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# ALTERATION CHARACTERISTICS OF THE MANAVALAKURICHI BEACH PLACER ILMENITE, TAMILNADU

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## Abstract

The mineralogy and alteration characteristics of beach placer ilmenite from the Manavalakurichi coast were investigated by optical microscopy and electron probe microanalysis. Mineral chemistry by electron probe micro-analysis indicated enrichment of $TiO_2$, MgO, $Al_2O_3$, $Cr_2O_3$, $SiO_2$, $K_2O$, $V_2O_5$, CaO and $Na_2O$ in the altered products of ilmenite, while there was a loss of iron oxide, maganese oxide and zinc oxide from the ilmenite grains during weathering leading to leucoxene and pseudorutile formation.

*Keywords* : Beach placer, Ilmenite, Alteration, EPMA, Manavalakurichi.

## 1. Introduction

Ilmenite ($FeTiO_3$), an important and the most abundant ore mineral of titanium, occurs in India along the coastal beach sands of Orissa, Andhra Pradesh, Tamilnadu and Kerala states. Manavalakurichi deposit, Kanyakumari district, Tamilnadu is one such deposit extending over a length of 6 kilometers with an average width of 44 meters. The total heavy mineral content of the deposit is 39% (upto an average depth of 7.5 meters). Ilmenite is the predominant mineral with a grade of 24% (in raw sand); up to 8% rutile; 0.9% leucoxene; 2% zircon, 1% monazite; 3.5% sillimanite and 5.5% garnet (Ali et al., 2001). The Indian Rare Earths Limited (IREL), a public sector undertaking of the Government of India under the administrative control of the Department of Atomic Energy, has mined and processed ilmenite along with other heavy minerals like garnet, monazite, rutile, sillimanite and zircon from these sands.

The beach placer ilmenite shows significant variation in the degree of weathering-related alteration, which, in turn, is independent of the provenance and for which it forms the object of research by scientists of different disciplines with totally different approaches (Suresh Babu et al., 1994, 1996 and Rao et al., 2002). Several workers have studied ilmenite from across the world to assess the qualitative variation from deposit to deposit (Bailey et al., 1956; Temple, 1966; Wort and Jones, 1980; Mitra et al., 1992), literature on the alteration of ilmenite is also plentiful (Frost et al., 1983; Hugo and Cornell, 1991; Suresh Babu and Mohan Das, 1999; Chernet, 1997 and Nimis, 1997). Although Suresh babu et al., (1994) have studied the alteration of ilmenite from this area, their study was based on magnetic fractionation of the ilmenite, which is an indirect approach to decipher the alteration characteristics of ilmenite. In the present paper, the authors present detailed characteristics of ilmenite from the beach sands of Manavalakurichi, which is a direct approach, and place a special emphasis on its alteration by optical microscopy and electron probe micro-analysis.

## 2. Materials and methods

Concentrated ilmenite sample from the Manavalakurichi coast was obtained from IREL. A representative sample was prepared from the concentrate and characterised by optical microscopy, XRD and electron probe microanalysis (EPMA). The sample was mounted in epoxy resin (cold mounting) and polished using conventional methods for optical and electron microscopic studies. The polished section of ilmenite was examined and analysed with a JEOL, Super Probe JXA-8600 model electron microprobe operating with a current setting of $2\times10^{-8}$A and with Standard Programme International (SPI) mineral standards, using on-line ZAF correction procedures. Individual ilmenite grains (both altered and unaltered) were selected from the polished specimen for EPMA before coating with carbon. Particle size analysis of the ilmenite grains was done using CILAS 1180 Particle Size Analyser.

## 3. Results and discussion

The Manavalakurichi placer ilmenite occurs mostly as sub-rounded to sub-angular grains, marked by numerous surface pits, etch marks/

grooves, crescentic pits and mesh like patterns. The particle size analysis plot is shown in Fig. 1, where the mean particle diameter is 169.12 microns (size ranges from 13 microns to 500 microns). Reflected light microscopy as well as XRD studies (Table 1) suggest that ilmenite is the major phase. Quartz, hematite and rutile were observed under the microscope rarely. Alteration of ilmenite was occasionally observed and seen to proceed along grain boundaries and/or fractures giving rise to an amorphous to crypto- or micro-crystalline mass resembling leucoxene (Fig. 2). The intensity and mode of alteration also varies from grain to grain.

The major and minor elemental composition, using electron probe microanalyses, of the ilmenite specimens from the Manavalakurichi coast is reported in Table 2. The ilmenite shows good stoichiometry of $TiO_2$ (52.193 to 54.151%) and FeO (42.034 to 45.885%). Significant amount of $V_2O_5$ (nil to 0.306%) is also present. In the analyses of all 4 grains of unaltered ilmenite, $SiO_2$ and $K_2O$ were not detected. Presence of significant amounts of magnesium (0.025 to 2.015%) and manganese (0.096 to 0.902%) indicates that the ilmenite of Manavalakurichi constitutes a solid solution series with geikielite and pyrophanite, respectively. As a result of these solid solutions, the $TiO_2$ content of the ilmenite is lower or higher than the ideal value (52.65%). The bulk sample analysis (Table 3) is comparable with that of the ilmenite grain analysis by EPMA. However, Manavalakurichi ilmenite sample shows higher content of ferric iron as well as titania and low content of ferrous iron compared to the ilmenite sample from Chatrapur (Rao et al., 2002)

Major and minor elemental analyses of the altered and unaltered portions of two different ilmenites grains were also carried out (Table 2). The analysis of unaltered ilmenite portions compares well with those in altered ilmenites. The altered ilmenite portions are enriched in $TiO_2$ (66.906 to 95.243%), MgO (0.012 to 0.945%), $Al_2O_3$ (0.789 to 2.727%), $Cr_2O_3$ (0.178 to 0.0.381%), $SiO_2$ (0.035 to 2.668%), $V_2O_5$ (0.303 to 0.0.555%), CaO (0.001 to 0.005%), $K_2O$ (0.001 to 0.005%) and $Na_2O$ (0.195 to 0.581%), and depleted in MnO, FeO and ZnO. Similar observations were made by Grey and Reid (1975), Anand and Gilkes (1984), Suresh Babu et al. (1994) and Rao et al. (2002). Dissolution and/or oxidation of iron of ilmenite in natural or acidic water leads to an enrichment of titanium and other elements in the residuum, which may be the main cause for ilmenite alteration (Dimanche and Bartholome, 1976). Though ilmenite alteration is neither uniform nor continuous, the weathering mechanism is illustrated as a two stage process (Grey and Reid, 1975) or a multistage process (Frost et al., 1983; Hugo and Cornell, 1991). However, the present mineral chemistry suggests that the initial step (ferrous-ferric iron transformation stage) is relatively advanced (indicated by a relatively low content of iron or removal of iron and enhancement of titanium), which is a common low temperature geochemical process. Such a process leads to the incomplete alteration of ilmenite and co-existence of ilmenite, pseudorutile and leucoxene. Similarly, the data on samples 7, 8 and 9 (Table 2) indicate that the end product of alteration leads to pseudo-rutile/rutile, which supports the theory of Temple (1966); Grey and Reid (1975); Frost et al. (1983) and Anand and Gilkes (1984).

The composition and grade/quality changes noticed in these ilmenites could only be due to the exogenic processes undergone by the mineral after its release from the Precambrian metasedimentary crystalline rocks. The heavy mineral assemblage in this sector is suggestive of provenance consisting principally of high-grade metamorphic (granulite facies) rocks, principally of khondalite (garnet-sillimanit-graphite-gneisses), charnokites and granitic gneisses (unclassified crystalline rocks), bordered by the sedimentary rocks exposed along the eastern coastal plains which are the rock types of Tamilnadu (Chandrashekharan and Murugan, 2001). However, the extent of alteration depends on the geological history of the deposit and also to the weathering environments (Hugo and Cornell, 1991; Suresh Babu et al., 1994). The degree of alteration of different ilmenite deposits in the world is quite varied; those of Zululand (South Africa) and Brazil being relatively very little altered while those of Australia and Florida (U.S.A.) are extensively altered (Hugo and Cornell, 1991 and Haseeb et al., 1997). In the present case, the ilmenite from Kerala state suffered maximum alteration whereas that of Tamilnadu state suffered moderately and that of Chatrapur coast in Orissa state has undergone least weathering (Suresh Babu et al., 1996).

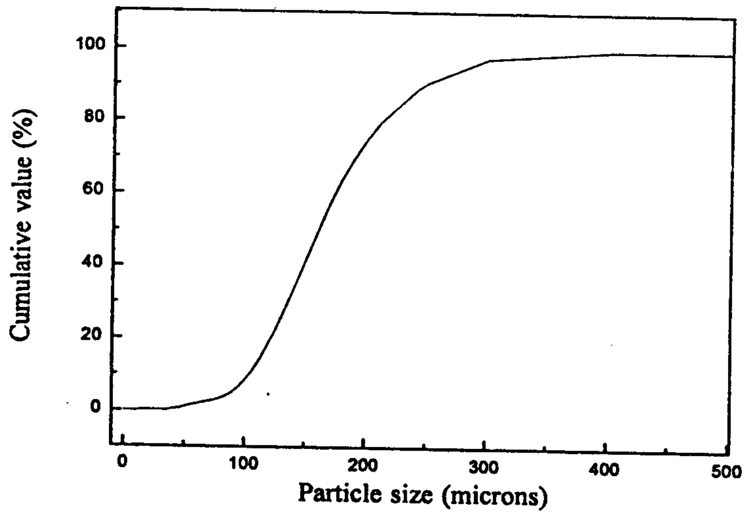


Fig. 1. Particle size analysis plot for the ilmenite from Manvalkuruchi.

Table 1. X-ray diffraction data of ilmenite from Manavalakurichi.

| 2 θ (degrees) | d (Å) | Phase |
|---|---|---|
| 27.759 | 3.728 | Ilmenite |
| 38.030 | 2.745 | Ilmenite |
| 41.249 | 2.539 | Ilmenite |
| 47.200 | 2.234 | Ilmenite |
| 57.310 | 1.865 | Ilmenite |
| 62.575 | 1.722 | Ilmenite |
| 63.963 | 1.688 | Ilmenite |
| 66.677 | 1.627 | Ilmenite |
| 73.082 | 1.502 | Ilmenite |
| 75.208 | 1.465 | Ilmenite |
| 80.688 | 1.381 | Ilmenite |

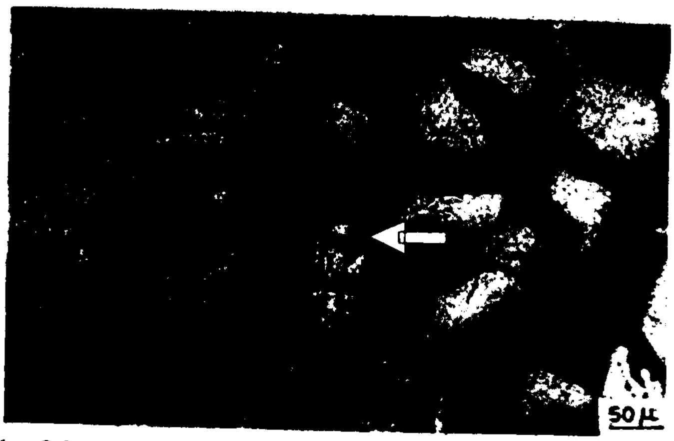


Fig. 2. Photomicrograph of the ilmenite grains of Manvalakurichi. I is ilmenite and S is quartz. Altered portion of ilmenite is shown by arrow.

Table 2. Electron probe microanalysis data of ilmenites and altered ilmenites (in wt.%) from Manavalakurichi.

| | Ilmenite | | Altered ilmenite | | Altered ilmenite | | Altered ilmenites | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | Altered portion | Unaltered portion | Altered portion | Unaltered portion | 7 | 8 | 9 |
| $TiO_2$ | 54.151 | 52.601 | 94.243 | 52.193 | 85.007 | 53.178 | 66.906 | 76.654 | 91.248 |
| FeO | 43.404 | 42.034 | ND | 45.632 | ND | 45.885 | ND | ND | ND |
| $Fe_2O_3$ | ND | ND | 1.547 | ND | 6.002 | ND | 28.195 | 18.995 | 3.151 |
| $Al_2O_3$ | 0.251 | 0.746 | 0.841 | 0.452 | 2.727 | 0.369 | 0.789 | 1.613 | 1.816 |
| MgO | 1.003 | 2.015 | 0.027 | ----- | 0.042 | 0.025 | 0.945 | 0.025 | 0.012 |
| MnO | 0.902 | 0.796 | 0.009 | 0.863 | ----- | 0.096 | 0.127 | 0.135 | 0.022 |
| ZnO | 0.008 | ----- | ----- | 0.055 | 0.010 | 0.054 | ----- | 0.007 | 0.025 |
| $Cr_2O_3$ | 0.066 | 0.093 | 0.250 | 0.018 | 0.179 | ----- | 0.262 | 0.381 | 0.178 |
| $V_2O_5$ | ----- | 0.225 | 0.510 | 0.290 | 0.521 | 0.306 | 0.303 | 0.456 | 0.555 |
| $SiO_2$ | ----- | ----- | 1.170 | ----- | 2.668 | ----- | 0.573 | 0.390 | 0.035 |
| $Na_2O$ | ----- | ----- | 0.581 | 0.414 | 0.596 | 0.350 | 0.295 | 0.357 | 0.195 |
| $K_2O$ | ----- | ----- | 0.001 | ----- | 0.005 | ----- | 0.002 | 0.001 | 0.001 |
| CaO | 0.003 | ----- | 0.142 | ----- | 0.136 | 0.004 | 0.078 | 0.111 | 0.082 |
| Total | 99.788 | 98.510 | 99.321 | 99.917 | 97.893 | 100.267 | 98.475 | 99.125 | 97.320 |

----- = not detected; ND - not determined

Table 3. Bulk chemical composition of the ilmenite sample (wt.%).

| Compounds | Manavalakurichi |
|---|---|
| $TiO_2$ | 55.10 |
| FeO | 20.30 |
| $Fe_2O_3$ | 19.90 |
| $Al_2O_3$ | 0.80 |
| $SiO_2$ | 1.50 |
| MnO | 0.40 |
| $V_2O_5$ | 0.22 |
| $Cr_2O_3$ | 0.08 |
| MgO | 1.00 |
| $P_2O_5$ | 0.12 |
| $ZrO_2$ | 0.06 |
| Rare Earths | 0.12 |
| Total | 99.60 |

## 4. Discussion and conclusions

Optical studies indicated the presence of ilmenite, trace amounts of hematite, altered ilmenite (leucoxene) and pseudorutile in the concentrate sample of the beach placers of ilmenite. The average diameter of these ilmenite grains is 169 microns. Electron probe microanalysis data indicate that ilmenite is in solid solution with pyrophanite and geikielite, and the alteration leads to enrichment of $TiO_2$, MgO, $Al_2O_3$, $Cr_2O_3$, $SiO_2$, $K_2O$, $V_2O_5$, BaO, CaO and $Na_2O$ with loss of FeO, MnO and ZnO. These alterations could be due to the exogenic processes that operated on these ilmenites after their release from the parent rocks. The studies further indicated that the alteration of ilmenite is not uniform.

Ilmenite is gradually converted to leucoxene and pseudorutile in this deposit under oxidising conditions, leaving enriched residue of $TiO_2$ and $SiO_2$ along with others, resulting in the formation of porous grains of ilmenite. The pores may remain open or get filled by a variety of secondary minerals which affect their grade/quality. These porous grains have low density and low magnetic susceptibility (because of change in content of iron) leading to concentration problems. The differences in physical properties between altered/ oxidised ilmenite and fresh/unaltered ilmenite are often many. The altered or oxidised ores behave differently to the beneficiation process compared to the fresh/unaltered ores. Altered/oxidised ilmenite generally adversely affects the treatment and the economic viability of any upgradation operation. Hence, it is necessary to comprehend the nature of both primary and altered ilmenites before going for any upgradation/beneficiation and further downstream utilisation. It is well known that ilmenite is soluble in $H_2SO_4$ whereas rutile is not. However, the degree of solubility of ilmenite varies depending on the extent of alteration. Regardless of the higher $TiO_2$ content in the altered ilmenite, its solubility in $H_2SO_4$ decreases with increasing degree of alteration (Sinha, 1979). In other words, the high ferric iron content of the altered ilmenite clearly demands a reduction process rather than a sulphate process for $TiO_2$ production (Chernet, 1999 a, b). Hence, the degree of weathering or alteration can be an indicator of its economic value. Compositional characterisation by such instrumental techniques not only helps to adopt better methods for industrial processing, but also facilitates production of different grades of synthetic rutile.

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## References

Ali, M.A., Krishnan, S. and Banerjee, D.C., (2001) Beach and inland heavy mineral sand investigations and deposits in India - An overview. Exploration and Research for Atomic Minerals, 13, pp.1-21.

Anand, R.R. and Gilkes, R.J., (1984). Weathering of ilmenite in a lateritic Pallid zone. Clays and Clay Minerals, 32, pp.363-374.

Bailey, S.W., Cameron, E.N., Spedden, H.R. and Weege, R.J., (1956). The alteration of ilmenite in beach sands. Econ. Geol., 51, pp.263-279.

Chandrasekharan, S. and Murugan, C., (2001). Heavy minerals in the beach and the coastal rd sand (Teris) of Tamilnadu. Exploration and Research for Atomic Minerals, 13, pp.87-109.

Chernet, T., (1997). Mineralogical study on Australian sand ilmenite concentrate, Australia. Proc. of 4th Biennial SGA meeting of Finland, pp.709-712.

Chernet, T., (1999a). Applied mineralogical studies on Australian sand ilmenite concentrate with special reference to its behaviour in the sulphate process. Min. Engg., 12, pp.485-495.

Chernet, T., (1999b). Applied mineralgical studies of the Koivusaarenneva ilmenite deposit, Kalvia, Western Finland, with special reference on the altered part of the ore. Chronique De La Rescherche Miniere, 535, pp.19-28.

Dimanche, F. and Bartholome, P., (1976). The alteration of ilmenite in sediments. Minerals Sci. Engg., 8, pp.187-201.

Frost, M.T., Grey, I.E., Harrowfield, I.R. and Mason, K., (1983). The dependence of alumina and silica contents on the extent of the alteration of weathered ilmenites from Western Australia. Mineral. Mag., 47, pp.201-208.

Grey, I.E. and Reid, A.F., (1975). The structure of the pseudorutile and its role in the alteration of ilmenite. Amer. Mineral., 60, pp.898-906.

Haseeb, A.S.M., Hug, M.Z. and Kurny, A.S.W., (1997). Characterization of Bangladesh ilmenite and study of its reduction mechanism by X-ray diffraction. Trans. Instn. Min. Metall., Sec.C, 106, pp.39-43.

Hugo, V.E. and Cornell, D.H., (1991). Altered ilmenites in Holocene dunes from Zululand, South Africa, Petrographic studies for multistage alteration. South Africa Jour. Geol., 94, pp.365-378.

Mitra, S., Ahmed, S.S. and Moon, H.S., (1992). Mineralogy and chemistry of the opaque of Cox's Bazar (Bangladesh) beach sands and the oxygen fugacity of their provenance. Sedimentary Geol., 77, pp.235-247.

Nimis, P., (1997). Weathering of ilmenite in southern Mozambique beach sands. Proc. of 4th Biennial SGA meeting of Finland. pp.741-742.

Rao, D.S., Murthy, G.V.S., Rao, K.V. Das, D. and Chintalapudi, S.N., (2002). Alteration characteristics of beach placer ilmenite from the Chatrapur coast, Orissa, India. Jour. of Applied Geochemistry, Vol.4, No.1, pp.47-59.

Sinha, H.N., (1979). Solubility of titanium minerals. Int. Conf. Advanced Chem. Metallurgy, 2, pp.1-16.

Suresh Babu, D.S., Thomas, K.A., Mohan Das, P.N. and Damodaran, A.D., (1994). Alteration of ilmenite in the Manavalakurichi deposit, India. Clays and Clay Minerals, 42, pp.567-571.

Suresh Babu, D.S., Das, D., Sudarsan, M., Reddy, V.R., Chintalapudi, S.N. and Majumdar, C.K., (1996). $^{57}Fe$ Mössbauer studies on natural ilmenites. Ind. Jour. of Pure and Applied Physics, 34, pp.474-479.

Suresh Babu, D.S. and Mohan Das, P.N., (1999). Mineralo-chemical assessment of ilmenites from the three Indian placers. Trans. Indian Inst. Met., 52, pp.73-79.

Temple, A.K., (1966). Alteration of ilmenite. Econ. Geol., 61, pp.695-714.

Wort, M. J. and Jones, M.P., (1980). X-ray diffraction and magnetic studies of altered ilmenite and pseudorutile. Mineral. Mag., 43, pp.659-663.

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