Characterization of FeTi-oxide species occurring in the Ranobe heavy mineral deposit, Madagascar

L. REYNEKE* and T. WALLMACH†
*Exxaro, Pretoria, South Africa
†GeoSphere (Pty) Ltd, Newlands, South Africa

Heavy mineral deposits are a source of the economic important element titanium, which is contained in minerals such as ilmenite, pseudorutile and rutile. In the Ranobe heavy minerals deposit these minerals occur not only as primary unaltered minerals but also display various degrees of alteration resulting in an increased titanium content of the deposit.

The presence of the various FeTi-oxide minerals’ textural relations is a reflection of geological processes and may ultimately be used to unravel the geological history of the deposit. These minerals have different chemical and physical properties that influence metallurgical tests and the quality of products produced from various mineral beneficiation streams. It is therefore of metallurgical importance that the minerals are well characterized, defined and monitored during preliminary beneficiation tests.

Introduction
The material used in this study originates from the Ranobe heavy mineral-bearing deposit in Madagascar. The bulk of the heavy mineral suite consists of ilmenite exhibiting various degrees and modes of alteration. This study presents a first stage characterization of the FeTi minerals and forms the basis to better understand and predict beneficiation behaviour of these minerals as well as to contribute to the proposal of a depositional model.

Geology
The Ranobe heavy mineral deposit is located approximately 40 km north of the town of Toliara (Tulear) situated in the south-western part of Madagascar (Figure 1). Two other mineralized areas are found between the Manombo River and Morombe to the north. The Ranobe deposit is located approximately 15–20 km inland from the coast at an elevation of 120–150 m, generally within a shallow linear valley along the base of a limestone cliff (Figure 2). The deposit, which is around 1.5–2 km wide, extends around 20 km south from the northern extremity of the dune system south of the village of Tsiafanoka.

The basic stratigraphy of the area comprises a basement of cemented Eocene limestone locally unconformably overlain by series of unconsolidated quartz dunes, of probable Pleistocene age. The Ranobe deposit, which is hosted by the easternmost dunes comprises three units largely distinguished on the basis of colour and clay content as follows (with increasing stratigraphic height) (Figure 2):

- A white limestone basement with weathered or Ca/Fe cemented surface. No heavy minerals are contained in the limestone unit
- A lower sand unit of brown, orange brown or yellow brown medium grained quartz sands with >3% HM and 5–10% slime and up to 30 m thick. This is interpreted as a tidal flat or barred lagoonal
- An upper sand unit of pale orange-brown, well sorted, well rounded, fine-medium grained quartz sand with >3% HM and <7% slime and up to 30 m thick. This is interpreted as a dune or sand pit that extends south from the Manombo River along the base of the cliff.

Figure 1. Locality map showing heavy mineral deposits in the Toliara area

Figure 2. Basic stratigraphy of the Ranobe deposit

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The origin of the deposit is possibly related to a period when the sea level was around 100 m higher than present. At such a time the sea would have eroded an irregular platform into the limestone basement terminating in a cliff at the limit of inundation. Sand transported to the coast by the Manombo River would have been carried south and reworked by the sea and wind to form a beach and foredune system, rich in heavy minerals, along the edge of the platform. At some stage it is possible that the sea retreated before advancing again. At this time a new beach would have formed further offshore with a protected lagoon behind it into which suspended fine clay particles from flood waters would have settled. As the sea continued to rise, the new beach and its foredune system would have advanced over the clay-rich sediments at the base of the lagoon until it reached the base of the cliff.

Thus we find a buried beach and dune system (lower sand unit) lying beneath a clayey sand (intermediate clay sand unit) which was formed in a protected lagoon. This unit has a relatively regular upper surface due to its mode of deposition in a protected lagoon. The upper sand unit which overlies both the intermediate unit and limestone, by contrast reaches an elevation of around 150 m due to its formation by both water and wind.

Mineralogy

The basic mineral chemical properties of ilmenite and associated phases are presented in Figure 3 and Table I. Pseudobrookite and ulvöspinel have relatively low TiO₂ contents, and are shown in Figure 3 only for reference purposes as they play no significant role in the Ranobe ore deposit. Natural weathering of ilmenite involves the removal of Fe, thus resulting in an increase in the Ti content. The products from ilmenite alteration are generally referred to as ‘altered ilmenite’ and/or ‘leucoxene’. The distinction between ‘altered ilmenite’ and ‘leucoxene’ is unclear and very much dependent on economic factors and specific mining operations (i.e. determined by deposit specific mineral assemblages). Generally the term ‘leucoxene’ is used in the heavy minerals industry as a collective description for ilmenite alteration products with TiO₂ components ranging from 65–90%. The most abundant iron oxides and hydroxides (not shown in Figure 3) associated with the ilmenite are hematite (Fe₂O₃) and goethite (Fe₃O(OH)).

Detail descriptions, genetic aspects, as well as reviews of research on the above minerals are presented by Frost et al. (1986), Haggerty (1976), Reyneke and Van der Westhuizen (2001).

Origin of samples

Samples for mineralogical studies originate from laterally and vertically different areas and horizons of the Ranobe deposit. It should be noted that variable ilmenite characteristics as described below were not correlated to geological settings at this preliminary stage of the study.

Analytical methods

The minerals occurring in the samples were identified, described and characterized using a combination of analytical methods depending on the nature and extent of the characterization required. Methods used include X-ray fluorescence (XRF), X-ray diffraction (XRD), stereomicroscopy, optical microscopy and scanning electron microscopy (supported with energy dispersive X-ray (EDX) analyses). As part of the ongoing study the observed qualitative mineralogy is in the process of being quantified using a combination of conventional manual microscopic counting as well as automated analytical methods (QemSCAN and XRD).

Details of the equipment used are:

- X-ray fluorescence (XRF) analyses using the fusion method and rhodium radiation
- Qualitative X-ray diffraction (XRD) analyses using the powder method and CuKα-radiation
- Unmounted samples were studied using a Leica MZ APO stereomicroscope with transmitted and reflected light
- Samples were set in resin and polished for reflected light optical microscopy using Zeiss Axioplan and Zeiss Axioscop binocular microscopes
- Scanning electron microscopy was performed using a Jeol JSM-5800 LV scanning microscope at 20 kV.

Mineral Formula Theoretical TiO₂ content

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<tr>
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<tr>
<td>Pseudorutile</td>
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</tr>
<tr>
<td>Ferropseudobrookite</td>
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</tr>
<tr>
<td>Rutile/Anatase</td>
<td>TiO₂</td>
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Figure 3. Theoretical TiO₂ content in FeTi oxide phases (wt %). The x-axis is based on wt% TiO₂ with FeO and Fe₂O₃ being the second end-member component of this binary system

Table I

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As this document aims to provide an indication of the minerals and mineral textures encountered in the Ranobe deposit, only some of the microscopic observations are presented below and other analyses are excluded except where EDX analyses are presented to support microscopic identification of mineral phases.

**Characterization of minerals**

**Stereomicroscopy**

The following oxide ore minerals could be distinguished under the stereomicroscope (Figures 4–6).

- Shiny, iron-black, opaque ilmenite with partial alteration often recognizable
- Brown, dark-brown and dark-mustard Fe-oxide (hematite) and Ti-enriched FeTi-oxides (pseudorutile and ferropseudobrookite)
- Yellowish to white leucoxene
- Red, deep-red and black rutile.

**Optical microscopy**

The main ore minerals observed in the deposit are:

- *Goethite/ilmenite*:
  - Occurring as secondary mineral either from ilmenite and hematite alteration or as a precipitate from Fe-bearing solutions, often acting as cement in agglomerates of various other mineral grains.
- *Hematite*:
  - Predominantly primary hematite, commonly containing exsolved ilmenite.
  - Secondary hematite, originating from martitization and ilmenite alteration.
- *Ilmenite*:
  - Ilmenite with exsolved hematite where the ilmenite component may be weathered while the hematite remained essentially unaltered.
- Homogeneous, unaltered ilmenite with TiO₂ contents of 50–54%.
- Ilmenite with incipient alteration along grain boundaries and micro-fractures resulting in Ti enrichment along these zones.
- Moderate to extensive altered ilmenite but original ilmenite often still present.
- Essentially homogeneous FeTi-oxide resembling pseudorutile with TiO₂ contents in the order of 59–65% and less often in the ferropseudobrookite range.
- Localized ‘Spotty’ alteration of ilmenite resulting in heterogeneous, multi-phased particles involving ilmenite, ilmeno-hematite, pseudorutile, ferropseudobrookite, anatase and rutile.

* Rutile:
- Primary homogeneous rutile with TiO₂ contents from 96% to almost 100%.
- Secondary, often porous, rutile resulting from ilmenite alteration. These particles often contain rutile and/or anatase crystals (with TiO₂ levels close to 100%) but the porous natures commonly introduce contaminants (Si in the form of quartz and Al and Si in the form of clay material) to the particle.

Ilmenite from Ranobe displays a number of textural and mineralogical variations that reflect various stages and processes of alteration. During alteration ilmenite decomposes into other more Ti-rich phases such as pseudorutile, ferropseudobrookite and anatase/rutile, resulting in a finely dispersed, spotty appearance under the microscope. As alteration advances the spotty appearance and internal reflection of the alteration products becomes more prominent. During the alteration process the Fe may be leached, resulting in porous grains while the Ti may recrystallize as rutile and/or anatase. The abundance of anatase and to a lesser extent rutile rims around ilmenite grain boundaries testify to this process. With advancing alteration, ilmenite is increasingly replaced by pseudorutile and ferropseudobrookite and original ilmenite is no longer recognizable. Under the microscope, the grains then have a complete dispersed spotty appearance with high internal reflections or may even again approach a homogeneous appearance as a specific phase dominates. Frequently anatase-rich leucoxene is a direct alteration product, and replaces ilmenite along grain boundaries along micro-fractures within ilmenite. Leucoxene can also replace ilmenite pervasively, resulting in leucoxene pseudomorphs after ilmenite. Limonite is also a major mineral phase in the Ranobe deposit, frequently including and replacing FeTi-oxides.

The complexity and heterogeneity of the FeTi-oxide minerals are illustrated in Figures 7–20. These figures were obtained by optical microscopy and back-scattered electron (BSE) microscopy; elemental analyses of individual phases and areas are measured by energy dispersive X-ray (EDX) spectrometry.

![Figure 7. Ilmenite grain (pink) replaced by pseudorutile (white) along micro-fractures and grain boundaries](image)

![Figure 8. Exsolved ilmenite-hematite with the curvature of the lamellae suggests that the grain was subjected to physical strain after its crystallization](image)

![Figure 9. Ilmenite grain altered to anatase-rich leucoxene along fractures](image)
Figure 10. Ilmenite altered to pseudorutile (white) and ferropseudobrookite (light red) along cracks and grain boundaries.

Figure 11. Pervasively altered ilmenite grain with ferropseudobrookite (red) and anatase (white) as alteration products.

Figure 12. Pseudorutile (centre of grain) altered to anatase (white).

Figure 13. Extensive altered grain comprising anatase-rich leucoxene (orange-red) and anatase (white).

Figure 14. Recrystallized mosaic-patterned ferropseudobrookite (red) with anatase as a replacement product along fractures and grain boundaries.

Figure 15. Recrystallized anatase (yellow) and recrystallized lepidocrocite (red).
Thus, in summary, the FeTi-oxides were categorized as:

- **Unaltered ilmenite** refers to ilmenite without any optical visible signs of alteration or incipient alterations concentrated along grain boundaries, micro-fractures and as clusters scattered through the grains.
- **Moderate altered ilmenite** refers to particles where original ilmenite is no longer the dominant component.
- **Highly altered ilmenite** refers to particles where most of the grain or the entire grain is affected by alteration. Original ilmenite is rarely present and increasingly difficult to distinguish and sometimes only discernable under very high magnification or not at all.

These particles typically exhibit pseudorutile-type compositions.

Figure 16. Ilmenite grain showing two stages of crystal growth separated by an anatase alteration rim on the earlier crystal surface (arrow)

Figure 17. Rhythmically layered limonite (red) overgrowing ilmenite (opaque) together with anatase-rich limonite (bright orange)

Figure 18. Progressive alteration of ilmenite depicting (a) unaltered ilmenite, (b) incipient alteration of ilmenite along grain boundaries and fractures, (c) extensive alteration throughout the grain and (d) ‘spotty’ alteration of ilmenite involving the formation of hematite, pseudorutile, ferropseudobrookite and rutile/anatase

Figure 19. Altered ilmenite with varying extents of alteration resulting in a heterogeneous particle containing various Ti-bearing phases, including original remnant ilmenite, pseudorutile, ferropseudobrookite and rutile/anatase

Figure 20. A porous, secondary particle containing ilmenite, pseudorutile, ferropseudobrookite and rutile/anatase and associated with the introduction of Si-contaminants
Pseudorutile is still present, but becoming subordinate, with increasing ferropseudobrookite and leucoxene contents replacing pseudorutile along grain boundaries and fractures.

- Leucoxene refers to particles where ilmenite is clearly absent. These particles are often porous (associated with the introduction of contaminants) and may contain re-crystallized Ti-laths (rutile and/or anatase). However, many particles have a homogeneous appearance with ferropseudobrookite and leucoxene-type compositions.

**Scanning electron microscopy**

SEM and micro-analyses confirmed the initial optical microscopic observation of different ‘ilmenite’ occurrences and subsequent correlation with Ti contents (Figures 21–22).

It is thus evident that FeTi-oxides with varying compositions, from typical ilmenite to pseudorutile to ferropseudobrookite to ‘leucoxene’, are present and that these phases can be distinguished by optical microscopy.

**Textures and physicochemical constraints**

The following paragraphs discuss suggested mineral reactions that could have taken place during the alteration of ilmenite into pseudorutile, ferropseudobrookite, anatase/rutile and limonite/goethite. Although a detailed thermodynamic investigation of these reactions still has to be performed, it is highly unlikely that alteration occurred under the same physicochemical conditions. Although no information is available on the alteration conditions of pressure and temperature, it is obvious that different Eh and pH conditions are required to facilitate the reactions presented in Table II. This is also supported by the textural evidence suggesting complex alteration history of ilmenite in the Toliara orebody.

- *Ilmenite alteration to pseudorutile*—reaction [1] in Table II is proposed to explain the alteration of ilmenite into pseudorutile; the resulting mineral texture is shown in Figure 7. Relative low pH and oxidizing conditions are required to drive this reaction.
- *Ilmenite alteration to anatase-rich leucoxene with and without limonite*—alteration of ilmenite into anatase-rich leucoxene and limonite according to Reactions [2] and [3] in Table II, depicted in Figures 9 and 17, could occur also under relatively low pH and oxidizing conditions, respectively.
- *Pseudorutile alteration to ferropseudobrookite*—Progressive alteration of pseudorutile into ferropseudobrookite, of which mineral textures are shown in Figures 10 and 14, could occur according to Reaction [4] in Table II. This reaction, compared to Reactions [1] to [3], requires different Eh and pH conditions, implying that chemical conditions have changed during time and/or that the minerals were transported and subjected to a different environment. The scarcity of ferropseudobrookite suggests that these conditions were met only very locally and/or temporarily.
- *Pseudorutile alteration to anatase-rich leucoxene and limonite*—alteration of pseudorutile to leucoxene and anatase according to Reaction [5] in Table II is pH and Eh independent. The resulting anatase-rich leucoxene-limonite mineral assemblage looks very similar to that of the ‘limonitization’ of ilmenite but due to the higher anatase-rich leucoxene contents has a bright yellow appearance.
- *Ferropseudobrookite alteration to anatase-rich leucoxene*—Reaction [6] in Table II explains the alteration of ferropseudobrookite into anatase as shown in Figure 14. Reactions [1], [2], [4] and [6] in Table II release Fe\(^{2+}\) into fluids and solutions of which the presence is essential for the discussed alteration processes.
- *Secondary formation of limonite from mobilized Fe\(^{2+}\)—under oxidizing conditions Fe\(^{2+}\) will precipitate according to Reaction [7] in Table II in the form of limonite or lepidocrocite, as shown in Figures 15 and 17. Limonite and/or lepidocrocite frequently display mineral inclusions of all other observed minerals, suggesting that Fe\(^{2+}\) was mobile throughout the ilmenite alteration stages and processes that occurred under reducing conditions.

Incomplete alteration in the majority of the observed mineral textures also suggests that the fluid phase was buffered with respect to oxygen fugacity and pH by the mineral assemblages. Multi-phase crystallization of
Ilmenite (Figure 16), recrystallization and annealing textures of ferropseudobrookite and anatase (Figures 14 and 15) also testify to the general observation that the Ranobe orebody underwent a complex alteration process. It therefore stated that it is highly unlikely that alteration processes occurred under the same conditions of time and space.

**Metallurgical implications**

A thorough study and understanding of minerals and mineral textures is of paramount importance to ascertain the pertinent insight and understanding during beneficiation and separation of different minerals. In the case of ilmenite and its alteration products, physical and chemical properties vary drastically depend on the quality and quantity of the various mineral phases. Considering the magnetic, conductive and density properties used during heavy mineral separation, it is obvious that unaltered and altered ilmenite behave differently. Unaltered ilmenite has a higher specific gravity and a better electrostatic and magnetic response than the Fe-poorer and Ti-richer ilmenite alteration products. Intimate intergrowths of unaltered and altered ilmenite need to be identified under the microscope as they may cause serious implications during separation processes. The feasibility of liberating the individual mineral phases before applying density, electrostatic and magnetic separation techniques, greatly depends on the mineral textures and the mode and occurrence of mineral intergrowths.

Based on the above discussion of mineral textures, it suffices to state that the complexity of the observed minerals textures from Ranobe samples present an extreme metallurgical challenge for mineral separation and beneficiation. Some of the alteration products form coatings on mobilized Fe2+

### Conclusion

Ranobe samples present a metallurgical challenge for mineral separation and beneficiation. Ilmenite is a major economic mineral in the Ranobe heavy mineral deposit. The majority of ilmenite grains show alteration textures ranging from incipient to pervasive and complete alteration. The replacement products of ilmenite in order of progressive alteration are pseudorutile, ferropseudobrookite, leucoxene and anatase/rutile. During the alteration of ilmenite, relatively mobile Fe2+ is released, whereas the relatively immobile Ti4+ remains behind as part of the newly formed secondary mineral phases. In this process the Ti content increases in the newly formed minerals with progressive alteration. Some of the observed limonite also forms as an alteration product of ilmenite, resulting in a fine-grained mineral assemblage together with anatase-rich leucoxene. The observed mineral assemblages and textures suggest a complex alteration history during transportation and/or deposition involving fluids that interacted with ilmenite and its alteration products at different Eh and pH conditions. Ilmenite replacement with pseudorutile requires higher oxidation potentials than the replacement of pseudorutile with ferropseudobrookite. The relative scarcity of ferropseudobrookite in the Ranobe deposit suggests that the physicochemical conditions were attained less frequently than those that led to the formation of the other ilmenite alteration products. The ultimate alteration end-member is anatase/rutile, suggesting that TiO2 is the only component left behind after all Fe2+ has been ‘leached out’.

In the Ranobe orebody the alteration processes yielded a variety of highly intricate mineral textures. A detailed microscopic analysis and description of the various mineral phases and alteration textures is of profound importance to efficiently apply mineral separation methods. Electrostatic and magnetic response as well as density decreases with intensity of ilmenite alteration. Only once the quality, quantity and textural appearance of the alteration phases have been established, can the physical behaviour of the minerals during separation be explained and predicted. It is, therefore, particularly challenging to qualify and quantify the mining potential of this deposit.

### Acknowledgement

The authors greatly appreciate the contribution from Dumi Sibiya, Principal Geologist, Exxaro.

### References

