Oldfield, 1986).

Though the research field of rock magnetism has grown dramatically over the last two decades, particularly with regard to its application for palaeoclimatic interpretation, the magnetic properties of minerals in the natural regime and their variation with regard to weathering and transportation and alteration has not been a major topic of work among the scientists. Such studies will have important role to delineate the effect of environment and geochemistry on the magnetic properties of minerals. Their importance in the characterization of minerals, when correlated with chemistry and mineralogy and the industrial implications has yet to be properly understood.

The magnetic properties like susceptibility and isothermal remenance of minerals have been widely applied in palaeoclimatic interpretation (Kharbhassi and Shanker, 1994) and estimation of heavy mineral deposits (Shanker et al, 1996). However, in this work, the aim would be to deal with the magnetic susceptibility of ilmenite under varying composition and environments.

For carrying out magnetic measurements, different methods were used in this work. The calculation of magnetic susceptibility based on the amperage used for separating out the ilmenite fractions (Flinter, 1959) have been applied for the factory grade ilmenite. Such measurements were confined to the ore grade ilmenite because large quantities are required to separate out the ore into the different magnetic crops. Such methods could not be applied to the field samples, particularly those from the hinterland, where the crop of ilmenite mineral separated out from each location is quantitatively scanty. Further, such methods are found to be far from the accurate and could be, at the most, used for comparative studies of the samples. Still, the data obtained were sufficient to highlight the role of magnetic properties for the characterization of the ore.

The determinations of the absolute measurements of magnetic susceptibility were carried out using a Bartington MS2 Susceptibility System considering its record of satisfactory sensitivity in measurements for a wide variety of applications. The results have been found to be satisfactory and the variation of the magnetic properties consequent to alteration and chemical composition could be worked out.

### 4.3.2 Fractionation using isodynamic separation

Different magnetic fractions of selected samples of factory grade ilmenite (2.75Φ) were separated out and their magnetic susceptibility $(\chi)$ was calculated using empirical formula of Flinter (1959). The results are presented in Table 4.3.1. Accordingly, a range of fractions of varying susceptibility ranging from (230 - >26) x $10^6$ cgs units were obtained. In the case of Manavalakurichi samples, the lowest susceptibility values obtained were around 32 x $10^{-6}$ cgs units. It is observed that about 60% of the total weight of the MK samples has susceptibility exceeding the theoretical values for pure ilmenite (96 x $10^{-6}$ cgs units). In contrast, only about 12% Of the Chavara samples define this highly magnetic fraction. The largest single fraction by weight (~31%) of the Chavara samples, CH4 has a low susceptibility value of 58 x $10^{-6}$ cgs units, while in Manavalakurichi samples, MK2 (129 x $10^{-6}$ cgs units) is the dominant fraction, constituting about 35% of the bulk sample.

As mentioned earlier, the susceptibility values obtained by this method is not absolute and could be used for comparative studies between the different magnetic fractions of a bulk mineral sample or between two deposits. Since the formula used is empirical and depends on the separating current applied, the fractions separated out at the same amperage gives the same susceptibility values for different deposits,

Table 4.3.1 Weight distribution of the magnetic fractions of ilmenite of Chavara (CH) and Manavalakurichi (MK) deposits

| Sample | Current (Amp) | Susceptibility ($\times 10^{-6}$ cgs units) | Weight (%) | |
|---|---|---|---|---|
| | | | CH | MK |
| 1 | 0.15 | 230 | 4.57 | 24.37 |
| 2 | 0.2 | 129 | 7.28 | 35.17 |
| 3 | 0.25 | 82 | 10.47 | 20.07 |
| 4 | 0.3 | 58 | 31.72 | 11.38 |
| 5 | 0.35 | 42 | 13.9 | 6.54 |
| 6 | 0.4 | 32 | 16.3 | 1.07 |
| 7 | 0.45 | 26 | 9.58 | 1.4 |
| 8 | 0.5 | <26 | 6.17 | -- |

irrespective of their content and ionic state of iron. Thus the values obtained by this method are arbitrary, in an absolute sense. Thus more emphasis should be given to the separating amperage rather than the magnetic susceptibility calculated in isodynamic separation.

The mineralogical analysis of the different magnetic fractions of various size grades has been dealt with in the preceding chapter on XRD analysis. The compositional difference depending on the various size grades of the ilmenite fractions separated out at the same amperage have been found to significant. These are confirmed by the absolute measurements of the ilmenite samples using susceptibility meter, which imply the significance of grain size in the processing and beneficiation of the ore grade ilmenite.

### 4.3.3 Determination of susceptibility using Bartington susceptibility Meter

The magnetic susceptibility of the ilmenite from the beach and the hinterland were measured using a Bartington susceptibility meter. The influence of weathering on the magnetism of mineral is discussed with respect to the contents of ferrous and ferric ions in the mineral.

#### 4.3.3.1 Ilmenite from beach:

The magnetic susceptibility of the ilmenite samples from Chavara beach are given in Table 4.3.2. The theoretical value of ilmenite calculated from the stochiometric proportions is 1.2 x $10^6$ $m^3/kg$. But the natural ilmenite samples show significant variations in the susceptibility from the above value depending on the alteration undergone by the sample and the consequent proportions of the ferrous and the ferric states of iron. The magnetic susceptibility values range from 0.72 to a maximum of 1.55

Table 4.3.2 Magnetic susceptibility data of the samples of Chavara beach ilmenite

| Sample (Chavara) | Content (%) | | | | Fe/Ti | Mag sus $(\times 10^{-6})m^3/kg$ |
|---|---|---|---|---|---|---|
| | $Fe^{3+}$ | $Fe^{2+}$ | Fe | Ti | | |
| C1 | 17.90 | 11.00 | 28.90 | 43.50 | 0.63 | 1.084 |
| C2 | 19.81 | 8.38 | 28.19 | 45.75 | 0.62 | 1.257 |
| C3 | 21.40 | 7.93 | 29.33 | 45.03 | 0.65 | 0.718 |
| C4 | 18.92 | 8.91 | 27.83 | 44.37 | 0.63 | 1.208 |
| C5 | 18.27 | 9.42 | 27.69 | 44.75 | 0.62 | 1.545 |
| C6 | 18.1 | 10.5 | 28.6 | 44.70 | 0.64 | 1.408 |

Table 4.3.3 Magnetic susceptibility data of the samples of Manavalakurichi beach ilmenite

| Sample (Manavalakurichi) | Content (%) | | | | Fe/Ti | Mag sus $(\times 10^{-6})m^3/kg$ |
|---|---|---|---|---|---|---|
| | $Fe^{3+}$ | $Fe^{2+}$ | Fe | Ti | | |
| M1 | 20.96 | 12.57 | 33.53 | 40.45 | 0.83 | 1.553 |
| M2 | 18.30 | 13.90 | 32.20 | 40.50 | 0.80 | 1.430 |
| M3 | 17.70 | 11.62 | 29.32 | 44.09 | 0.67 | 1.165 |
| M4 | 15.79 | 18.41 | 34.20 | 41.04 | 0.83 | 1.377 |

x $10^{-6}$ $m^3/kg$. The most altered sample as seen from the various analyses, C3 exhibits the least susceptibility, while relatively less altered samples like C5 and C6 show higher values of susceptibility (Table 4.3.2).

The susceptibility has been reported to depend on the content of iron particularly in the ferric form. The higher spin state of the ferric ions when compared to that of the $Fe^{2+}$ ions has been assigned the reason for the enhanced susceptibility property of these ions (Lindsley, 1991). However in the Chavara deposit, the magnetic susceptibility has been observed to show a decreasing trend (r =-0.69) with the ferric content in ilmenite (Fig 4.3.1). A similar trend with slightly lowered correlation is shown by the Fe/Ti values pointing to similar trends in the case of iron enrichment (Fig 4.3.2). This behaviour is explained by the highly altered state of the Chavara ilmenite. As discussed earlier when the magnetic fractionation of ore grade ilmenite was discussed, the Chavara ilmenite is composed mainly of low magnetic fractions, where, in the case of the lower magnetic fractions, the ferric content shows an increase with decreasing magnetism. This has been a general trend noted in the magnetic fractions of ilmenite in deposits elsewhere (Wort and Jones, 1980; Suresh Babu et al, 1994).

In the Manavalakurichi deposit, ilmenite exhibit on an average, higher value for the magnetic susceptibility when compared to the Chavara samples (Table 4.3.3). This is consistent with the enhanced iron enrichment in the ilmenite of this deposit. The values are slightly higher than the theoretical value of magnetic susceptibility for ilmenite. In contrast with the trend shown by Chavara ilmenite, the susceptibility in the Manavalakurichi fractions shows a marked increasing trend (r =0.93) with ferric enrichment (Fig. 4.3. 3). This nature of correlation is also reflected in the Fe/Ti values with r value of 0.88 (Fig 4.3.4). Interestingly, though the ferric/ ferrous ratio is higher in Chavara, the

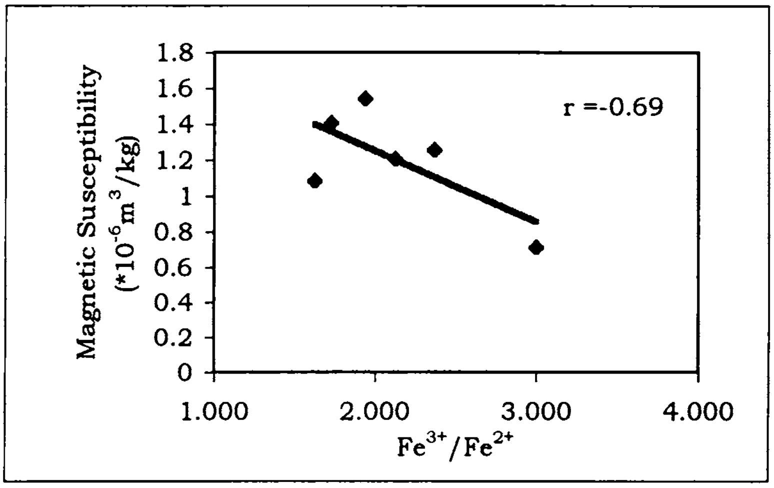


Fig 4.3.1. Variation in magnetic susceptibility with alteration (indicated by increasing $Fe^{3+}/Fe^{2+}$ ratios) in Ilmenite samples from Chavara beach.

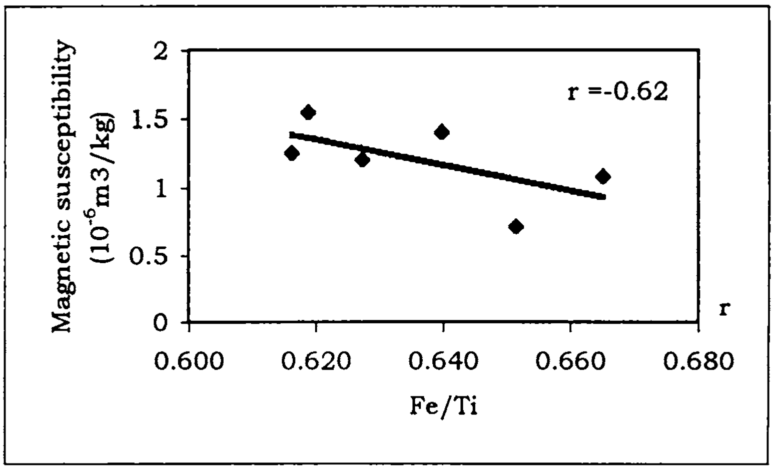


Fig4.3.2.Variation in magnetic susceptibility with iron enrichment (indicated by Fe/Ti ratios) in Ilmenite samples from Chavara beach

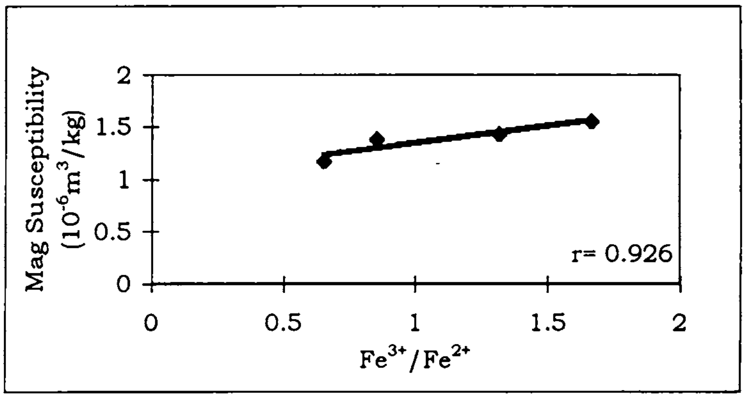


Fig4.3.3. Variation in magnetic susceptibility with alteration (indicated by increasing $Fe^{3+}/Fe^{2+}$ ratios) in Ilmenite samples from Manavalakurichi beach.

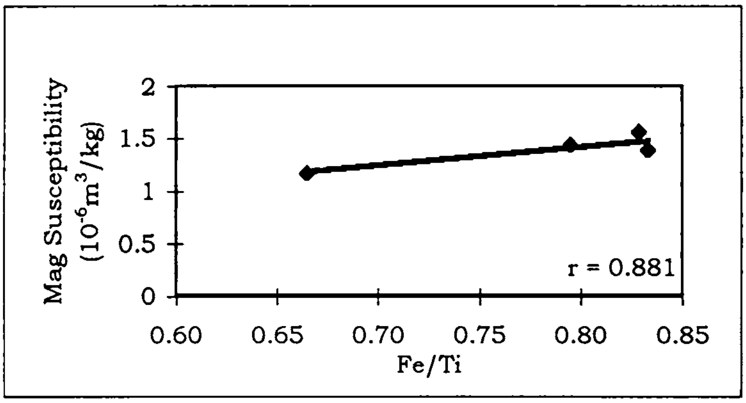


Fig4.3.4.Variation in magnetic susceptibility with iron enrichmen (indicated by Fe/Ti ratios) in Ilmenite samples from Manavalakurichi beach.

Manavalakurichi ilmenite follows the established expected pattern of increase of susceptibility with higher $Fe^{3+}$ content. This different pattern in the magnetic behaviour of the two deposits, which are adjacent to each other under similar environmental settings, could only be explained on the basis of the differential alteration suffered by the deposits, which harks to the older age of the Chavara deposit. The textural studies indicate that the Manavalakurichi ilmenite is made up of differentially magnetic fractions of the mineral, with a bias towards the higher magnetic crops.

4.3.3.1.1 Magnetic fractions of the bulk ilmenite: As indicated in the preceding section, the ore grade ilmenite of the two deposits was split up into different fractions by separating them under progressively varying amperages in an Isodynamic separator. Such fractionation provides crops of grains, which had undergone different stages of alteration. The susceptibility measurements of the magnetic analysis of the fractions are given in Table 4.3.4. The CH1 sample exhibits a susceptibility value much higher than the rest of the samples and the theoretical value for ilmenite. In fact, it is about 2.3 times that of the next magnetic sample. The increased susceptibility of the high magnetic fractions have been explained as due to presence of solid solution of haematite in the ferric oxide of the grains (Wort and Jones, 1980). Such a solid solution has been reported to produce a highly magnetic fraction (Nagata, 1961; Stacey and Banerjee, 1974). The progressive decrease of magnetic properties for fractions separated from 0.2A onwards is due to the increasing alteration forming poorly magnetic products like pseudorutile and rutile. Shanker et al (1996) suggested that the higher magnetic properties shown by the Chavara ilmenite, could be due to the solid solution with haematite. Probably, such grains are predominantly separated out at the lowest ampere. However, no evidence of the presence of haematite/maghaemite is seen in the beach ilmenite samples of

Table 4.3.4 Magnetic susceptibility data of the magnetic fractions of ilmenite from Chavara (CH) deposit

| Amperage (A) | Sample | Content (%) | | | | Fe/Ti | Mag sus (x10$^{-6}$)m$^3$/kg Mag Sus |
|---|---|---|---|---|---|---|---|
| | | $Fe^{3+}$ | $Fe^{2+}$ | Fe | Ti | | |
| 0.15 | CH1 | 22.68 | 8.12 | 30.8 | 33.76 | 0.912 | 3.200 |
| 0.20 | CH2 | 21.66 | 7.85 | 29.51 | 35.25 | 0.837 | 1.406 |
| 0.25 | CH3 | 16.61 | 11.06 | 27.67 | 36.44 | 0.759 | 0.801 |
| 0.30 | CH4 | 16.10 | 9.84 | 25.94 | 36.52 | 0.710 | 0.635 |
| 0.35 | CH5 | 17.69 | 8.48 | 26.17 | 36.57 | 0.716 | 0.399 |
| 0.40 | CH6 | 19.93 | 5.08 | 25.01 | 37.15 | 0.673 | 0.245 |
| 0.45 | CH7 | 20.05 | 2.99 | 23.04 | 38.16 | 0.604 | 0.158 |
| >0.45 | CH8 | 15.10 | 1.57 | 16.67 | 39.03 | 0.427 | 0.093 |

Table 4.3.5 Magnetic susceptibility data of ilmenite fractions of various size grades

| Size Grade (ASTM) | Sample | Mag sus (x10$^{-6}$)m$^3$/kg |
|---|---|---|
| +60 | CH2 | 0.855 |
| | CH4 | 0.873 |
| | MK2 | 2.439 |
| | MK4 | 0.830 |
| +140 | CH2 | 2.083 |
| | CH4 | 1.016 |
| | MK2 | 2.909 |
| | MK4 | 0.958 |

Chavara after microscopic, XRD, chemical and Mössbauer studies during the present investigations.

When the magnetic susceptibility values are plotted against ferric contents of the fractions, it is found that the susceptibility generally decreases with increase of the $Fe^{3+}/Fe$ ratios (Fig 4.3.5). However, it is found that the total iron content has a positive influence on the susceptibility values. The CH1 and CH2 fractions are found to be more altered than the CH3 and CH4 samples, in spite of their higher magnetic susceptibilities, as discussed in the preceding section concerning XRD studies. Further the $Fe^{3+}/Fe^{2+}$ ratios show higher values (2.79 and 2.76 for CH1 and CH2 respectively) for these samples than the successively magnetic CH3 and CH4 fractions (Table 4.3.4). This lends credence to the suggestions by Subrahmanyam et al (1982) that presence of the ferric ions influence magnetic susceptibility than the ferrous content due to the higher spin state of the $Fe^{3+}$ ions. Thus, they argued that moderately altered samples may exhibit higher magnetic susceptibility than the unaltered fractions due to the higher content of the ferric iron in them. Among the least magnetic fractions, the susceptibility decreases with increasing $Fe^{3+}/Fe^{2+}$ ratios (Figs 4.3.5 and 6; Table4.3. 4). In these fractions, the total iron content steadily decreases, even though the proportion of ferric content in the total iron increases to a considerable extent. The dependence of iron on the magnetic susceptibility is reflected in Fig. 4.3.7, where the Fe/Ti plots indicate the depletion of iron in the lower magnetic fractions. Obviously, the enhanced ferric content with respect to the ferrous content becomes relevant only when the total iron content tends to the theoretical values for pure ilmenite. With progressive alteration as indicated by the decreasing Fe/Ti ratios, the predominance of ferric state in iron sharply increases as the total Fe content falls. The iron enrichment with respect to the susceptibility exhibits a healthy relationship ($r = 0.80$), pointing to the significance of the total iron

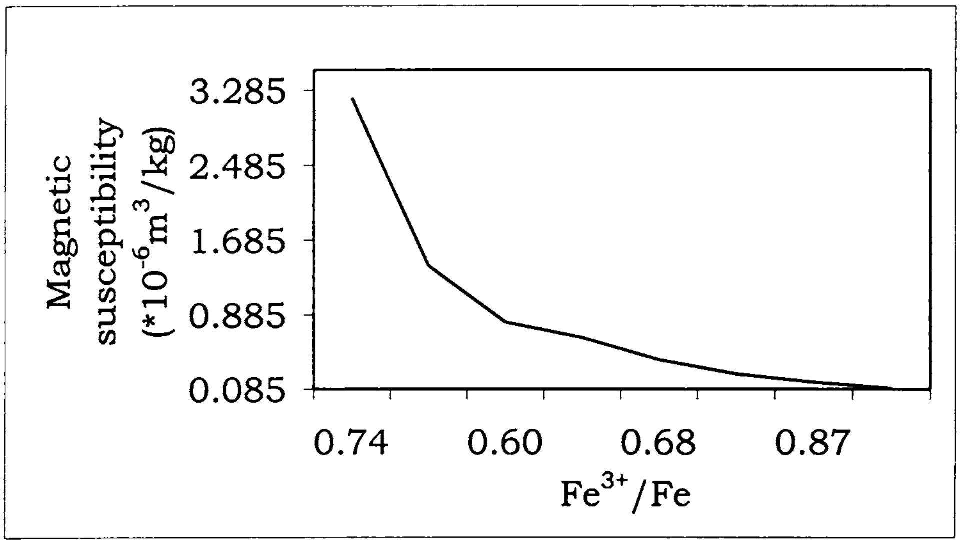


Fig 4.3.5. The variation of magnetic susceptibility with Ferric content in total iron in the magnetic fractions of bulk Ilmenite from Chavara beach.

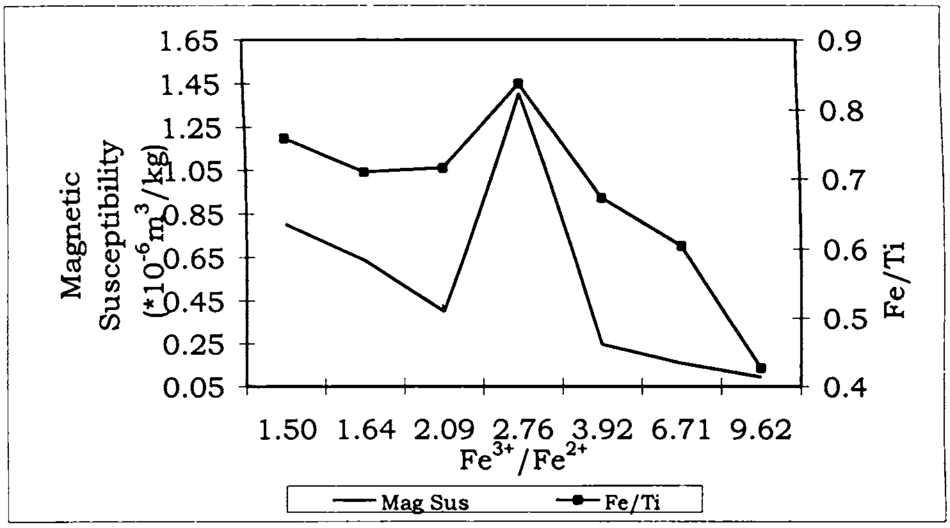


Fig 4.3.6. Relationship between magnetic susceptibility and iron enrichment with increasing ferric - ferrous ratios in the magnetic fractions of bulk ilmenite from. Chavara beach

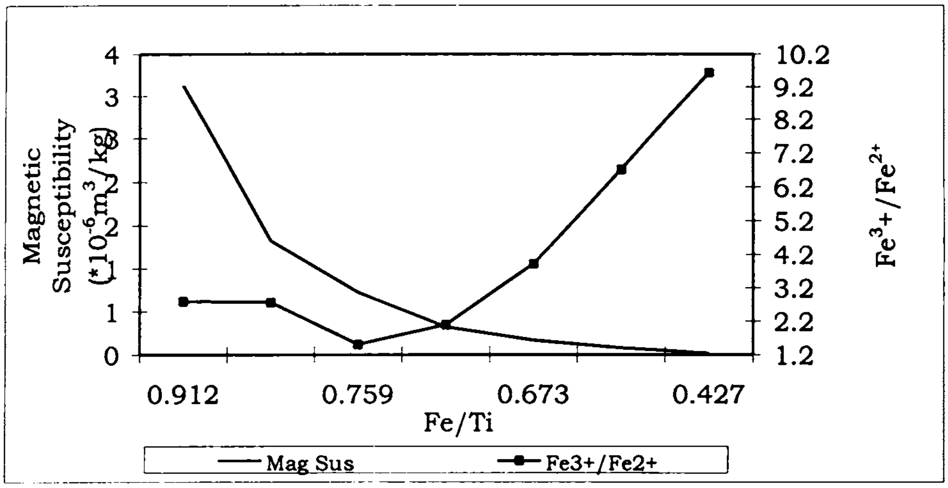


Fig. 4.3.7 Relationship between magnetic susceptibility and ferric-ferrous ratios with enrichment of total iron (Fe/Ti) in the magnetic fractions of bulk ilmenite from Chavara

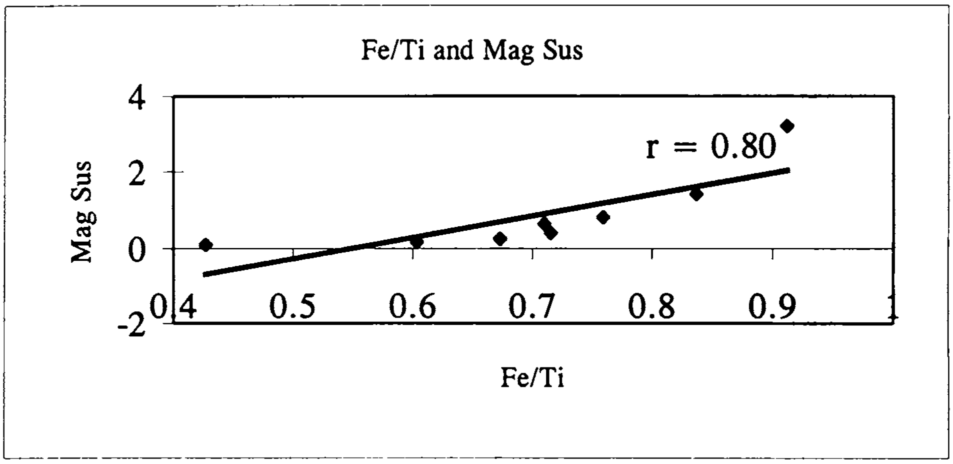


Fig. 4.3.8 Correlation of magnetic susceptibility with total iron enrichment (Fe/Ti) in the magnetic fractions of bulk ilmenite from Chavara beach

contents on the magnetic susceptibility (Fig. 4.3.8). The very low magnetism by the fractions separated by <0.45A complements the dominance of rutile peaks shown by them in the XRD analysis.

The different size grades of the same fraction separated at the same amperages were measured for their magnetic susceptibility, to assess the influence of the grain size of ilmenite ore on the magnetism of the mineral. Thus two very different size grades were selected namely the grains retained between –45 (1.5 Φ) and +60 (2 Φ) and –80 (2.5 Φ) and +140 (3.75 Φ) mesh sizes (ASTM). It is found that, invariably, irrespective of the deposits, the finer sized grains will present greater susceptibility values than their coarser counterparts (Table 4.3.5). The presence of enhanced amount of silicate minerals have been reported in the coarser fractions of Australian ilmenite deposits (Chernet, 1999). In the beach deposits, quartz is the major silicate mineral, particularly in the Chavara beach. The presence of such minerals, which are usually seen in the coarser fractions, could be the reason for the depleted susceptibility values for the coarser fractions of a given magnetic crop.

It is seen from the magnetic susceptibility data that the samples belonging to different size grades of any given fraction separated at the same amperage present very characteristic trends (Table 4.3.5). In the higher magnetic fractions as given by the samples separated at 0.2A, the susceptibility shows a higher value for the Manavalakurichi ilmenite. This is consistent with the patterns in the beach ilmenite where the Manavalakurichi samples are on an average more magnetically susceptible than Chavara. The presence of silicates as impurities is commonly observed in ilmenite crops, particularly in the coarser size grades (Chernet, 1999). In the Chavara beach quartz is reported to be the very predominant silicate mineral (Thampi et al, 1994).

The Manavalakurichi ilmenite, on the other hand, contain significant contents of silicates like garnet, pyroxenes, amphiboles etc., which all tend to be paramagnetic in character. Such minerals, may give rise to elevated values of magnetism, when even present in marginal quantities, compared to the corresponding Chavara samples. However, the low magnetic fractions of Chavara and Manavalakurichi are very similar in their susceptibility behaviour of their respective size fractions. In the lower magnetic fractions (below 0.35A) of ilmenite of these deposits, the composition of the major elements tends to be very similar as the magnetism decreases (Table 4.3.4). This leads to the similar magnetic susceptibility for the low magnetic fractions.

A fractionation based on the grain size of the ore ilmenite of the two deposits were carried out at 0.5$\phi$ interval, it was found that the Chavara and Manavalakurichi ilmenite samples exhibit similar magnetic values except in that retained in the +100 (2.75$\Phi$) mesh (Table4.3. 6). This particular fraction of Manavalakurichi ilmenite has a relatively very high value of about 3.2 x $10^{-6}$ $m^3$/kg. The explanation could be given either by suggesting higher concentration of ferrian ilmenite phase in the grains of this particular fraction or the presence of impurities like haematite and magnetite in this particular fraction than the other crops. Generally it is found that the factory grade ilmenite has marked quantities of ferromagnetic impurities, which could be separated out by a hand magnet.

4.3.3.1.2 IRE graded samples of ilmenite Commercial grade ilmenite from the Chavara deposit was separated in a pilot plant scale again into seven fractions (IRE 1-7) based on their magnetic principles. Out of these, IRE1 represents ilmenite grade, while IRE 2-4 rutile and the last three fractions correspond to rutile (Table 4.3.7). The susceptibility of the

Table 4.3.6 Magnetic susceptibility data of the different size grades of the bulk ilmenite from Chavara (CH) and Manavalakurichi (MK) deposits

| Size Grade | Magnetic susceptibility $(\times 10^{-6})m^3/kg$ | |
|---|---|---|
| | CH | MK |
| +60 | 1.346 | 1.193 |
| +80 | 1.459 | 1.402 |
| +100 | 1.582 | 3.211 |
| +120 | 1.99 | 1.619 |
| +140 | 1.690 | 1.760 |
| +170 | 1.329 | 1.077 |

Table 4.3.7 Magnetic data of the IRE factory graded samples of ilmenite

| IRE grading | Samples | Fe (%) | Mag sus $(\times 10^{-6})m^3/kg$ |
|---|---|---|---|
| Ilmenite | IRE1 | 22.92 | 0.887 |
| Rutile | IRE2 | 1.34 | 0.010 |
| | IRE3 | 1.70 | 0.006 |
| | IRE4 | 10.70 | 0.009 |
| Leucoxene | IRE5 | 4.08 | 0.034 |
| | IRE6 | 3.00 | 0.030 |
| | IRE7 | 5.67 | 0.072 |

Ilmenite product is very similar to the values obtained for ilmenite from Chavara beach sample. The leucoxene grade (IRE 5 to 7) and the rutile grade products present low susceptibilities. The susceptibilities of leucoxene grades range from 0.030 to 0.072 x $10^{-6}$ $m^3/kg$. These values are consistent with the iron content of these samples. The rutile products posses much lower susceptibility values ranging from 0.009 to a maximun of 0.01 x $10^{-6}m^3/kg$.

### 4.3.3.2 Ilmeite from laterite:

The susceptibility values for the sample in this environment range from 0.5 to about 1.18 x $10^{-6}$ $m^3/kg$ (Table 4.3.8). Among the laterite samples over crystalline rocks, the magnetic susceptibility range around 1. In spite of the relatively fresh state of the samples as attested by microscopic, XRD and high FeO contents, the values are on an average lower than the reputedly altered Chavara ilmenite. The content of iron in the samples and the ratio of its ionic state in determining the magnetic susceptibility of the mineral is illustrative in the study of the samples. Although, the iron enrichment is high, the magnetism is apparently dependent on the ferrous iron in the laterite ilmenite samples. The spin moments of these are lower than that of the ferric ions. Thus, though an amount of magnetism is developed the lower proportion of the ferric ions give rise to susceptibility value lower than the ferric rich beach sample. A similar relationship is observed in the laterite over sedimentary formations. Though the sample L11 is depleted in iron, which forms only about 27.26% (38% in the oxide form), the magnetic susceptibility is significantly higher than that of the L2 sample, even though in this sample the iron is more enriched to about 35%. The ferric contents of these samples vary, being richer in the L11 (18%), than the more unaltered L2 (6%). Apparently, the content of $Fe^{3+}$ determines the magnetic susceptibility for comparable contents of total iron. A marked

Table 4.3.8 Magnetic susceptibility data for the ilmenite samples of the different geological environments of hinterland

| Sampling Environment | Sample | Composition (%) | | | | Fe/Ti | Mag sus $(\times10^{-6})m^3/kg$ |
|---|---|---|---|---|---|---|---|
| | | $Fe^{2+}$ | $Fe^{3+}$ | Fe | Ti | | |
| Laterite | L1 | 30.48 | 6.34 | 36.82 | 30.82 | 1.19 | 1.175 |
| | L2 | 29.31 | 5.47 | 34.78 | 31.34 | 1.10 | 0.583 |
| | L3 | 28.69 | 8.32 | 37.01 | 30.52 | 1.21 | 0.961 |
| | L6 | 27.32 | 7.83 | 35.15 | 30.66 | 1.14 | 1.060 |
| | L7 | 27.93 | 8.21 | 36.14 | 29.63 | 1.21 | 1.087 |
| | L8 | 24.45 | 10.78 | 35.23 | 30.10 | 1.17 | 0.712 |
| | L9 | 30.57 | 5.93 | 36.50 | 29.99 | 1.21 | 0.805 |
| | L10 | 30.42 | 6.58 | 37.00 | 30.63 | 1.20 | 0.678 |
| | L11 | 9.21 | 17.95 | 27.26 | 36.14 | 0.75 | 0.734 |
| | L12 | 27.74 | 7.26 | 35.04 | 30.10 | 1.16 | 0.334 |
| Sandstone | S1 | 2.20 | 20.98 | 23.18 | 38.81 | 0.59 | 0.290 |
| | S2 | 6.58 | 24.05 | 30.63 | 32.93 | 0.93 | 2.364 |
| | S4 | 29.00 | 7.33 | 36.33 | 32.58 | 1.11 | 0.804 |
| Teri | T1 | 19.37 | 14.41 | 33.78 | 36.76 | 0.92 | 1.600 |
| | T2 | 22.11 | 13.00 | 35.11 | 37.98 | 0.92 | 1.339 |
| Rivers | Valliyar | | | | | | |
| | 1 | 22.08 | 13.42 | 35.5 | 31.96 | 1.11 | 1.607 |
| | 2 | 21.8 | 13.86 | 35.66 | 32.07 | 1.11 | 1.237 |
| | 4 | 18.07 | 12.12 | 35.90 | 32.14 | 1.11 | 1.883 |
| | Karamana | | | | | | |
| | 1 | 27.30 | 8.98 | 36.28 | 31.14 | 1.16 | 0.829 |
| | 3 | 28.12 | 8.64 | 36.76 | 31.53 | 1.16 | 0.610 |
| | 5 | 28.45 | 6.62 | 35.07 | 32.34 | 1.08 | 0.593 |
| | Ithikkara | | | | | | |
| | 1 | 30.22 | 6.68 | 36.90 | 31.21 | 1.18 | 0.542 |
| | 2 | 27.19 | 9.52 | 36.71 | 31.44 | 1.16 | 0.653 |
| | 3 | 28.64 | 7.94 | 36.58 | 31.80 | 1.15 | 0.763 |
| | Kallada | | | | | | |
| | 1 | 23.88 | 13.57 | 37.46 | 30.52 | 1.22 | 1.889 |
| | 3 | 20.57 | 22.79 | 36.50 | 30.62 | 1.19 | 1.983 |
| | 6 | 23.16 | 14.27 | 37.43 | 31.67 | 1.18 | 1.226 |
| | 7 | 24.28 | 10.40 | 34.69 | 32.41 | 1.07 | 1.284 |
| Estuary | E1 | 8.50 | 17.88 | 26.37 | 37.76 | 0.69 | 0.975 |
| | E2 | 8.21 | 19.16 | 29.37 | 36.00 | 0.81 | 1.270 |
| | E3 | 7.85 | 20.75 | 28.60 | 34.93 | 0.81 | 1.067 |
| | E5 | 11.30 | 15.84 | 27.14 | 34.85 | 0.77 | 1.368 |

correlation between the magnetic susceptibility values and the $Fe^{3+}/Fe^{2+}$ and the Fe/Ti ratios are not observed in the laterite samples unlike in the beach. This could be due to the lower ferric content when compared to the ferrous ions, which does not give a sharp variation in the magnetism with change of content.

### 4.3.3.3 Ilmenite from the Tertiary sedimentary rocks:

Among the ilmenite samples from the Tertiary formations, the magnetic susceptibility shows a wide range from about 0.3 for S1 to rather value of 2.4 x $10^{-6}$ $m^3/kg$ for S2 (Table 4.3.8). S1 has reached a very advanced alteration stage that it is almost leucoxenized and the iron values is a very low of 23%, of which around 21% is ferric. On the other hand, the S2 sample is enriched in iron and possesses high ~~and~~ $Fe3+/Fe2+$ and Fe/Ti values that give rise to the considerable susceptibility of 2.36 x $10^{-6}$ $m^3/kg$. In S4, though the iron enrichment is slightly higher, when compared with the above sample the ferric content is much lower, accounting for only 7% of the composition of the sample. The difference in susceptibility for samples from the same formation, which are located close to each other point to the variation in the nature of the alteration in ilmenite of the samples. This could be due to the local change in nature of the sediments, which went on to form the Warkkalli formation or to the difference in post depositional changes occurring in the formation. Morad and Aldahan (1986) have argued that the post depositional diagenetic changes account for the dominant part of the alteration of ilmenite in sedimentary rocks.

### 4.3.3.4 Ilmenite from the Teri deposit:

The hinterland of the Manavalakurichi area is characterized by the occurrence of a reddish sandy deposit consisting of loosely consolidated material. These sediments are known as Teris. They primarily consist of quartz coated with iron derived from the leaching of associated minerals. The heavy mineral content of the Teris is about 10%. The chemical analysis indicates that the ilmenite from this environment is enriched in iron. The Teri ilmenite samples record higher values when measured for the magnetic susceptibility. Here alteration has succeeded in the oxidation of ferrous (19%) to ferric (14%) but the total iron values are high (about 45%), giving rise to enhanced values as shown in the Table 4.3.6.

### 4.3.3.5 Ilmenite from the rivers:

In the rivers, a similar pattern to that of the laterite ilmenite is seen (Table 4.3.8). Compositional studies indicate that the river ilmenite is relatively unaltered, except those from the very down stream locations. The reasons have been described in the section dealing with the chemistry of the work, which attributed to the relatively short course of the rivers of Kerala, the high gradient, which imparts significant erosive power and velocity to the flow of water. The river not only, carry the sediment load brought from upstream, but also carry out weathering and erosion as it flows along. This ensures a constant supply of fresh material in the rivers studied. Thus, like laterite samples, the lower ferric contents ensure a lower magnetic susceptibility values in spite of high iron enrichment of the samples. The exception is shown by the ilmenite samples of the Kallada River, were rather high values with an average of 1.5 x $10^{-6}$ $m^3$/kg are recorded. This is consistent with the minerdogical and chemical studies, which have indicated to the very high iron content in the samples. The XRD and Mössbauer analyses have suggested the presence of a ferromagnetic content in the ilmenite and the microscopic observations have identified the presence of magnetite/maghematite in laterite and river samples of the drainage basin of this river. As in compositional patterns, the other rivers more or less show a similarity in the variation in magnetism too.

#### 4.3.3.6 Ilmenite from the Ashtamudi estuary:

In the Ashtamudi estuary, the ilmenite sample shows the characters of both riverine and marine influence on the location of the sample in the various analyses carried out. The magnetic methods too exhibit results, which complements this trend. The sample E1 and E2 represent sample from the creeks of the estuary where a shaded environment is seen. These zones are not much disturbed by the effects of the riverine discharge or the currents of the estuary or of marine origin. The slightly depleted iron and ferric content is reflected by their marginally lower magnetic susceptibilities when compared to E3, which is from the open main body of the estuary (Table 4.3.8). The sample E5 is from near the estuarine mouth, which remains open through out the year givingrise to the important influence for the marine processes in this zone of the estuary. The consequent sediment influx determines the detrital regime in this part of the estuary. The magnetic susceptibility of the sample is akin to that of certain samples from the Chavara beach.

## Part 4.4. THERMOGRAVIMETRIC ANALYSIS

### 4.4.1 Introduction

The technique of thermogravimetry is one in which the change in sample mass is determined as a function of temperature and/or time (Wendlandt, 1986). Dynamic thermogravimetry is one mode of the thermogravimetry in which the sample is heated in an environment whose temperature is changing in a predetermined manner, preferably at a linear rate. The main parameter measured is the change in sample mass, which is recorded as the function of increasing temperature. This is the method used for the present study and will be hereafter referred to as thermogravimetry (TG). Other techniques of thermal analysis measure parameters like heat flow, thermal conductivity, dielectric constant, change in dimensions of the sample etc. to delineate and characterize the thermal properties of the samples.

Thermogravimetric analysis of the samples was carried out to decipher the behaviour of ilmenite under progressively increasing temperatures. The method of TG is quantitative in nature in that the mass change can be accurately determined. However, the temperature ranges in which the mass changes occur are qualitative in that they depend on the nature and type of instrumentation and sample characteristics (Wendlandt, 1986). In the case of ilmenite, the patterns of the curves depend on the release of the water included in the mineral and the oxidation of ferrous ions to the ferric form. These, in turn, are characters intrinsically related to the state of alteration and weathering undergone by the mineral. The nomenclature used in the work is based on the terminology adopted by the International Confederation of Thermal Analysis in 1967 for reporting the DTA and TG data.

Since a mass change is observed, when ilmenite samples are heated to high temperatures, thermogravimetry is preferred to other thermal techniques like DTA and DSC. However, this technique has been sparely used for the study of the mineral, in spite of the encouraging results obtained (Kharkhanawala and Momin, 1959; Suresh Babu et al, 1994; Ramakrishnan et al, 1997) in delineating the alteration and composition. The purpose of TG in this work is to determine its behaviour of ilmenite samples at progressively increasing temperature and to understand the effect of alteration based on the trend and pattern of the curves.

In the following sections, the TG analysis of the ilmenite samples from the beach and the different geological set ups of the hinterland are discussed to understand the variation in the behaviour of differently altered ilmenite samples at increasing temperatures.

### 4.4.2 Ilmenite from beach

The ilmenite samples from the beach are found to occur in a two-stage process in the TG curves (Fig. 4.4.1). The initial weight loss due to the escape of water content and hydroxyls forms the first stage. Grey et al (1983) has on the basis of DTA analysis, identified two endothermic peaks in this temperature range corresponding to the weight loss as a result of the release of the hygroscopic water at around 50$^{0}$C and the structurally bound water at around 370$^{0}$C. However, in the case of clays, the temperature of evolution of sorbed water and dehydroxylization are around 200$^{0}$C and at a range of 400-700$^{0}$C respectively (Wendlandt, 1986). In Chavara, the ilmenite is found to suffer a loss in mass in the range of about 0.72 to 1.89% for samples C1 and C3 respectively at a temperature of about 500$^{0}$C (Table 4.4.1). The sample C2 and C3 show the maximum weight loss due to the release of water molecules. These water found in the mineral structure associated with ferric ions related to the formation of

Table 4.4.1 TG data of the ilmenite from Chavara and Manavalakurichi beaches

| Deposit | Sample | Weight loss due to water content (~500°C) | Weight gain/loss at 1000°C |
|---|---|---|---|
| Chavara | C1 | -0.72 | 0.95 |
| | C2 | -1.40 | -0.42 |
| | C3 | -1.89 | -0.58 |
| | C6 | -0.97 | 0.77 |
| Manavalakurichi | M1 | -0.39 | 1.73 |
| | M3 | -0.86 | 1.30 |
| | M5 | -0.21 | 2.15 |

Table 4.4.2 TG data of the magnetic fractions of ilmenite from Chavara (CH) and Manavalakurichi (MK)

| Sample | Weight loss due to water content at 500°C (%) | Weight gain/loss due at 1000°C (%) |
|---|---|---|
| CH1 | -1.48 | -1.26 |
| CH2 | -2.00 | -1.88 |
| CH3 | -0.42 | 3.6 |
| CH4 | -0.32 | -0.07 |
| CH5 | -0.69 | -1.76 |
| CH6 | -2.14 | -2.02 |
| CH7 | -4.23 | -4.03 |
| CH8 | -4.60 | -4.20 |
| MK1 | -0.25 | 0.60 |
| MK2 | -0.25 | 1.45 |
| MK3 | 0 | 3.00 |
| MK4 | -0.30 | 0.20 |
| MK5 | -1.75 | -2.30 |
| MK6 | -2.30 | -2.80 |
| MK7 | -2.80 | -2.80 |

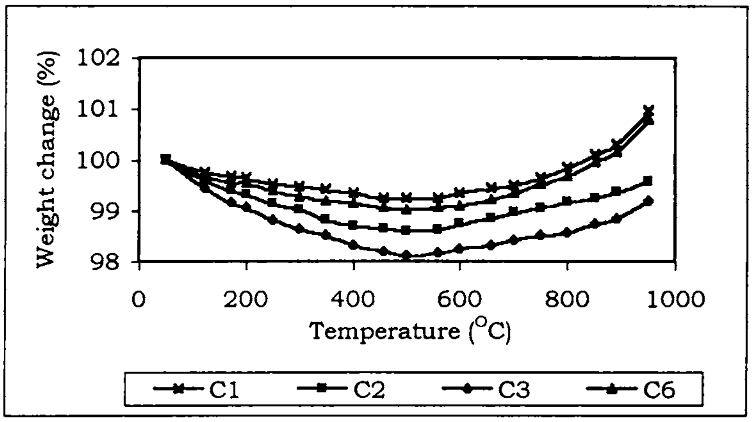


Fig. 4.4.1. TG patterns of ilmenite samples from Chavara beach

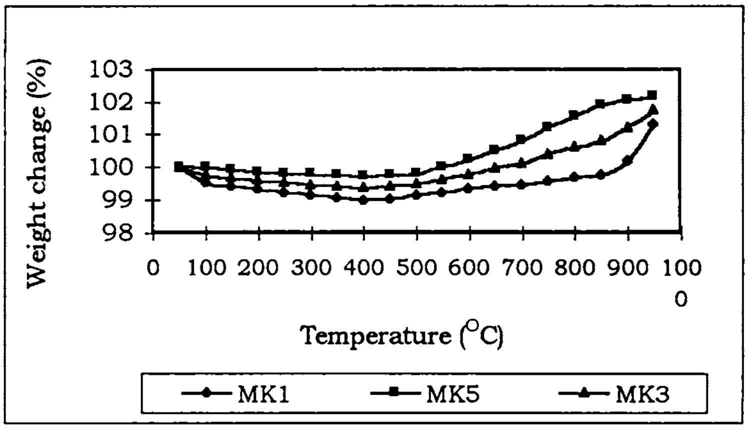


Fig. 4.4.2. TG patterns of Ilmenite samples from Manavalakurichi beach.

pseudorutile phase during alteration (Ramakrishnan et al, 1997). On the other hand, the samples C1 and C6, which are known to be relatively less altered as seen in the XRD data show marginal loss of weight (0.72 and 0.9% respectively) due to the release of structural water (Table 4.4.1). The gain in weight due to the conversion of ferrous oxide to the ferric form from about 500$^{0}$C forms the second stage of the process. In Chavara, the final effective weight variation is expressed as a gain of about 0.95 and 0.77% for samples C1 and C6 respectively. These samples from the southern and northern part of the Chavara deposit have been found to be less weathered as discussed in other sections of this work. However, samples C2 and C3 represent the more altered of the ilmenite samples, as noted from their lower ferrous contents. These samples trace a weight loss of about 0.42 and 0.58% respectively.

The Manavalakurichi samples exhibit a different behaviour in that all the samples analysed show an effective final increase in weight (Table 4.4.1 and Fig 4.4.2). The sample M5 from the northern part of the deposit, which is the least weathered shows the maximum weight gain (2.15%) and least weight loss due to water content (0.21%). The higher state of alteration in MK3 is reflected in its lower weight gain (1.3%) and higher water loss (0.86%). The weight gain shown by the Manavalakurichi ilmenite in all the samples echoes the higher ferrous ions present as found in the chemical analysis. The lower state of alteration of the ilmenite compared to that of Chavara is highlighted by the TG analysis as in the other techniques carried out in this study.

### 4.4.2.1 Magnetic fractions of bulk ilmenite:

The different magnetic fractions of ilmenite were separated out using progressively increasing amperages and undertaken for TG analysis (Fig 4.4.3, a-b). By this way, the progressive alteration undergone by the mineral in the beach could be better understood, since the various

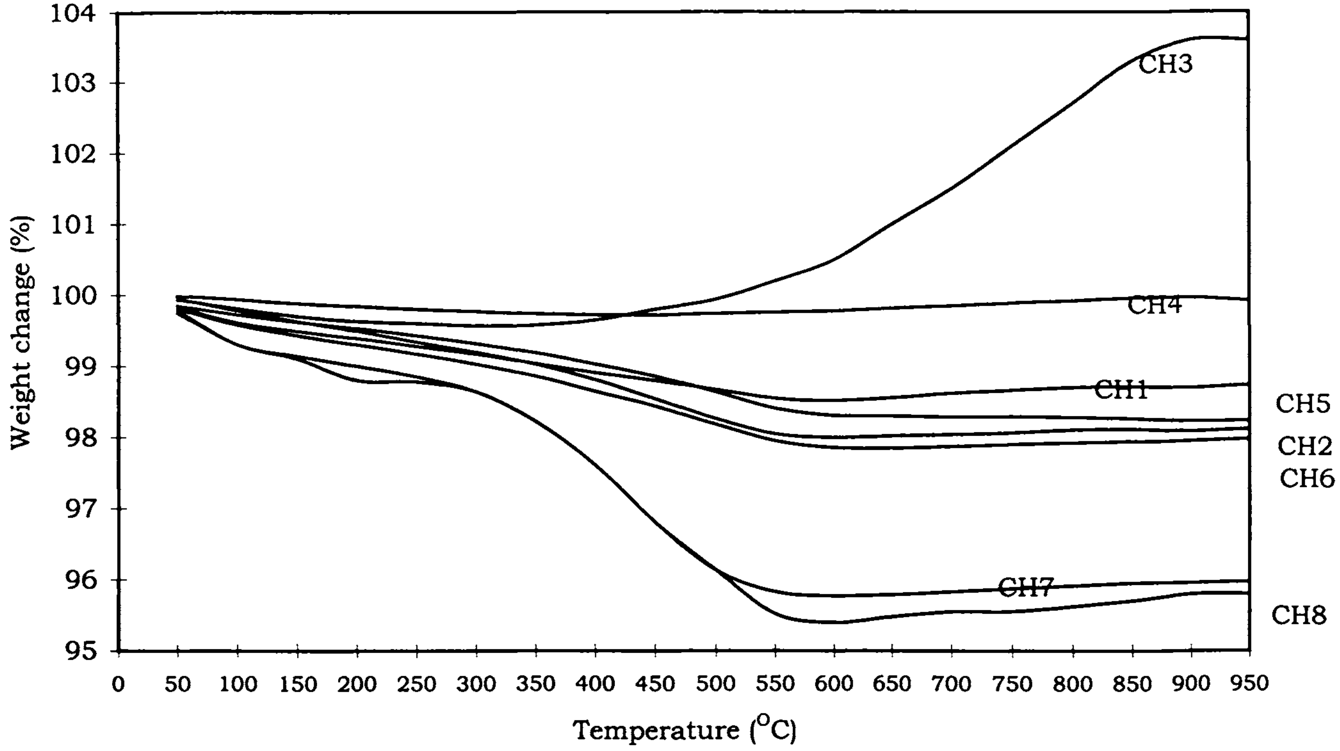


Fig 4.4.3.a. TG patterns of the magnetic fractions of bulk Ilmenite from Chavara deposit.

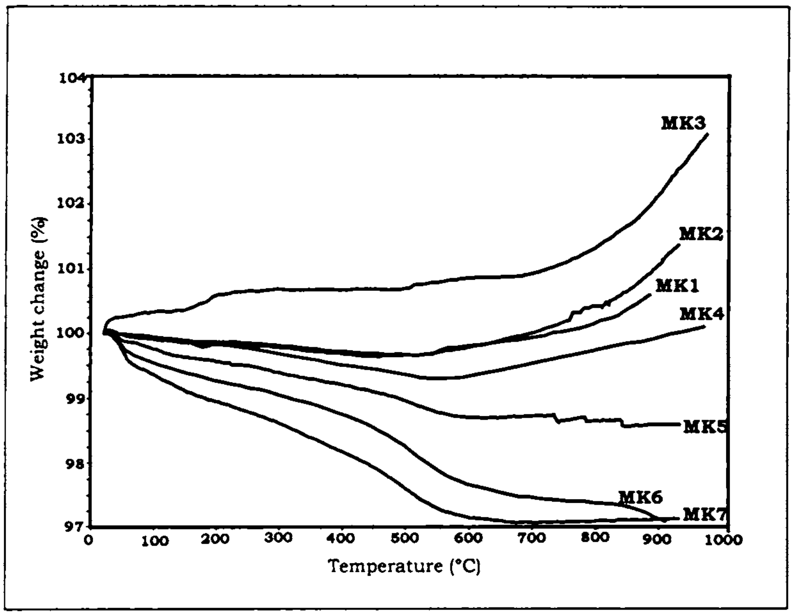


Fig. 4.4.3.b. TG patterns of the magnetic fractions of bulk Ilmenite from Manavalakurichi deposit.

magnetic fractions represent, crops of ilmenite, which have reached different stages of alteration. The curves present an initial fall in weight corresponding to the release of hydroxyls till around $500^{0}$C (Table 4.4.2). This process is more acute in Chavara ilmenite fractions, when compared to the data on Manavalakurichi (Fig 4.4.3b) as published by Suresh Babu et al (1994). The weight loss in Chavara fractions extends up to about $600^{0}$C, as a result of the higher water content, echoing the enhanced content of ferric ions. In the highly magnetic fractions of ilmenite, the more prominent variation in weight is defined by the oxidation of ferrous to ferric state. The weight loss due to the water content is prominent. The weight loss due to the escape of water is marked from MK5 onwards ranging from 1.25 to about 2.3% in MK6, while in Chavara the loss experienced due to the escape of water ranges from 2.14 to 4.6% in the low magnetic fractions. In these fractions, the effective change of mass is defined by the loss of hydroxyls. Since the water content in the mineral structure increases with the increase in ferric content with alteration, particularly with regard to the formation of pseudorutile and leucoxene (Grey et al, 1983; Mucke and Chaudhuri, 1991), the weight loss due to the release could be correlated with the content of these phases. Thus the Chavara ilmenite reveals a higher altered state than the fractions of the mineral from Manavalakurichi.

In the Chavara ilmenite fractions, an effective weight gain is shown by only the sample of CH3, which records a gain of 3.6% (Table 4.4.2; fig. 4.4.3b). Chemical data indicates this sample to be the least altered as it shows the highest FeO values among the fractions. The CH4 fraction exhibits a slight effective weight loss of 0.07%. The most magnetic fractions of CH1 and CH2 present a fall in weight of about 1.26 and 1.88% respectively at final temperatures, which contrasts drastically with the effective weight gain experienced by the corresponding fractions of Manavalakurichi ilmenite. In the first four fractions of the Manavalakurichi ilmenite, though a marginal weight loss consequent to the loss of structural water is recorded (0-0.3%), the weight gain obtained in the reaction interval from around 600$^0$C dominates. In Chavara ilmenite, the corresponding fractions suffer a weight loss of 0.32 to 2%, as weight loss due to the release of water present in the mineral structure. Thus, a high effective increase in weight is shown by MK3 (3%) to a minimum increase in MK4. The MK3 is found to be the least altered fraction based on the chemical and XRD analysis. Thus the considerable FeO content of 32% is being converted into the ferric form, accounting for the increase of mass exhibited. This sample does not show any indication of even the marginal hint of a loss in weight, pointing to its very unaltered nature. The sharp difference in the behaviour of the magnetic c rops of ilmenite of Chavara and Manavalakurichi deposits point ot the higher altered nature of Chavara ilmenite when compared to the Manavalakurichi ilmenite. The influence of the ferrous-ferric transformation on the effective change in weight of the samples is shown by the plot in Fig. 4.4.4(a-b). A significant positive correlation (r =0.94 and 0.88 in Manavalakurichi and Chavasra samples, respectively) is seen underscoring the fact that the oxidation of the ferrous constituent concomitant with alteration proceeds in the mineral. There seems to be a strong negative relationship (r =-0.93 and -0.80 respectively for Manavalakurichi ilmenite magnetic fractions) between the content of water in the ilmenite structure and weight gained by the mineral at higher temperature due to the oxidation of ferrous oxide conversion, attesting to the association of water molecules with the ferric content in ilmenite (Fig. 4.4.5, a-b). This validates the observation of increased water content associated with progressive alteration and consequent ferric conversion. Interestingly, this relation is seen more strongly in the Chavara beach ilmenite than in the magnetic fractions (Fig 4.4.6). In fact, Mucke and Chaudhuri (1991) suggest that alteration of ilmenite, particularly in the advanced stages are characterised by the processes of hydrolization and leaching.

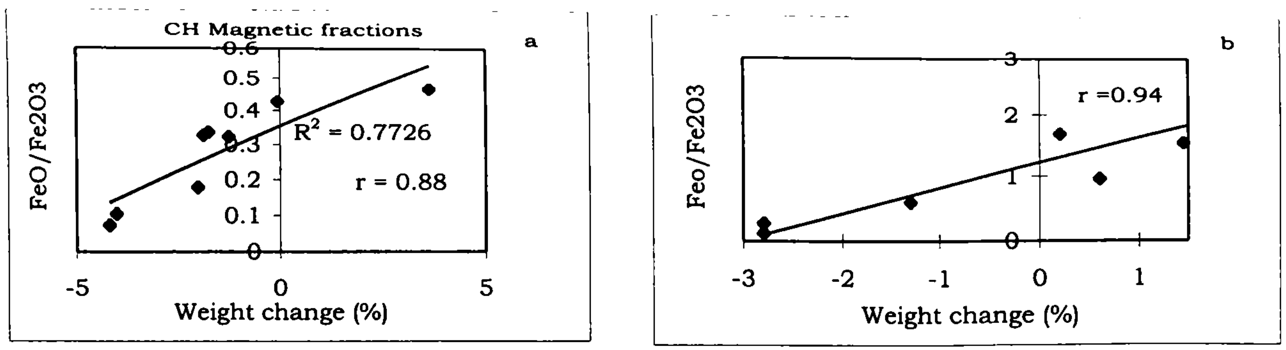


Fig. 4.4.4 Relationship between the final weight change and the ferrous-ferric conversion in magnetic fractions of ilmenite from a) Chavara and b) Manavalakurichi deposits

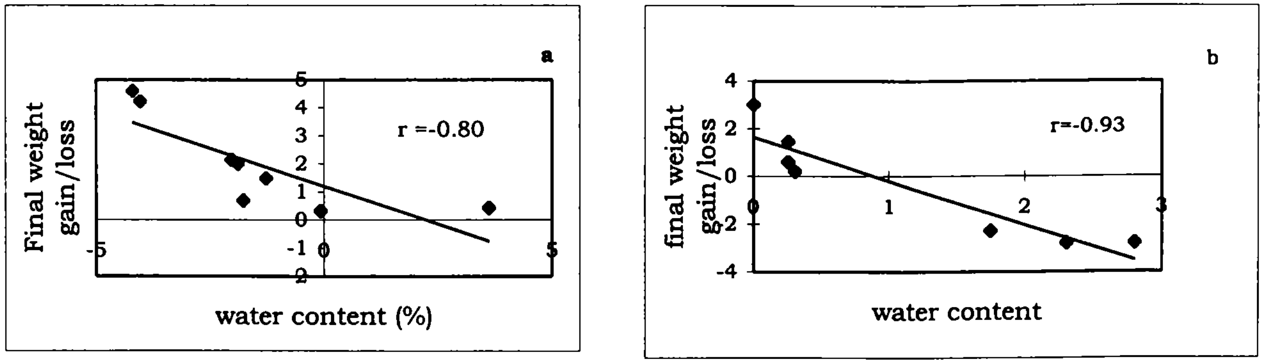


Fig. 4.4.5 Relationship between the water content and the final weight gain/loss in magnetic fractions of ilmenite from a) Chavara and b) Manavalakurichi deposits

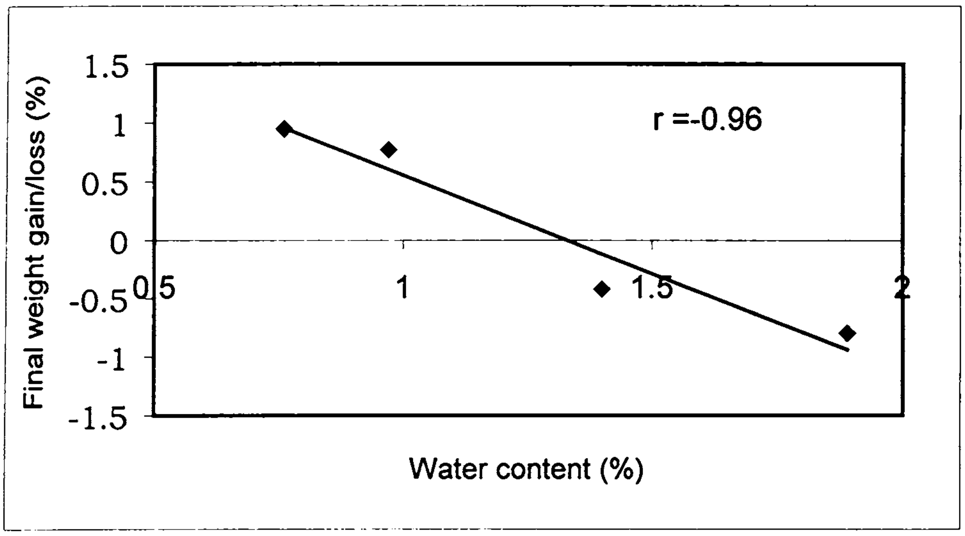


Fig. 4.4.6 Relationship between the water content and the final weight gain loss in the magnetic fractions of Manavalakurichi ilmenite

In the less magnetic fractions, there is a slight but discernible increase in weight of the samples, indicative of the oxidation of the ferrous iron present, even though the contents of iron is relatively insignificant.

#### 4.4.2.2 TG analysis on magnetic fractions of various size grades:

Two samples of significantly different susceptibilities were taken from each deposit for the purpose. They are the high magnetic fractions CH2 and MK2, separated out at 0.2 A from each placer deposit and the CH6 and MK6, obtained at 0.4A. The size factors of the samples, from each deposit vary with the highest magnetic fractions (CH2 and MK2) belonging both to 2 Φ and 3.25 Φ size grade each, and the lesser magnetic grades (CH6 and MK6) to the 3.25 Φ. The CH2 and MK2 fractions of 2 Φ size show an effective increase of 0.29 and 1.33% respectively around 800°C, while in the corresponding samples of 3.25 Φ grade, there is a marginal weight loss of 0.04% for CH2 and a gain of 1% for MK2 (Fig. 4.4.7, a-b). Thus the TG curves vary for samples separated out at the same amperages depending on their size. This is in agreement with the results of the XRD analysis, where the composition difference of the same magnetic fraction of different size grades was observed. The sample CH2 of finer size grade shows a fall in weight of around 1% at 450°C relating to the loss of hydroxyls. The corresponding MK sample traces a gain of 1.4% after the loss of structural water and then around 700°C shows a slight fall to the maximum temperature of about 950°C. The notable difference in the effective weight difference of the corresponding fractions of the Chavara and Manavalakurichi deposits could be ascribed to the compositional difference, which has been observed in the chemistry and other analyses. The loss in effective weight or the subdued gain in weight of the CH samples underscore the highly altered nature of these samples, which have had been well documented. The CH6 and MK6 samples too follow afore mentioned patterns, striking an effective decrease of total mass (1.27 and 1.98% respectively) around 400°C

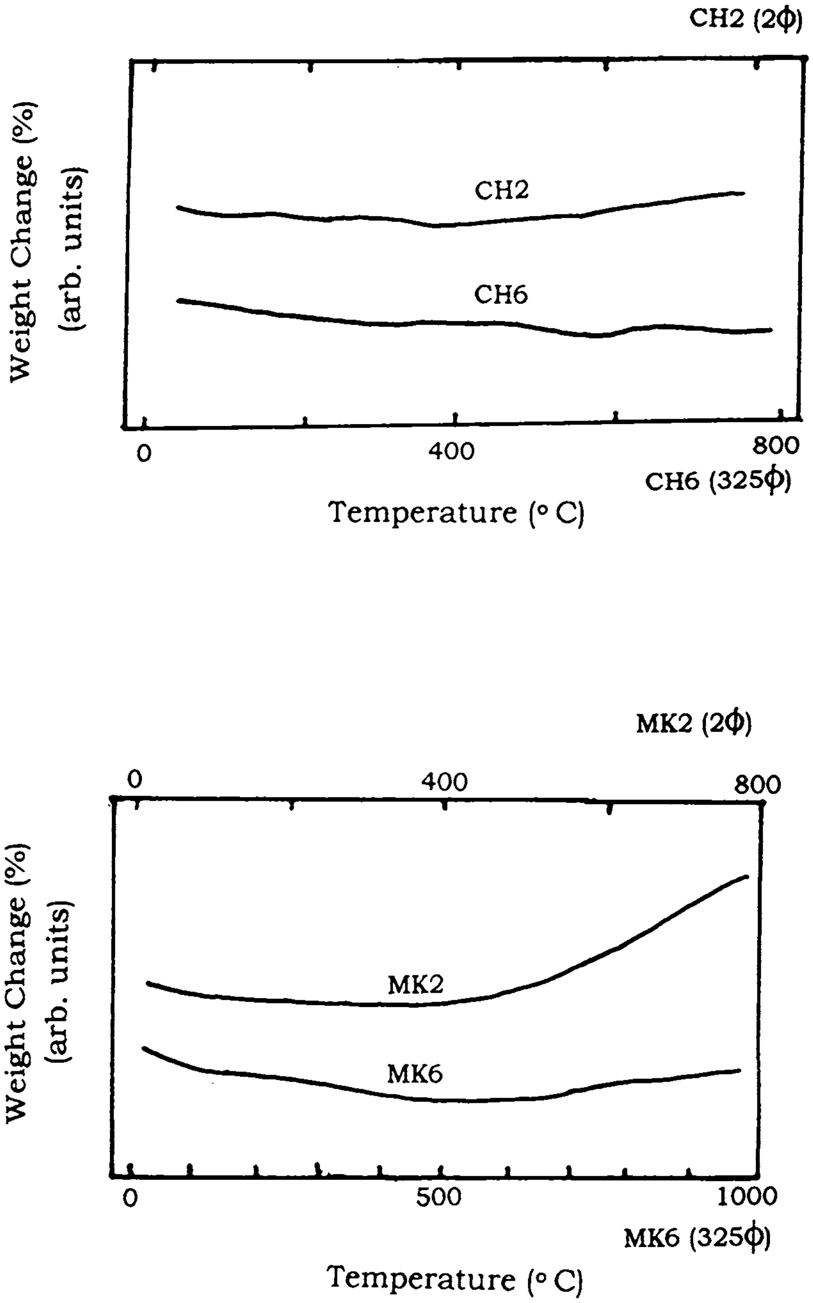


Fig. 4.4.7 TG patterns of different size grades of magnetic fractions of bulk ilmenite from a) Chavara and b) Manavalakurichi

and 600°C respectively. It may be noted that the weight increase persists up to a temperature of about 1000°C.

### 4.4.3 Ilmenite from laterite

The ilmenite samples show an effective increase in weight when heated to a temperature of 1000°C (Fig 4.4.8). Samples from the laterite formation over the crystalline rocks of the study area, in general, offer a relatively less altered state as evidenced from XRD, microscopic and chemical data. Among the lateritic ilmenite samples, the final effective weight gain is maximum at about 3.8% for L12. The least values are for sample L13 at about 2.4%. The hygroscopic free water is released around 50°C and the structurally bound water around 450 and 500°C for L6 and L13 respectively. The weight loss consequent to these processes is only 0.21% for L6. In the case of L13, this loss is slightly larger at about 0.5%. The weight gain after the release of structural water at around 500°C is indicative of the oxidation of ferrous ions and is defined by a steep rise in the curves. The higher weight gain exhibited by the sample L12 is reflected in its high ferrous oxide content (~36%). The relatively lower weight gain shown by the TG cuve of L13 indicates the relatively low FeO content. However, the sample L5 exhibits a higher effective weight gain at 950°C, though its ferrous oxide content is similar to L13. It should be noted that sample L13 is different from other laterite samples by the presence of intergrowths of magnetite/maghaemite, as observed under the microscope and indicated by other analyses. In general, it could be stated that the relatively unaltered state of ilmenite in laterite results in a marked weight gain at the maximum temperature.

The relationship between the $FeO/Fe_2O_3$ ratios and the final effective weight gained by the ilmenite samples describe a moderate positive correlation (r=0.79) as presented in Fig. 4.4.9. The composition of the ilmenite samples from the laterite falls with in a narrow range and

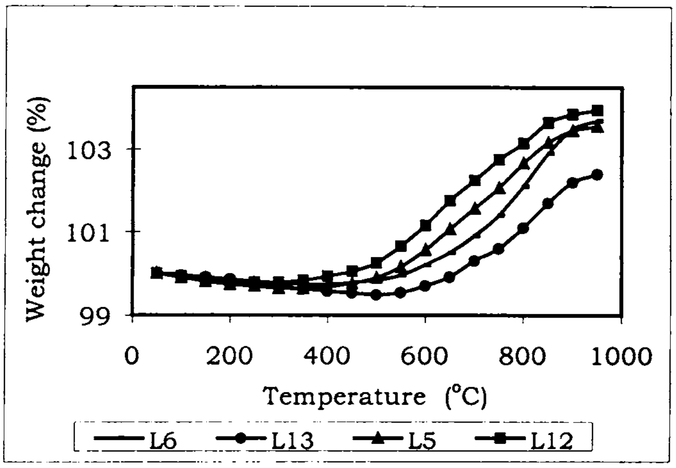


Fig. 4.4.8. TG patterns of ilmenite samples from laterite.

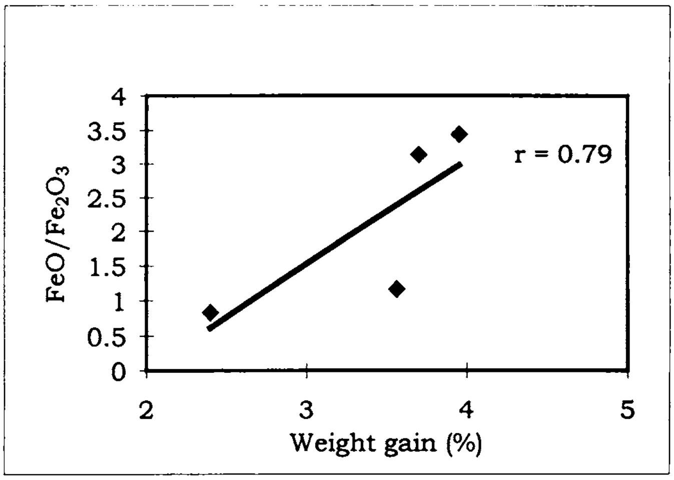


Fig. 4.4.9. Relationship between effective weight gain and ferrous - ferric conversion.

does not posses samples which fall into the entire spectrum of alteration stages as in the case of the magnetic fractions.

### 4.4.4 Ilmenite from the Tertiary sedimentary rocks

Three samples from the Tertiary formation of the southwest coast were selected for the TG analysis, which represent ilmenite of varying degree of alteration (Fig 4.4.10). S1 is a sample that had under gone a high degree of leaching as evidenced by its chemical data. The very low content of FeO of about 2% proves its highly altered state which is about 15 % ~~times~~ lower than the ferric oxide value. Compositionally, this sample can be considered to be of pseudorutile stage. A break in slope around 300$^{0}$C defines the release of the structural water which continues to a final temperature of about 600$^{0}$C. A very slight increase of about 0.19% is observed as a result of the conversion of the insignificant FeO present and the reaction interval from 650$^{0}$C can be considered to be a plateau till the final temperature of 950$^{0}$C. In the sample from Akkulam, S3, a weight loss is suffered from 50$^{0}$C to about 300$^{0}$C corresponding to the loss of hygroscopic free water. Another break in the pattern, which continues to 500$^{0}$C defines the release of water bound to the mineral structure. There after, a steady weight gain is plotted, amounting to about 3.1%. In the highly altered Thiruvallam sandstone, S2, the sample undergoes a net weight loss of 0.12% where as in S3, a gain of more than 1.8% is noted. The structurally bound water is completely released at 450$^{0}$C, with a weight loss of 1% in S2. The considerable value for ferric oxide of about 34.3% points to the presence of significant pseudorutile phase, the hydroxyl content of which is indicated in the weight loss at 450$^{0}$C. Though the FeO present is oxidized, as shown by the weight gain in the reaction interval from 600$^{0}$C, a net weight loss is recorded at the maximum temperature. In the case of S3, the higher value of FeO (22.77%) ensures a weight gain as high as about 2%.

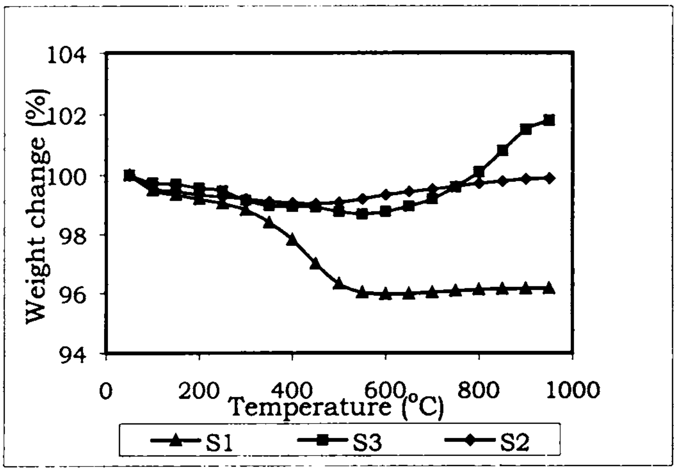


Fig 4.4.10. TG patterns of Ilmenite samples from Tertiary sandstone.

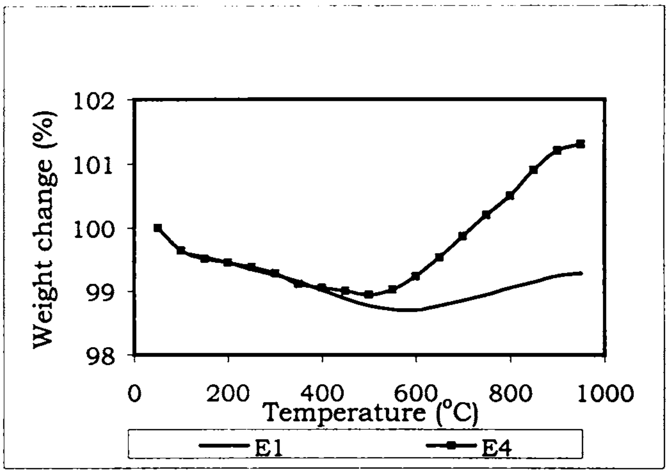


Fig. 4.4.11. TG patterns of ilmenite samples from Asthamudi estuary.

### 4.4.5 Ilmenite from the Ashtamudi estuary

Two samples were selected for the TG analysis (Fig 4.4.11). E1 represents from the typical estuarine portion where the sediments are rich in clay and organic matter is enriched pointing to the 'sheltered' nature. Hydrodynamic processes are low that flushing out of the sediments or the deposition of fresh materials takes place at a minimal rate. Such conditions are ideal for the undisturbed alteration of minerals leading to progressive leaching. A considerable drop in weight (1.3%) is charted by E1 to about 600$^0$C, associated with the escape of hygroscopic free water and that trapped with in the mineral structure. The subsequent increase in weight is subdued accounting to 0.5% due to the ferrous-ferric transformation. This is not sufficient to effect an overall increase in weight at the maximum temperature of 950$^0$C. The net difference in weight in the analysis is a loss of about 0.7% from the original weight at the room temperature. E4, in contrast, shows a net increase in weight of 1.3%. The difference in weight associated with the loss of the escape of hydroxyls is about 0.98%, followed by an increase of about 2.1%. The low magnitude of water loss and the higher effective weight gain point to the high content of FeO and low ferric oxide composition in the sample. This sample from the area around the mouth of the Kallada River is fresh material brought from the hinterland.

## Part 4.5. MÖSSBAUER ANALYSIS

### 4.5.1 Introduction

Mössbauer spectroscopy is a relatively a new entrant in the field of determinative mineralogy. However, the limited work carried out reveals the effectiveness of this technique in studying the chemical properties of minerals. Important information regarding the site population of the ferrous and ferric state in iron in minerals, magnetism, and chemical properties like bonding and atomic structure has been collected over the past few years using this spectroscopic method.

Mössbauer spectroscopy is based on the phenomenon of Mössbauer effect whereby certain nuclei in solids can emit and absorb gamma radiation without energy loss due to recoil. This recoilless emission and absorption produces a resonant absorption process with a narrow gamma radiation wavelength. The resulting narrow Mössbauer line widths can be used to investigate the very small energy changes produced by the hyperfine interactions between nuclei and their surrounding electrons. In mineralogical terms, these properties can be interpreted to determine the oxidation state of iron and the magnetic behaviour in the mineral. Mössbauer properties like isomer shift, quadrupole splitting and hyperfine field are the parameters, which are made use in this analysis.

In the present work, the Mössbauer technique has been applied to a selected number (14) of ilmenite samples. The samples include both field samples representing different geologic environments and factory grade samples from the Chavara and Manavalakurichi deposits of varying size grades and magnetism. The purpose of applying this rather modern method in the study is to understand the viability of this technique in its use as a simple and effective tool for the determination of mineral phases and the degree of weathering, in comparison with the results of other techniques like chemical methods and XRD analyses. Samples are subjected to this analysis and the results compared with that of their chemical data and based on their comparative evaluation, the viability of using this technique for other samples are assessed.

### 4.5.2 Mössbauer analysis of ilmenite in natural settings

The Mössbauer spectra of the field samples are given in Fig. 4.5.1. The peaks of unequal intensities indicate overlapping of closely lying peaks. In general, the spectra show the presence of doublets, indicating the paramagnetic nature of ilmenite. The samples are fitted by constraining the heights and widths of the peaks of a particular doublet to be equal. The Mössbauer parameters like isomer shift (IS), quadrupole splitting (QS), magnetic hyperfine fields of the samples are presented in Table 4.5.1.

The parameters for one set of doublets resemble closely, that are characteristic of paramagnetic ferrous component in a non-cubic environment. The IS and QS values for the doublet of pure ilmenite has been identified to be 0.94 mm/s and 0.84 mm/s respectively (Babu et al, 1996). The values for the samples fall near these parameters of pure ilmenite and is, thus considered to be caused due to this mineral. However, the parameter values are more close to the IS and QS values for the doublet of natural ilmenite samples as reported by Subrahmanyam et al (1982). It is found that the, unlike XRD values, which show a slight variation with alteration and leaching, the IS and QS values fall with in a narrow range and do not show any considerable variation with alteration. The Mössbauer parameters for the remaining set of doublets, agree closely with the values for $Fe^{3+}$ in a non-cubic

Table 4.5.1 Mossbauer data of some ilmenite samples from the beach and the hinterland. See Fig. 3.1 and Tables 5.1.1,5,6,7 & 8 for details

| Sample | Ionic charge | IS (mm/s) | QS (mm/s) | $Fe^{3+}/Fe^{2+}$ | $Fe^{3+}/Fe^{2+}$ $ |
|---|---|---|---|---|---|
| L13 (laterite | $Fe^{3+}$ | 0.44 | 0.53 | 44.22 | 52.01 |
| | $Fe^{2+}$ | 1.10 | 0.72 | 49.36 | 48.99 |
| | $Fe^{3+}$ (m) | 0.25 | 0.10 | 6.42 | -- |
| L8 (laterite) | $Fe^{3+}$ | 0.46 | 0.64 | 21 | 20.86 |
| | $Fe^{2+}$ | 1.03 | 0.72 | 79 | 79.14 |
| S2 (sandstone) | $Fe^{3+}$ | 0.39 | 0.65 | 78.52 | 81 |
| | $Fe^{2+}$ | 1.03 | 0.79 | 21.48 | 19 |
| Valliyar 2 (river) | $Fe^{3+}$ | 0.35 | 1.00 | 13 | 14.11 |
| | $Fe^{2+}$ | 1.04 | 0.69 | 86 | 85.89 |
| E1 (estuary) | $Fe^{3+}$ | 0.40 | 0.65 | 76.8 | 68.31 |
| | $Fe^{2+}$ | 1.03 | 0.79 | 23.2 | 31.69 |
| E4 (estuary) | $Fe^{3+}$ | 0.33 | 0.54 | 35.45 | 34.4 |
| | $Fe^{2+}$ | 1.08 | 1.66 | 64.55 | 65.6 |
| C3 (beach) | $Fe^{3+}$ | 0.39 | 0.62 | 77.12 | 75.01 |
| | $Fe^{2+}$ | 1.04 | 0.76 | 22.82 | 24.99 |

$ Ratios based on the chemical data m –magnetite/maghaemite

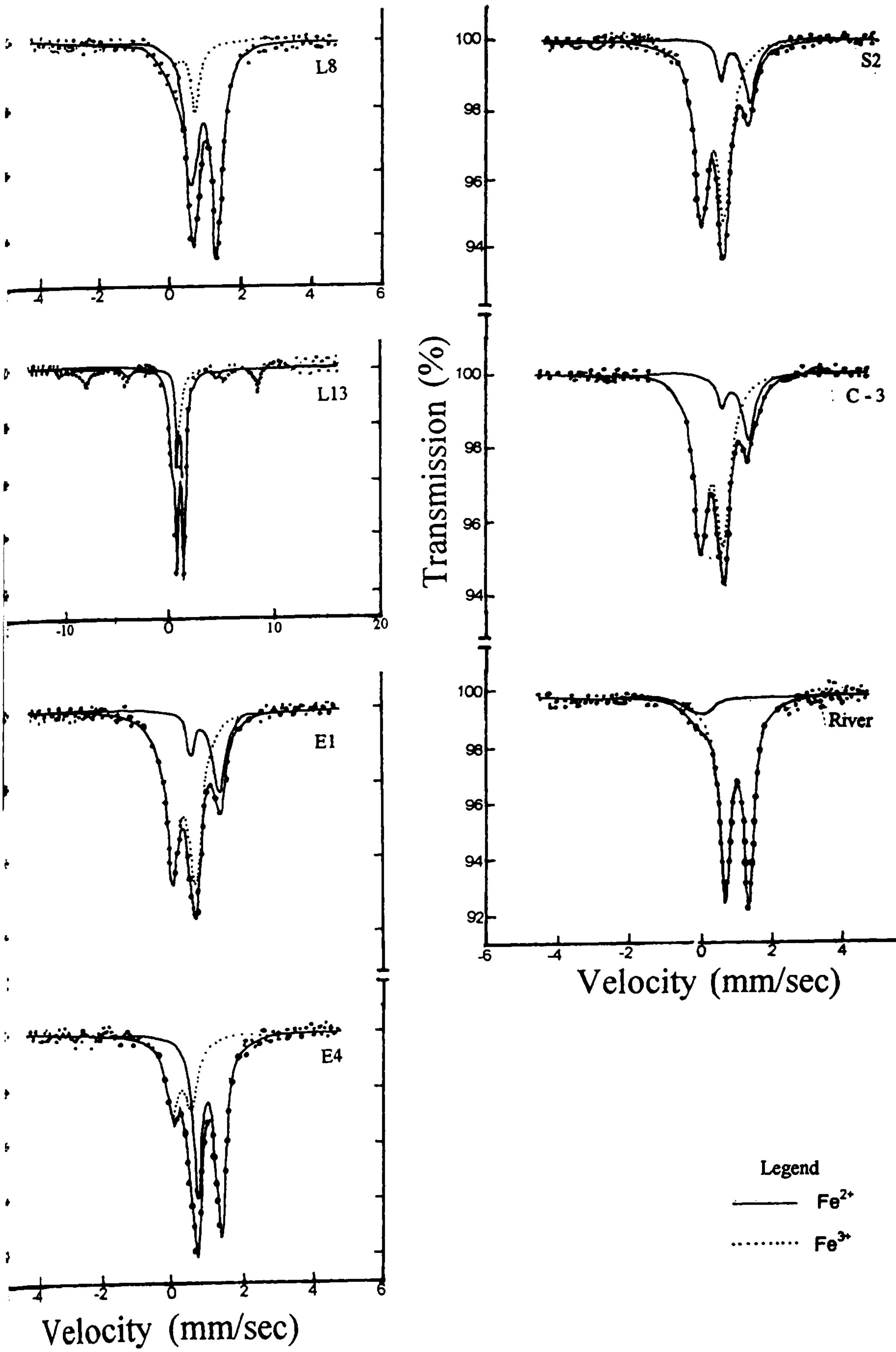


Fig. 4. 5. 1. Mössbauer spectra of ilmenite samples from different natural settings.

environment. Minerals like magnetite, haematite and maghaemite has known to be occurring associated with ilmenite as intergrowths. But the absence of any sextet pattern in most of the patterns, precludes the possibility of these minerals. The QS value of about 0.65mm/s, points to the distortion of lattice structure resulting in large electric field gradient. Also, the parameter values do not come close to the doublet formed by ferric ions in a non-cubic environment formed by substitution of $Ti^{4+}$ in ilmenite structure (Ahmed et al, 1992). However, the Mössbauer values are fairly similar to those given by Subrahmanyam et al (1982) for the weathered intermediate phase of ilmenite, pseudorutile. The variation in the parameters could be a result of the characteristic non-stochimetry exhibited by this product. Other causes may be due to the finer grain size (Gibb et al, 1969) and presence of foreign ions. Thus, the second doublet is taken to represent the content of pseudorutile in the ilmenite samples.

In the sample from the lateritized corderite gneiss, the Mössbauer spectrum exhibits the sextet pattern, indicating the presence of ferro-magnetic content. The study of the ilmenite grains with exsolved mineral phases particularly ilmenite has been published. The Mössbauer parameters, particularly the QS values for the exsolved phases show appreciable difference in these studies. The variation noted could be attributed to the reasons cited above for the variation of parameters by pseudorutile and to the possible presence of other iron oxides in them. However, the values obtained for the sextet in the present work do not indicate haematite (IS values of 0.39mm/s and QS values of 0.12mm/s). But the values are very close to those given for magnetite and maghaemite. The Mössbauer analysis of this sample supports the impression obtained from the results of XRD, microscopic and magnetic studies of this sample. However, the QS values (0.1 mm/s) are closer to the parameters reported for maghaemite (0.08 mm/s) rather than magnetite. Maghaemite is known to occur usually as the alteration product of magnetite (Lindsley, 1976). It is possible that in the sample under discussion the intergrowths in the ilmenite sample may be magnetite partially altered to maghaemite during lateritization.

Since the Mössbauer factors were assumed to be identical for all the components present in the samples, the area of the phases of a sample are measured and their relative intensities are used to calculate the ferrous-ferric ratios of the samples. The ratio of ferrous-ferric calculated from the chemical analysis and those determined from the Mössbauer spectra are given in the Table 4.5.1. In general, it could be seen that that the Mössbauer values are in good agreement with those obtained from the chemical data.

### 4.5.3 Magnetic fractions of bulk ilmenite

The factory grade ilmenite samples of various size grades and magnetism are also undertaken for the Mössbauer analysis (Fig 4.5.2). Of these, only selected samples were compared for the agreement between the chemical and Mössbauer data on the $Fe^{2+}/Fe^{3+}$ ratios, as an appreciable quantity of ilmenite is separated out at lower amperages of 0.2 and 0.3 A. The results of the chemical and Mössbauer analyses were found to be satisfactorily similar (Table 4.5.2). The weight frequency distribution of the magnetic fractions show that only low quantities of ilmenite are separated below 0.35 A. For such samples, the Mössbauer analysis is found to be suitable than chemical analysis because of the low quantities required for this technique. The ferrous and ferric contents were estimated and considered to be dependable based on the precedence of the good tallying of the chemistry and Mössbauer values.

Table 4.5.2 Estimation of the oxidation state of iron in the different magnetic fractions of ore grade ilmenite using Mossbauer analysis. See Table 5.1.3 for details

| Sample | Ionic charge | IS (mm/s) | QS (mm/s) | $Fe^{3+}/Fe^{2+}$ | $Fe^{3+}/Fe^{2+}$ $ |
|---|---|---|---|---|---|
| CH2 | $Fe^{3+}$ | 0.40 | 0.66 | 70.6 | 72.55 |
| | $Fe^{2+}$ | 1.03 | 0.79 | 29.4 | 27.55 |
| MK2 | $Fe^{3+}$ | 0.43 | 0.72 | 38.52 | 39.5 |
| | $Fe^{2+}$ | 0.94 | 0.78 | 61.48 | 60.5 |
| CH4 | $Fe^{3+}$ | 0.32 | 0.70 | 62.79 | 62.07 |
| | $Fe^{2+}$ | 0.93 | 0.84 | 37.21 | 37.93 |
| CHa | $Fe^{3+}$ | 0.38 | 0.63 | 89.20 | -- |
| | $Fe^{2+}$ | 1.03 | 0.55 | 10.90 | -- |
| MKa | $Fe^{3+}$ | 0.40 | 0.67 | 80 | -- |
| | $Fe^{2+}$ | 1.02 | 0.83 | 20 | -- |
| CHb | $Fe^{3+}$ | 0.38 | 0.64 | 100 | -- |
| | $Fe^{2+}$ | - | - | - | |
| MKb | $Fe^{3+}$ | 0.39 | 0.65 | 92.90 | -- |
| | $Fe^{2+}$ | 1.04 | 0.91 | 7.10 | -- |

$ Ratios based on the chemical data
CHa and MKa are ilmenite fractions separated at 0.5A
CHb and MKb are ilmenite fractions separated at 0.7A

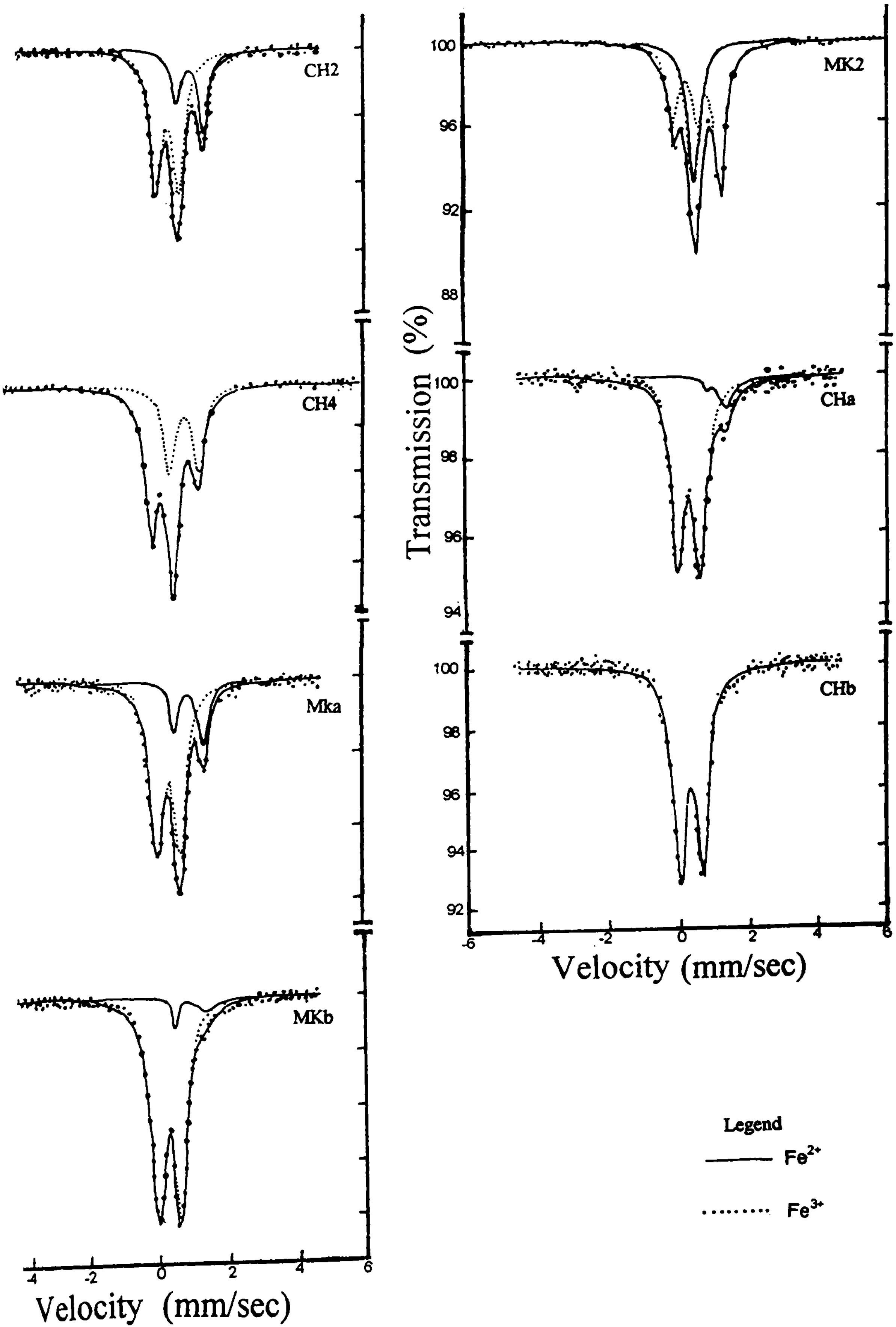


Fig. 4. 5. 2. Mössbauer spectra of magnetic fractions of bulk ilmenite from Chavara and Manavalakurichi deposits.

The fractions separated at 0.2 and 0.5A of the ilmenite from these two deposits, present very notable variations (Table 4.5.2). Thus the percentage of ferric ions in the crops separated at 0.2A of Chavara ilmenite is around 71%, while in Manavalakurichi mineral, the content is only about 39%. In the 0.5A fractions for which the chemical analysis could not be carried out as pure ilmenite separation is difficult at higher ampere levels, the above trend is maintained. Thus for Chavara ilmenite, the ferric content for this very altered fraction is about 89%, while the corresponding Manavalakurichi sample is apparently less altered with the ferric content forms about 80% of the total Fe content. The Chavara ilmenite fraction obtained at 0.7A, is found to be consisting of iron completely in the ferric state, indicating the total conversion of ilmenite into pseudorutile. The IS and QS values of this sample corresponds closely with the ferric component of the highly altered samples among the field samples and the magnetic fractions. In the Manvalakurichi ilmenite, the corresponding magnetic split is almost fully oxidized, with about 97% of iron in the ferric form.

The isomer shift in the MK2 fraction is 0.43mm/s, while in CH2 it is around 0.40m/s for the ferric ionic state. This is comparable with the values reported in literature for the samples from the study area (Babu et al, 1996). For the magnetic fractions separated at 0.5A, the values for IS are 0.38 and 0.40mm/s for ilmenite samples of Chavara and Manavalakurichi respectively. Similar pattern is noted in the differently weathered samples from the coast and hinterland. The isomer shift depends on the electron charge density at the nucleus. Thus chemical changes like the oxidation of ferrous iron to ferric is reflected on the IS. Various parameters like the grain size and the compositional drift from the stochiometic values due to oxidation and hydroxylization of altered ilmenite and the fine grain size may all account for the difference of the Mössbauer values with alteration.

### 4.5.4 Significance of Mössbauer studies on ilmenite

It is seen from the section of XRD analysis that the X ray patterns of the samples show overlapping of the pseudorutile peaks with that of rutile (leucoxene). This is caused by the similar d values of the peaks of these minerals. Also, the peaks of these phases are broad and diffuse due to their poor crystallinity. Thus, the quantitative estimation of the pseudorutile and leucoxene in the ilmenite samples are difficult in practice. The available methods, as given by the different authors, are semi quantitative and need not be dependable. One reason is the crystallinity of ilmenite phase is relatively well defined, whereas the weathered products are generally microcrystalline. The chemical methods do give accurate values for the content of elements, but the quantitative determination of the content of other phases like those seen as intergrowths is not possible. The chemical data of L13 indicates the possible presence of some iron oxide in ilmenite grains due to the high values for iron exceeding that of the theoretical limits. But this could not be confirmed or any estimation of the phase, if present could be carried out. The Mössbauer is found to be useful in such cases where the ionic state of iron in each phase could be measured. Unlike XRD lines, the spectra of both ilmenite and pseudorutile phases are sharp and well defined. These have been explained as due to the dependence of Mössbauer spectra on the local charge of and local symmetry around the iron ion and are only marginally broadened by the loss of longrange order (Subrahmanyam et al, 1982). Chemical analyses are cumbersome and time consuming involving the use of a large number of reagents.

Thus the Mössbauer analysis has been noted to be a dependable method which affords an easy way for the quantitative estimation of the degree of alteration and phases present. Most of the chemical analytical techniques are also destructive and would require a considerable quantity of the sample. This would be difficult, when the sample obtained is very less which may be needed to carry out various mineralogical and chemical analyses. In Mössbauer analysis, the quantity required is much less (about 15-30 mg). This does not involve the use of any chemical and the process is non destructive.

Different authors have listed out the quantitative contents of ilmenite and pseudorutile as well as the presence of intergrowths based on the ferrous-ferric ratios in the samples (Gibb et al, 1969; Subrahmanyam et al, 1982). But, such estimation would be, at best, an approximation, as the Mössbauer data is based on the ionic state of iron. Further, these authors assume that ferric iron formed is due to pseudorutile phase in the mineral. But more recent work on alteration of ilmenite has suggested that many intermediate products formed during the alteration of ilmenite has ferric iron as one of their constituents. Thus, the term pseudorutile is used in this context to denote all intermediate alteration phases formed during the weathering and leaching of ilmenite to form leucoxene/rutile. Mössbauer analysis at low temperatures of 77K and 100K are required to reveal more about the properties of ilmenite like the hyperfine filed and the magnetic ordering (Ahmed et al, 1992; Babu et al, 1996).

## CHAPTER 5

# CHEMICAL STUDIES

## Part 5.1. CHEMICAL CHARACTERISATION – MAJOR ELEMENTS

### 5.1.1 Introduction

The chemistry of iron and titanium in the ilmenite mineral structure is the most evident and direct indicator of the stage of alteration undergone. While the oxidation state of iron is defined by the ferrous–ferric conversion, as the first stage of alteration, the latter process is the function of the leaching of iron from the mineral structure and the corresponding enrichment of titanium. Thus the study of the major elements of ilmenite has implications in the assessment of the quality of ilmenite ore.

The alteration of ilmenite and the different mechanisms suggested by earlier workers has been discussed in Part 4.1. Whatever may be the processes, which define the weathering of ilmenite, the essential chemical reactions are the conversion of ferrous iron to the ferric state and the leaching of the ferric iron from the mineral lattice. The titanium by virtue of its high stability, remains in the structure and is progressively enriched.

Different elemental ratios have been proposed to delineate the weathering mechanisms in ilmenite. While parameters like $FeO/Fe_2O_3$ (Morad and Aldahan, 1986), $Fe^{2+}/Fe^{3+}$ and $Fe^{2+}/Fe$ (Bailey et al, 1956) are indices which high light the first stage of alteration, ie, the oxidation of ferrous iron forming pseudorutile, the Fe/Ti and $FeO/TiO_2$ point to the enrichment of iron/titanium. Frost et al (1983) has classified ilmenite alteration into four stages based on the Ti/(Ti+Fe) ratios. The terminology of those stages in the order of increasing stage of alteration is as follows. The Ti/(Ti+Fe) values are given in brackets. 'Ferrian Ilmenite' (<0.5), 'Hydrated Ilmenite' (0.5 – 0.6), 'Pseudorutile' (0.6 – 0.7) and 'Leucoxene' (>0.7). This system has been adopted and has been used in this work for the chemical characterization of ilmenite based on the major element chemistry.

A report on the weathering of ilmenite in the different geologic set ups of the hinterland and the beaches are described below. The author has attempted to verify whether the chemistry of ilmenite is a progressive sequence from the ilmenite of laterite through that in the rivers and estuary and finally the beach, as expected, or it represents a complex mechanism involving a host of processes of significant contribution from each set up. A road map of the ilmenite alteration in the Chavara and Manavalakurichi deposits has been worked out based on the chemistry of different magnetic fractions of ilmenite of these deposits. This helps to understand the patterns of weathering of these two deposits, which are located in a reasonable geographical proximity and in similar set ups.

The relative content of iron and titanium is very important in determining the raw mineral quality of ilmenite. The theoretical content of total iron oxide in ilmenite is about 47%, which represent the iron in ferrous ionic state. But in nature, invariably, a considerable amount of ferric iron is present, some times exceeding that of the ferrous oxide. The iron present in the mineral and the proportion of its ionic states is essentially a function of the nature of alteration and weathering. Since iron is highly leachable when compared to titanium, the content of iron would be below the theoretical value of 47% in pure ilmenite grains as alteration proceeds.

The chemical analysis is presented in the following sections and the distribution pattern of iron and titanium in ilmenite samples of various geological set ups is discussed below.

### 5.1.2 Ilmenite from beach

In the Chavara beach, the samples bear relatively low content of total iron oxide over a narrow range of about 38.24 to 40.80% (Table 5.1.1). However, a more striking variation is noted in the distribution patterns of the individual oxides of iron in the ferrous and ferric form (Fig. 5.1.1). The ferrous content shows a maximum value of 11.01% in the southern most sample from Neendakara, C1, while the sample C3 has the minimum FeO content (10.20%). A corresponding opposite trend is noted in the case of ferric oxide in these samples. The northern most part of this deposit (C6), a low content of ferric iron and the titanium contents and a higher value for the FeO is observed. These figures are in contrast to the chemistry of sampling locations adjacent to it. The relatively fresh grains could point to a younger part of the deposit body, where supply of fresh material is being constantly provided. Ramakrishnan et al (1997) has credited the above observation to the fresh material provided by the Quilon promontory and/or the sediments provided by river Kallada.

In the southern deposit of Manavalakurichi, the total iron oxide (40.26-46.26%) is found to be significantly higher than those of Chavara (38.24-40.8%). While a higher content in iron is noticed in the ilmenite from the northern and southern extremities of the Manavalakurichi deposit, the samples from the deposit proper has suffered acute leaching as indicated by the lower iron oxide value (40%). A general increase in the ferrous content of the ilmenite samples could be observed towards north in this deposit.

It could be observed from the compositional diagram that in the Chavara samples, the major elements are in a narrow range along the deposit. In Manavalakurichi the variation in the contents of the elemental chemistry is more impressive. Though, the Chavara deposit is much voluminous than able 5.1.1 Major elemental distribution in beach ilmenite

| posit | Sample No | $Fe^{2+}$ (%) | FeO (%) | $Fe^{3+}$ (%) | $Fe_2O_3$ (%) | Total Oxide (%) | $TiO_2$ (%) | $\frac{Ti}{Ti+Fe}$ | Alteration Stage |
|---|---|---|---|---|---|---|---|---|---|
| [illegible] | C1 | 11.00 | 14.19 | 17.90 | 25.60 | 39.79 | 58.00 | 0.61 | PR |
| | C2 | 8.38 | 10.78 | 19.81 | 28.32 | 39.10 | 61.00 | 0.62 | PR |
| | C3 | 7.93 | 10.20 | 21.40 | 30.60 | 40.80 | 60.04 | 0.61 | PR |
| | C4 | 8.91 | 11.46 | 18.92 | 27.05 | 38.51 | 59.16 | 0.62 | PR |
| | C5 | 9.42 | 12.12 | 18.27 | 26.12 | 38.24 | 59.67 | 0.62 | PR |
| | C6 | 10.50 | 13.51 | 18.10 | 25.88 | 39.39 | 59.60 | 0.61 | PR$ |
| [illegible] | M1 | 12.57 | 16.17 | 20.96 | 29.97 | 46.14 | 0.55 | 0.55 | HI$ |
| | M2 | 13.90 | 17.88 | 18.30 | 26.17 | 44.05 | 54.21 | 0.56 | HI |
| | M3 | 11.62 | 14.95 | 17.70 | 25.31 | 40.26 | 58.79 | 0.60 | PR |
| | M4 | 18.39 | 23.66 | 13.80 | 19.73 | 43.39 | 54.03 | 0.56 | HI |
| | M5 | 18.41 | 23.68 | 15.79 | 22.58 | 46.26 | 54.72 | 0.55 | HI |

CH -Chavara *MK -Manavalakurichi

PR -pseudorutile $HI – hydrated ilmenite

able 5.1.2 Weight distributions of the magnetic fractions of CH and MK
menite

| Amperage | CH (wt%) | MK(wt%) |
|---|---|---|
| 0.15 | 4.57 | 24.37 |
| 0.2 | 7.28 | 35.17 |
| 0.25 | 10.47 | 20.07 |
| 0.3 | 31.72 | 11.38 |
| 0.35 | 13.9 | 6.54 |
| 0.4 | 16.3 | 1.07 |
| 0.45 | 9.58 | 1.4 |
| >0.45 | 6.17 | -- |

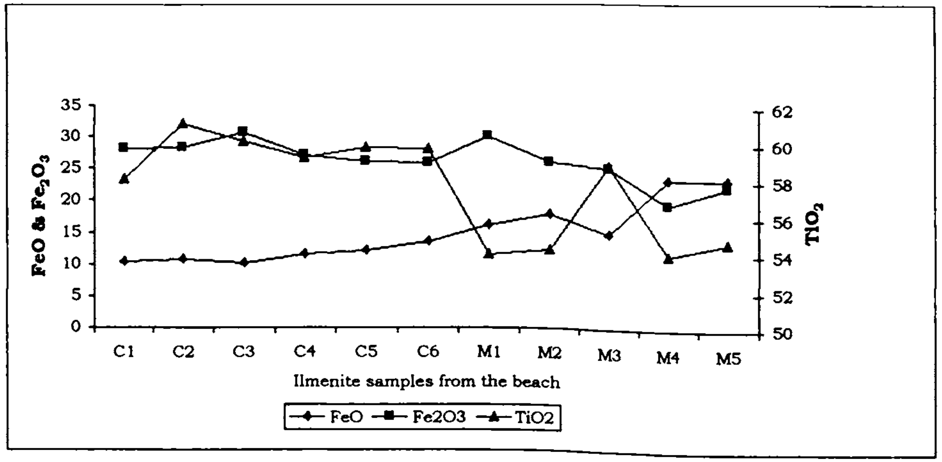


**Fig. 5.1.1 Distribution of major elements in the ilmenite samples from Chavara and Manavalakurichi beach**

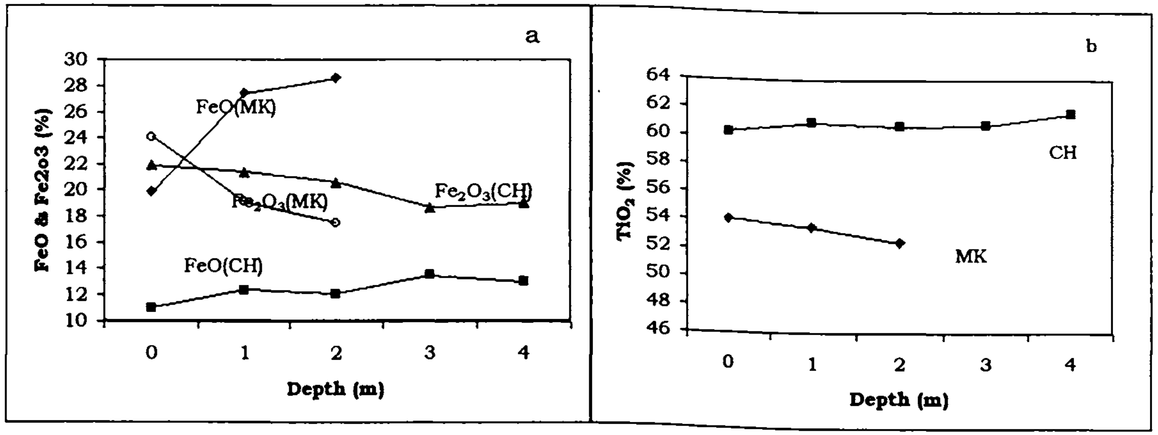


**Fig 5.1.2 Variation of a) Iron and b) Titanium Dioxide in the ilmenite samples with depth from Chavara and Manavalakurichi beach**

the Manavalakurichi deposit, it presents a uniform chemistry along its length. Chavara deposit is considered to be the older than the Manavalakurichi deposit (Thampi et al, 1994; Nair et al, 1995). Such a conclusion is drawn on the basis of its higher $TiO_2$ content, the paucity in garnet in the Chavara deposit and the studies on the micromorphology of the sediments from the two deposits.

The compositional homogeneity exhibited by the ilmenite samples along its longitudinal stretch of the Chavara deposit is echoed in its vertical extent (Fig. 5.1.2, a-b). Though samples were taken from a depth up to about 4 meters, the values for the elemental contents range only within a narrow range. The ground water environment is found to be conducive for the oxidation and alteration of ilmenite forming pseudorutile and the mineral is enriched in titanium near surface conditions leading to the formation of leucoxene (Bailey et al, 1956; Frost et al, 1983). However, in Chavara, the subsurface samples in the ground water conditions (at a depth of about 1.25 metres) do not show a difference in composition (expressed by the enrichment of ferric iron or titanium depletion) as expected. The compositional variability expressed by the Manavalakurichi deposit along its length, is reflected in the ilmenite samples along the vertical profile of the deposit. The ferric oxide content shows a marked increase below the water table (at a depth of about 1 m.), while the titanium defines a significant reduction.

The more or less uniformity in composition of the Chavara ilmenite along the longitudinal and vertical extent of the deposit could be a reflection of the repeated cycles of reworking undergone by the sediments in this area giving *rise to a body of highly mature,* well-mixed homogenous deposit (Thampi et al, 1994). In the MK deposit, in spite of its smaller bulk, the composition is more varied along its spatial dimensions, as the sediments represents a body of sediments, where the processes of reworking are limited. Then textural investigations reveal that the sediments are not well sorted, finer or platykurtic as those in Chavara. This discrepancy in the sediment texture irrespective of the comparable geographical and mineralogical characters could be attributed to the relative immaturity of the Manavalakurichi deposit.

The Fe/Ti values of ilmenite are an index of the relative enrichment of iron with respect to the amount of titanium present. Titanium being relatively immobile, this ratio indicates the effect of weathering on ilmenite and the consequent leaching of iron from the mineral structure. Fig. 5.1.3 illustrates the contrast between the Chavara and Manavalakurichi samples. The Chavara samples show low values for the relative iron concentration, with no pronounced variation among the samples. On the other hand, in Manavalakurichi, the samples exhibit values near to 1 for these ratios. The relative variation of the values is more considerable than in Chavara, with M3 dipping to a low of about 0.85. The samples from the northern and southern extremities of the Manavalakurichi deposit, exhibits iron values exceeding that of Ti, ie Fe/Ti>1.

Like Fe/Ti, the $Fe^{3+}/Fe^{2+}$ ratios also serve as an indicator of the alteration undergone by the mineral (Fig. 5.1.4). In the Chavara samples, this ratio shows a value of more than 2, highlighting the dominance of the ferric state, compared to the $Fe^{2+}$ contents. In Manavalakurichi, for the ilmenite from the southern sector (samples M1-M3), the ratio has values <1, attesting to the relative low ferric content. However, in the northern part of the deposit, the ferric iron dominates over the ferrous state in the samples.

During leaching, the ferric ions formed by the oxidation of ferrous iron is ultimately removed from the crystal lattice, enriching the stable $Ti^{4+}$ions in the grain. The $TiO_2$ content in the Chavara deposit ranges from 58 to 61 %, with an average of 59.5%, the maximum being in C2. In the

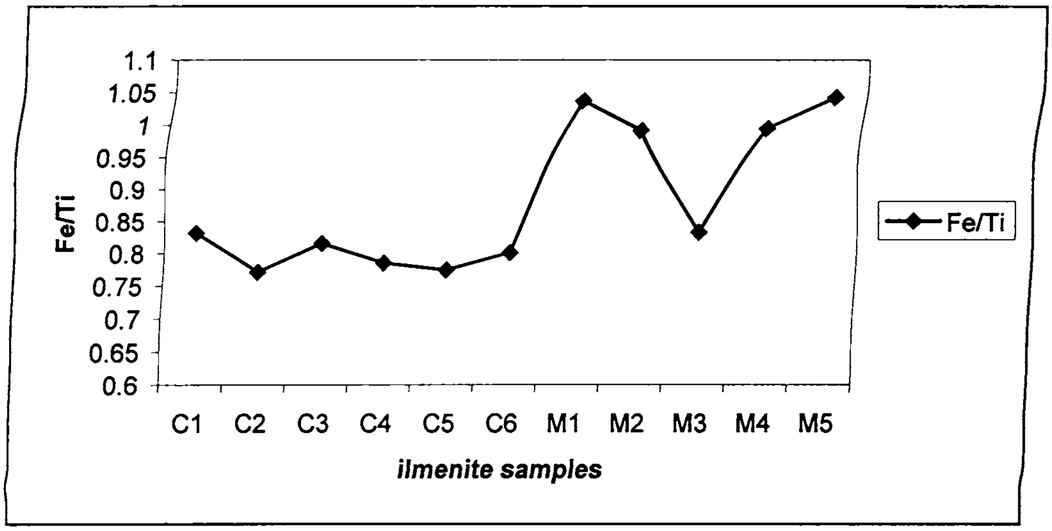


Fig.5.1.3 Iron Titanium relationship in ilmenate samples from the beach

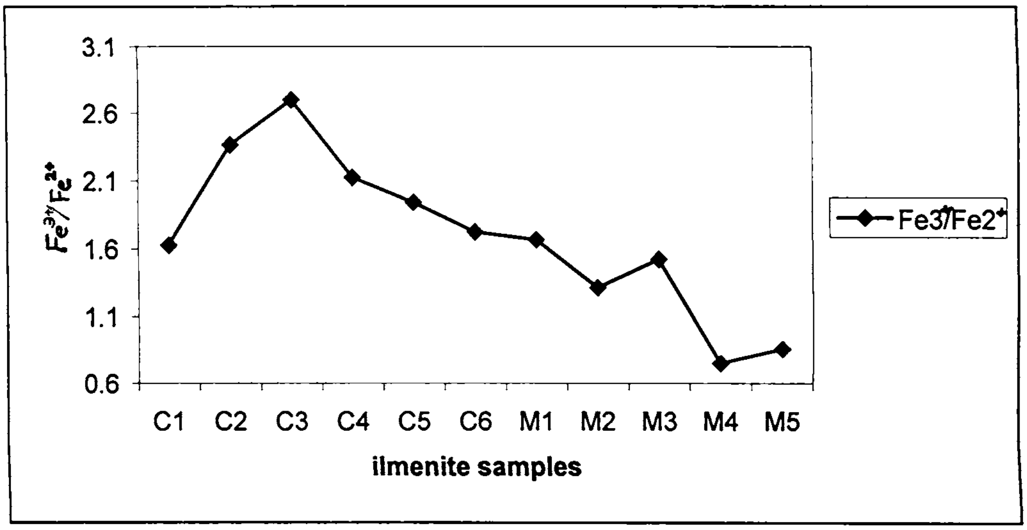


Fig.5.1.4 Inter relationship between Fe3+ and Fe2+ in the ilmenate sample from the beach

Manavalakurichi samples, the maximum content is 51%, as exhibited by the sample M1 from the deposit, complementing the low iron oxide.

The relationship of iron and titanium as given in Table 5.1.1 and Fig. 5.1.3 indicates the difference in the degree of alteration suffered by the two deposits. In Chavara, the Ti content has enriched at the expense of iron to an extent that all the samples have reached an advanced alteration stage of 'Pseudorutile' as defined by Frost et al (1983). In Manavalakurichi, the samples fall under the category of 'Hydrated ilmenite', except the ilmenite from sample M3, which is relatively more weathered to the limits of the 'Pseudorutile stage'.

The chemical analyses of the ilmenite samples from various geological environments of the hinterland, which are considered to be the source of the heavy mineral assemblage of the south west of India, are discussed below

### 5.1.2.1 Magnetic fractions of bulk ilmenite

The magnetic susceptibility of the various fractions corresponding to the separating amperages and their weight distribution, which was discussed in part 4.3.2 are shown in Table 5.1.2. The fractions separated at amperages of 0.25 - 0.45 A form about 70% of the bulk ilmenite concentrate. The major elemental distribution of the magnetic fractions is given in Table 5.1.3 and Fig. 5.1. 5a. The ferrous content of the fractions range from 10.81 to 2 % for the lowest magnetic fractions. The ferric oxide dominates over the ferrous part in all the fractions. As mentioned earlier, the ferrous-ferric transformation defines the alteration of ilmenite in its primary stage.

Table 5.1.3 Major element chemistry in the magnetic fractions of Chavara and Manavalakurichi ilmenite

| Amperage | Sample | Content (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $Fe^{2+}$ | FeO | $Fe^{3+}$ | $Fe_2O_3$ | Fe | Ti | $TiO_2$ |
| 0.15 | *CH1 | 8.12 | 10.44 | 22.68 | 32.43 | 30.8 | 33.76 | 56.31 |
| 0.20 | CH2 | 7.85 | 10.10 | 21.66 | 30.97 | 29.51 | 35.25 | 58.80 |
| 0.25 | CH3 | 11.06 | 14.22 | 16.61 | 23.75 | 27.67 | 36.44 | 60.78 |
| 0.30 | CH4 | 9.84 | 12.65 | 16.1 | 23.02 | 25.94 | 36.52 | 60.92 |
| 0.35 | CH5 | 8.48 | 10.91 | 17.69 | 25.30 | 26.17 | 36.57 | 61.00 |
| 0.40 | CH6 | 5.08 | 6.53 | 19.93 | 28.50 | 25.01 | 37.15 | 61.97 |
| 0.45 | CH7 | 2.99 | 3.85 | 20.05 | 28.67 | 23.04 | 38.16 | 63.65 |
| >0.45 | CH8 | 1.57 | 2.02 | 15.1 | 21.59 | 16.67 | 39.03 | 65.10 |
| | | | | | | | | |
| 0.15 | *MK1 | 16.3 | 20.96 | 15.3 | 21.88 | 31.6 | 33.59 | 56.03 |
| 0.20 | MK2 | 20.6 | 26.49 | 13.45 | 19.23 | 34.05 | 32.53 | 54.26 |
| 0.25 | MK3 | 25.04 | 32.20 | 9.1 | 13.01 | 34.14 | 33.39 | 55.69 |
| 0.30 | MK4 | 20.31 | 26.12 | 10.92 | 15.62 | 31.23 | 34.08 | 56.85 |
| 0.35 | MK5 | 11.94 | 15.35 | 18.12 | 25.91 | 30.06 | 34.68 | 57.85 |
| 0.40 | MK6 | 6.2 | 7.97 | 20.82 | 29.77 | 27.02 | 36.37 | 60.67 |
| >0.40 | MK7 | 2.61 | 3.36 | 20.21 | 28.90 | 22.82 | 39.02 | 65.09 |

*CH1 – Magnetic fractions of Chavara bulk ilmenite
*MK1 – Magnetic fractions of Manavalakurichi bulk ilmenite

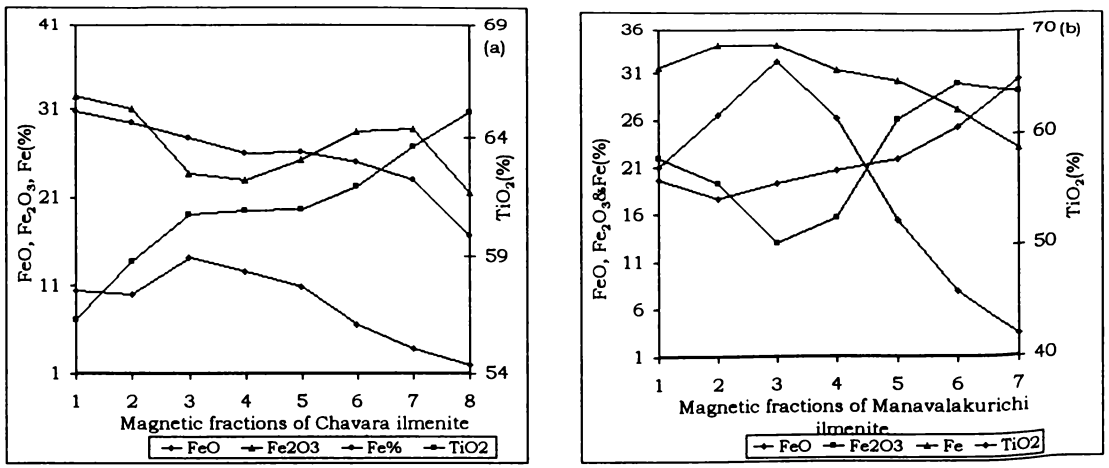


**Fig 5.1.5. Distribution of major elements in the magnetic fractions of bulk ilmenite from a) Chavara and b) Manavalakurichi deposits.**

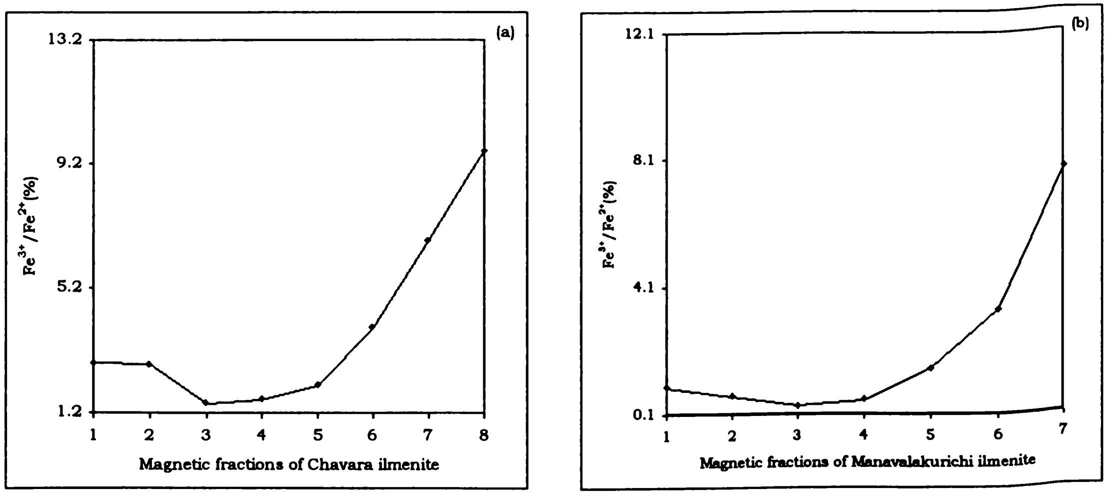


**Fig 5.1.6. Relationships of ferric - ferrous contents in the magnetic fractions of bulk ilmenite from a) Chavara and b) Manavalakurichi deposits**

The Chavara (CH) ilmenite is compared to the ilmenite samples of the nearby Manavalakurichi (MK) deposit based on the data published by Suresh Babu et al, 1994 (Fig 5.1.5b). The Manavalakurichi ilmenite represent a less altered occurrence as seen from the total iron oxide values, which approaches the theoretical level of 47% in its highly magnetic fractions compared to the corresponding Chavara fractions. The elemental distribution in Manavalakurichi shows the high correlation between the ferrous and ferric oxides, as the alteration proceeds, the $Fe^{2+}$ is oxidized to the ferric ions. In the Chavara ilmenite, the magnetic fractions exhibit only a weak correlation between the FeO and the $Fe_2O_3$ contents. Different parameters like $Fe^{3+}/Fe^{2+}$, Fe/Ti and Ti/(Ti+Fe) (Frost et al. 1983) are used as an index for progressive alteration undergone by ilmenite (Figs 5.1.6 (a-b), 7 & 8). While the former represent the oxidation of ferrous to ferric state during alteration, the later is an index of the titanium enrichment with the leaching out of iron from the mineral structure. In the Chavara magnetic fractions, the $Fe^{3+}/Fe^{2+}$ ratio is generally higher than 2 except in the CH3 and CH4 fractions where the values shown are 1.5 and 1.6 respectively (Fig. 5.1.6a). In Manavalakurichi, this ratio is less than 1 except in the least magnetic, highly altered fractions separated from 0.35A. The Fe/Ti (Fig. 5.1.7) ratios always are seen to be greater in the MK magnetic fractions of ilmenite than in the CH samples, highlighting once again, the depleted content of iron in the latter as a result of the leaching of this element from the mineral structure.

This qualitative difference confirms the higher alteration undergone by the Chavara (Nair et al, 1995; Ramakrishnan et al, 1997). The Ti/(Ti+Fe) parameters indicate that the Chavara fractions exist in a range from the relatively altered 'Hydrated Ilmenite' stage to the upper boundary of the 'Pseudorutile- Leucoxene' stages (Fig. 5.1.8). In contrast, some of the highly magnetic samples in Manavalakurichi fall in the 'Ferrian ilmenite' stage attesting to the marked difference in weathering suffered by the two

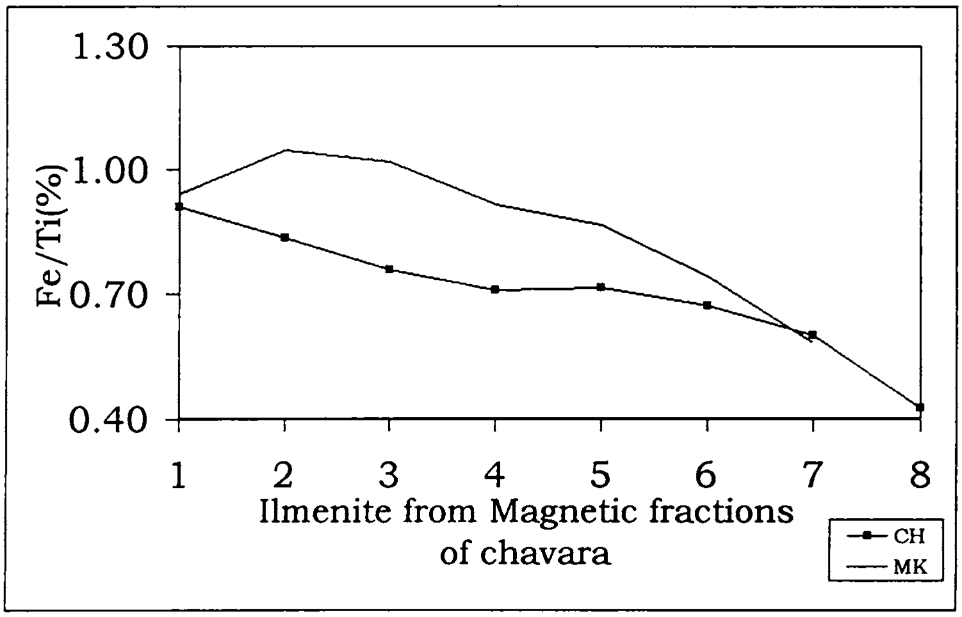


**Fig 5.1.7. Iron enrichment in the magnetic fractions of Ilmenite *from Chavara and Manavalakurichi deposits***

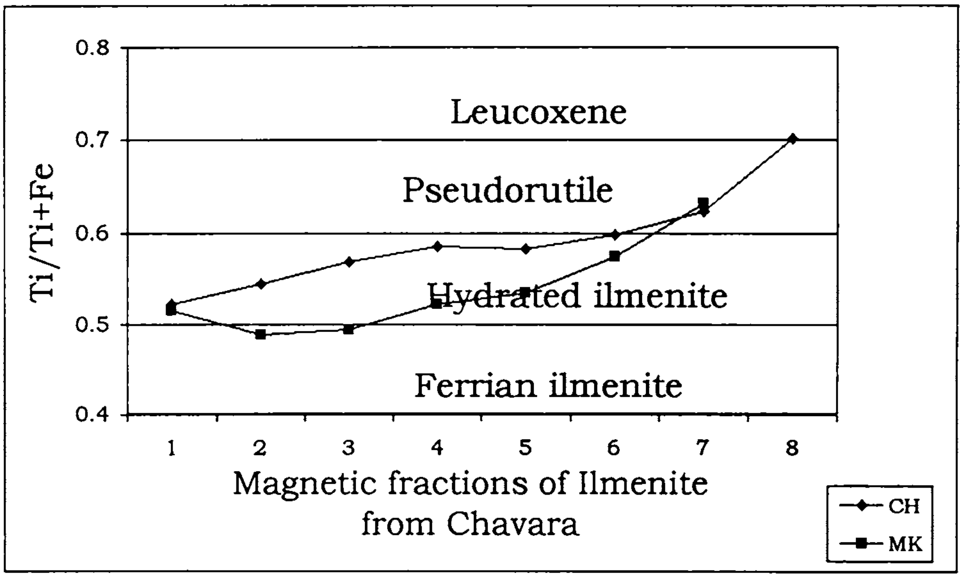


**Fig 5.1.8. Alteration stages of magnetic fractions of ilmenite from Chavara and Manavalakurichi deposits.**

deposits. The ferric formation due to the oxidation of ferrous ions has a strong negative bearing on the iron content with respect to titanium in ilmenite (Fig. 5.1.9 a-b). As shown in all the instances above discussed, the ferric transformation is accompanied by the removal of iron from the mineral. The correlation is stronger in the case of MK fractions ($r = -0.94$) than shown by CH ilmenite ($r = -0.82$). The oxidation of ferrous ions are very significant in the initial stages of alteration. The MK fractions have not reached the degree of alteration suffered by CH ilmenite. The CH deposit is at an advanced stage of alteration, where the leaching of iron is the prominent phenomenon than the ferrous-ferric transformation. The MK fractions, on the other hand, are relatively immature, where the oxidation of ferrous ions are the prominent phenomenon. These aspects are further discussed in the statistical analysis of the chemical data.

Many authors have discussed the magnetic properties of ilmenite and concluded that magnetism decreases with progressive alteration. Though magnetism has been often described as inversely related to the alteration undergone (Bailey et al, 1956; Flinter, 1959; Temple, 1966; Frost et al, 1986), it could be seen that the third and fourth magnetic fractions CH3 and CH4 form the least altered ones as shown by their highest FeO content (~14%) among the magnetic fractions. Since the ferrous-ferric transformation defines the alteration of ilmenite in its primary stage, the higher ferrous content of these fractions is an indicator of the relative 'fresh' state of the fractions. Similar observations have been recorded for the highly magnetic fractions in other deposits by Wort and Jones (1980) and Suresh Babu (1994). It is observed that the XRD results complement the above-discussed observations. The major ilmenite peaks of these fractions are sharp and prominent than those of the higher magnetic fractions. The higher presence of the poorly crystalline altered phases like pseudorutile and rutile in CH1 and CH2 is exhibited by the broad and diffused nature of the peaks. For fractions separated at amperages above

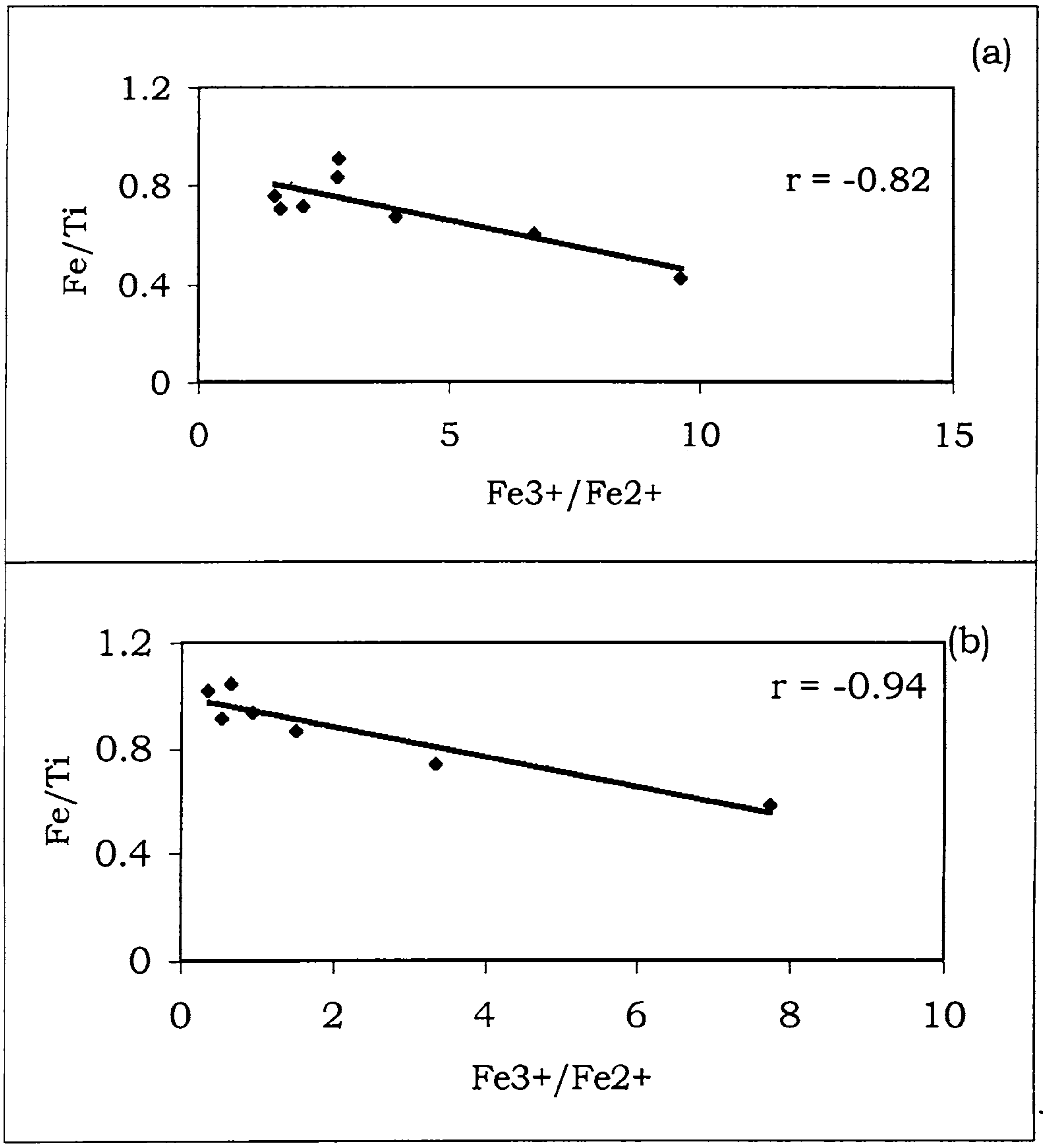


**Fig 5.1.9. Correlation between iron enrichment and ferric - ferrous contents in the different magnetic fractions of ilmenite from a) Chavara and b) Manavalakurichi deposits.**

0.35A, alteration undergone, as evidenced by the dominant peaks of the altered phases, is related to the decrease in magnetic susceptibility. The chemical data too bears out this view (Table 5.13, Fig. 5.1.5).

It could be noted that though, the Chavara and Manavalakurichi fractions present a similar pattern in their magnetic behaviour with respect to alteration, they present some very notable difference in their composition. In Manavalakurichi, the first four fractions are similar in their total iron oxide contents, with the least altered, MK3, bearing the maximum iron oxide content. Their significant FeO contents justify the XRD data, which exhibits prominent ilmenite peaks. The ferrous, ferric and the total iron oxide contents in the Manavalakurichi fractions are compatible with trends expected during alteration, ie. the fractions having higher ferrous ions being relatively less weathered contains total iron oxide comparable to that of unaltered ilmenite. In Chavara, except for the first two fractions, the total iron oxide content is significantly less compared to theoretical values of 47% for ilmenite.

The relative enrichment of iron of the magnetic fractions of the Manavalakurichi ilmenite compared to those of Chavara is shown in Fig. 5.1.7. It has been understood from the discussions in the previous sections that ferric content increases with progressive leaching of iron in ilmenite. Still, the CH3 and CH4 crops contain high ferrous content in spite of their lower total iron oxide values of about 38 and 36% respectively, as supported by the XRD plots. The CH3 and CH4 samples may represent the grains that had undergone prominent oxidation in ground water condition in beaches according to the first stage of the alteration mechanism as discussed earlier and as exhibited by their higher ferric contents than the ferrous iron. They would have been transported to near surface zones by reworking processes where the ferric iron starts leaching out of the mineral lattice enriching the ferrous content. Such observations have been reported

Table 5.1.4 Major element contents in the various IRE factory graded samples of ilmenite products

| IRE factory graded samples of ilmenite | | Total Fe (%) | $TiO_2$ (%) |
|---|---|---|---|
| Ilmenite | | 22.92 | 60.02 |
| RUTILE | IRE2 | 1.34 | 93.85 |
| | IRE3 | 1.70 | 94.21 |
| | IRE4 | 1.70 | 96.23 |
| LEUCOXENE | IRE5 | 4.08 | 89.50 |
| | IRE6 | 3.00 | 91.94 |
| | IRE7 | 5.67 | 85.42 |

earlier (Hugo and Cornell, 1991). In the most magnetic crops of CH1 and CH2, the ferrous -ferric conversion is more advanced and/or where the leaching out of iron has not reached the stage of the CH3 and CH4 fractions, thereby hindering the considerable relative enrichment of ferrous content.

The segregation of the products of the different alteration stages based on their magnetic susceptibilities was discussed by Frost et al (1986). The results obtained in this work too present the differently altered ilmenite grains in their 'arrested' state in the various magnetic fractions. The chemical data highlights the intense alteration suffered by the Chavara ilmenite, as indicated by the high ferric contents and lower total iron content of the individual magnetic fractions when compared to those of the Manavalakurichi ilmenite. The Chavara deposit represents a highly weathered compositionally homogenous mass (Ramakrishnan, et al, 1997).

#### 5.1.2.2 The IRE factory graded samples of ilmenite:

The various ilmenite fractions of Indian Rare Earths, were analyzed for the major ions to under stand the compositional framework (Table 5.1.4). The iron content in rutile grade portion in ilmenite ranges from 1.34 to 1.7 % of the composition. Leucoxene shows a maximum content in Ti values in the sample, IRE6 with as much as 92 % of the compositional weight.

### 5.1.3 Ilmenite from laterite

The ilmenite samples were collected from the laterites, which prevails over a dominant part of the study area. Since the unaltered rock type is not exposed in many cases, the samples were classified based on the predominant country rock of the area, as indicated by the nearby exposures of the crystalline rocks and the geological map of the area. Thus the ilmenite samples from this particular environment are generally organized based on the parentage of the enclosing laterite, as belonging to lateritised khondalite or charnockite, as it is difficult to identify the specific rock type immediately below the sampling location. Intercalations of charnockite and mafic rocks are known to occur in the Khondalite-Migmatite Complex of South Kerala (Soman, 1997), in which the major part of the study area falls. Thus the characters applied to ilmenite with respect to the rock suites are at best approximations and should be treated with an amount of caution. A detailed work based on the ilmenite samples from individual crystalline rocks belonging to the khondalite and charnockite suite of south Kerala and their lateritized equivalents would throw light on the variation in the chemical patterns of the ilmenite of the crystalline country rocks.

The samples from laterites generally have composition tending to the stochiometric proportions with regard to the total iron and titanium oxide contents of pure unaltered ilmenite (Fig. 5.1.10; Table 5.1.5). The laterites are basically weathered rock masses and the ilmenite is found relatively unaltered as indicated by the chemistry. However, in the sample from L5 (laterite over khondalite), the total iron oxide value (44%) is lower than the theoretical threshold for iron oxide. Meanwhile, ilmenite from the lateritised cordierite gneiss (L13) from near Punalur show iron oxide values for ilmenite exceeding that of the titanium dioxide, pointing to the presence of other iron phases associated with ilmenite.

It may be observed from the chemical data of the lateritic ilmenite samples that no clear and definite discrimination could be marked based on the major elements. Most of the samples have maintained the total iron contents very near to that of the theoretical values for pure ilmenite, and the absence of intense oxidation undergone by the samples, are indicated by the high ferrous contents, which ranges from about 27 to 30 % in most

Table 5.1.5 Major elements in the ilmenite from laterite developed over different source rocks

| Source Rocks Laterite | Content (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| Sample | Fe | $Fe^{2+}$ | FeO | $Fe^{3+}$ | $Fe_2O_3$ | Total oxide | $TiO_2$ |
| L1-CH | 36.82 | 30.48 | 39.20 | 6.34 | 9.07 | 47.26 | 51.47 |
| L2-SSt | 34.78 | 29.31 | 37.69 | 5.47 | 7.82 | 45.51 | 52.34 |
| L3-CH | 37.01 | 28.69 | 36.90 | 8.32 | 11.90 | 48.79 | 50.96 |
| L4-KH | 35.5 | 28.45 | 36.59 | 7.05 | 10.08 | 46.67 | 50.73 |
| L5-KH | 33.01 | 18.61 | 23.93 | 14.4 | 20.59 | 44.52 | 52.71 |
| L6-KH | 35.15 | 27.32 | 35.13 | 7.83 | 11.20 | 46.33 | 51.21 |
| L7-KH | 36.14 | 27.93 | 35.92 | 8.21 | 11.74 | 47.66 | 49.49 |
| L8-KH | 35.23 | 24.45 | 31.44 | 10.78 | 15.42 | 46.86 | 50.26 |
| L9-CH | 36.5 | 30.57 | 39.31 | 5.93 | 8.48 | 47.79 | 50.09 |
| L10-CH | 37 | 30.42 | 39.12 | 6.58 | 9.41 | 48.53 | 51.15 |
| L11-SSt | 27.26 | 9.31 | 11.97 | 17.95 | 25.67 | 37.64 | 60.35 |
| L12-KH | 35.04 | 27.74 | 35.67 | 7.26 | 10.38 | 46.06 | 50.26 |
| L13-KH | 38.78 | 18.61 | 23.93 | 20.17 | 28.84 | 52.78 | 44.45 |

CH _Charnockite derived KH -khondalite derived Sst - Sedimentary formation

Table 5.1.6 Distribution of the major elements in the ilmenite of sedimentary rocks and the Teri formation

| Tertiary sedimentary formation | Content (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Fe | $Fe^{2+}$ | FeO | $Fe^{3+}$ | $Fe_2O_3$ | Total Oxide | $TiO_2$ |
| S1 | 23.18 | 2.2 | 2.83 | 20.98 | 30.00 | 32.93 | 64.82 |
| S2 | 30.63 | 6.58 | 8.46 | 24.05 | 34.39 | 42.85 | 55.00 |
| S2a | 28.95 | 8.18 | 10.52 | 24.85 | 35.54 | 46.15 | 51.29 |
| S3 | 34.88 | 22.72 | 29.22 | 12.11 | 17.32 | 46.54 | 49.40 |
| S4 | 36.33 | 29 | 37.29 | 7.33 | 10.48 | 47.78 | 50.25 |
| S5 | 30.27 | 14.24 | 18.31 | 16.03 | 22.92 | 41.24 | 57.15 |
| Teri | | | | | | | |
| 1 | 33.78 | 19.37 | 24.91 | 14.41 | 20.61 | 45.52 | 53.67 |
| 2 | 35.11 | 22.11 | 28.52 | 13.00 | 14.43 | 42.95 | 55.45 |

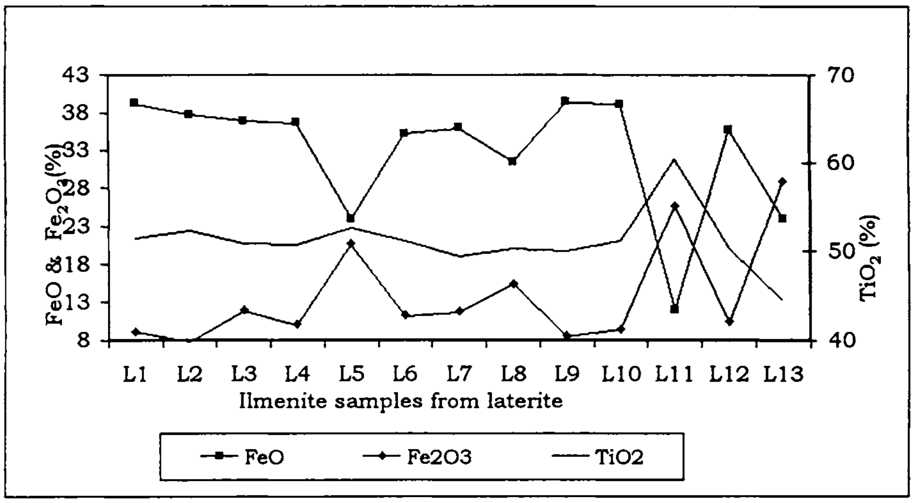


**Fig 5.1.10. Distribution of major elements in ilmenite from laterite**

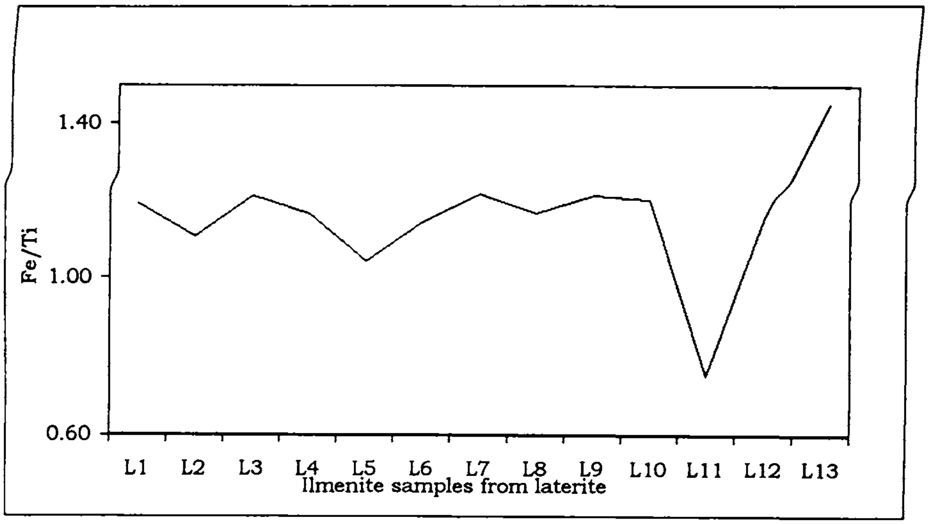


**Fig 5.1.11. Iron enrichment in ilmenite samples from laterite**

of the samples. Among the samples from laterites owing their parentage to the crystalline rocks, only L5 has a low ferrous content (18.61%). The laterites developed over the Tertiary sedimentary formations present different patterns of chemical composition. While the sample from laterite over the Tertiary sandstone at Thiruvallam, L2 has a high value for the ferric content comparable to the samples from the laterite over the crystalline rocks. The Warkallai laterite are marked by a very low ferric content of 9.31% for ilmenite. Although laterites are ubiquitous in the area, the degree of lateritisation is not uniform through out the extent and the alteration of ilmenite could be a direct function of thisprocess. In addition, three lateritisation phases are reported to have been occurred in Kerala in the past (Soman, 1997). The chemistry of the ilmenite of the laterites formed over the Tertiary formations is a direct consequence of the nature of the formations prior to the lateritisation process.

Even though the L5 has a low FeO content and rather a high ferric value, the total iron oxide content is not very different from the corresponding values for most of the other samples. This may be ascribed to the low mobility of iron in the laterite environment, even after the oxidation of much of the iron to the ferric state. The laterite ilmenite samples in general, almost bear an aggregate composition of leached ilmenite or that intermediate between ilmenite and leached ilmenite as worked out by Chernet (1999)

The Fe/Ti values present the enrichment of iron in the laterite samples (Fig. 5.1.11). The values are in a similar range except for the laterite over the Warkallai sand stone (L11) and the laterite over the corderite gneiss (L13). While in the former the iron defines very low values (27%), the latter is a study in contrast presenting a high value of about 39%. The ferrieferrrous ratios also reflect this trend (Fig. 5.1.12). This value is consistent with the observations in the microscopic and Mössbauer studies, which indicated

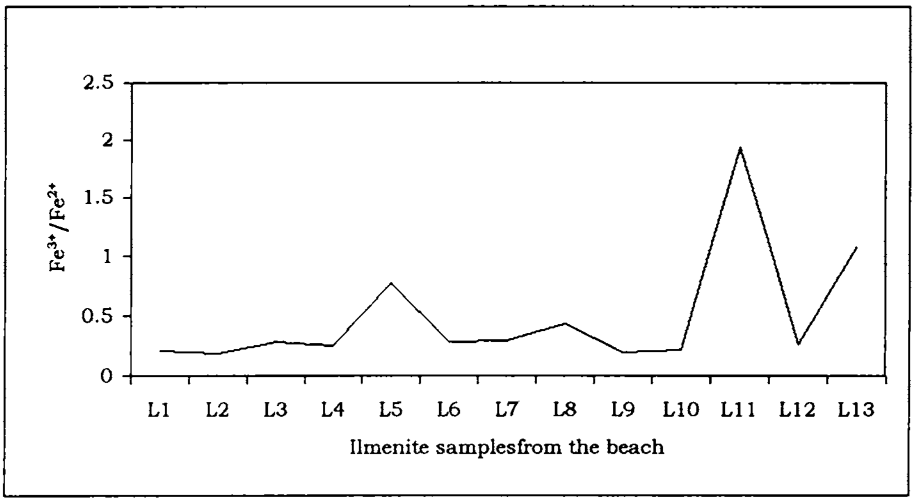


**Fig 5.1.12. Relationship between ferric-ferrous content from ilmenite samples from laterite**

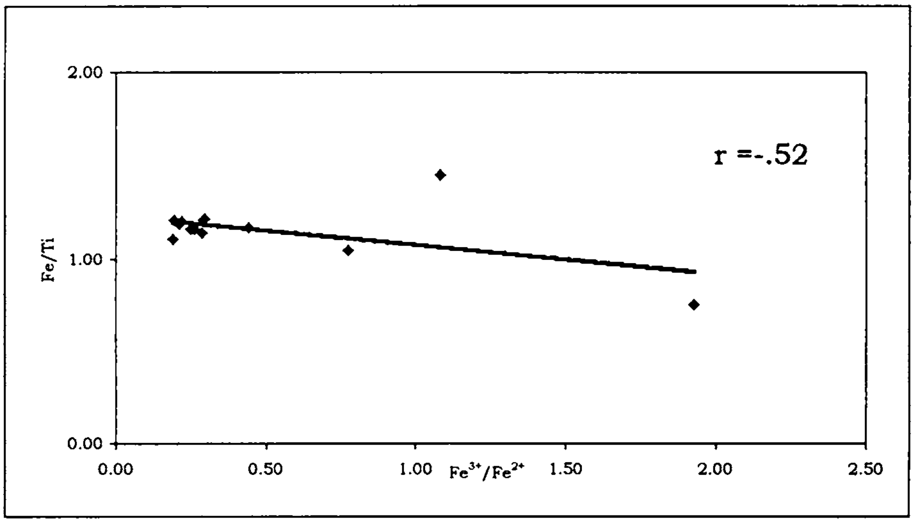


**Fig 5.1.13 Correlation between iron enrichment and ferric- ferrous contents in ilmenite samples from laterite**

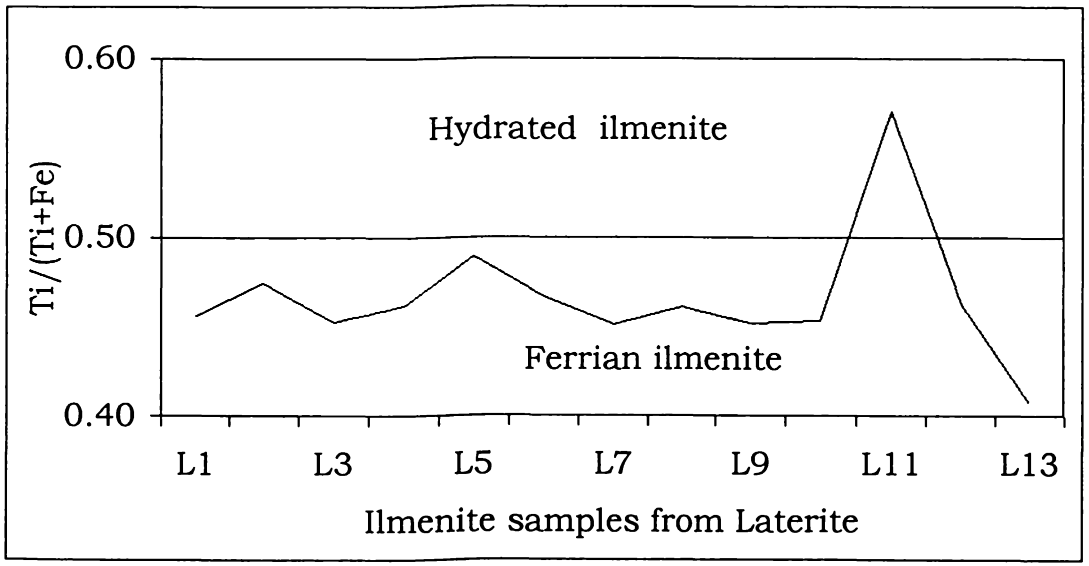


**Fig. 5.1.14. Alteration stages of ilmenite samples from laterite.**

presence of magnetite/maghaemite. The $Fe^{3+}/Fe^{2+}$ values present a slight antipathetic relationship (r = -0.52) to the Fe/Ti curves (Fig. 5.1.13). As the oxidation of ferrous ions takes place the iron content is slowly leached away with progressive alteration.

The characterization of the laterite based on the method of Frost et al (1983), classifies almost all the samples as having reached the 'Ferric ilmenite' stage of alteration (Fig. 5.1.14). The only exception to this trend is the Warkallai laterite. As observed earlier it has undergone much leaching of iron from its structure. Consequently, this sample falls in the field of the more advanced 'Hydrated ilmenite' stage.

The alteration behaviour of heavy mineral, under lateritic set up has not been subjected to much research by geochemists. Though in this work, the ilmenite samples from laterites show an apparent state of limited alteration, the dynamics of the weathering patterns, still demands a more detailed investigation.

### 5.1.4 Ilmenite from the Tertiary sedimentary rocks

The ilmenite from the Tertiary sedimentary sequence shows wide variation in their composition, depending on their spatial location (Table 5.1.6; Fig. 5.1.15). While the S4 sample, has a chemistry almost identical to that of the theoretical value of ilmenite, (~47% of the total iron oxide), with a low ferric content; in the case of both the two samples from the sandstone profile, S2 and S2a, the ferric oxide content (34.4 & 35.5 %) is almost four and three times that of the ferrous iron (8.46 and 10.52%) respectively. In S3, the pattern of composition reflects an alteration trend intermediate between the above samples ($FeO$-29% & $Fe_2O_3$-17%). The sample from the southern most area (S1) of the study area at Karichal is the most altered

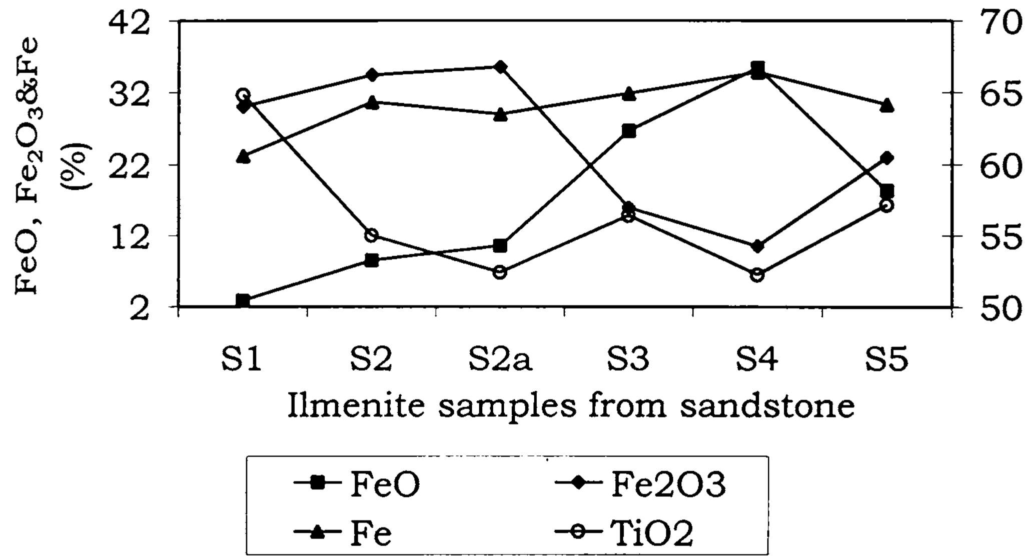


**Fig 5.1.15.** **Distribution of major elements in Ilmenite samples from Tertiary sandstone**

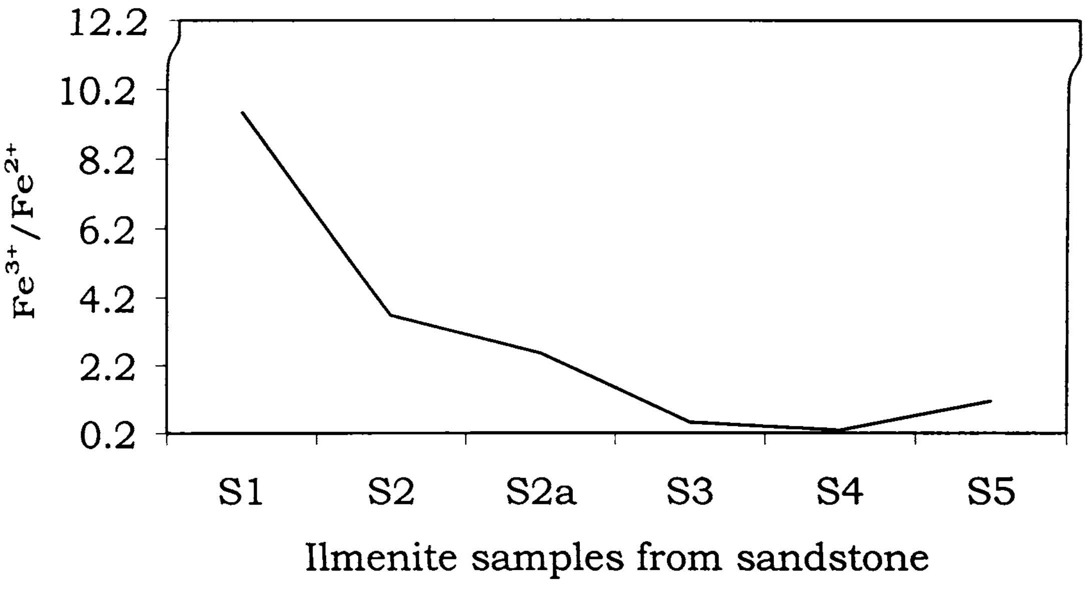


**Fig 5.1.16. Relationship of ferric - ferrous contents in Ilmenite samples from Tertiary sandstone.**

with a low oxide content of about 33%. Thus this samples almost bears the composition of pseudorutile.

The ilmenite samples from different locations of the Tertiary formations show varied chemical characteristics, although the locations fall within a limited spread of the area. While in the Warkallai proper, in sample S5, the ilmenite shows moderate values of around 41% of the iron oxides and 57.5% of $TiO_2$. These values are significantly more than that in ilmenite in the overlying laterite capping. In the Thiruvallam section of the Tertiary formation (S2 and S2a), the ilmenite chemistry shown is in contrast to the above observation. The chemical trend describes the maximum iron enrichment in the overlying laterite sample. The Tertiary formation in this location is exposed to height of more than four meters. The unit formations, which make up the Tertiary sedimentary rock, are known to possess different textural and mineralogical attributes (Raha et al, 1983; Soman, 1997). This may be a reflection of the differing environment of deposition, the provenance, and the diagenetic changes undergone by the formation. The sample from near the bottom of the section is composed of coarse-grained arkosic sandstone, while the top sampling location is made up of finer laminations. The two samples along the vertical section of the formation exhibit a difference in composition, concurrent with the variance observed for the nature of the different units. The presence of higher ferric content in the bottom sample and lower value for the ferrous iron when compare to that of the upper sample can be explained as due to the more favourable condition for pore water circulation aided by the higher permeability of the formations (Morad and Aldahan, 1986).

The high variation of weathering shown by the ilmenite samples from the Tertiaries is more illustrated by the plots of ferric-ferrous ratios of the samples (Fig. 5.1.16). The sample S1 shows extreme picture of alteration with ferric values at about 10 times that of the ferrous content. In fact, this is the most altered of all the field samples in this study. The sample S4 presents a case on the other side of the spectrum, with ferric iron to a tune of only about one fourth of the ferrous content. The S3 sample, show a half way oxidation stage in the ionic state of iron. Most of the samples, however, show the excess of ferric iron over ferrous ions. The Fe/Ti values traced stresses the differential alteration of samples from the different locations of the Tertiaries (Fig. 5.1.17). The sample S4 is seen to be the most iron enriched sample. In S1 sample this ratio is almost half of that in S4, indicating the high degree of leaching out of iron from the former. This point is brought out more clearly by the sharp inverse relationship ($r = 0.9$) between the $Fe^{3+}/Fe^{2+}$ and the Fe/Ti plots, indicating the role of ferric state of iron in the weathering and leaching process (Fig. 5.1.18). It may be noted that this relation is much stronger than observed for laterite samples. It means that the ferric enrichment is essentially a process which results in the leaching of iron. As most of the sandstone ilmenite samples are in advanced states of alteration, this process is much enhanced than in laterites.

The alteration stages of the sandstone samples show wide extremities in their nature based on the Ti/Ti+Fe values (Fig. 5.1.19). While the sample S1 from the southern section of the Tertiaries have weathered to the extent of 'Pseudorutile' stage of alteration, the samples from the type section of the Warkallai Tertiary sandstone (S5) and both samples of the vertical profile (S2 and S2a) show a moderate weathering trend of 'Hydrated ilmenite' stage. The other two samples, as indicated by their chemistry, fall in the 'Ferrian ilmenite' field, indicating their higher iron enrichment.

### 5.1.5 Ilmenite from the Teri deposits

The major element chemistry of the Teri beds is given in Table 5.1.6. The ferrous oxide content ranges around 33.78%. The titanium oxide content is

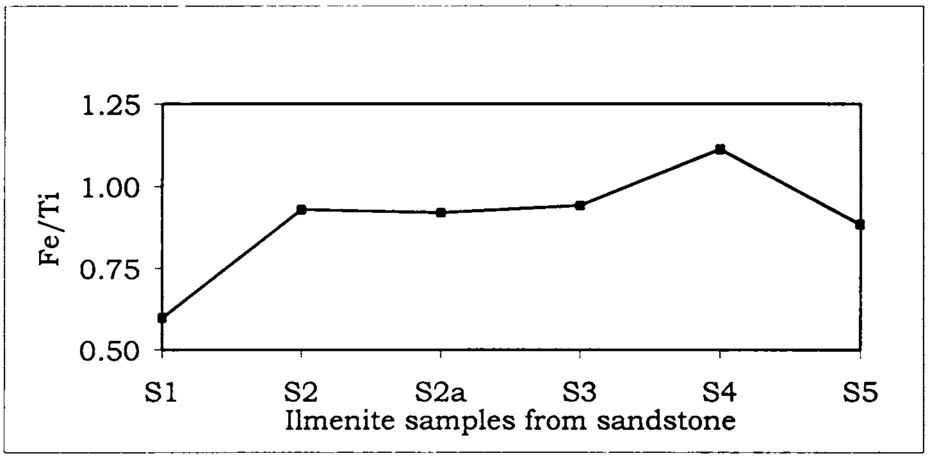


**Fig 5.1.17. Iron enrichment in ilmenite samples from Tertiary sandstone**

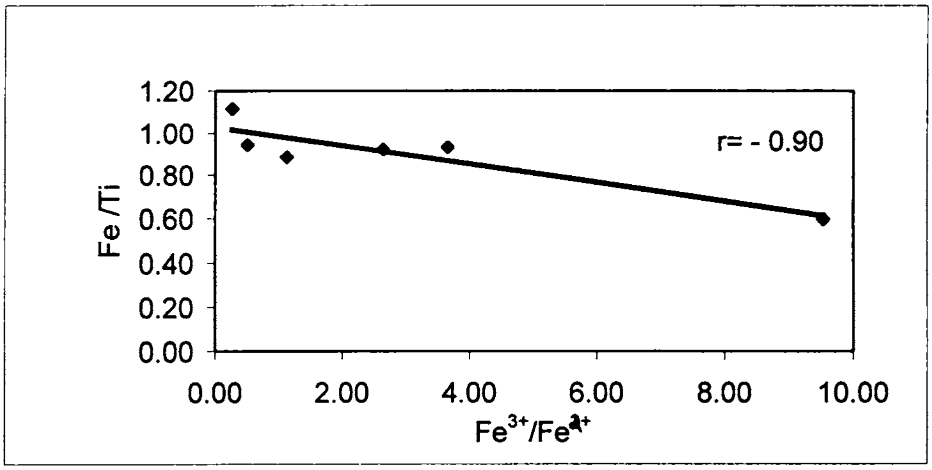


**Fig 5.1.18. Correlation between iron enrichment and ferric - ferrous contents in ilmenite samples from Tertiary sandstone**

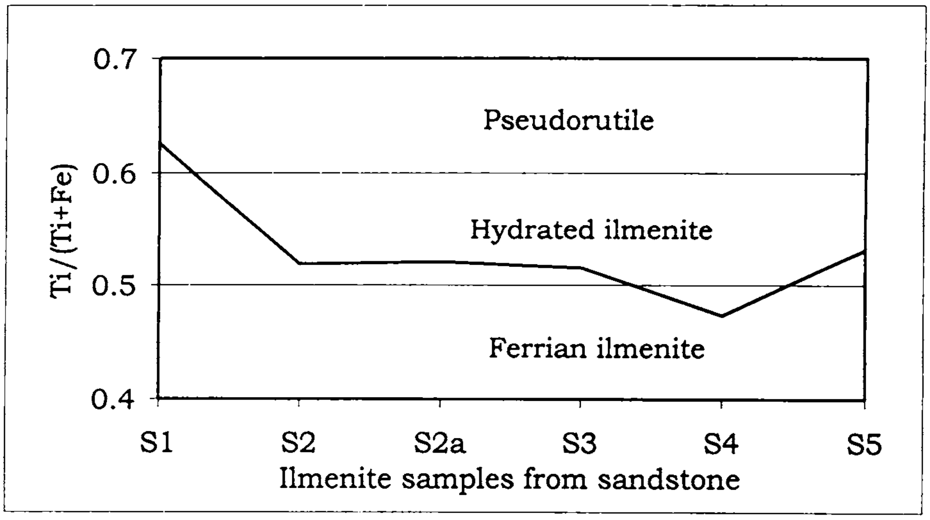


**Fig 5.1.19 Alteration of Ilmenite samples from Tertiary**

around 54%. The chemistry of the ilmenite samples of the Teri beds is similar to that of the ilmenite of the southern part of the Manavalakurichi deposit. The altertion is marginal as indicated by the slight decrease in the total iron content. Exsolution with haematite has been observed in the ilmenite grains. These samples have just managed to reach an alteration stage of 'Hydrated ilmenite' of Frost et al (1983).

The Teri sands are suggested to be the result of aeolian processes along the southern part of India. The minerals other than the quartz have been almost weathered away and the iron coatings are reported to be the result of this weathering activity. A limited fluvial influence in these deposits has been observed (Thampi et al, 1985). The similar elemental distribution as that of the beach ilmenite may point to the comparable emplacement of these two features in this region.

### 5.1.6 Ilmenite from the rivers

The degree of weathering in the path of migration depends on the stream gradient, nature and velocity of water flow, the type of country rocks and the water chemistry. There are four important rivers in the hinterland of the Chavara deposit, namely Karamana, Vamanapuram, Ithikkara and Kallada. Among these the Kallada falls in the vicinity of the southern part of the deposit and forms the largest river with a length of about 121kms and a run off about 76MC ft. The samples were collected from the mid-stream of main steam in each river system. Since the rivers insouth Kerala have comparably short courses than the rest of the peninsula, an average of five samples covered the stretches of river in the highland, midland and the coastal plain.

The ilmenite samples from the rivers, do not exhibit a high degree of alteration as indicated by the iron contents around 45% (Table 5.1.7; Fig.

Table 5.1.7. Major elements in the ilmenite from the rivers of the hinterland of Chavara and Manavalakurichi areas

| Rivers | Content (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Fe | $Fe^{2+}$ | FeO | $Fe^{3+}$ | $Fe_2O_3$ | Total oxide | $TiO_2$ |
| Karamana | | | | | | | |
| 1 | 36.28 | 27.30 | 35.22 | 8.98 | 12.836 | 48.056 | 52.01 |
| 2 | 32.33 | 29.90 | 38.57 | 2.43 | 3.48 | 42.05 | 53.11 |
| 3 | 36.76 | 28.12 | 36.28 | 8.64 | 12.35 | 48.63 | 52.65 |
| 4 | 37.52 | 30.53 | 39.38 | 6.99 | 10 | 49.38 | 54.39 |
| 5 | 35.07 | 28.45 | 36.7 | 6.62 | 9.47 | 46.17 | 54.01 |
| Vamanapuram | | | | | | | |
| 1 | 36.59 | 22.55 | 29.09 | 14.04 | 20.08 | 49.17 | 52.01 |
| 2 | 36.60 | 31.42 | 40.53 | 5.18 | 7.41 | 47.94 | 53.3 |
| 3 | 31.32 | 29.39 | 37.91 | 1.94 | 2.77 | 40.68 | 53.55 |
| 4 | 38.01 | 27.52 | 35.5 | 10.49 | 15 | 50.5 | 54 |
| 5 | 33.56 | 24.20 | 31.22 | 9.36 | 13.38 | 44.6 | 55.75 |
| Ithikara | | | | | | | |
| 1 | 36.90 | 30.22 | 38.99 | 6.68 | 9.55 | 48.54 | 52.12 |
| 2 | 36.71 | 27.19 | 35.08 | 9.52 | 13.61 | 48.69 | 52.5 |
| 3 | 36.58 | 28.64 | 36.95 | 7.94 | 11.35 | 48.3 | 53.11 |
| 4 | 36.11 | 25.60 | 33.02 | 10.52 | 15.04 | 48.06 | 53.41 |
| Kallada | | | | | | | |
| 1 | 37.46 | 23.88 | 30.81 | 13.57 | 19.41 | 50.22 | 50.97 |
| 2 | 35.46 | 24.09 | 31.07 | 11.37 | 16.26 | 47.33 | 54.64 |
| 3 | 36.50 | 20.57 | 26.53 | 15.94 | 22.79 | 49.32 | 51.14 |
| 4 | 36.17 | 29.11 | 37.55 | 7.06 | 10.1 | 47.65 | 53.12 |
| 5 | 36.88 | 26.08 | 33.54 | 10.80 | 15.44 | 48.98 | 52.1 |
| 6 | 37.43 | 23.16 | 9.78 | 14.27 | 20.41 | 50.19 | 52.89 |
| 7 | 34.69 | 24.28 | 31.22 | 10.41 | 4.89 | 46.11 | 54.13 |
| Valliyar | | | | | | | |
| 1 | 35.5 | 22.08 | 28.41 | 13.42 | 19.19 | 47.60 | 53.38 |
| 2 | 35.66 | 21.8 | 28.05 | 13.86 | 19.56 | 47.61 | 53.55 |
| 3 | 35.9 | 23.78 | 30.59 | 12.12 | 17.33 | 47.92 | 52.60 |
| 4 | 32.38 | 18.07 | 23.25 | 14.31 | 20.46 | 43.71 | 53.68 |
| 5 | 31.68 | 14.77 | 19.00 | 16.91 | 24.18 | 43.18 | 54.45 |

5.1.20, a-d). The ferrous content is prominently higher than the ferric values, pointing to the limited oxidation in the ionic state of iron. The rivers in the study area are reported to have steep gradients of more than 1/250 (Soman, 1997) thus retaining their youthful behaviour for most of their course. Consequently, the erosive power due to stream action is very high and large bulk of sediments are transported downstream. The high current action ensures that the sediments are not reworked and weathered to high levels. These factors contribute to the lower state of alteration of the river ilmenite samples. The erosive power of the stream also constantly contributes more sediment along their course. The major element chemistry of the samples down stream also does not reveal a gradual lowering in the ferrous content downstream. The samples show a slight but significant fluctuation in the values down stream. A number of tributaries join the main stream along its course in these rivers, which contribute relatively fresh sediments. This may account for the irregular variation in the content of the major elements.

The river samples from the Kallada, particularly in its upper course, exhibit large iron values for ilmenite, noticeably higher than the theoretical values for the mineral. In the samples from other rivers, the iron content though high is near the iron values for pure ilmenite. Thus the high values of iron are interesting, particularly when the tendency of iron to leach out of the mineral structure is considered. The Kallada river system, occurs in an area, where in addition to the charnockite and khondalites, significant intercalations of mafic rocks like corderite gneiss and calc ganulites occur (GSI, 1995; Soman, 1997). The ilmenite grains from the corderite gneiss have been observed to contain suspected intergrowths of magnetite/maghaemite. This accounts for the high ferrous and iron values. In the samples from the lowest stretches of the stream, the alteration has been more successful in the leaching of iron from the mineral.

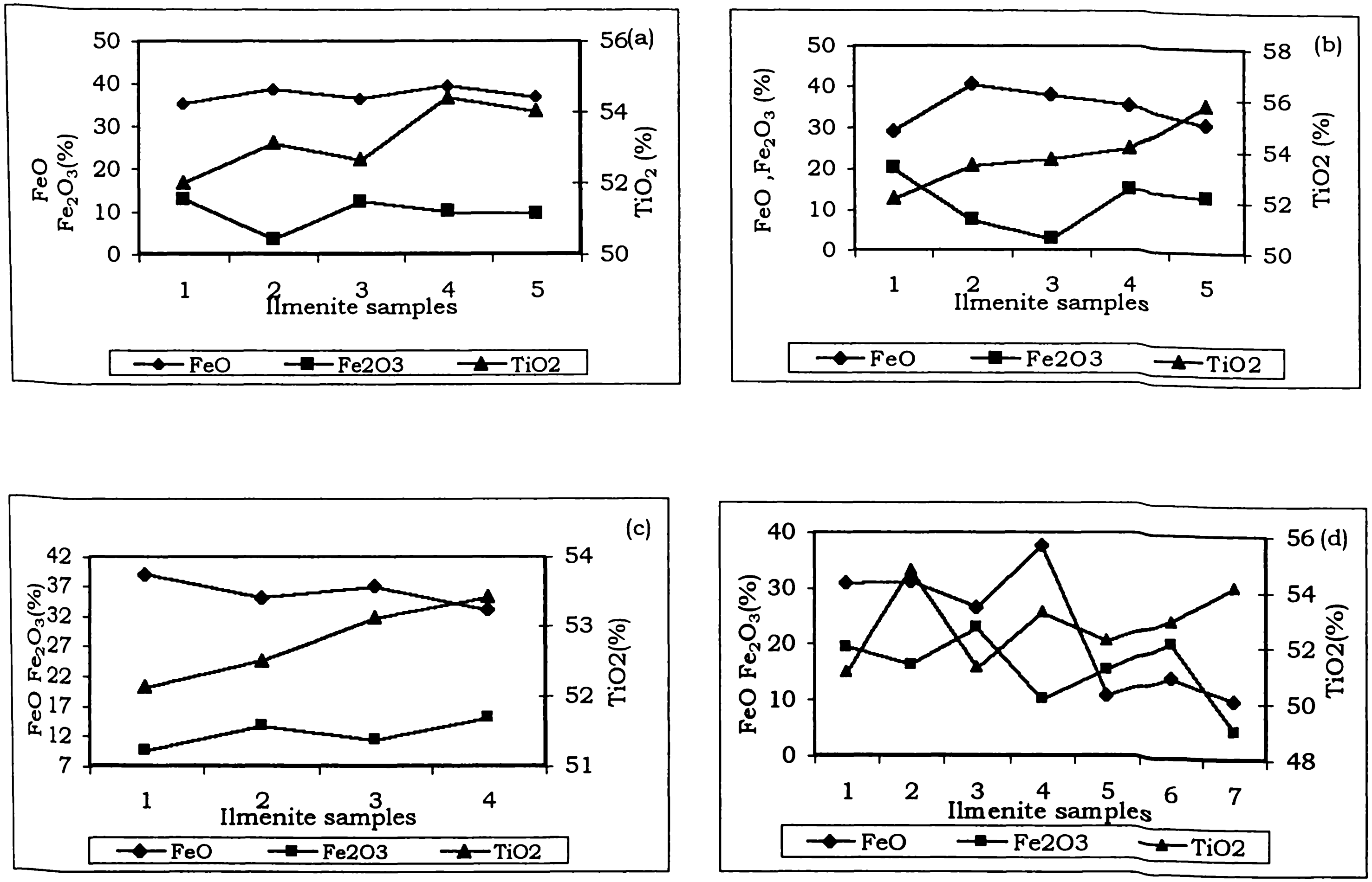


Fig 5.1.20. Distribution of major elements in rivers in the hinterland of Chavara deposit
a) Karamana , b) Vamanapuram, c) Ithikara and d) Kallada

The ferric content is very low ranging from 9% in Killiar to 16% in Kallada. Valliyar is the only river in the vicinity of the Manavalakurichi deposit (Table 5.1.7). The ilmenite from this stream has a total iron oxide value of 47.6% at the upstream part, which decreases to a value of 43% near the mouth. The ferric oxide shows a corresponding range of 19 to 24%.

### 5.1.7 Ilmenite from the Ashtamudi estuary

It represents a zone of fluvio-marine interaction. Thus the sediments in this zone include, those brought from the hinterland by the rivers and those transported from offshore by coastal waves and currents. The ilmenite generally shows higher $TiO_2$ contents (Table 5.1.8; Fig 5.1.21). In E1, these values go to as high as 63%, while the lowest value (55%) is shown near the Ashtamudi area (E4), which is near the mouth of Kallada river. This particular sample shows a value of 36% for FeO, much higher than the other estuarine ilmenite sample (around 12%), indicating the fresh supply of grains from the hinterland. Near the mouth of the estuary, the influence of the marine sediments is very significant. The marginal but noticeable depletion of the ferric contents and the increase of the FeO in E5 is noticed.

The ferric enrichment with progressive alteration is highlighted in Fig. 5.1.22. While the ferric content in E1 is lower than that in the other more altered samples, its enrichment compared to the ferrous iron is the point of interest. This trend has been noticed for the other geological environments earlier in this account. The slightly lower value shown by the E1, in spite of the high alteration shown by the high $TiO_2$ content, is indicative of the starting of the marked depletion of ferric iron from the mineral structure. This phase with an aggregate composition of $TiO_2$, which is more than that for pseudorutile, is defined by the increased rate of iron leaching.

Table 5.1.8 Major elemental distributions in the estuarine ilmenite

| | Content (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Sample | $Fe^{2+}$ | FeO | $Fe^{3+}$ | $Fe_2O_3$ | $TiO_2$ | Fe |
| Ashtamudi Estuary | E1 | 8.74 | 11.27 | 18.89 | 27.01 | 63.07 | 27.64 |
| | E2 | 8.39 | 10.82 | 20.96 | 29.97 | 60.12 | 29.37 |
| | E3 | 7.98 | 10.3 | 22.57 | 32.27 | 58.33 | 30.58 |
| | E4 | 27.85 | 35.93 | 5.27 | 7.54 | 55.07 | 33.2 |
| | E5 | 11.27 | 14.54 | 15.84 | 22.65 | 58.2 | 27.14 |

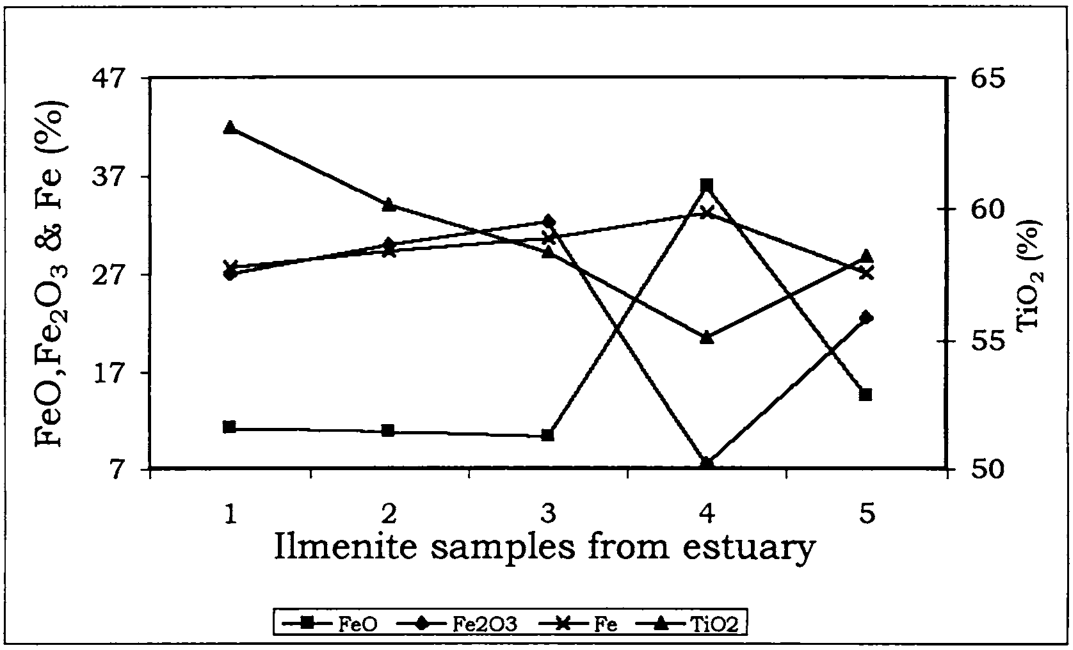


**Fig. 5.1.21.** Distribution of major elements in ilmenite samples from Ashtamudi estuary

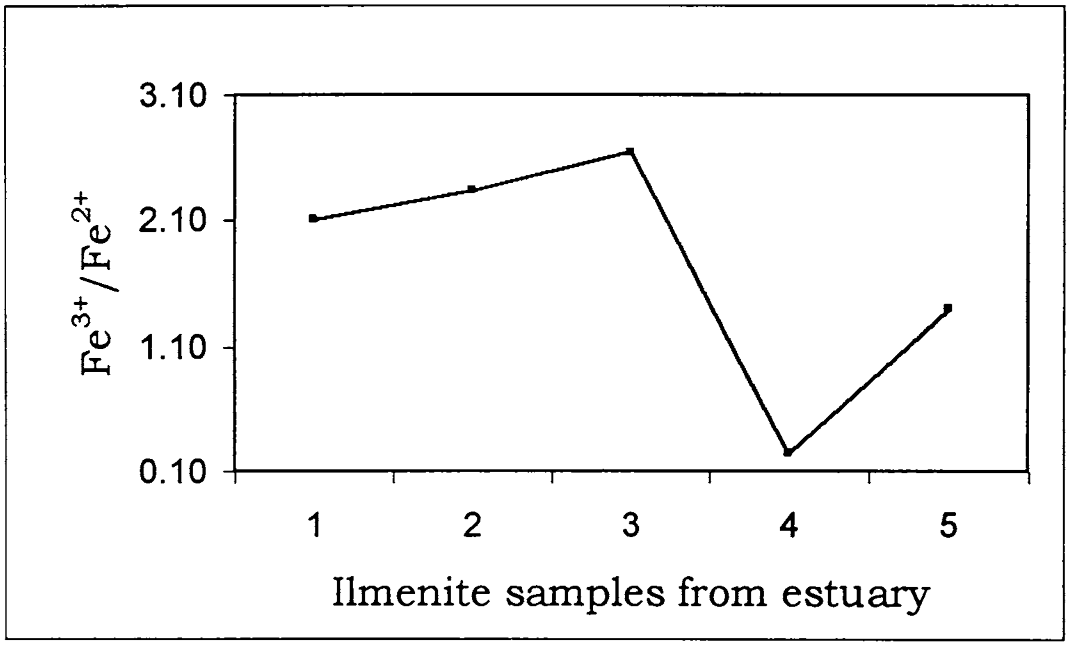


**Fig. 5.1.22.** Relationship of ferric - ferrous contents in ilmenite samples from Ashtamudi estuary.

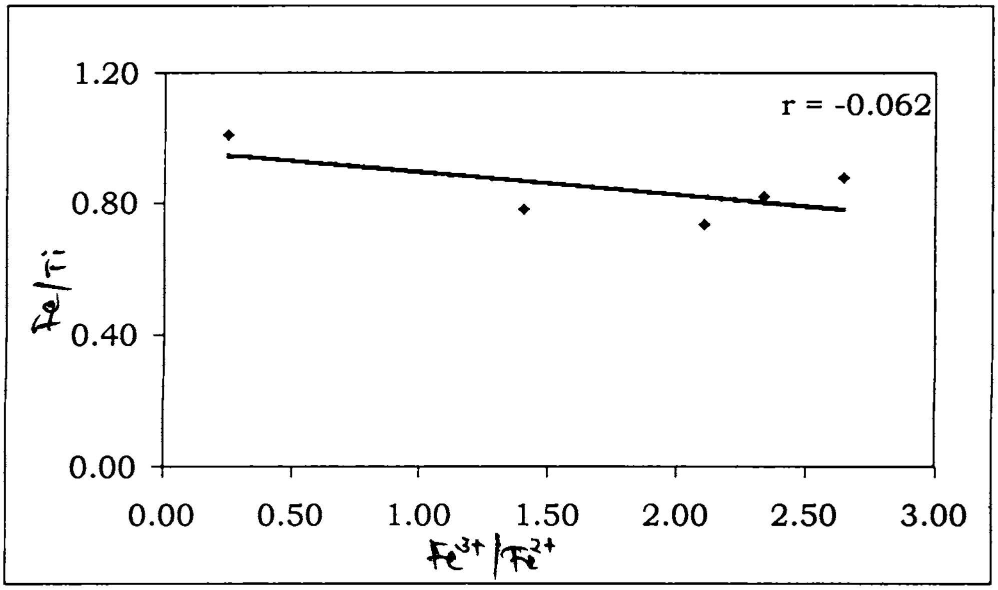


**Fig 5.1.23. Correlation between iron enrichment and ferric - ferrous contents in ilmenite samples from Ashtamudi estuary.**

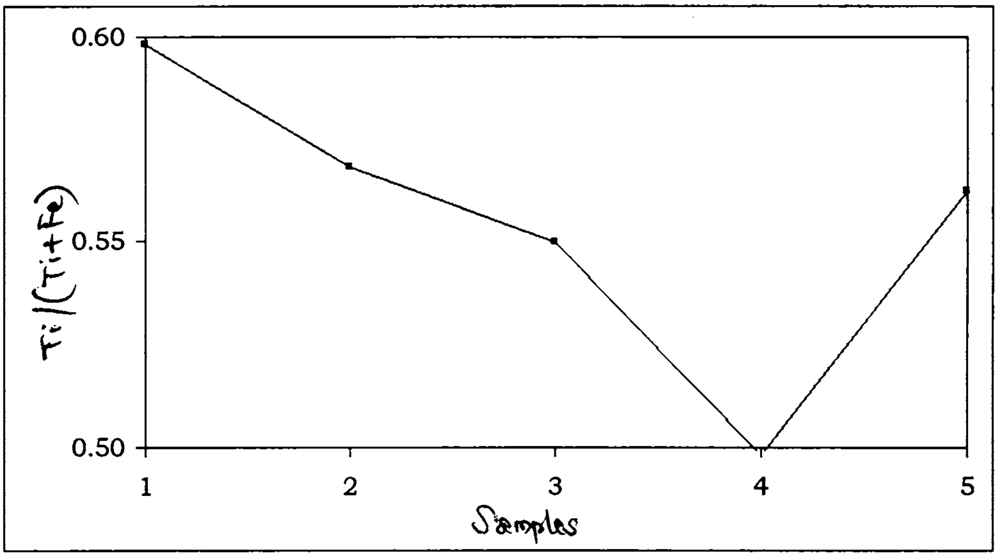


**Fig 5.1.24.Alteration stages of ilmenite samples from Ashtamudi estuary**

The Fe/Ti plots, for this set up is characterized by one noticeable trend (Fig. 5.1.23). While in the environments mentioned so far, plots showed a possible negative correlation between the ferric/ferrous and the Fe/Ti plots, implying the total iron depletion with ferric conversion. In the estuarine samples the same general trend is observed attesting to the sway of ferric iron in the content of the total iron in ilmenite. The leaching of ferric iron seems to be at a low momentum in these samples. The behaviour of ilmenite alteration under reducing and slightly basic conditions has not been well studied. The difference in the apparent degree of leaching patterns of iron in the estuarine conditions from other sampling locations could be a function of the characteristic geochemical environment which slows down the leaching process.

The samples of the estuary all fall in the 'Hydrated ilmenite' stage of alteration of ilmenite, defining various phases of alteration of this field (Fig. 5.1.24). Thus E4 is the most unaltered of the samples, which lie in the boundary of 'Ferrian ilmenite' and 'Hydrated ilmenite'. The explanation for their relative freshness has been attempted before. On the other hand, the sample from the sheltered regions, especially E1, has reached the termination of the hydrated ilmenite phase. The varying degrees of alteration are a result of the difference in the physical environments occurring in the estuary. Factors like the geochemical environment, the supply of fresh material from the hinterland and the marine conditions, the disturbance to sediments in the form of transportation and deposition determine the chemistry of the ilmenite in the estuarine condition.

## Part 5.2. CHEMICAL CHARACTERISATION – MINOR AND TRACE ELEMENTS

### 5.2.1 Introduction

Minor and trace elements are important in the modern mineralogical scene, as they provide clues for (1) the provenance of mineral suite, (2) the alteration patterns and trends of minerals and (3) the quality of raw mineral ores before industrial processing. Ilmenite trace element variation is dependent on its paragenesis (Hutton, 1950; Deer et al, 1962; Buddington and Lindsley, 1964). The delineation of the provenance based on trace elements, is preferred nowadays to the study of mineralogy of the heavy mineral suites. Such studies based on the mineralogy of heavy minerals are limited in their application due to problems caused by the weathering of more unstable minerals of the suite and the dependence of the mineralogy on the sorting processes. Such drawbacks are eliminated by the use of trace elements for provenance discrimination (Darby, 1984).

The chemical changes consequent to weathering and alteration since the release of the mineral from the country rocks indicates the nature of the transportation and the depositional environments of the minerals through which the mineral has passed (Blatt, 1967; Force, 1976; Darby, 1984; Anand and Gilkes, 1984; Morad and Aldahan, 1982,1986; Darby and Tsang, 1987, Basu and Molianroli, 1989; Grigsby, 1992;). Ilmenite and its intermediate products during alteration and their chemical variation have been well documented (Bailey et al, 1956; Temple, 1966; Wort and Jones, 1980; Frost et al, 1983, 1986; Chaudhuri and Newsley, 1990; Mucke and Chaudhuri, 1991, Chernet, 1999). Although the chemistry of the major elements of the Indian ilmenite ore has been worked upon (Suresh Babu et al, 1994; Sukumaran and Nambiar, 1994; Nair et al, 1995; Ramakrishnan et al, 1997), the minor and trace element distribution of these ilmenite deposits have been scanty and only a few elements have been studied. These elements have important implications in the benefication and processing of the ilmenite ore, since the chemistry determines the quality and recoverability of the ore (Wort and Jones, 1980). The adoption of the various process of beneficiation and their suitable modifications also is based on an understanding of chemistry (Temple, 1966; Wort and Jones, 1980; Suresh Babu et al, 1994, 1996; Chernet, 1999). Thus, the research on the minor and trace element chemistry of ilmenite is not confined to the realm of academic interest and economic and industrial considerations complement such studies. The minor and trace elements may be included in the mineral structure either during the crystallization of the mineral at high temperatures or they may be accommodated in the mineral structure during the alteration stages affecting the mineral. Certain elements are freed from the crystal lattice leading to the enrichment of the remaining elements during weathering and transportation. The ilmenite samples in the present study were analyzed for nine minor and trace elements, namely, Mn, Mg, Al, Cr, Si, V, Zn, Cu and Ni. These elements were selected based on their relevance in the delineation of weathering history and parentage.

In this work, ilmenite of the beach deposits along the southwest coast of India has been analyzed for their minor and trace element chemistry. The differently weathered fractions of the beach ilmenite have also been analyzed to understand the pattern of the progressive weathering and resultant chemical changes. The ilmenite from the various geological conditions of the hinterland has also been observed keeping in view their relevance as the ultimate source of the beach placers.

The alteration of ilmenite from the hinterland has not been well documented as that from the beach in the literature. Hence, the geochemical behaviour of ilmenite with progressive alteration has been 'standardized' over the years with out taking into consideration their environment of occurrence. The weathering and alteration of different minerals, which take place in a particular geologic set up would be dictated by the geochemical environment prevailing at the time of the formation and emplacement of such a setup. Many minerals formed consequent to weathering are products of reactions involving oxidation and reduction under varying pH conditions. Thus the nature of alteration of minerals would be different under varying geologic conditions, dictated by the local Eh and pH conditions at the formation and emplacement of each setup.

An attempt has been made in this work to explain the leaching patterns of the minor and trace elements based on the Eh-pH conditions of each geologic environment. Since the data on the geochemical environment of the different geologic conditions of the study area in a micro level scale is not now adequately available, broad generalizations about the Eh and pH configuration of each sampling set up was assumed based on the general idea about the formation processes of the different depositional environments. Hence the outcome of this study on the leaching patterns during alteration should be treated as approximations based on gross presumptions rather than definite trends of geochemical behaviour.

The minor and trace element analysis of ilmenite samples from the Chavara and Manavalakurichi deposits are given below along with the chemical composition of the ilmenite from different geological settings of the hinterland.

### 5.2.2 Ilmenite from beach

The minor and trace element data is given in Table 5.2.1. The elements Mn, Mg, Al, Si, Cr and V dominate the chemical scenario. These elements, particularly Mg, Mn, Al and Cr are reported to be very significant in the chemical composition of the mineral. In the Chavara deposit, the Mn shows a high content and varies from 0.18 – 0.3 %. The Cr values range from 860 to 960 ppm (Fig. 5.2.1, a-h). The variations of

5.2.1 Distribution of minor and trace elements in the ilmenite samples Chavara and Manavalakurichi beach

| posit | Sample | Content (%) | | | | Content (ppm) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Mn | Mg | Al | Si | Cr | V | Zn | Cu | Ni |
| avara | C1 | 0.3 | 0.13 | 0.49 | 0.26 | 900 | 1479 | 112 | 50 | 39 |
| | C2 | 0.19 | 0.35 | 0.41 | 0.32 | 860 | 1099 | 300 | 39 | 23 |
| | C3 | 0.25 | 0.26 | 0.31 | 0.46 | 960 | 1086 | 214 | 67 | 71 |
| | C4 | 0.18 | 0.19 | 0.4 | 0.29 | 860 | 1084 | 150 | 47 | 69 |
| | C5 | 0.23 | 0.28 | 0.43 | 0.36 | 890 | 971 | 201 | 60 | 39 |
| | C6 | 0.22 | 0.17 | 0.38 | 0.37 | 860 | 1095 | 188 | 57 | 42 |
| anavala<br>urichi | M1 | 0.24 | 0.32 | 0.31 | 0.45 | 540 | 1021 | 500 | 62 | 43 |
| | M2 | 0.24 | 0.31 | 0.54 | 0.32 | 810 | 1042 | 447 | 78 | 20 |
| | M3 | 0.2 | 0.12 | 0.41 | 0.22 | 511 | 1164 | 396 | 52 | 144 |
| | M4 | 0.23 | 0.28 | 0.36 | 0.41 | 650 | 968 | 361 | 71 | 69 |
| | M5 | 0.22 | 0.23 | 0.24 | 0.09 | 860 | 1375 | 99 | 69 | 40 |

5.2.2 Distribution of minor and trace elements in the magnetic fractions of ilmenite from Chavara and Manavalakurichi deposits

| | Content (%) | | | | Content (ppm) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| CH<br>(amp) | Mn | Mg | Al | Si | Cr | V | Zn | Cu | Ni |
| .15 | 0.23 | 0.31 | 0.48 | 0.45 | 1060 | 1103 | 169 | 71 | 79 |
| 0.2 | 0.26 | 0.29 | 0.45 | 0.42 | 900 | 953 | 184 | 69 | 58 |
| .25 | 0.22 | 0.31 | 0.37 | 0.35 | 960 | 1079 | 238 | 68 | 14 |
| 0.3 | 0.21 | 0.32 | 0.45 | 0.41 | 960 | 1028 | 264 | 62 | 53 |
| .35 | 0.15 | 0.29 | 0.52 | 0.42 | 1170 | 1079 | 408 | 132 | 54 |
| 0.4 | 0.13 | 0.28 | 0.62 | 0.42 | 1540 | 1136 | 429 | 85 | 39 |
| .45 | 0.12 | 0.3 | 0.66 | 0.47 | 1810 | 1135 | 519 | 92 | 72 |
| 0.45 | 0.16 | 0.31 | 0.6 | 0.44 | 1240 | 998 | 385 | 80 | 53 |
| p) | | | | | | | | | |
| .15 | 0.29 | 0.3 | 0.3 | 0.43 | 930 | 1214 | 334 | 125 | 66 |
| 0.2 | 0.29 | 0.7 | 0.25 | 0.5 | 720 | 924 | 315 | 71 | 58 |
| .25 | 0.16 | 0.35 | 0.23 | 0.41 | 560 | 1053 | 410 | 109 | 82 |
| 0.3 | 0.16 | 0.34 | 0.23 | 0.42 | 530 | 984 | 395 | 69 | 51 |
| .35 | 0.2 | 0.31 | 0.52 | 0.43 | 980 | 2000 | 431 | 130 | 65 |
| 0.4 | 0.09 | 0.22 | 0.54 | 0.41 | 1880 | 1160 | 119 | 58 | 29 |
| 0.40 | 0.17 | 0.26 | 0.46 | 0.42 | 1130 | 1104 | 350 | 92 | 59 |

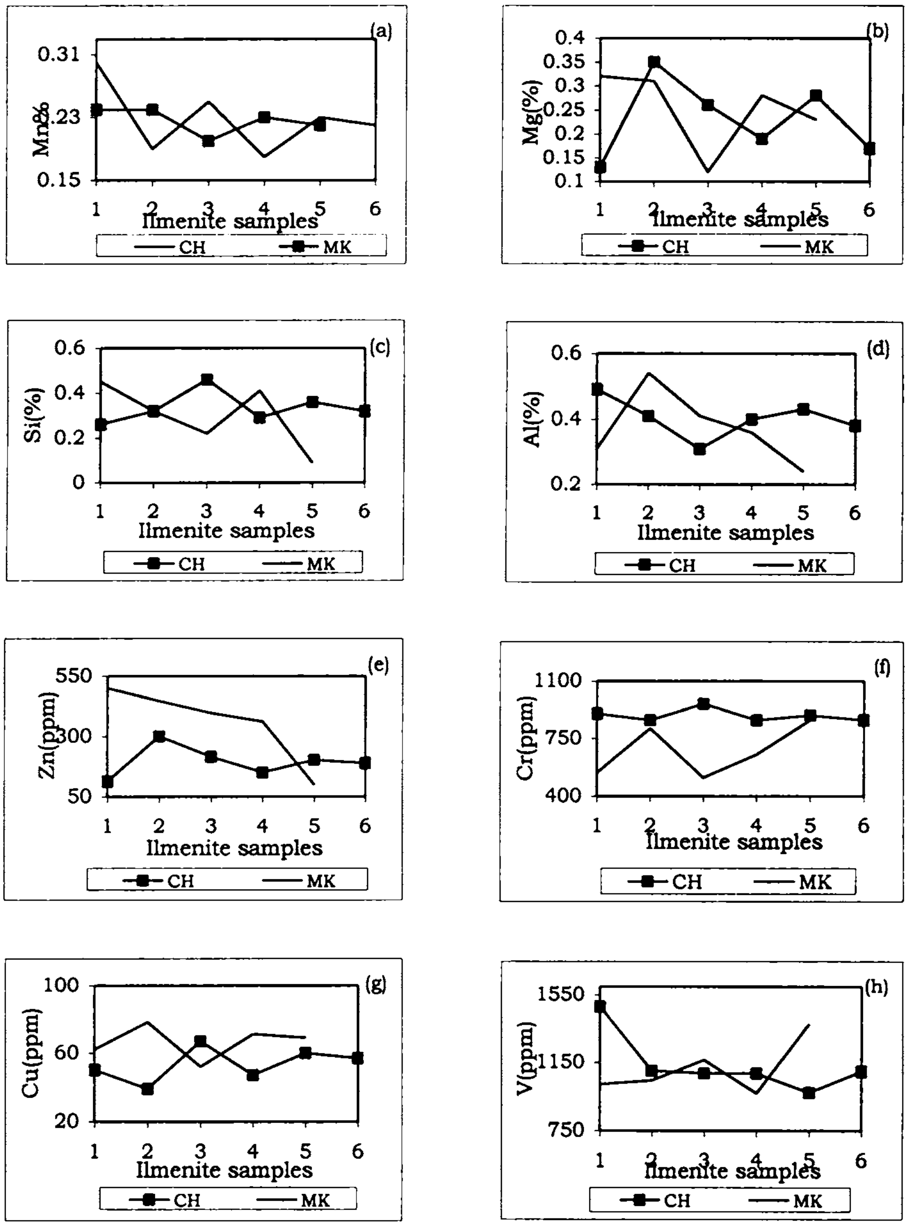


Fig 5.2.1(a-h). Distribution of minor and trace elements in the ilmenite samples from Chavara and Manavalakurichi

other important elements are as follows, Mg (0.13 – 0.35%), Al (0.31 – 0.49 %), Si (0.26 – 0.46 %) and V (971 – 1479 ppm). The C4 sample shows the lowest content of Cr and Mn. On the other hand, C3 exhibits the maximum values for Cr, Si and Mn while the lowest contents among the beach samples for Al are reserved in the this sample. The sample C1 from the southern extremity of the deposit at Neendakara defines a different pattern in the elemental distribution in its high values of Mn, Al and more significantly V. The average pattern of abundance of the elements is Al>Si>Mg>Mn>V>Cr>Zn>Cu>Ni.

The Manavalakurichi ilmenite exhibits notable difference with the Chavara ilmenite, particularly with respect to some elements like Cr and Zn. The sample M5 from the northern part off the Manavalakurichi deposit report lowest values for Al (0.24 %), Si (0.09 %) and Zn (99 ppm), while maximum values of Cr (860 ppm) and V (1375 ppm) are credited to this sample. The pattern of abundance based on the average values of the elements are Al>Si>Mg>Mn>V>Cr>Zn>Cu>Ni.

As mentioned above, the samples C1 from Chavara and the sample M5 from Manavalakurichi show significant differences from other samples of their respective area. The distinct chemistry of C1 indicates that progressive enrichment is taking place from the southern side of the deposit. These observations agree with those of Ramakrishnan et al (1997), who argued in favour of enrichment of the Chavara deposit. Such an explanation seems plausible when the deposition of Kallada River near this part of the deposit is considered.

Among the ilmenite samples of the Manavalakurichi deposit, the sample M5 from Kolachel exhibits a deviation in the minor and trace element chemistry. When the major element chemistry was considered in the preceding section, it was the sample M3, which presented a different nature, as indicated by the higher stage of alteration. As in the case of the Chavara deposit, an enrichment of the extremity could be suggested.

The dominant coastal currents are southward in this region, which carry out the bulk of the transport of sediments, which are subsequently deposited (Baba, 1998). This region represents the portion of the deposit, where the influence of the fluvial process is minimum when the elemental distribution of the deposit and the adjacent Valliyar river is compared. The mineral ilmenite here thus represents those concentrated by the sorting process of waves from the offshore. The ilmenite released from the Kolachel headland by weathering cannot also be discounted.

The average values of the elemental contents of the ilmenite of two deposits are compared in Fig. 5.2.2 (a-i). The most striking difference between the two deposits is characterized by the very high concentration of Cr in Chavara than in the Manavalakurichi deposit. Significant depletion in the contents of Mg, Mn, Zn, Cu and Ni is found in the Chavara ilmenite. Al, Si and V are three elements, which are suggested in the literature to be immobile and consequently increase with alteration. But there is no significant difference in the contents of these elements in the two deposits although higher values of these elements are expected in Chavara ilmenite. The depositional environment in the beaches of these two areas has to be investigated for throwing light on the alteration patterns in these two deposits.

The well-mixed and mature state of the Chavara placer deposit, compared to that of the Manavalakurichi area has been explained based on the distribution of the major elements. This is reflected in the distribution of most of the minor and trace elements of the Chavara ilmenite with in a narrow range, when compared to that of Manavalakurichi. Some elements like Mg show a more similar nature in the range of distribution in ilmenite from the two deposits. However, the effect of local weathering environments has not been studied, which is essential for the delineation of the detailed alteration patterns.

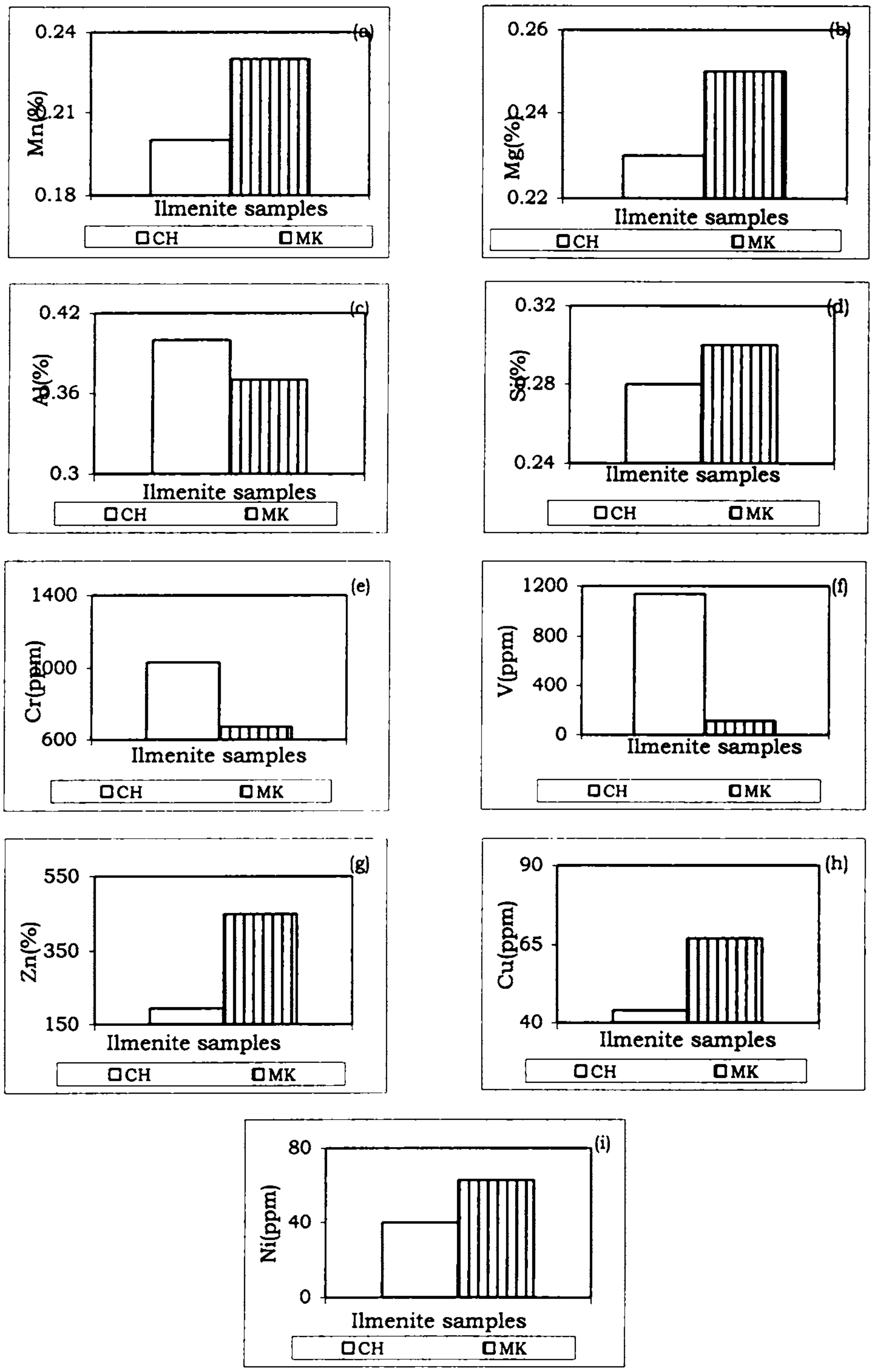


Fig 5.2.2(a-i). Variation in the average contents of the minor and trace elements in ilmenite from Chavara and Manavalakurichi beach.

The distribution of the minor and trace elements along the vertical profiles of the Chavara and Manavalakurichi deposits present strikingly different patterns. The individual elemental concentrations in ilmenite of the two deposits are plotted in Fig. 5.2.3 (a-e) to convey the degree of contrast in the contents of each element in the Chavara and Manavalakurichi ilmenite. Temple (1966) has reported that the in a vertical profile of a placer deposit, the ilmenite in the topmost layer near the surface regions exhibit the most altered state. Below the water table, which is at depth of around 1.3 meters in the Chavara area, the alteration slightly decreases. However, in this study the Chavara deposit, echoes the pattern of the major elements and do not show much range in the minor and trace element contents. This is interesting when the considerable dimensions of the placer deposit are taken in account. The sampling has been carried to a depth of about 4 metres of the reported maximum depth of about 15 metres. The repeated cycles of reworking led to the deposition of a mature well-mixed sediments forming the present placer deposit.

A contrasting picture is seen in Manavalakurichi (Fig. 5.2.3, a-e), in spite of the smaller dimensions of the deposit here (6 kms in length and about 6 m in depth). Here, the most altered ilmenite is above the water table, which occurs at a depth of about 1 meter from the surface as indicated by the lower FeO content. The minor elements correlate with the variation shown by the major elements. Mg and Mn are enriched below the surface, while Al and V are depleted. V shows further depletion with depth. This element is leached out at reducing and acidic conditions. Reducing and acidic environment prevail below the surface of the Manavalakurichi beach, as indicated by the occurrence of peat at shallow depths (Murugan et al, 2000). The subsurface sampling locations at Manavalakurichi may have conducive conditions for V removal. Only Cr signifies an unexpected behaviour, where it increases in the bottom ilmenite samples. This element is known to be soluble at a pH below 5. Cr shows enrichment in the sample below the water table

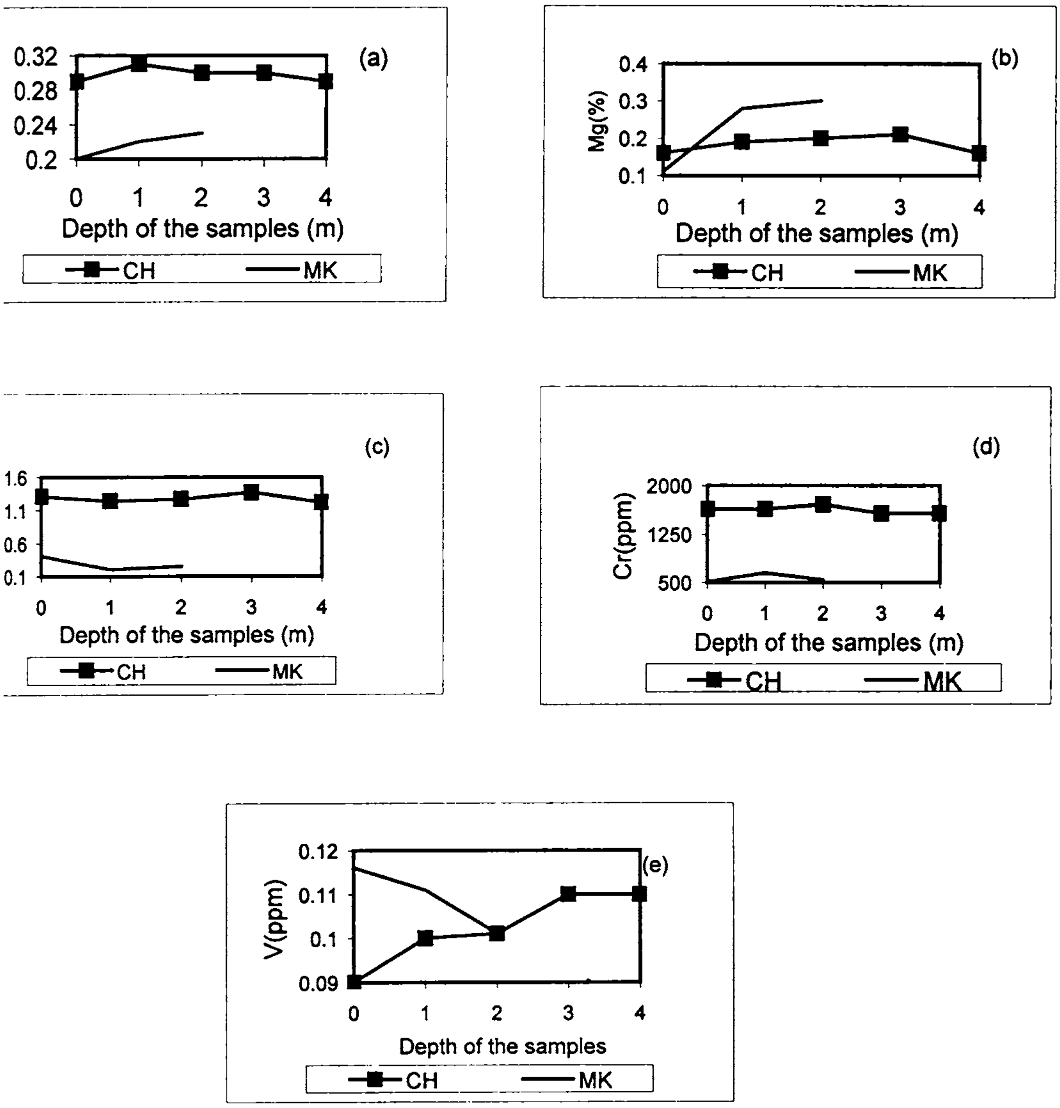


Fig 5.2.3 (a-e). Variation in the minor elements with depth in ilmenite samples from Chavara and Manavalakurichi deposits

above the peat bed. In deeper portions of the deposit, the pH values may tend toward still lower values, leading to chromium depletion.

Though the Chavara and Manavalakurichi deposits are explained to be of differential origin, the characteristic depositional environments of each deposit and their influence on the geochemistry during alteration of ilmenite has not been looked into. The higher amount of ferrous iron and depleted contents of iron in ferric state and titanium in ilmenite deposit of Manavalakurichi, together with enrichment of Cr in Chavara ilmenite is often pointed to as the evidences supporting the older age of the Chavara placers. The paucity of garnet in this deposit is also another argument in support of the sequential origin of these deposits (Thampi et al, 1994). The premise is that the climatic setting, ground water condition and country rocks of the hinterland are similar in both the deposits and hence they are comparable based on the mineralogy of the deposit and the chemistry of ilmenite. Though the country rocks in the vicinity of the deposits belong to the Khondalite- Migmatite and the Charnockite suites, the relative proportion of the constituent rocks of these suites have to be considered along with the study of the ilmenite samples from them. The intercalations of mafic and ultra mafic rocks in the country rocks would influence the chemistry of ilmenite carried by the rivers to the sea. e.g. The Khondalite complex near Chavara shows presence of basic intrusive rocks like pyroxenites and considerable intercalations of calc granulites and corderite gneiss. Lateritisation is more prominent in the Chavara area. This is a unique process of in situ weathering, which takes place in crystalline and sedimentary rock environments where the chemical change is characterized by the enrichment of iron and aluminium and the leaching out of silica.

As shown above, the geochemical nature of the alteration process is different depending on the type of the geological environment of the samples. On the other hand, the Manavalakurichi is characterized by the Teri deposits, which are assumed to be mainly aeolian in origin. The present investigation indicates a slightly different pattern of elemental distribution between the beach ilmenite and that in the Teris. Its role as one of the likely parent materials of the Manavalakurichi deposit has to be investigated further. The fluvial component is very prominent as the agents of transportation of sediments from the hinterland to the sea. The nature of the sediments carried along each fluvial system depends on the proportion of the rocks belonging to the Khondalite and Charnockite suites, the extent of the Tertiary formations through which they flow and the development of estuarine facies at the river mouths. Except for the presence of a small river, Valliyar, there are no rivers in the vicinity of the Manavalakurichi deposit. Judging by its size and sediment out put, the contribution from this river cannot be overstressed.

The most dominant factors which control the concentration and enrichment of the placer deposit of the southwest coast of India, in the present age, has been the coastal processes like waves and currents (Kurian et al, 1997; Prakash et al, 1991, 1997; Thampi et al, 1994). The sway of these processes must have been marked since the super imposition of an estuarine regime on the southwest coast. The relict sediments, which occur in the shelf zone in the form of palaeo beaches and sand ridges, which are products of the low sea levels in the past. The sorting processes by the coastal processes and subsequent transportation lead to the reworking and enrichment of denser heavy sand on the shore. The high replenishment observed in the southwest coastal region points to the transportation of reworked sediments to the beach from the shelf zone. The chemical trends of weathering in the shelf zone would influence the chemistry of the reworked sediments deposited on the beach.

### 5.2.2.1 Magnetic fractions of bulk ilmenite:

The minor element data of the different magnetic fractions are given in Table 5.2.2. Aluminium and silicon are the elements present in the largest contents. The contents of magnesium and chromium are markedly greater than the corresponding values for the Manavalakurichi samples (Suresh Babu et al, 1994). The distribution of the minor elements with increasing alteration (expressed as the function of Ti%) is shown in Figs. 5.2.4 ((a-b)& 5 (a-b)). The initial slight increase in Mg and Cr and decrease in Al, Si, and Mn could be linked to the relative variation of these elements related to the oxidation of ferrous ions and the simultaneous leaching of the ferric iron from the ilmenite structure. A sharp and striking deviation in the distribution trends is noticed for all the elements studied. Accordingly, Al and Cr define a marked increase, while Si shows a more subdued rise. On the other hand, the corresponding Mg and Mn contents show significantly lower values. The Ti amounts at this point correspond to the theoretical values assigned to this element in the composition of pseudorutile (Temple, 1966). This is well defined in the Chavara magnetic fractions.

The structural change undergone by mineral during its transformation from hexagonal ilmenite to the poorly crystalline pseudohexagonal pseudorutile is accompanied by compositional changes in the ionic state of iron and the titanium contents as well as the distribution of minor and trace elements, depending on their compatibility in the mineral structure. While Mn and Mg leach out of the mineral structure during the alteration of ilmenite (Anand and Gilkes, 1984; Frost et al, 1983; Suresh Babu et al, 1994), Cr, Al and Si are generally seen to increase with advanced alteration, either by relative enrichment consequent to the loss of other elements present in the ilmenite lattice (Suresh Babu et al, 1994) or the adsorption from surrounding medium during the dissolution-reprecipitation process leading to the formation of leucoxene (Frost et al, 1983). The elements exhibit a reversing trend from the above discussed patterns towards the last fraction, but it may be noted that this particular crop represents a composite group containing all magnetic fractions that could be separated above 0.45A.

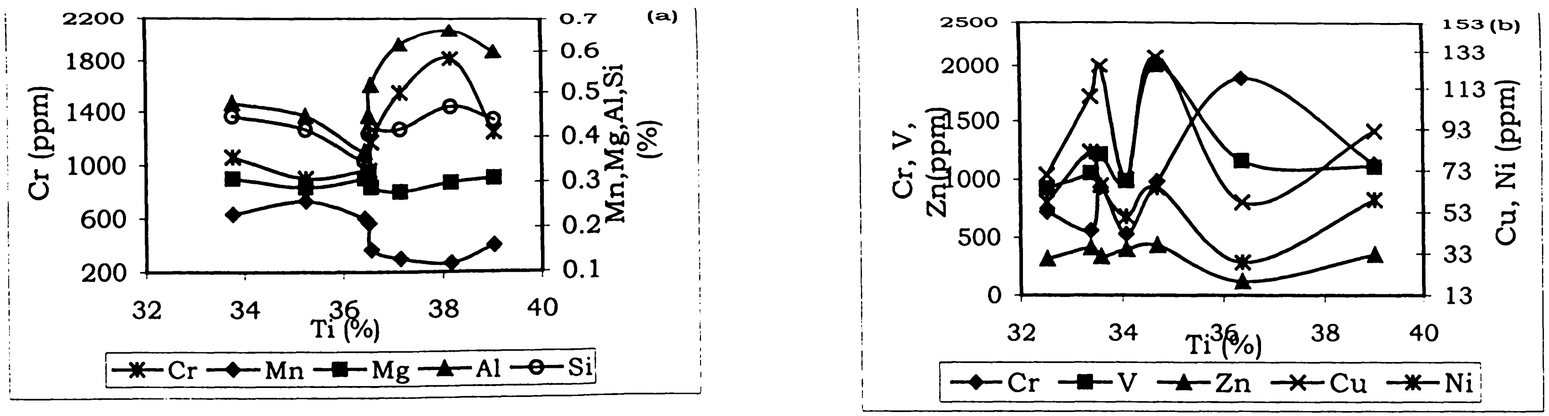


Fig 5.2.4(a-b). Variation of minor and trace elements in the magnetic fractions of bulk ilmenite from Chavara deposit with increasing Ti content.

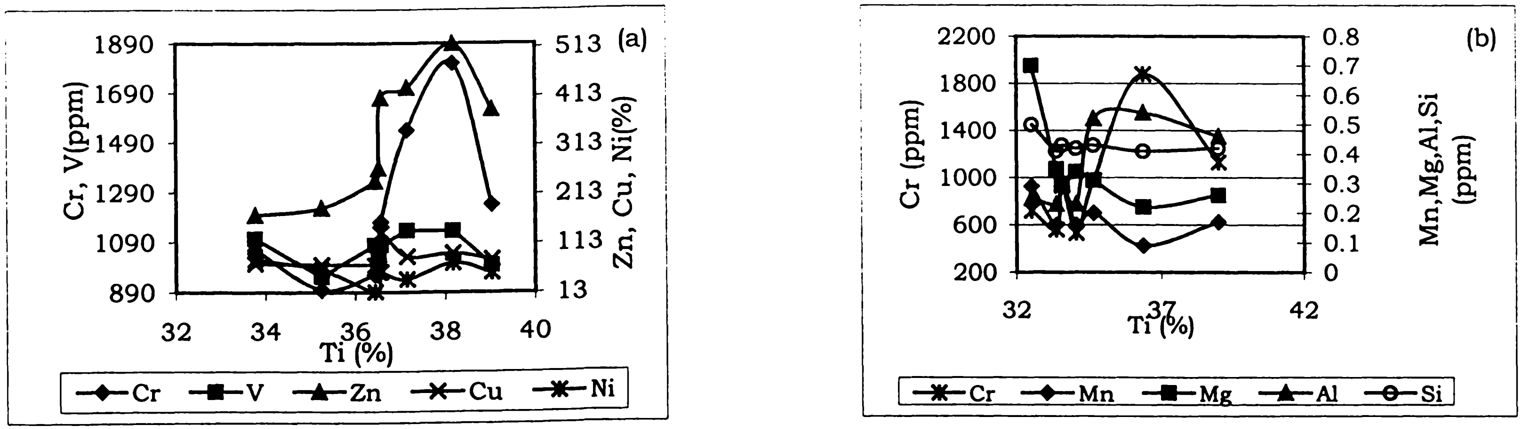


Fig 5.2.5 (a-b). Variation of minor and trace elements in the magnetic fractions of bulk ilmenite from Manavalakurichi deposit with increasing Ti content

In Manavalakurichi, the above plot reveals another interesting feature (Fig. 5.2.5 a-b). The abrupt and noticeable variation is observed corresponding to the stochiometric pseudorutile composition. But the more prominent variation of the elemental distribution takes place near the Ti content of around 34%. This composition corresponds to the titanium composition of the phase, pseudoilmenite (Chaudhuri and Newesley, 1990). The patterns of the compositional trends indicate that major structural changes are likely associated with the formation of this phase. Unlike pseudorutile, this phase has not been identified as a separate mineral. However, the very notable variation in the concentration of elements calls for more investigations on the structural aspects of this phase. The difference in the compositional trends of the ilmenite samples of the two deposits again point to the differential weathering suffered by them. The possible difference in the geochemical environment as discussed would also influence the leaching patterns of elements in the two deposits. Al and Zn exhibit a decreasing tendency with advanced alteration in MK, contrary to the patterns shown in CH ilmenite. The leaching and interrelationship of the elements are further discussed later in the light of the cluster analysis of the chemical data.

The chemical data of the magnetic fractions where subjected to the method of cluster analysis to understand better the interrelationship of the elements with alteration (Table 5.2.3 and 4). This method of statistical investigation is useful, when the correlation of a large number of variables have to be taken up. The inter relationship between the elements were not considered when the significane is less than ±0.5. As revealed by the various mineralogical and chemical analyses on ilmenite discussed so far, the Manavalakurichi deposit is found to be relatively less altered than the Chavara deposit. Hence, the results of the cluster analysis on the crops of ilmenite from this deposit are first attempted.

The most striking is the relationship between the ferrous and the ferric ions in the fractions. They exhibit a very high negative correlation with r

Table 5.2.3 Interrelationship between the elements in the magnetic fractions of ilmenite from the Manavalakurichi.

| | Fe$^{2+}$ | Fe$^{3+}$ | Ti | Mn | Mg | Al | Si | Cr | V | Zn | Cu | Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fe$^{2+}$ | 1.000 | | | | | | | | | | | |
| Fe$^{3+}$ | -.959 | 1.000 | | | | | | | | | | |
| Ti | -.901 | .749 | 1.000 | | | | | | | | | |
| Mn | .371 | -.247 | -.542 | 1.000 | | | | | | | | |
| Mg | .542 | -.434 | -.619 | .638 | 1.000 | | | | | | | |
| Al | -.873 | .922 | .691 | -.45 | -.547 | 1.000 | | | | | | |
| Si | .287 | -.144 | -.474 | .731 | .939 | -.32 | 1.000 | | | | | |
| Cr | -.791 | .857 | .589 | -.48 | -.486 | .83 | -.284 | 1.000 | | | | |
| V | -.282 | .396 | .084 | -.01 | -.327 | .615 | -.183 | .179 | 1.000 | | | |
| Zn | .462 | -.541 | -.280 | .35 | .153 | -.425 | .033 | .846 | .286 | 1.000 | | |
| Cu | .113 | -.061 | -.151 | .406 | -.216 | .044 | -.170 | -.294 | .645 | .625 | 1.000 | |
| Ni | .549 | -.576 | -.374 | .452 | .197 | -.492 | -.051 | -.739 | .134 | .817 | .745 | 1.000 |

Table 5.2.4 Interrelationship between the elements in the magnetic fractions of ilmenite from the Chavara.

| | Fe$^{2+}$ | Fe$^{3+}$ | Ti | Mn | Mg | Al | Si | Cr | V | Zn | Cu | Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fe$^{2+}$ | 1.000 | | | | | | | | | | | |
| Fe$^{3+}$ | .022 | 1.000 | | | | | | | | | | |
| Ti | -.677 | -.660 | 1.000 | | | | | | | | | |
| Mn | .646 | .234 | -.728 | 1.000 | | | | | | | | |
| Mg | .223 | -.434 | -.030 | .358 | 1.000 | | | | | | | |
| Al | -.901 | .080 | .620 | -.850 | -.399 | 1.000 | | | | | | |
| Si | -.710 | .421 | .132 | -.400 | -.127 | .753 | 1.000 | | | | | |
| Cr | -727 | .131 | .576 | -.880 | -.387 | .904 | .584 | 1.000 | | | | |
| V | -.088 | .234 | .039 | -.608 | -.212 | .399 | .167 | .665 | 1.000 | | | |
| Zn | -.671 | -.247 | .793 | -.973 | -.374 | 847 | .409 | .886 | .494 | 1.000 | | |
| Cu | -.187 | -.063 | .249 | -.617 | -.520 | .409 | .235 | .382 | .324 | .613 | 1.000 | |
| Ni | -.198 | .568 | -.358 | .117 | .242 | .190 | .749 | .150 | .097 | -.105 | .009 | 1.000 |

value of –0.96. The alteration in ilmenite is initialized by the transformation of ferrous into ferric form by oxidation (Temple, 1966; Grey and Reid, 1975). This process is very active in the Manavalakurichi ilmenite and points to the less advanced state of weathering and leaching. The marginal positive correlation of the elements like Mg and Ni with ferrous iron indicates that these elements may occupy similar structural sites in the lattice structure and slightly mobilized by the oxidation of ferrous ions. Al and Cr have been reported as stable elements known for their immobility. This is brought out by their strong correlation with $Fe^{3+}$. Their enrichment does not progress during the mature state of weathering at rates as appreciable as in the initial stages, as indicated by their depleted relation to Ti enrichment. The oxidation of ferrous iron to the ferric state seems to be very significant than the leaching of the latter from the mineral structure, as indicated by its positive relationship with Ti. Mn is slightly negatively correlated with Ti which shows a slight depletion with alteration. Zn is leached out of the structure in a marginal way as shown by their feebly inversely proportional bearing with $Fe^{3+}$. Mn and Mg are well known for their strong mobility (Morad and Aldahan, 1986; Mucke and Chaudhuri, 1991). The probable reasons for the deviant behaviour in the Manavalakurichi ilmenite have been discussed in the previous sections of this chapter (5.1.2).

The fractions of the Chavara ilmenite exhibit a marked difference from the magnetic splits of the Manavalakurichi sample in the insignificant correlation between the ferrous and ferric ions ($r= 0.02$). The considerable negative bearing of both ferrous and ferric ions with Ti indicates that the leaching of iron is the main phase of alteration taking place in Chavara. Al and Cr are mobilized by the oxidation of ferrous ions than by the enrichment of Ti. These elements are reported to be enriched even after the culmination of the leaching process (Chernet, 1999). Si exhibits a pattern of increase with alteration. Zn, which is known for its mobility presents a positive relationship with Ti. Probably, as seen in the

Table 5.2.5. Distribution of minor and trace elements in the IRE factory graded samples of ilmenite

| Sample No. | IRE graded sample of ilmenite | Content (%) | | | Content (ppm) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Si | Mg | Al | Mn | Cr | V | Zn | Cu | Ni |
| Ilmenite | IRE1 | 0.23 | 0.11 | 0.48 | 1546 | 1260 | 1084 | 701 | 53 | 124 |
| Rutile | IRE2 | 0.39 | 0.10 | 0.28 | 63 | 1340 | 4245 | 244 | 45 | 84 |
| | IRE3 | 0.50 | 0.11 | 0.19 | 66 | 1500 | 4000 | 152 | 46 | 103 |
| | IRE4 | 0.15 | 0.02 | 0.28 | 38 | 1187 | 2453 | 167 | 40 | 138 |
| Leucoxene | IRE5 | 0.50 | 0.05 | 1.16 | 90 | 2040 | 4430 | 326 | 64 | 109 |
| | IRE6 | 0.50 | 0.07 | 0.49 | 103 | 1920 | 5280 | 168 | 53 | 116 |
| | IRE7 | 0.15 | 0.05 | 1.1 | 142 | 1702 | 2164 | 171 | 61 | 133 |

chemical data, this element may already has reached the base level of leaching out of the mineral structure and thus is selectively enriched with respect to the other elements. Ni is being enriched in Chavara ilmenite, unlike in Manavalakurichi. Mg is found to present a more or less similar content through out in the magnetic fractions.

### 5.2.2.2 IRE factory graded samples of ilmenite:

The chemical analysis of the seven grades of ilmenite were carried out (Table 5.2.5). Since the various grades show sharp difference in their iron contents, such an analysis gives an overview of the patterns of elemental distribution in the alteration in ilmenite.

The concentrations of Mn and Zn decrease from ilmenite to rutile. Al, Cr and V are enriched from IRE1 to IRE7, while in rutile they are slightly depleted. In the fractions of IRE1, the ilmenite strikes a very high Mn content (1546 ppm). Among the rutile grades, IRE4 shows a notable difference from IRE 2 and IRE3 in their lower concentrations of Mn (38 ppm), Mg (0.02%), Si (0.15%), Cr (1187 ppm) and V (2453 ppm). Titanium oxide contents indicate that this is the most altered among the seven samples. Among the leucoxene samples, IRE 7 is distinguished by low values for Si (0.15%), Cr (1702 ppm) and V (2164 ppm). It is seen that even among the grades IRE 2- 4, which represent the final stages of ilmenite alteration, the elemental distribution exhibit significant difference in their concentrations.

### 5.2.3 Ilmenite samples from laterite

The chemical behaviour during lateritisation is very unique due to the characteristic geochemical environment of its formation. In this condition of oxidizing set up and pH (about 9), the response of elements to weathering of ilmenite in laterite is also possibly unique to this particular environment. Even though lateritisation is a relative operation in that the degree of this process undergone at each sampling location varies depending on the favourable conditions of formation, some discernable trends could be delineated. The samples from laterites over khondalite and charnockites show different patterns of geochemical distribution.

In general, it could be noted from Table 5.2.6 and Fig 5.2.6 (a-b) that the ilmenite from the laterite samples over khondalitic terrain shows a higher values for Mg, Al, V, Zn and Cu. The discrimination based on the content of Mg is the most striking with a significant difference between the contents in ilmenite samples from khondalite and charnockite provenance. While in the former this metal ranges from 0.29 to 0.51 % with an average value of 0.39%, in 'charnockite' ilmenite it ranges from 0.1 to 0.14% (average value = 0.12%). The Ni content at an average of 28 ppm, on the other hand, is lower for the ilmenite of this parentage than that with charnockite provenance (57 ppm). Mn shows a depleted value for the charnockitic ilmenite, except for the sample L1. The other elements do not show any significant trend. The sample L13 exhibits a different distribution of the trace elements, from the other samples of crystalline rock origin. Accordingly, this sample which owes its origin to the cordierite gneiss occurrence near the northern extremity of the study area, has a higher content of Mn, Al, V and lower content of Mg, Si and Zn. Sukumaran and Nambiar (1994) argued that ilmenite from basic rocks would contain high amounts of Cr, V and Ni than those from felsic rocks. But this observation is in contrary to the work of Grigsby (1992). The observations from laterite ilmenite in this work, too support Grigsby rather than the former authors. Similarly, Bhattacharya et al (1997) opined that the provenance of the southwest coastal placers should be attributed basic rocks like gabbro/diorite gneisses and not to the rocks of the khondalite-charnockite suite. They based their view on the low Mn/Mg ratios exhibited by the ilmenite of the coastal placers, which are characteristic of a basic rock provenance. But the chemical data of ilmenite from ferrogabbro published by Deer et al (1978) shows a high value of 4.6 for Mn/Mg ratio.

Table 5.2.6 Distribution of minor and trace elements in ilmenite samples from laterite

| terite imple | Likely provenance | Content (%) | | | | Content (ppm) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Mn | Mg | Al | Si | Cr | V | Zn | Cu | Ni |
| L1 | *CH | 2269 | 0.12 | 0.3 | 0.38 | 850 | 1275 | 232 | 60 | 62 |
| L2 | *SSt | 1266 | 0.11 | 0.39 | 0.39 | 380 | 838 | 78 | 57 | 62 |
| L3 | CH | 1053 | 0.11 | 0.21 | 0.15 | 250 | 647 | 340 | 47 | 75 |
| L4 | *KH | 1357 | 0.39 | 0.35 | 0.36 | 400 | 1286 | 421 | 53 | 10 |
| L5 | KH | 962 | 0.4 | 0.37 | 0.43 | 490 | 1139 | 570 | 77 | 30 |
| L6 | KH | 1388 | 0.29 | 0.31 | 0.39 | 730 | 1246 | 315 | 70 | 41 |
| L7 | KH | 781 | 0.36 | 0.58 | 0.32 | 540 | 1076 | 680 | 80 | 18 |
| L8 | KH | 826 | 0.51 | 0.44 | 0.34 | 580 | 1127 | 609 | 55 | 41 |
| L9 | CH | 1099 | 0.1 | 0.37 | 0.4 | 300 | 952 | 230 | 52 | 41 |
| .10 | CH | 1146 | 0.14 | 0.31 | 0.49 | 270 | 950 | 637 | 60 | 62 |
| .11 | SSt | 1674 | 0.11 | 0.51 | 0.07 | 1270 | 1551 | 104 | 85 | 49 |
| .12 | KH | 1068 | 0.36 | 0.89 | 0.45 | 480 | 870 | 549 | 76 | 29 |
| .13 | KH | 2685 | 0.03 | 0.87 | 0.15 | 401 | 1763 | 190 | 52 | 40 |

*CH –Charnockite *SSt –Tertiary sand stone *KH -khondalite

Table 5.2.7 Distribution of minor and trace elements in the ilmenite samples from Tertiary sandstone and the Teri deposits

| | Content (%) | | | | Content (ppm) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sand Stone | Mg | Mn | Al | Si | Cr | V | Zn | Cu | Ni |
| S1 | 0.11 | 0.14 | 0.41 | 0.41 | 770 | 1025 | 143 | 56 | 20 |
| S2 | 0.16 | 0.1 | 0.54 | 0.19 | 601 | 1076 | 364 | 47 | 133 |
| S2a | 0.22 | 0.26 | 0.42 | 0.38 | 710 | 1055 | 271 | 62 | 30 |
| S3 | 0.08 | 0.26 | 1.05 | 0.45 | 1110 | 1351 | 418 | 987 | 41 |
| S4 | 0.12 | 0.16 | 0.49 | 0.11 | 420 | 1668 | 193 | 61 | 70 |
| S5 | 0.16 | 0.15 | 0.35 | 0.06 | 660 | 1385 | 120 | 61 | 40 |
| Teri | | | | | | | | | |
| T1 | 0.32 | 0.24 | 0.32 | 0.32 | 550 | 1176 | 405 | 62 | 50 |
| T2 | 0.38 | 0.22 | 0.19 | 0.38 | 390 | 950 | 268 | 52 | 41 |

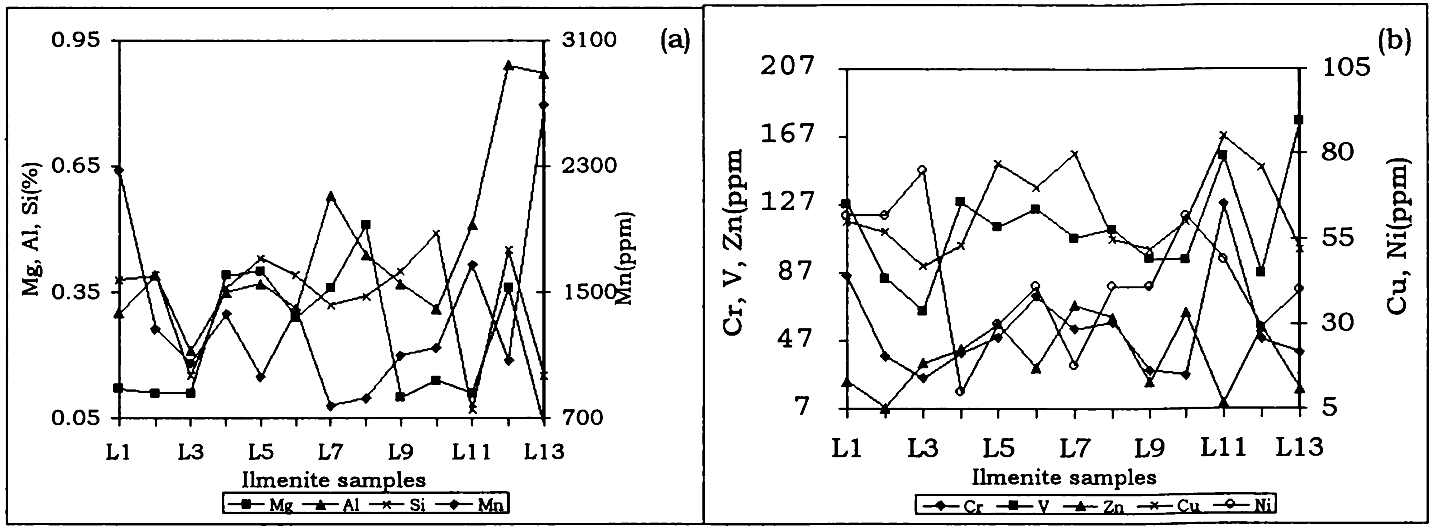


**Fig 5.2.6(a-b). Variation of minor and trace elements in the ilmenite samples from laterite.**

The two samples from the laterite over the Tertiary sedimentary formations show a deviation from those of the crystalline parentage and among themselves, reflecting their major element chemistry. While the sample L2 presents a similarity with the charnockite derived ilmenite in its Mg, Cr, V contents, the Zn content is very lower than the crystalline derived ilmenite. The L11, the sample from the laterite over the type section of the Tertiaries at Warkkallai presents a different picture. Higher Mn, Al, Cr, V, Cu and lower Si, Zn (than the crystalline ilmenite) characterizes this sample.

The difference in the trends shown by the laterite samples are more striking when the inter relationship of the trace elements are taken into account. The trace elemental contents of ilmenite from laterite samples derived over crystalline rocks are traced against ferrous iron to reveal the behaviour of elements with oxidation and consequent alteration in ilmenite (Fig. 5.2.7, a-b). Only plots showing a considerable correlation of r= ±0.5 or greater (or lesser when r = -0.5) are taken into account in this work. In the case of laterite samples, V and Cr are seen to show a marked negative correlation. These elements are known for their relative immobility and their concentrations increase with progressive oxidation of ferrous iron. However, silicon, which is generally considered to be one of the more immobile elements show a considerable positive correlation (r= 0.77), with ferrous iron. This is accounted by the unique phenomenon of the leaching of this element during laterite forming processes.

When the Mg values are plotted against the ferrous content, it could be seen that the sample plots fall in two clusters (Fig. 5.2.8). Other plots do not exhibit any such sharp discriminatory feature. While the khondalite derived samples fall in the upper field, the charnockite derived ilmenite define the lower cluster. In this plot the samples L11 and L13 form isolated points away from the two main clusters. While the former is the

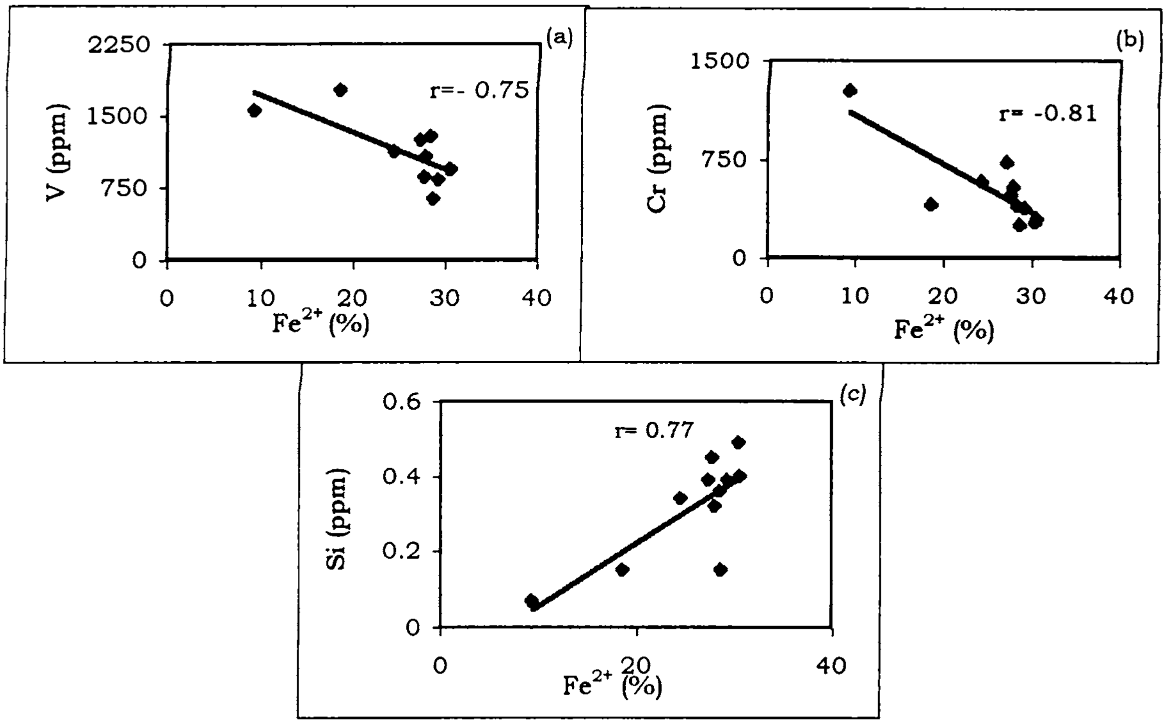


Fig 5.2.7(a-c). Correlation between a) V, b) Cr and c) Si and ferrous Iron content in ilmenite samples from laterite.

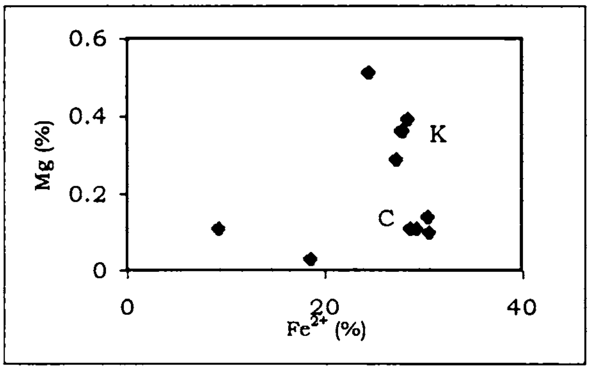


Fig 5.2.8. Variation of Magnesium (Mg) contents with the ferrous content in ilmenite. Note the distinctive separation between ilmenite from lateritised khondalite (KH) and charnockite (CH)

sandstone derived laterite sample, the latter forms the ilmenite from the lateritised corderite gneiss. This behaviour is in tune with their chemistry as observed above. The charnockite originated L1 also fall in a horizontally different position from the other samples of similar origin.

The geochemical pattern of the laterite ilmenite points to the differing chemistry of the ilmenite, based on the parent rocks. Though a general trend in weathering could be worked out, this is not by any means conclusive on the alteration studies of ilmenite since the chemistry of the ilmenite of the provenance rocks is not known. But still, since the crystalline rocks of the study area have been affected by lateritisation, the chemistry of ilmenite samples from this particular setup, points to the difference in the chemistry of ilmenite in the country rocks. Though it has been shown that ilmenite is affected by diagenetic processes (Anand and Gilkes, 1984; Morad and Aldahan, 1982; 1986), data on work of similar lines in the southwest of India is insufficient to delineate the chemical signatures of alteration in this environment.

Though L2 and L11, belong to near by locations from the same formations, the chemistry shown is different. This is echoed by the distribution of the major elements. Though the increase in Cr (1270 ppm), V (1551 ppm) and, Al (0.51 %) could indicate the higher alteration of the L11 sample (Anand and Gilkes, 1984; Morad and Aldahan, 1986), there could be other reasons like the difference in the nature and provenance of the original sediments and the degree of lateritisation undergone. This observation is suggested based on the depleted contents of elements like Si (0.07 %) in L11 in contrast to the higher content (0.39%) in L2 in the samples, which is reported in the literature to be enriched with progressive alteration. Similarly, higher values of Mn and Zn in L11, is not expected of a highly altered ilmenite sample. These deviations from the expected lines of behaviour, could be due to the difference in the pattern of alteration of ilmenite in this particular geologic setup.

The laterite samples show a different chemical distribution of the elements, which is not always along predicted trends, when sequential variation in elemental content is expected. Thus, Al, Cr, V and Si are expected to show lower values in ilmenite from laterite than from that in beach. This should be true, when the high iron values (especially ferrous) are observed, indicating limited alteration. But the elemental distribution follows a different pattern. The lateritisation progresses along around a pH of around 9 and in oxidizing conditions as attested by the formation of oxides of iron (Mason and Moore, 1985). The pattern of their leaching in the mineral is given below. The explanation of the leaching patterns of elements in this report is based on the work of Goldschimdt (1962) and Brookins (1988).

The Eh-pH diagrams indicate that Mn is not removed by solution in the oxidizing and the particular pH associated with lateritisation. This could account for its concentration, in spite of its reputation as an easily mobile element in beach ilmenite. Magnesium is known to be soluble in acidic and mildly basic solutions. Thus during lateritisation it is mostly leached out. Al is reputed to be stable in all environments under natural conditions. The removal of silica is characteristic of laterite forming environments. Cr, like Al, is known to be very stable in nature, making it very unlikely to be removed by solution activity. V is known to be concentrated during the formation of laterites (Goldschmidt, 1962). The reports of the very high mobility of zinc are offset by its concentration in laterite setup, where its content is not radically reduced in the beach environment. Cu is known to be generally mobile in basic conditions in nature. Cu and Ni do not exhibit any particular trend of concentrations. Their low contents discourage the delineation of any significant pattern in the various alteration setups.

### 5.2.4 Ilmenite from the Tertiary sedimentary rocks

The six ilmenite samples from five locations of the Tertiary sedimentary formation of the southwest coast show a general absence of uniformity in the chemical composition (Table 5.2.7). The major element chemistry and mineralogical analysis point to wide variation in the alteration of ilmenite in these samples (Fig. 5.2.9, a-c). The sample S1 is in a very advanced state of alteration of 'Pseudorutile' stage while the S4 and 5 samples fall in the least altered state of 'Ferrian ilmenite'. The other samples fall into intermediate position between the above two stages. The varying composition is reflected in the trace elemental distribution. The stark difference within a single geologic formation among samples of close proximity has been suggested in the preceding chapters as due to the provenance of sediments constituting the Tertiary formation and/or due to the variation in the diagenetic changes in different locations after the deposition of the sediments. Such observations have been reported in the sandstones of Sweden by Morad and Aldahan (1982, 1986). They have suggested the post depositional changes to be the main agent for the alteration of ilmenite. The ultimate alteration product has been identified as predominantly brookite, even though rutile and anatase are present. Our results, however, show only the presence of rutile. Such changes could be due to the diagenetic changes suffered by the mineral since proterozoic, while the Warkallai is relatively very younger. The high content of Al and Si could be ascribed to the precipitation of these elements in clays, which tend to accumulate in altered ilmenite grains (Frost et al, 1983; Morad and Aldahan, 1982, 1986).

The sample S1 from Karichal is the most altered of the field samples, exceeding even the beach ilmenite in its titanium content, certain observations are worth noting. The elemental distribution of minor and trace elements shows a deviant behaviour from the reported trace element chemistry of altered ilmenite grains (Fig. 5.2.9, a-c). Thus, considering its highly advanced weathered state, when compared to the other samples, the contents of Cr, Al, Si and V should be highest in this sample. But relatively high concentrations of these elements are reported

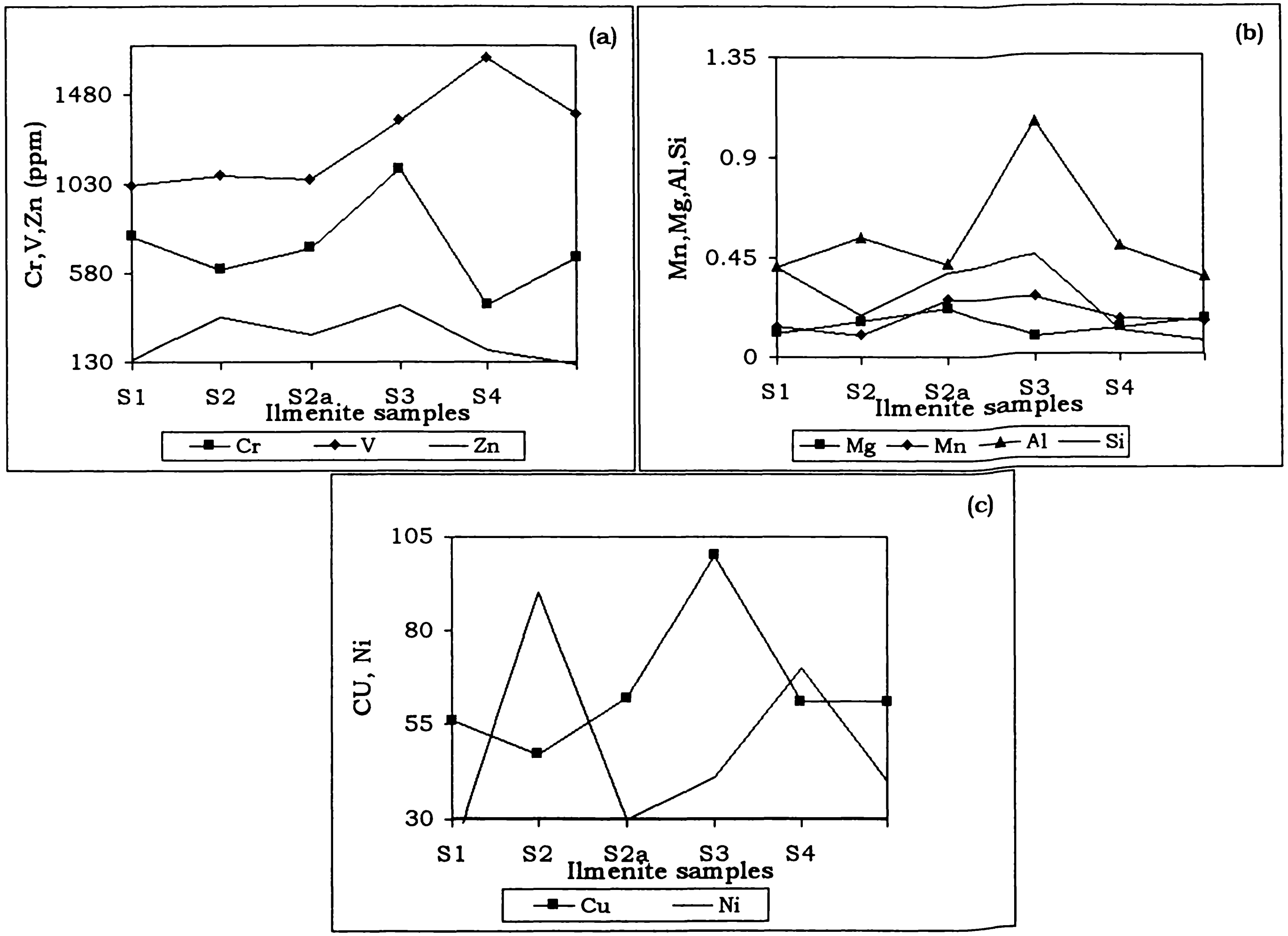


Fig 5.2.9(a-c). Variation of minor and trace elements in ilmenite samples from Tertiary sandstone.

in much less altered samples like S2 and S3 which are characterized by higher contents of Al. S2a and S3 exhibit high Cr values, while V content is lowest in sample S1. Similarly the reportedly mobile elements like Mn and Mg are enriched in almost all other samples irrespective of the alteration suffered. The above stated suggestion of difference in the provenance of the sediments and the nature of the diagenetic reactions may account for the chemical patterns. The geochemical environment of the Tertiary sedimentaries during its deposition and diagenesis could be the determining component in the weathering and leaching processes.

A similar anomalous character is shown by the S3 sample. The high ferrous content and lower titanium content attests to the limited alteration undergone by this sample. But low Mg (0.08%) and high values for Al (1.05%), Si (0.45%), Cr (1110 ppm) and V (1351 ppm) characterizes the mineral in this location.

The Thiruvallam cliff section shows significant variation in chemistry along their vertical profile (Fig. 5.2.10, a-b). The laterite part is the least weathered as indicated by the higher FeO content in ilmenite from that location. The Al, V, Cr, Ni and Cu variation is sympathetic with the titanium variation in the formation. Mn, Mg and Si exhibit an inverse relation. The elemental variation pattern, interestingly is more in tune with the accepted variation trends reported earlier.

The correlation of elements during alteration is traced as the correlation with ferrous iron in ilmenite (Fig. 5.2.11, a-b). Cu and V show positive relationship in the plots. V is very highly correlated with ferrous iron ($r = 0.95$). This element is known for its concentration in ilmenite with alteration. This unexpected behaviour could only be explained with due consideration with the chemical conditions prevailing in the sandstone body.

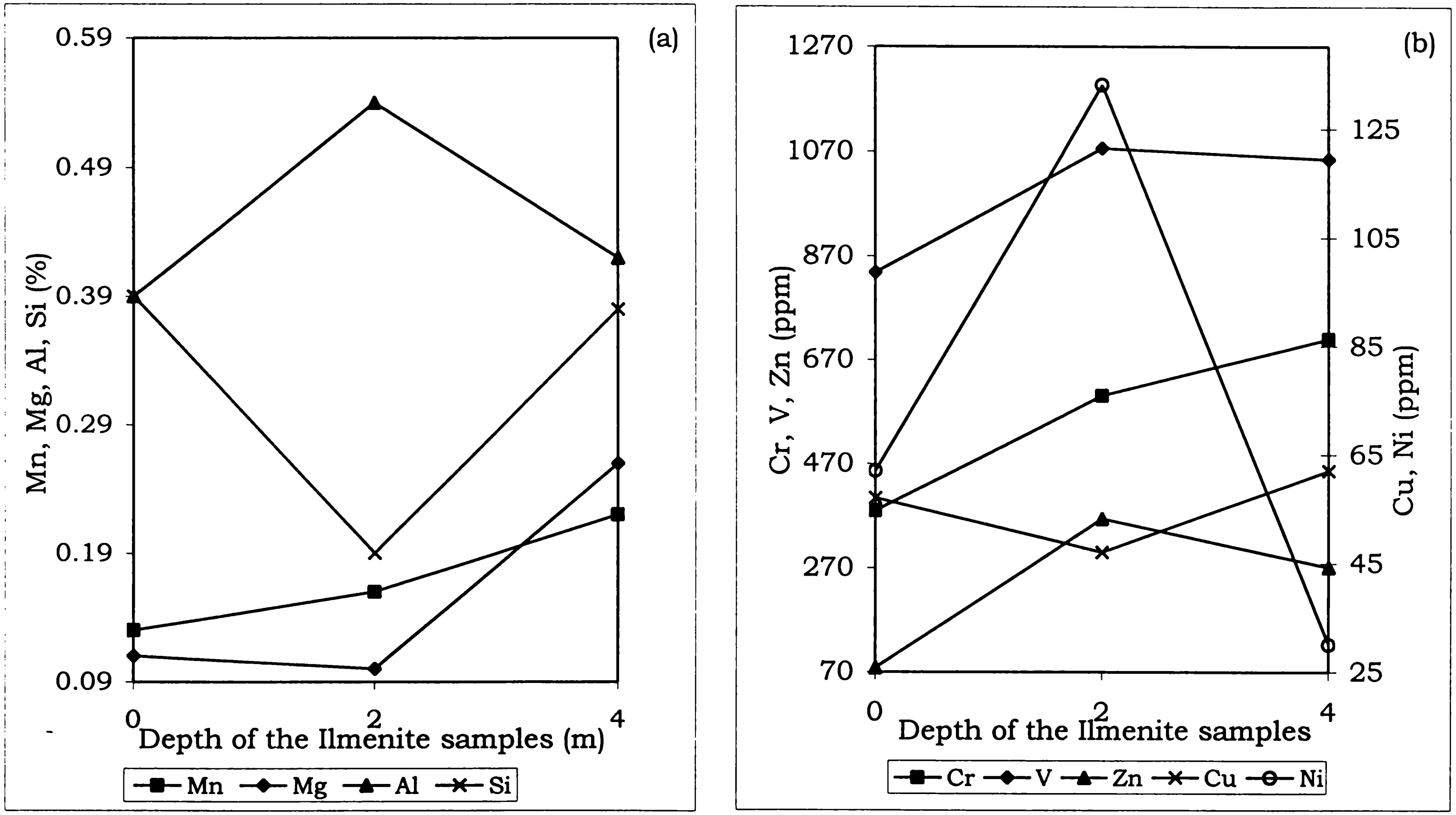


Fig 5.2.10(a-b). Variation of minor and trace elements from ilmenite samples along the vertical profile of the Tertiary sedimentary formation.

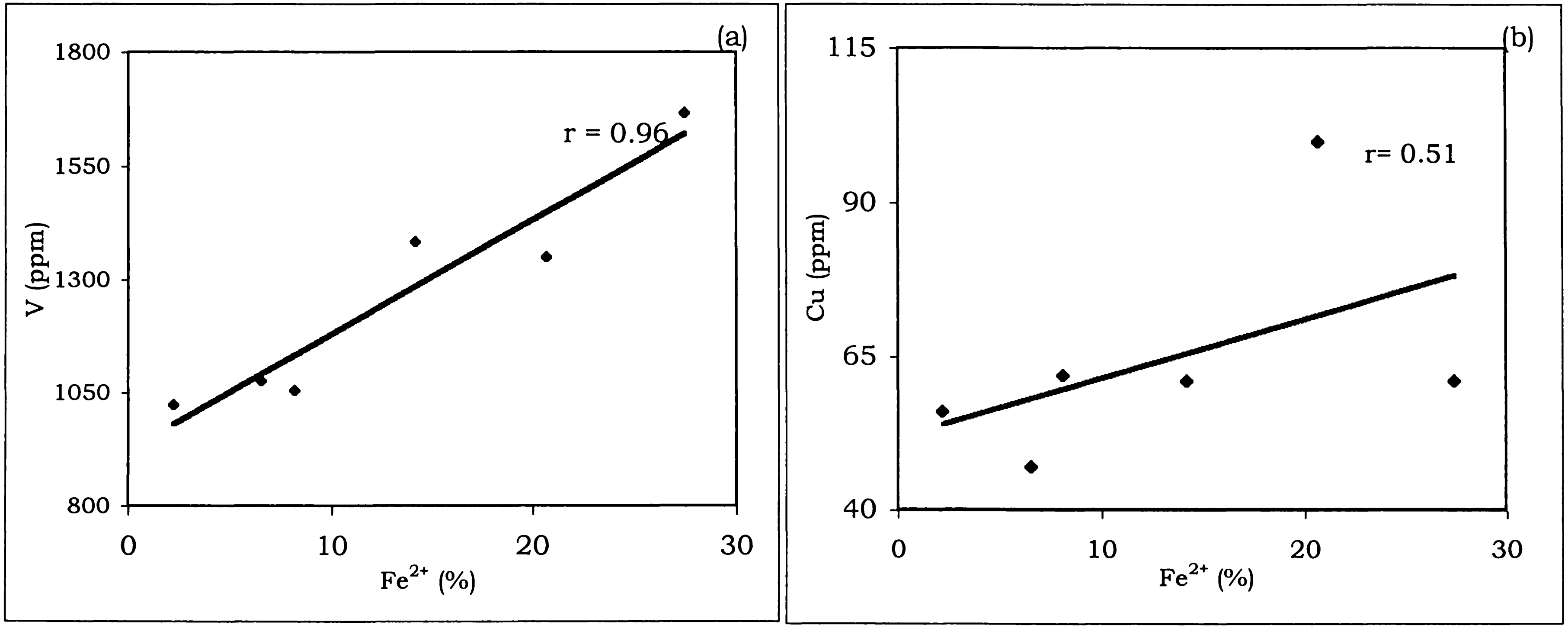


Fig 5.2.11(a-b). Correlation between a) V and b) Cu with ferrous content in ilmenite samples from the Tertiary sandstone.

The Eh-pH conditions of the Tertiary formations have not been well studied. The occurrence of peat in the Warkallai sandstone indicates a reducing environment of occurrence (Soman, 1997). Christ and Garrels (1965) state that peat is formed under acidic conditions. Thus the paucity of sufficient data compels one to generalize the geochemical environment and suggest a reducing and acidic setup for the Tertiary formations. This has to be treated with caution, since the environments must have changed continuously over the time of deposition and consolidation of the sediments, though reducing and acidic conditions may have been dominant.

Mn goes into solution in the ionic state under such environment, which may explain its depleted state when compared to that of the ilmenite in the beach placers. Mg too is leached out, which account for its lowest average value among the field samples. Al and Cr are usually stable in nature under all geochemical conditions. V exhibits the highest average value in the sedimentary ilmenite among all the field samples. The slight depletion of Si with respect to the laterite ilmenite could not be accounted for, but the general post-Warkallai age of the laterite and the limited alteration undergone by the ilmenite in this setup could be the reason for these decreased values of Si. Zn is less mobile under the present conditions and this is echoed in the general higher values for this element than in ilmenite samples from beaches.

### 5.2.5 Ilmenite from the Teri deposits

Samples were collected from the Teri sand deposits, which cover vast stretches of the immediate hinterland of Manavalakurichi area. The two samples analyzed exhibit considerable difference in their elemental contents, particularly for elements Al, Cr, V and Zn (Table 5.2.7).

### 5.2.6 Ilmenite from the rivers

The four rivers in the hinterland of the Chavara deposit vary in their runoff and discharge (Soman, 1997), the Kallada, being the longest and having the maximum discharge. The rivers, though relatively short with steep gradients, they show maturity in their final stages (Soman, 1997). However, this is not reflected in the chemistry of ilmenite, which exhibits a comparatively unaltered state.

A gradational distribution in the elemental contents downstream was not encountered reflecting the major element distribution (Table 5.2.8 and Fig. 5.2.12, a-g). This could be a function of the lithology of the country rocks through which they flow, the difference in the proportion of the different constituent rocks of the khondalite and charnockite suites and the laterites and the Tertiary sedimentary formation along their course and the control exerted by the tributary discharge. In fact, it has been observed that the ilmenite shows significant variation where the sample is collected from the area of confluence of tributary with the main stream.

The Kallada River exhibits a composition very different from the other rivers. Higher contents of Mg and Al, slightly enhanced quantities of V and Mn and lower values for zinc and copper differentiate this river from other fluvial systems (Table 5.2.8 and Fig. 5.2.12, a-g). The other three rivers show a similar compositional pattern, but subtle differences can be made out. The different patterns of enrichment in the drainage basins, though they flow through a terrain with similar petrology, suggest the importance of ilmenite chemistry constituent rock units of Khondalite and Charnockite suites of the hinterland and their contribution to the sediment flux of the streams. The geochemical behaviour of the elements varies in each drainage basin as shown in Fig. 5.2.13 (a-d). Such observations could be ascribed to the reasons discussed earlier.

Table 5.2.8 Distribution of minor and trace elements in rivers of the hinterland of Chavara and Manavalakurichi deposits

| Rivers | Content (%) | | | | Content (ppm) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Karamana | Mn | Mg | Al | Si | Cr | V | Zn | Cu | Ni |
| 1 | 0.11 | 0.28 | 0.23 | 0.42 | 430 | 899 | 401 | 74 | 50 |
| 2 | 0.08 | 0.38 | 0.57 | 0.36 | 390 | 1062 | 503 | 55 | 86 |
| 3 | 0.1 | 0.21 | 0.28 | 0.36 | 630 | 1081 | 670 | 77 | 40 |
| 4 | 0.01 | 0.29 | 0.36 | 0.42 | 760 | 1035 | 411 | 87 | 84 |
| 5 | 0.08 | 0.26 | 0.3 | 0.35 | 530 | 1039 | 405 | 68 | 15 |
| Vamanapuram | | | | | | | | | |
| 1 | 0.12 | 0.35 | 0.34 | 0.44 | 810 | 908 | 746 | 87 | 71 |
| 2 | 0.11 | 0.22 | 0.22 | 0.4 | 440 | 840 | 536 | 69 | 34 |
| 3 | 0.09 | 0.29 | 0.54 | 0.32 | 320 | 793 | 410 | 49 | 15 |
| 4 | 0.21 | 0.26 | 0.42 | 0.39 | 850 | 941 | 277 | 69 | 80 |
| 5 | 0.11 | 0.35 | 0.26 | 0.41 | 550 | 1053 | 505 | 75 | 68 |
| Ithikkara | | | | | | | | | |
| 1 | 0.1 | 0.2 | 0.43 | 0.5 | 550 | 729 | 399 | 68 | 64 |
| 2 | 0.08 | 0.46 | 0.55 | 0.35 | 600 | 1095 | 636 | 76 | 27 |
| 3 | 0.08 | 0.38 | 0.41 | 0.37 | 410 | 971 | 550 | 60 | 10 |
| 4 | 0.1 | 0.29 | 0.25 | 0.51 | 560 | 1020 | 544 | 87 | 49 |
| Kallada | | | | | | | | | |
| 1 | 0.25 | 0.36 | 0.67 | 0.35 | 540 | 1418 | 392 | 50 | 36 |
| 2 | 0.12 | 0.26 | 0.3 | 0.38 | 890 | 815 | 401 | 76 | 56 |
| 3 | 0.3 | 0.41 | 0.78 | 0.42 | 600 | 1396 | 386 | 59 | 50 |
| 4 | 0.09 | 0.44 | 0.46 | 0.43 | 440 | 1100 | 472 | 64 | 44 |
| 5 | 0.23 | 0.44 | 0.81 | 0.43 | 480 | 1042 | 449 | 63 | 26 |
| 6 | 0.26 | 0.38 | 0.62 | 0.35 | 500 | 1274 | 365 | 51 | 32 |
| 7 | 0.24 | 0.4 | 0.53 | 0.44 | 470 | 1215 | 384 | 55 | 30 |
| Valliyar | | | | | | | | | |
| 4 | 0.17 | 0.18 | 0.21 | 0.39 | 490 | 1047 | 350 | 57 | 33 |
| 5 | 0.21 | 0.26 | 0.28 | 0.31 | 770 | 1150 | 461 | 222 | 100 |

Table 5.2.9 Distribution of minor and trace elements in ilmenite samples from the Ashtamudi estuary

| Ashtamudi Estuary | Content (%) | | | | Content (ppm) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Mn | Mg | Al | Si | Cr | V | Zn | Cu | Ni |
| E1 | 0.19 | 0.11 | 0.49 | 0.1 | 994 | 1519 | 184 | 52 | 40 |
| E2 | 0.12 | 0.26 | 0.58 | 0.45 | 1510 | 1029 | 646 | 62 | 23 |
| E3 | 0.22 | 0.12 | 0.39 | 0.15 | 761 | 1368 | 201 | 94 | 79 |
| E4 | 0.21 | 0.34 | 0.7 | 0.39 | 600 | 974 | 586 | 106 | 66 |
| E5 | 0.22 | 0.26 | 0.53 | 0.38 | 950 | 980 | 276 | 79 | 74 |

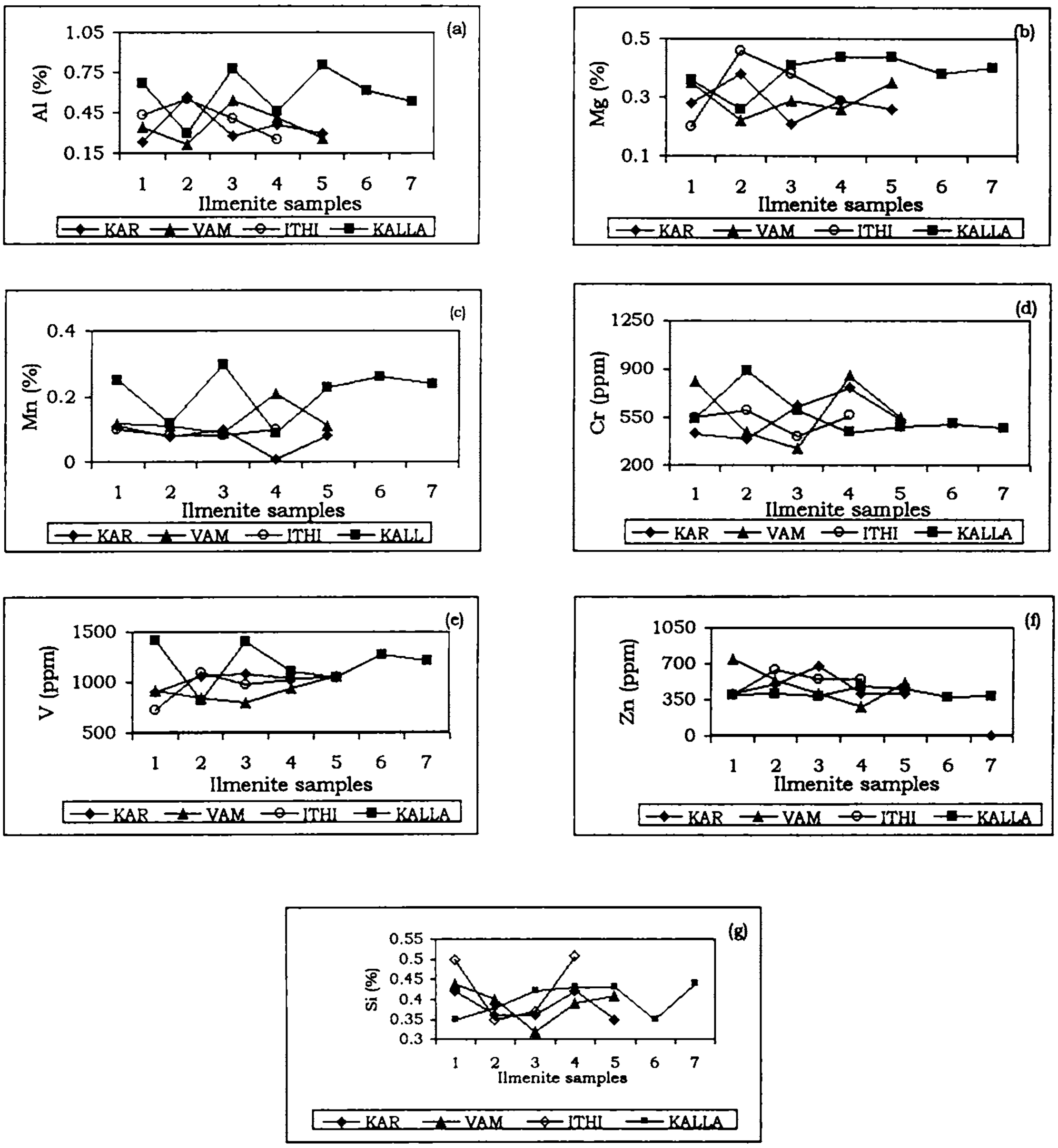


Fig 5.2.12(a-g). Distribution of minor elements in ilmenite samples from the rivers of the hinterland of the Chavara deposit

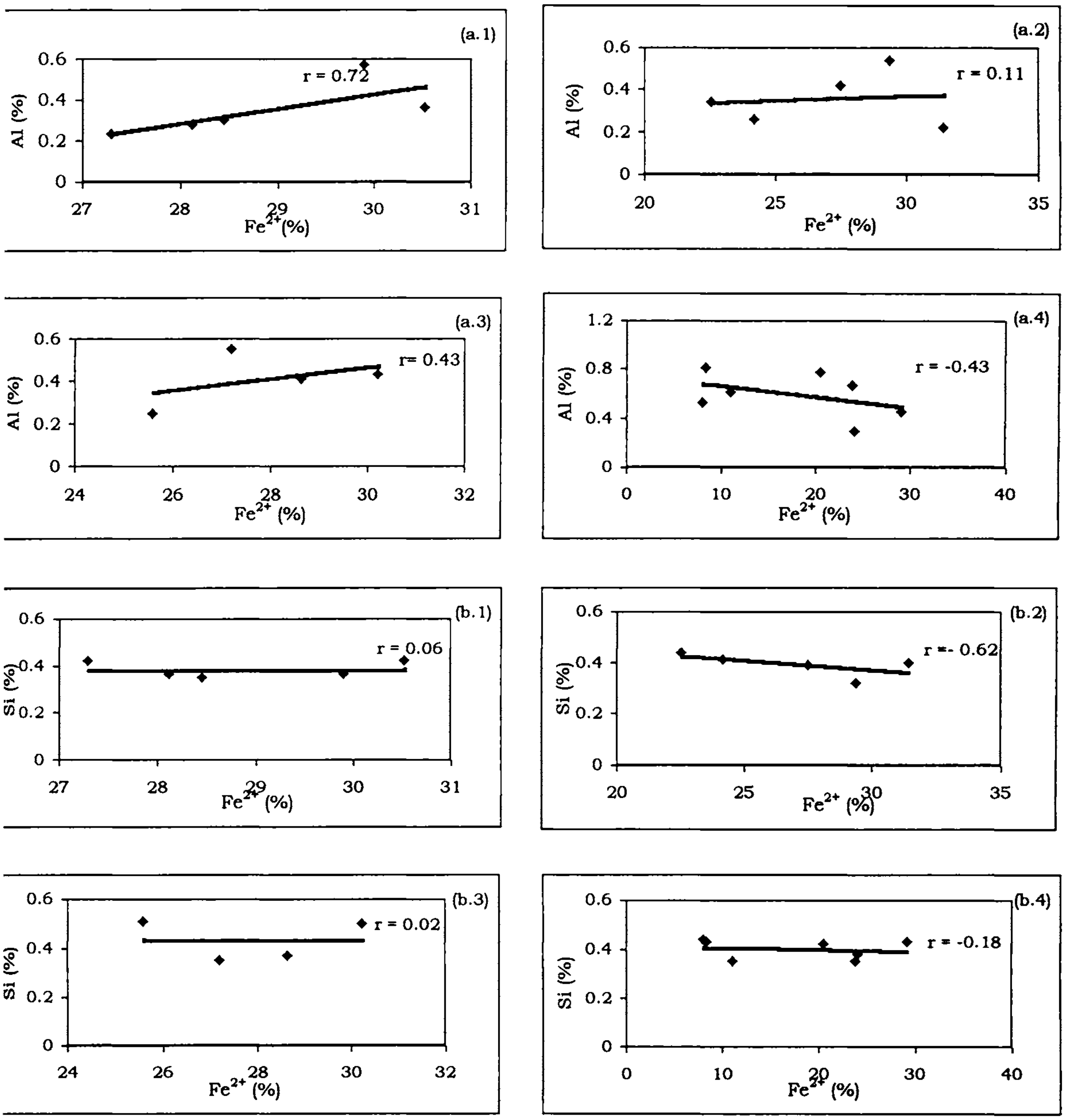


**Fig 5.2.13.(a-b). Variation of a) Al b) Si against ferrous contents in the ,**
**[1) Karamana river 2) Vamanapuram river c) Ithikkara river d) Kallada river**
**rivers of the hinderlands of Chavara area.**

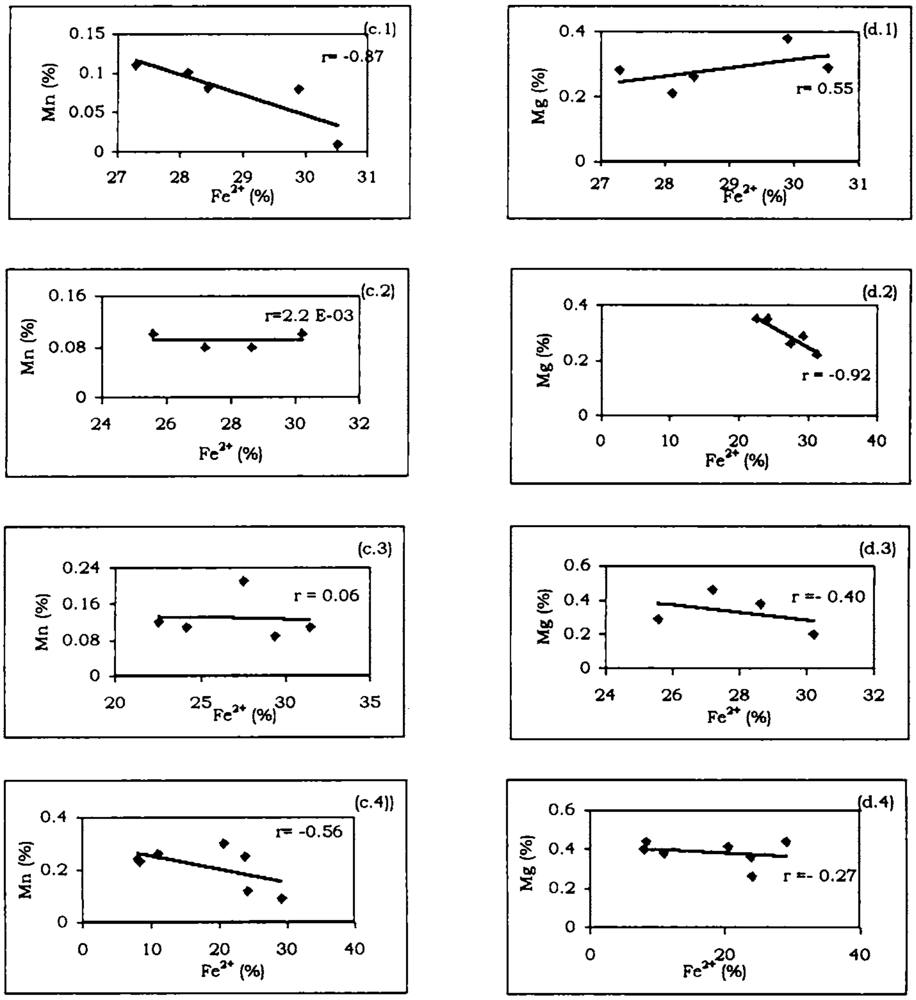


**Fig 5.2.13(c-d). Variation of c) Mn and d) Mg aginst ferrous contents in the, [1) Karamana river 2) Vamanapuram river c) Ithikkara river d) Kallada river] rivers of the hinterlands of Chavara area.**

Lithological variation in the Khondalite complex is suggested to be due to varying provenance and depositional conditions of the sediments, which were subsequently metamorphosed (Soman, 1997). In addition, the presence of intrusions of pyroxene granulites and calc granulites have been reported. The rivers Karamana, Vamanapuram and Ithikkara, flow through a terrain characterized by Khondalites and their migmatitised equivalents, with zones of charnockites and pyroxene granulites. Migmatitisation is more prominent in the Ithikkara drainage basin than in the more southern rivers. The Tertiary sedmentary formation of Warkkallai gain prominence towards the downstream of the rivers and this is more evident in the Ithikkara River. The Kallada flows through the Tenmala Shear zone, which divides the southern Khondalite-Migmatite complex from the northern Charnockite suite of rocks, in its upper reaches. In addition, some of the tributaries course through this region cutting across the lineaments. This region contains intercalations of calc granulites and corderite gneisses, which govern the nature of the sediment out by this riverine system. The ilmenite of the corderite gneiss indicates a genesis different in other rock types, as indicated by the presence of intergrowths of magnetite/maghaemite.

These factors contribute to the variation in the nature of ilmenite of this river when compared to the other rivers of the region. As seen in the chemistry of the ilmenite of sedimentary rocks, the composition of the minerals varies widely even among samples of close geographical proximity. The Tertiaries, is again a source of sediments for the streams and thus, can claim part of the parentage of the beach deposits. The laterites, which form another contributor to the river sediment input, manifest different trends depending on their origin from rocks of charnockite and khondalite rocks. The rivers carry sediments from the source rocks while at the same time eroding and transporting detritus along their way. Given the relatively short length and their high gradients and consequent erosive power, the sediments are prone to reach sea quickly and therefore the geochemical changes on the mineral, is more dominated by the nature of the sediment into the fluvial systems than factors like the Eh-pH conditions of the system.

Valliyar is the only significant fluvial system in the hinterland of the Manavalakurichi deposit. The trace elemental analysis was carried out on two samples, which are from the down stream portion of the river. The considerable difference in the chemistry of the samples indicates that the ilmenite from Valliyar has not reached chemical maturity, even at final stages of the fluvial system. The chemical analysis points to the supply of fresh material between the sampling locations or the relatively short length of the river. The difference in the chemical populations of the provenance could be due to the enhanced importance of the Teri sands towards the coastal line or the influx of material from the sea due to tidal movements.

### 5.2.7 Ilmenite from the Ashtamudi estuary

E4 and E5 represent ilmenite near the river and estuarine mouths respectively (Table 5.2.9; Fig. 5.2.14, a-b). The chemistry of this ample to a great extent is similar to the samples from Kallada and the beach ilmenite. The slight increase Zn and Cu in E4 than in ilmenite from the river is the only marked deviation in their similarity. Like the other geologic setups, the elemental distribution is not always along the reported leaching trends. Though E1 is the most altered, as shown by its Ti/(Ti+Fe) values, the contents of Cr (994 ppm) and Al (0.49%), very stable elements in through the alteration of ilmenite do not show expected values, when compared to relatively fresh E5. Similarly the Mn values do not exhibit much variation in the samples irrespective of the degree of alteration undergone. The characteristic elemental patterns could be due to the very nature of estuaries, where the mixing of riverine and marine sediments takes place with a difference in the degree of mixing from location to location. The leaching patterns of elements in the

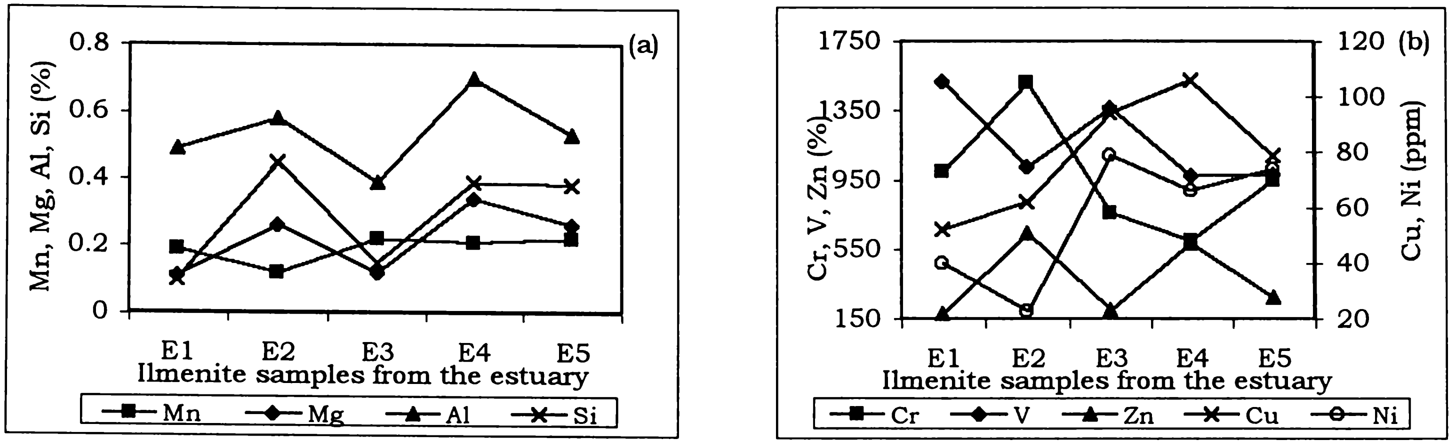


**Fig 5.2.14.(a-b). Distribution of minor and trace elements in the ilmenite samples from the Ashtamudi estuary**

reducing and slightly basic nature of the estuary may differ from the normal weathering models in beaches.

The relationship of the elements with increasing ferrous content is given in Fig. 5.2.15 (a-f). Positive correlation with ferrous content is established even for relatively immobile elements like Al. Elements like Mn, Cr and Zn show expected correlation patterns. The plots seem to be biased with the high ferrous content of the E4 sample.

The Ashtamudi estuary presents an average pH of 7.5 representing slightly alkaline conditions and reducing environment (Muralikrishna, 2000). In the sheltered parts of the estuary, where the scope of dilution is much less, the pH rises up to around 8.8. The distribution of the elements is worked out, wherever possible, by referring to the pH conditions of the area in which each location falls. Mn is leachable under acidic to slightly basic conditions under reducing conditions. But the relatively higher content of this element for E1, could be due to its possible pH nearing 9. The concentration of Mn is depleted with progressive alteration. Al is concentrated with progressive alteration due to its well-known immobility. Another indication for the higher pH of location of E1 is given by the Si contents which are depleted at basic condition of pH around 9. For the rest of the samples, the leaching patterns suggested in previous literature is more or less followed. Cr shows a more conventional behaviour in this environment. The rather high value of this element in E5 has already been discussed. The highest concentration of V is in E1 and the element behaves in line with the reported immobility of the element. Below a pH of about 7.5, zinc leaches out, which is indicated by the irregular distribution of this element in the estuary, where the pH ranges from 7.2 to 8.8. Even though the content of zinc in the most altered sample E1 is the least among the samples in the estuary, compared to the beach ilmenite, which is less altered, the zinc content is still higher. Cu and Zn are concentrated in this

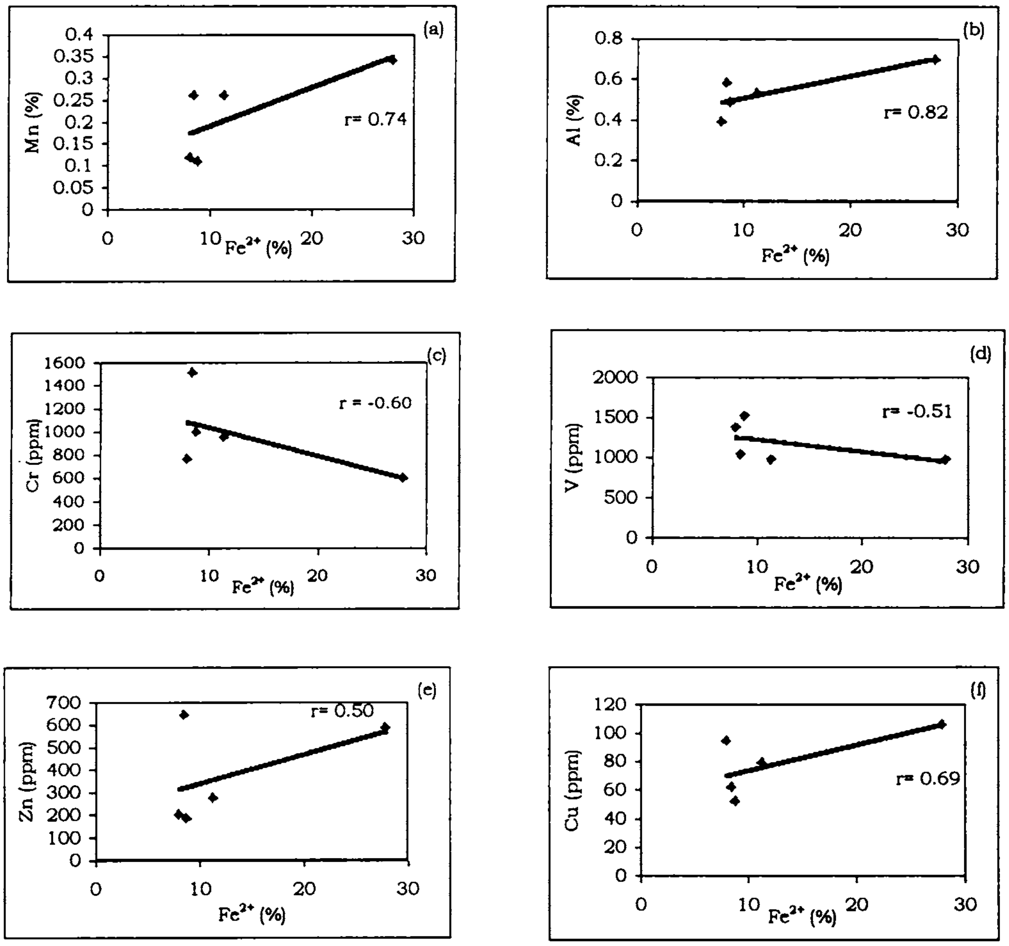


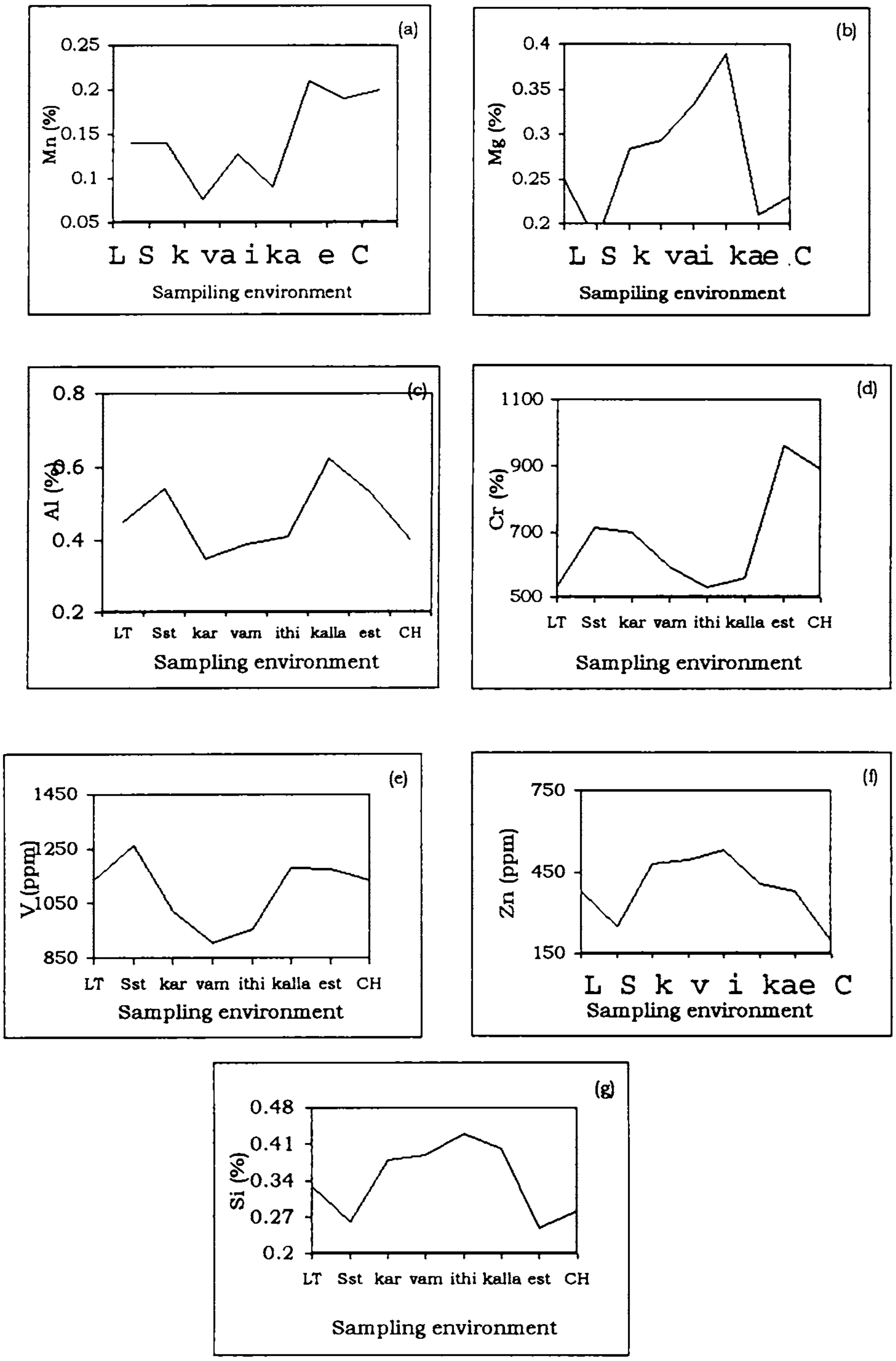
**Fig 5.2.15(a-f). Correlation between ferrous content and minor elements in the ilmenite samples from Asthamudi estuary.**

geochemical condition and the average values for these elements exceed those of the beach ilmenite.

The variation of average elemental concentrations in the different weathering environments of the hinterland to beach in the Chavara and Manavalakurichi was traced to obtain a synoptic view of the geochemical variation under different geological environments (Figs. 5.2.16, a-g & 5.2.17, a-g). This should not be taken as representing the progressive weathering in ilmenite taking place from source rocks, through different geological conditions in the hinterland to the beach. Such a process is not taking place as observed from the chemistry of the ilmenite samples from different environments. The elements of the ilmenite in the source rocks themselves show wide variation between samples from laterites and sedimentary formations, even between samples from lateritized charnockite and khondalite in their contents. In addition, the chemical distribution in each environment need not be along expected lines as discussed in the previous part of this section. The compositional dissimilarity with the hinterland ilmenite could also hint at the dominant role played by coastal processes.

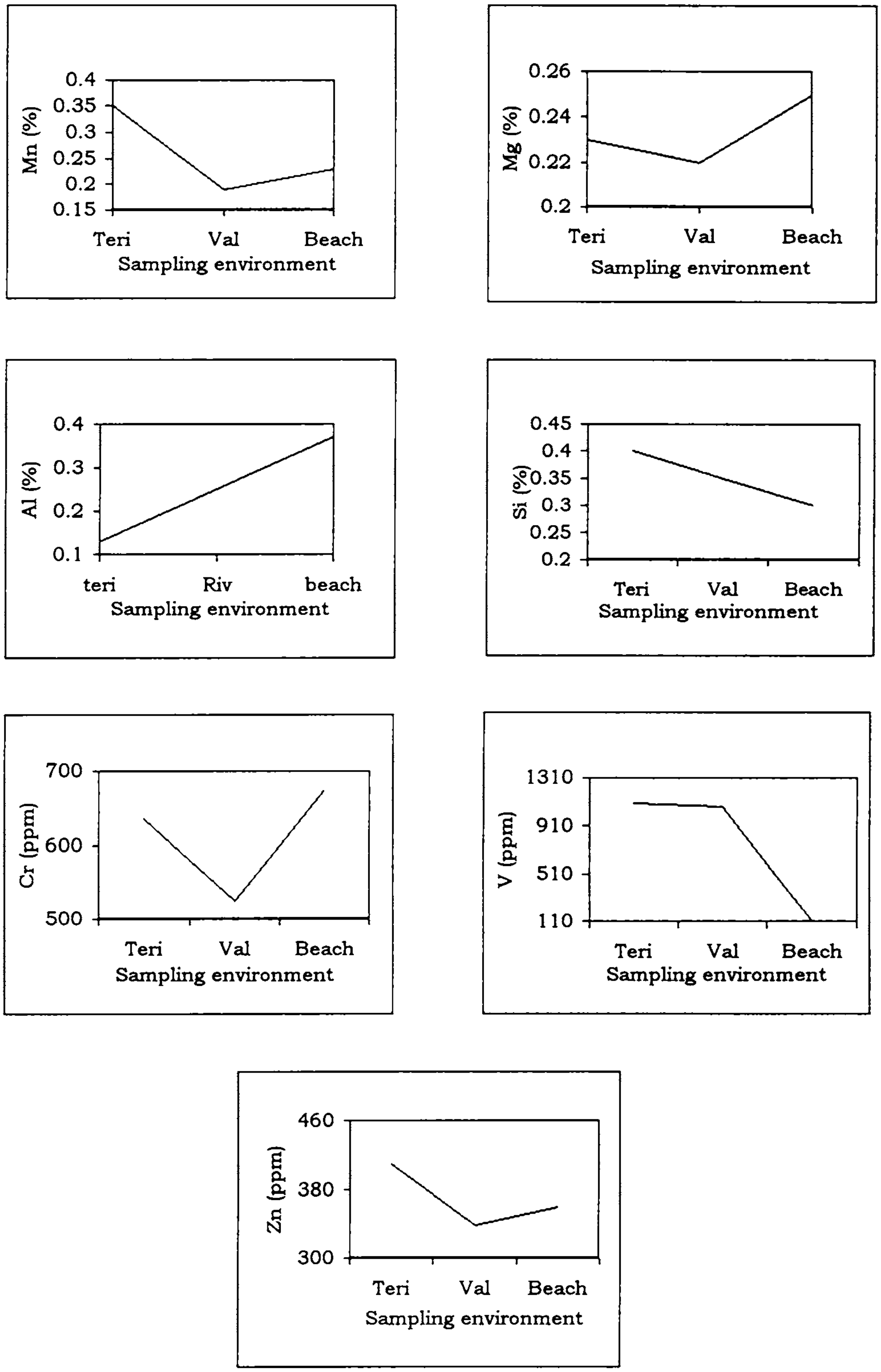
However, some definite trends could be observed from the above plots. The estuarine samples show maximum similarity to the beach ilmenite in Chavara. Such an affinity could be expected when the origin of estuary to the regression of the sea level and the present influence to the tidal influx is taken into account. Among the rivers of the hinterland, the southern rivers like Karamana, Vamanapuram and Ithikara show more similarity among themselves than with the Kallada river. This river which courses adjacent to the Chavara deposit appears to bear the most similar ilmenite, when compared to the ilmenite of the beach based on the elemental distributions.

In the Manavalakurichi area (Fig. 5.2.17, a-g), the chemical compositions show wide variations between ilmenite samples of the Teri sand, Valliyar



**LT -Laterite, S.st - Sandstone, Kar - Karamana river, Vam - Vamanapuram river, Ith - Ithikkara river Kall - Kallada river, Est - Estuary, CH - Chavara beach.**

**Fig 5.2.16(a-g). Variation in the average contents of minor and trace elements in ilmenite from different environments of the hinterland to the Chavara beach.**



**Val - Valliyar river, Beach - Manavalakurichi beach.**

**Fig 5.2.17(a-f). Variation in the average contents of the minor and trace elements in ilmenite from the different environments of the hinterland to the beach**

river and Beach. Though the river samples are more near to the concentrations of elements in beach ilmenite than the Teri sample, the notable variation between the ilmenite of beach and the adjacent river, indicate the limited fluvial influence on the deposit. This points to the role of palaeo placers in the formation of the present Manavalakurichi deposit brought about by the reworking processes of tides and currents.

# CHAPTER 6

# SUMMARY AND CONCLUSIONS

In keeping with the objectives of the work mentioned earlier in the thesis, different mineralogical (ore and scanning microscopy, XRD, magnetic measurements, TG methods and Mössbauer spectroscopy) and chemical (major and minor elements) analyses of ilmenite from two placer deposits of the southwest coast of India were carried out. In addition, the above techniques were applied to the magnetic and various size fractions of bulk ilmenite separated out in the laboratory at the Indian Rare Earths Ltd. Factory. The ilmenite samples from different geological settings of the hinterland like laterite, sedimentary formations, Teri sand, fluvial and estuarine systems, which forms the ultimate provenance source of the placer deposits were used for the above mentioned multifarious analyses and comparison.

## 6.1. Summary and Conclusions of the Mineralogical Analyses

The nature and patterns of alteration observed under the microscope was systematically recorded in the thesis with photomicrographs. It is found that in the Chavara and Manavalakurichi deposits, alteration apparently starts from the boundaries of grains and/or zones of weakness. Two types of alteration, namely continuous and discontinuous, as reported in literature are observed in the present work. The evidences suggested support an insitu alteration of ilmenite grains like the altered boundaries of rounded grains and the maintenance of the outline of the grains seem to indicate a post-depositional alteration for ilmenite. At the same time, the indications of reworking are observed like the truncation of the boundaries between the alteration phases by the grain surfaces. The ilmenite grains of the Chavara deposit are found to be more altered than those of the Manavalakurichi beach.

Among the ilmenite samples from the hinterland, the lateritic samples show limited alteration. In a few grains, however, the clay like bodies appears to be associated with the altered phases in sites of alteration like pits and cavities, supporting the dissolution-reprecipitation mode of formation of leucoxene. The ilmenite samples do not show any presence of high-temperature intergrowths of minerals, except in the grains from the lateritized corderite gneiss (S13), which show properties of magnetite/maghaemite. In the samples from Teri sand deposits which occurrs adjacent to the Manavalakurichi beach, a few grains exhibit intergrowth textures due to the ilmenite-haematite exsolution. The samples from the Tertiary sandstone are differentially weathered, depending on the sampling location. The reason shown by the different samples of close geographical proximity could be due to the difference of the diagenetic changes or the variation in the provenance of the source sediments of the sandstone formation. Since the discontinuous type of alteration is formed due to recrystallization, this type is generally favoured in insitu conditions. Similar alteration patterns are seen in grains from the undisturbed portions of the Ashtamudi estuary.

A total of sixty three ilmenite samples consisting of ilmenite from different geological settings and the magnetic fractions of bulk ilmenite were analyzed for XRD patterns. The Chavara ilmenite presents altered phases as high as 55%. In comparison, the Manavalakurichi ilmenite shows marginal weathering recording the content of the altered phases in the range of 16 to 23%. The northern and southern extremities of the Chavara deposit and the northern part of the Manavalakurichi placer body presents relatively lower altered grains of ilmenite. The altered phases found in the samples studied are pseudorutile and rutile.

Although in a few samples suspected peaks of anatase are observed. The XRD methods were applied to the magnetic fractions of bulk ilmenite from the Chavara and Manavalakurichi separated at progressively increasing amperages. The results indicate that the magnetism of the ilmenite need not be a simple inverse function of the degree of alteration undergone, as reported earlier. The results of the study show that the most magnetic fraction contains more content of altered phases than the relatively unweathered fractions. The fractions separated above 0.35A define a high grade of ilmenite ore enriched in Ti content. The lattice volume generally decreases with alteration.

The samples from the source rocks of laterite are generally unaltered. Intergrowths of other mineral phases are not observed in the samples, confirmed by the microscopic observations, except in the sample from the lateritized corderite gneiss. Similarly, the ilmenite samples from the Tertiary sandstone too agree with the microscopic data showing differential alteration, with some samples as altered as the beach samples. The river samples are generally found to be only slightly altered pointing to the fast nature of the streams and the constant supply of fresh grains along their course from the country rocks. The estuarine samples are generally weathered.

The magnetic studies reveal that the Chavara ilmenite are found to be made up of low magnetic crops with about 46% of the bulk ilmenite constituted by fractions separated at above 0.35A. In the Manavalakurichi ilmenite on the other hand, around 91% of the beach ilmenite is made up of fractions separated at or below 0.3A. The magnetic susceptibility is observed to be increasing with higher amounts of ferric ions and when the content of total iron approaching the theoretical values for ilmenite. The susceptibility is correlated with increasing ferric contents and iron enrichment in Manavalakurichi ilmenite, but shows poor relationship for samples of Chavara, pointing to the depletion of iron from the mineral structure. Thus higher magnetic susceptibility values are noted for Manavalakurichi ilmenite. The finer size grades of the grains are found to be more magnetically susceptible than coarser fractions. The IRE factory-graded samples show negligible susceptibility for the samples of the rutile grade (IRE2-4), as compared to the ilmenite and leucoxene grades (IRE5-7).

The latertic ilmenite present lower magnetic susceptibility in agreement with their marginal ferric contents, while samples from the sandstone shows a wide variance in their values from 0.29 to 2.3 $m^3/kg$. The Teri samples too present higher values, in part attributable to the reported presence of haematite intergrowths in some grains. Among the rivers, ilmenite from Kallada gives higher susceptibility. The lithology of the drainage basin off this river contains intercalations of basic rocks and intergrowths of magnetite/maghaemite have been observed in the ilmenite from corderite gneiss.

The thermogravimetic analysis was carried out on thirty-five ilmenite samples to understand the degree of alteration. The advanced nature of weathering suffered by the Chavara ilmenite is brought out bythe weight loss due to water content at 500°C and the relatively lower effective weight gain at about 950°C. The dependence of the water molecules in the ilmenite structure with the ferric ions is found to be strong. The TG patterns of the magnetic fractions of the bulk ilmenite confirm with the XRD plots in that the most magnetic fractions need not be the least altered. The size grades of the same magnetic fractions show difference in the TG patterns subscribing to the results of other analyses that weathering in ilmenite is related to the size of the fraction.

The samples undertaken for Mössbauer analysis indicates that this technique is found to be very viable to determine the oxidation states of iron and the presence of likely intergrowths in ilmenite. The intergrowths present in the ilmenite from the lateritized corderite gneiss could not be identified as magnetite or maghaemite due to the similar optical and XRD properties, but the Mössbauer parameters indicate values closer to maghaemite than magnetite.

## 6.2. Summary and Conclusions of the Chemical Analyses

The higher ferrous oxide content and lower ferric and titanium oxide contents of the Manavalakurichi ilmenite indicates the comparatively lower altered nature than the Chavara deposit. Accordingly, the Chavara ilmenite is found to have reached the advanced alteration stage of 'Pseudorutile', while the Manavalakurichi samples fall in the 'Hydrated ilmenite stage' of alteration. The Chavara ilmenite is found to present a more uniform distribution of the elements along its lateral and vertical dimensions, while the Manavalakurichi samples show more variation. These characters indicate that the Chavara placer deposit consists of mature and reworked sediments. The northern and southern extremities of the Chavara and the northern part of the Manavalakurichi deposits show the presence of comparably less altered samples pointing to the enrichment by coastal processes as exemplified by the XRD, magnetic and TG analyses. The low magnetic fractions of both the deposits define a high grade of ore consisting of high values of titanium oxide to a maximum of about 65% in both the deposits. The cluster analysis shows that the primary stage of alteration involving the oxidation of ferrous ions to ferric is the dominant process in Manavalakurichi ilmenite. In Chavara samples the leaching of iron from the mineral structure is the significant process. Among the IRE factory-graded samples of ilmenite, the leucoxene fractions show an average total iron content of about4%, while in the rutile samples this value is as low as about 1%.

The ilmenite samples from lateritized crystalline rocks exhibit a relatively unaltered state with iron oxide contents nearing to the theoretical limits for ilmenite (47%). On the other hand, the samples from laterite developed over the Tertiary formations are more depleted in iron oxide content particularly in the type section of the Warkkalai formation (S11) at Varkala. The sandstone shows samples consisting of very altered, iron poor grains to samples where the major elemental composition is close to theoretical values for ilmenite. The sample S1 from the Tertiary sandstone section at Karichal is the most altered among all the field samples with very low iron oxide content of 33%. The estuarine ilmenite samples, too present a similar pattern. The patterns shown by ilmenite samples from river and Teri sands reveal slightly weathered nature.

The most notable difference when the average compositions are considered, are the high values Al, V and Cr and the depleted contents of Zn and Cu in Chavara ilmenite when compared with samples of Manavalakurichi. The elements like Al, Cr and V are noted for their relative immobility leading to enrichment in the mineral structure with progressive weathering. Their enrichment indicates the advanced alteration undergone by the Chavara sample.

The minor and trace elements determine the quality of the grade of ilmenite and the industrial products manufactured from the mineral. Thus undesirable quantities of Cr in ilmenite will impart a greenish colouration to the titania pigment produced thereby affecting its quality, even though the ore may be rich in titanium. Thus the industrial processing techniques have to be suitable to remove the undesirable quantities of trace elements, if present from the ilmenite ore. It is found that most of the elements analyzed for ilmenite in this work, are present within the desirable limits specified by the Department of Atomic Energy, Government of India. The Cr content in Chavara ilmenite lie close to the threshold limits specified for this element (<0.1%). However, the Mn and Si contents in ilmenite of both the deposits are much higher than the upward limits of 0.01 and 0.15% specified. However, the contents of elements like V, Mg, Zn and iron are within the specified limits. Though its high Cr content is detrimental to the quality Chavara ilmenite, it is compensated by the low iron and high Ti values. The Cr content is very high in the Ti rich low magnetic fractions of the Chavara ilmenite

The elemental variation in ilmenite has been standardized based on the alteration of ilmenite in beaches. But each geological settings like the latetrite, sandstone formation, Teri sands, estuary etc. has its own environment based on factors like digenetic changes, Eh and pH conditions and the degree of weathering undergone. Thus the variation of ilmenite composition from the laterite (source) to beaches (sink) cannot be expected to follow any standard route. For example, the V and Cr describe a strong negative correlation with ferrous iron in lateritic ilmenite, while in the sedimentary rocks, V shows a well-defined positive relationship with ferrous iron contents. The Manavalakurichi ilmenite samples do not exhibit any marked compositional similarity with the likely provenance sources of the hinterland like Teri sand deposits and the Valliyar river, suggesting the dominant role played by the coastal processes in the enrichment of the deposit in the modern scenario. The influence of geochemical conditions like Eh and pH have been discussed in the text, albeit in a general way, due to the lack of any sufficient work on the different geological settings of the hinterlands in the study area. The ilmenite samples from the lateritized charnockites and khondalites could be discriminated based on the content of Mg. The analyses of ilmenite samples from the vertical section of a Tertiary formation at

Thiruvallam (L2, S2 and S2a) show that the composition exhibits considerable variation, indicating the difference in the source sediments and/or the nature of post-depositional changes in the sedimentary formation. Ilmenite samples from rivers show difference in their distribution even though they flow through similar lithological terrain.

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