ALTERATION OF ILMENITE IN THE MANAVALAKURICHI DEPOSIT, INDIA

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Abstract—Magnetic fractionation, chemical, and structural analyses prove that alteration of ilmenite from Manavalakurichi deposit extends only up to the formation of pseudorutile with traces of rutile. The data indicate that ferrous to ferric iron transformation, ferric iron oxide formation, and iron removal contribute to the alteration sequence. The first two highly magnetic fractions are not unaltered ilmenite. A reduction in ilmenite unit cell volume indicates the ferrous-ferric conversion occurred during alteration.

Key Words-Alteration, Ilmenite, Pseudorutile, Unit cell volume.

INTRODUCTION

Beach placer ilmenite concentrates of the world show significant variation in the degree of alteration that is independent of provenance. Differential weathering of ilmenite after its release from the country rock and natural mixing of fresh and altered grains during migration impart complexity to the placer sands. Various minerals have been identified as weathering products of ilmenite. We describe here the qualitative variation in different fractions isolated from the bulk ilmenite of the Manavalakurichi (MK) beach placer deposit located at the southwest coast of India. Earlier studies on MK ilmenite have shown that Mössbauer technique is suitable for the identification and estimation of pseudorutile (Subrahmanyam et al 1982) and that reactivity of the significantly-altered fraction is high compared to the less-altered fraction (Suresh Babu et al 1991).

MATERIALS AND METHODS

Factory grade MK ilmenite was washed several times with water, dried and sieved to get uniform size (+0.125)mm). This sample was separated with a Frantz isodynamic separator into seven magnetic fractions using different input currents and 15° sideward and forward slope combinations. Specific gravity was determined using a specific gravity bottle and water as the medium. Phase identification was done by a standard X-ray powder diffraction (XRD) method using a Philips diffractometer (CuK α radiation, Ni-filter). Hexagonal a and c lattice parameters for ilmenite and pseudorutile were calculated by a least-squares fitting method taking into consideration the four important reflections of ilmenite (110, 113, 204 and 116) and three of pseudorutile (100, 101, 102). Thermogravimetric analysis (TGA) was carried out using a Du Pont 2000 (model V5.IA) thermal analyser at a heating rate of 20°C/min. in air. Chemical analysis was done by the standard wet chemical methods, using the aluminium reduction method for TiO₂, dichromate titration for iron (Vogel Copyright © 1994, The Clay Minerals Society

1961) and atomic absorption and colourimetric methods for trace elements.

RESULTS AND DISCUSSION

A common ilmenite alteration mechanism can be explained as follows:

Ilmenite		Pseudoru	tile	
Fe ²⁺ TiO ₃	\rightarrow	Fe ₂ ³⁺ Ti ₃) ,	
Hexagonal		Primitive Her	kago	onal
		(Grey and Rei	d 1	975)
		Rutile/Anatas	e	Hematite
	\rightarrow	TiO ₂	+	Fe ₂ O ₃
		Tetragonal		Hexagonal
		(Temple 1966	;	(Morad and
		Anand and		Aldahan 1982;
		Gilkes 1984)		Frost et al 1983)

Several attempts have been made to characterize the sequence, mechanism, and products of alteration. The important alteration indicators are changes in Fe²⁺/ Fe³⁺ and Fe/Ti ratios; variations in magnetic susceptibility, density, hardness and reflectivity; structural and morphological changes, increases in impurities like Cr and V and decreases in Mn, Ni, Zn, Cu, Mg, Co and Ca (Grey and Reid 1975; Anand and Gilkes 1984; Wort and Jones 1980). The difference in the degree of ilmenite alteration in various heavy mineral placer deposits implies differential weathering due to age differences and/or in situ and multistage alteration of ilmenite (Hugo and Cornell 1991) and also due to different weathering environments. In nature, progressive alteration of ilmenite results in the formation and co-existence of different phases. Moreover, positive identification of all altered phases is difficult because of indistinct and similar structural as well as physical properties. Accordingly, degree of alteration may only be perceived as the degree of rutilization.

The magnetic susceptibility (χ) of each of seven fractions was calculated using the relation reported by Flin-

Ilmenite fraction	Current (A)	Mag. Susc. (×10 ⁻⁶)	Content (wt. %)	Sp. gravity
MK1	0.15	230	15.4	4.214
MK2	0.20	129	22.6	4.335
MK3	0.25	82	30.5	4.568
MK4	0.30	58	15.4	4.418
MK5	0.35	42	4.0	4.395
MK6	0.40	32	8.0	4.224
MK7	>0.40	<32	4.0	4.147

Table 1. Fractionation of MK ilmenite.

Table 2. Results of the chemical analysis.

ter (1959). It is seen that at a separation current of 0.25 A, corresponding to a χ of 82×10^{-6} cgs units, a maximum of 30.5 wt. % of the bulk ilmenite, with a sp. gravity of 4.568, can be separated (Table 1). In comparison with synthetic ilmenite ($\chi = 96 \times 10^{-6}$ cgs units, sp. gravity = 4.7), the MK3 fraction is thus the closest in magnetic susceptibility and specific gravity to ideal ilmenite. About 40 wt. % of the bulk ilmenite has higher values of χ than that of pure synthetic ilmenite (MK1 plus MK2).

The chemical analysis of the seven fractions is given in Table 2. In MK ilmenite, iron oxide varies between 44 and 32 wt. % and TiO₂ between 55 and 65 wt. %.



Figure 1. Powder XRD patterns of MK fractions showing ilmenite-rutile conversion. I—ilmenite; PR—Pseudorutile.

Ilmenite fraction	Composition (%)							
	FeO	Fe ₂ O ₃	FeO + Fe ₂ O ₃	TiO ₂	Mn	Cr		
MK1	20.96	21.88	42.84	56.02	0.195	0.079		
MK2	26.50	17.30	43.80	54.26	0.188	0.071		
MK3	32.20	11.70	43.90	55.70	0.123	0.104		
MK4	26.21	15.62	41.83	56.84	0.124	0.106		
MK5	15.35	25.91	41.26	57.84	0.139	0.144		
MK6	7.97	29.77	37.74	60.66	0.130	0.168		
MK7	3.36	28.90	32.26	65.06	0.106	0.232		

With increasing alteration as indicated by decreasing χ , the Mn content decreases while Cr content increases. The increase in Cr is presumably due to relative enrichment following the selective leaching of other constituents. The first four magnetic fractions, having an average Fe-oxide content of 43 wt. % and TiO₂ of 55.7 wt. %, are relatively unaltered ilmenite. In these fractions, the mean value of the FeO/Fe₂O₃ ratio is 1.73. In the fifth fraction, compared to the fourth one, the weight percentage of ilmenite sharply decreases from 15.4 to 4 and FeO/Fe₂O₃ ratio decreases from 1.68 to 0.59. The last three fractions, containing an average iron oxide content of 37 wt. % and TiO₂ of 61 wt. %, belong to the highly-altered variety of ilmenite with a mean FeO/Fe₂O₃ of 0.36.

Based on the chemical analysis, a cut-off grade can be fixed for unaltered and significantly-altered varieties of ilmenite at a χ of around 58 × 10⁻⁶ cgs units. This has been confirmed by XRD and TGA studies. XRD patterns (Figure 1) illustrate that sharp and prominent peaks of ilmenite persist only in the first four fractions whereas the remaining three fractions are pseudorutilerich. A similar observation has been reported for Capel ilmenite (Wort and Jones 1980). TGA data (Figure 2) show that the weight gain above 600°C occurs only for the first four fractions, implying the presence of substantial amounts of Fe²⁺. Weight loss due to bound



Figure 2. TGA curves of seven MK fractions.



Figure 3. Synoptic diagram showing differential alteration.

water increases as the degree of alteration increases. The pseudorutile structure may actually contain hydroxyl ions (Frost *et al* 1983; Waychunas 1991). Thus the content of bound water might be correlated with the presence of the pseudorutile phase.

While the Australian Capel ilmenite fraction having χ of 81 × 10⁻⁶ cgs units contains 14.8 wt. % Fe₂O₃ (Wort and Jones 1980), the similar MK3 contains only 11.7 wt. %, but with a common TiO₂ of 55.7 wt. %. Maximum-altered Capel ilmenite contains 25 wt. % Fe₂O₃ against 29 wt. % in the similarly-altered MK7 fraction with 63.2 and 65 wt. % TiO₂ respectively.

Though ilmenite alteration is neither uniform nor continuous, the weathering mechanism is illustrated as a two-stage (Grey and Reid 1975) or a multi-stage process (Hugo and Cornell 1991). The present chemical and XRD data suggest that the initial step (ferrousferric iron transformation stage) is relatively advanced compared to the next Fe-removal stage. In other words the first stage is conformable to the widespread ferrousferric iron conversion in nature, a common low-temperature geochemical phenomenon, while the leaching step takes place only in favorable environments. However, oxidation to ferric state and peripheral removal of iron from the system can take place simultaneously. The incomplete alteration leads to the coexistence of ilmenite, pseudorutile and rutile. Thus different fractions could be rich in one of these phases.

Though magnetic susceptibility is inversely related to the degree of alteration in ilmenite, it is reported that the highly magnetic fractions need not be those containing the least-altered ilmenite (Wort and Jones 1980). The present XRD, TGA, chemical analysis and sp. gravity studies (Figure 3) support this observation. Among the first three fractions the third one contains more FeO than the other two, total iron oxide being similar. Therefore ferrous-ferric iron conversion is less in the first two fractions. Neither Fe₂O₃ nor total Feoxides exceeds the equivalent amount of TiO₂ present in any of the ilmenite fractions. This points out that the Fe₂O₃ component cannot be due to ilmenite-hematite solid solution. Therefore, the ferric component can either form pseudorutile or hematite as a product of alteration. However, in the samples studied, pseudorutile was identified as the major product of alteration. Recently, our Mossbauer studies have confirmed that alteration in MK ilmenite stops at the pseudorutile stage (Das et al 1993).

Hexagonal a and c lattice parameters of ilmenite and the volume of the unit cell are illustrated in Figure 4. This has been done by the careful identification of the reflections of ilmenite and pseudorutile and assigning



Figure 4. Variation of the lattice parameters and cell volume.

the (hkl) values based on the reported standard reflections of ilmenite (JCPDS file No.3-781). In the case of $Fe_2Ti_3O_9$ (pseudorutile), different XRD data are reported with slight variations in d-values and intensity ratios (Overholt *et al* 1950; Teufer and Tample 1966; Grey and Reid 1975). XRD values quoted in the latest reference were taken into consideration for the analysis of the pseudorutile phase.

Both the *a* and *c* lattice parameters of ilmenite were found to progressively decrease resulting in a reduction in the unit cell volume. According to the ionic radius concept, this decrease is anticipated if there is a Fe²⁺-Fe³⁺ conversion as Fe³⁺ is smaller compared to Fe²⁺. This conversion of ferrous to ferric iron while retaining the hexagonal structure can be achieved either by assuming excess oxygen in the lattice (FeTiO_{3+x}) or by ejection of some Ti or Fe by diffusion or by the reduction of some of Ti⁴⁺ to Ti³⁺. The latter is very unlikely under natural conditions. Retaining the oxygen content during the ferrous-ferric iron transformation is possible by the simultaneous release of Fe³⁺ ions (Subrahmanyam *et al* 1982). In the 6th fraction, where both ilmenite and pseudorutile co-exist, the ilmenite a parameter shows an increase and the c parameter a decrease. This has resulted in an increase in the unit cell volume (Figure 4), showing that the ilmenite structure expands, thus facilitating the Feleaching from the ilmenite but only to form pseudorutile.

CONCLUSIONS

Intense alteration with loss of much Fe has affected less than 20% of the material and apparently weathering has not been able to convert a significant quantity of ilmenite to rutile. The 3rd magnetic fraction with an approximate magnetic susceptibility of 82×10^{-6} cgs units is considered as the relatively-pure ilmenite of the deposit. XRD analysis shows that the hexagonal ilmenite structure contracts in the initial stages of alteration followed by an expansion before transforming to pseudorutile. It is clear that identification of a relatively-homogeneous raw material or an effectivelyfractionated bulk ore is important for a given process and for a specific end product. Such an approach would lead not only to optimum utilization of ilmenite resources but also would facilitate the production of different grades of synthetic rutile.

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