

(1973), with six reflections (PDF 30-287), has many strong reflections missing compared with the calculated pattern, it was decided to collect powder data.

Specimen number 20292 of the American Museum of Natural History, New York, from Yellow Cat Wash, near Thompsons, Utah, USA was reported to contain rossite together with metarossite,  $\text{CaV}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ . A powder X-ray diffraction pattern of specimen 20292 was identified as only metarossite after comparison with PDF 29-392. Specimen 20292 was then placed over water in a dessicator for three months at room temperature, where the specimen rehydrated to rossite. Therefore the reaction between rossite and metarossite is reversible at room temperature.

Guinier films of rossite were taken with  $\text{Cu-K}\alpha_1$  radiation (1.5405 Å) with a graphite 0002 monochromator for 2 and 14 hour exposures, and then measured with a densitometer. The unit-cell para-

meters, which were refined by least-squares analysis starting from the unit-cell parameters of Ahmed and Barnes in space group  $\text{P}\bar{1}$ (no. 2), are  $a$  8.552(2),  $b$  8.576(2),  $c$  7.028(2) Å,  $\alpha$  101.50(2)°,  $\beta$  114.96(2)°, and  $\gamma$  103.39(2)°. The  $hkl$ ,  $d$  calculated,  $d$  observed, relative intensities ( $I/I_1$ ), and  $I$  calculated are presented in Table I.

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## Some alumina and silica in weathered ilmenite grains is present in clay minerals—a response to Frost *et al.* (1983)

IN a recent issue of this journal, Frost *et al.* (1983) reported electron microprobe analyses of altered ilmenite grains from West Australian beach sand deposits which they interpreted as showing that Al and Si levels increased with decreasing iron within those grains whose compositions lie between that of rutile and pseudorutile. These authors consider that during the latter stages of ilmenite alteration, when rutile crystallizes from solution, both alumina and silica are extracted from the ambient environment and are coprecipitated with, or adsorbed on, rutile. However, in the lateritic pallid zone, the increased Al and Si content of altered ilmenite grains is due to crystallization of halloysite, kaolinite and gibbsite from soil solution within pores rather than to incorporation of these elements into anatase crystals (Anand and Gilkes, 1984).

In view of the apparent difference in forms of Al and Si in altered ilmenite from the pallid zone and beach sand, samples of ilmenite from West Australian beach sand were investigated using the analyti-

cal procedures employed by Anand and Gilkes (1984). The samples studied were from the same deposits as those analysed by Frost *et al.* (1983) and were supplied by Associated Minerals Consolidated (AMC), Capel, Western Australia. A chemical analysis of a typical altered ilmenite concentrate is given in Table I and is similar to samples investigated by Frost *et al.* (1983), although containing more  $\text{TiO}_2$  and 2-3 times as much  $\text{Al}_2\text{O}_3$ . Highly altered ilmenite grains were separated in a Frantz isodynamic magnetic separator and hand-picked under the microscope. A powder X-ray diffractometer pattern showed that the sample consisted of ilmenite, pseudorutile and rutile; no reflections due to clay minerals were detected. Reflected light photomicrographs of polished sections showed that partly altered ilmenite grains consist of a core or bands of dark grey phase (pseudorutile) with rutile showing white internal reflections developed within and around the grains. This style of alteration of ilmenite to rutile via pseudorutile in beach

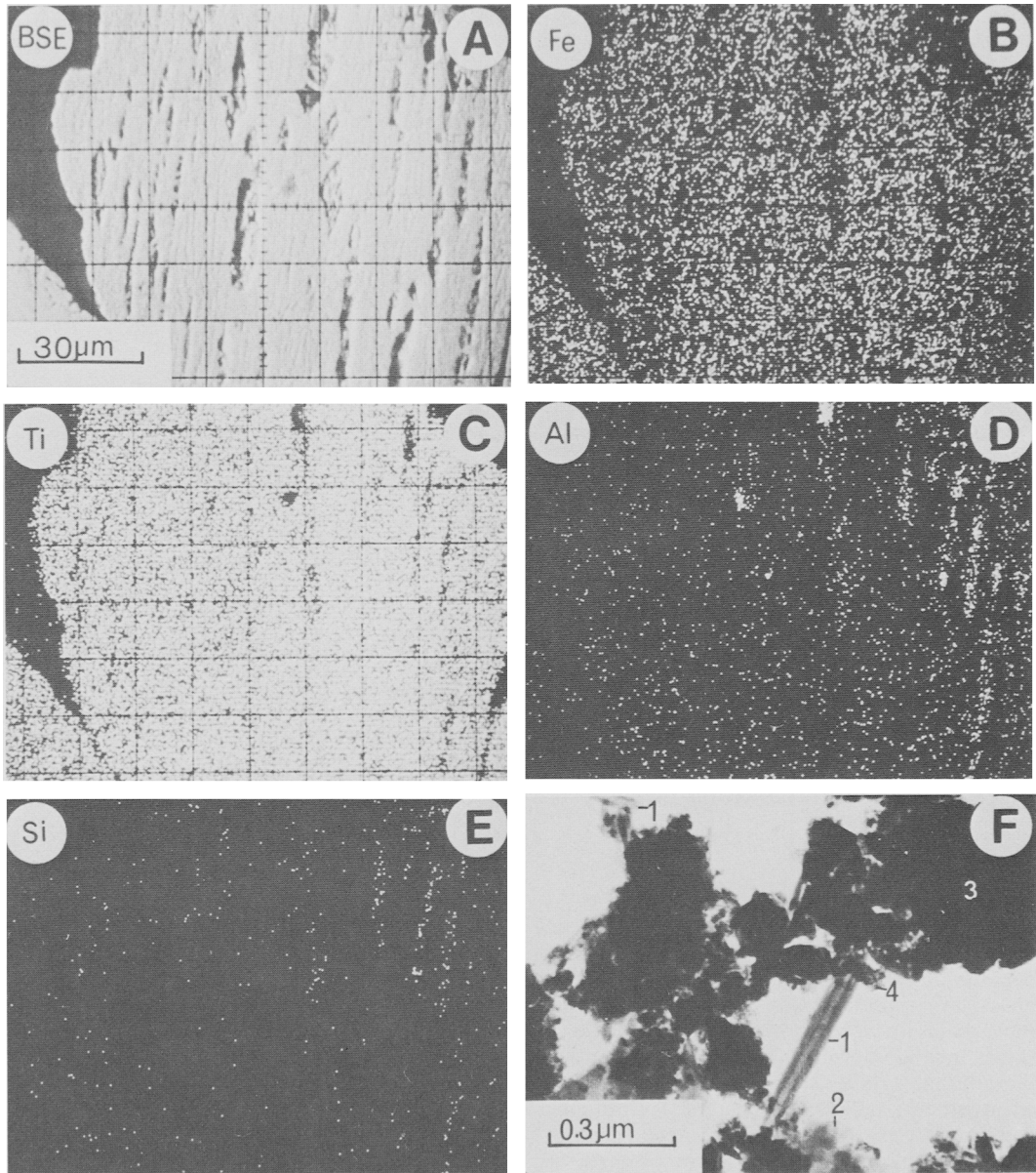


FIG. 1. Electron microprobe back-scattered electron (BSE) and X-ray images (B-E) of an altered ilmenite grain consisting mostly of a porous aggregate of very small rutile crystals. Much Si and Al is present as aggregates of halloysite, kaolinite and gibbsite in large elongated pores. (F) Transmission electron micrograph of the  $< 5 \mu\text{m}$  fraction of altered ilmenite showing tubular halloysite (1), platy kaolinite or gibbsite (2), large fragments of ilmenite/pseudorutile (3) and aggregates of small (*c.*  $0.01 \mu\text{m}$ ) crystals of rutile (4).

TABLE I. Chemical analysis (wt. %) of typical altered ilmenite concentrate from beach sand and its residue after caustic digest\*

	Concentrate	Residue
TiO <sub>2</sub>	60.5	—
FeO	14.2	—
Fe <sub>2</sub> O <sub>3</sub>	17.8	—
SiO <sub>2</sub>	0.90	0.60
Al <sub>2</sub> O <sub>3</sub>	2.0	1.2
MnO	1.1	—

\* Analysed by Associated Minerals Consolidated.

sands has been reported by several workers (e.g. Temple, 1966; Grey and Reid, 1975).

Si and Al are present in appreciable amounts in all altered ilmenite specimens from West Australian deposits (e.g. Table I). Electron microprobe X-ray images of altered ilmenite show Si and Al in patches within pores (fig. 1D, E) in rutile-rich regions, which is consistent with the presence of included clay. This interpretation was confirmed by XRD and TEM analysis. X-ray diffraction patterns of the basally oriented < 5  $\mu\text{m}$  fraction of crushed altered ilmenite showed the presence of dehydrated halloysite and/or kaolinite (7.2 Å) and gibbsite (4.84 Å); these identifications were confirmed by various heat treatments (fig. 2). The gibbsite peak (4.84 Å) disappeared on heating to 300 °C for 1 hour; the 7.2 Å halloysite/kaolinite peak disappeared on heating to 550 °C for 1 hour. Much larger amounts of ilmenite, pseudorutile, and rutile were also present in the < 5  $\mu\text{m}$  fraction.

Transmission electron micrographs of the < 5  $\mu\text{m}$  fraction showed the presence of tubular halloysite, platy kaolinite/gibbsite, large fragments of ilmenite/pseudorutile and aggregates of small (c. 0.01  $\mu\text{m}$ ) rutile particles (fig. 1F). The identity of halloysite, kaolinite, and gibbsite was confirmed by taking selected area electron diffraction patterns of single crystals. Halloysite crystals are c. 0.1–1.0  $\mu\text{m}$  tubes elongated along their *b* axes (fig. 3A, B). Kaolinite occurs as platy anhedral to euhedral hexagonal c. 0.3  $\mu\text{m}$  crystals and was identified from its *hk0* net of reflections with an 060 spacing of 1.49 Å (fig. 3C, D). Gibbsite crystals are generally c. 0.2  $\mu\text{m}$ , platy, anhedral, and gave typical arced *hk0* reflections with a 330 spacing of 1.46 Å (fig. 3E, F). These SAD patterns were calibrated by reference to a gold standard.

Several samples of altered ilmenite were treated with 15% NaOH (w/v) at 70 °C for 1 hour\* (40 g of

\* AMC assisted with this work.

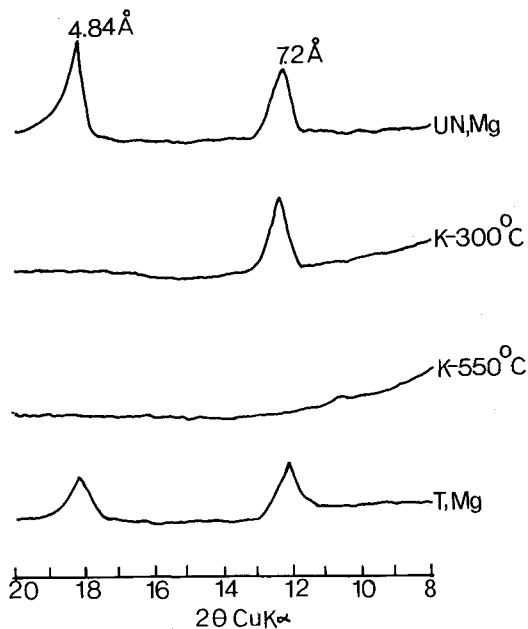


FIG. 2. X-ray diffractometer patterns of the basally oriented < 5  $\mu\text{m}$  fractions of treated (T, treated with NaOH) and untreated (UN) altered ilmenite. Mg = Mg saturated; K-300 °C, K-550 °C = K saturated and heated at 300 °C and 550 °C for 1 hr. The 7.2 and 4.84 Å reflections are due to dehydrated halloysite and/or kaolinite and gibbsite respectively.

mineral in 20 ml of solution). The titanium minerals did not dissolve but the altered ilmenite contained much less Al and Si after this treatment; in most cases the Al content was reduced by approximately 50%. The < 5  $\mu\text{m}$  fraction of NaOH-treated samples contained less gibbsite and halloysite/kaolinite, with XRD patterns indicating that a greater proportion of gibbsite had dissolved (fig. 2). The electron microprobe maps for Al and Si in the NaOH-treated material showed that these elements no longer occurred in deposits within the larger pores. This is probably due to the easy access of NaOH into the larger pores, compared with the smaller pores where gibbsite and halloysite/kaolinite would remain protected. TEM micrographs of treated material also showed a lower abundance of gibbsite and halloysite/kaolinite crystals relative to titanium minerals.

These results offer an explanation for the observed increasing Al and Si content with Ti/(Ti + Fe) ratio reported by Frost *et al.* (1983). The present investigation has clearly indicated that Si and Al are mostly present as clay minerals and gibbsite in

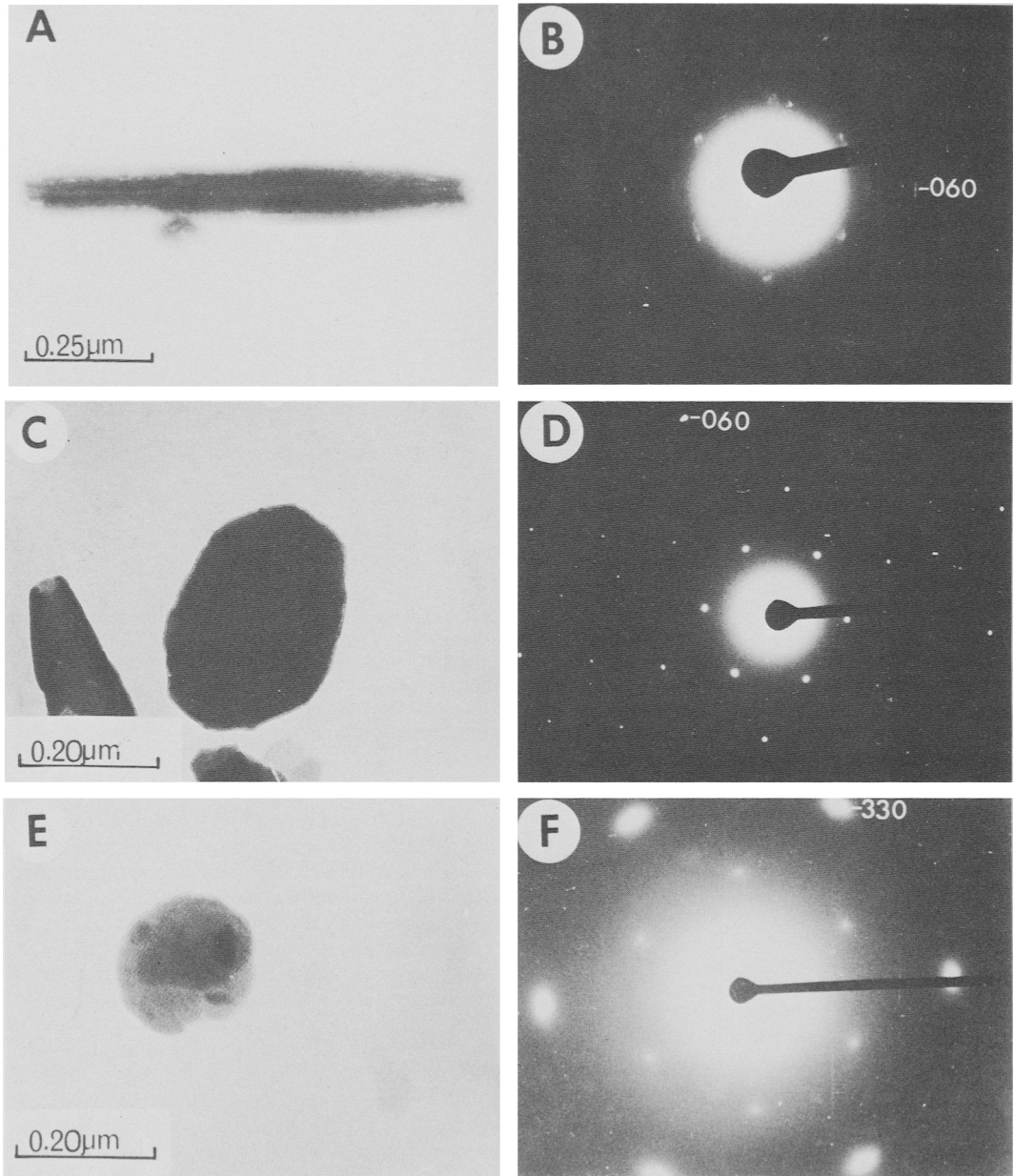


FIG. 3. Transmission electron micrographs and selected area electron diffraction patterns of halloysite, kaolinite, and gibbsite present in the  $< 5 \mu\text{m}$  fraction of altered ilmenite. (A) A tubular halloysite; (B) Its correctly oriented SAD pattern showing that it is elongated along the  $b$  axis; (C) A sub-hexagonal crystal of kaolinite; (D) Its SAD pattern consisting of an  $hk0$  net of reflections with an  $060$  spacing of  $1.49 \text{ \AA}$ . (E) A rounded crystal of gibbsite; (F) Its SAD pattern consisting of typical slightly arced  $hk0$  reflections with a  $330$  spacing of  $1.46 \text{ \AA}$ . The diffraction patterns were calibrated by reference to an evaporated gold standard.

pores within a rutile matrix. As massive ilmenite alters isovolumetrically with porous rutile, the increased abundance of pores allows for increased incorporation of Si and Al within the pores. Whereas Frost *et al.* propose that the Si and Al are coprecipitated with, or adsorbed on to the alteration products during the formation of rutile, we propose that the incorporation of these impurities in the pores of the altered grains is an integral, ongoing part of the soil-forming processes in the heavy mineral deposits. Thus incorporation of Al or Si into altered ilmenite grains in mineral sand deposits is identical to the mechanism proposed by Anand and Gilkes (1984) for altered ilmenite grains in lateritic pallid zones. This is a significant result, since existing methods of beneficiating the altered ilmenite ore are based on the assumption that Al or Si impurities are incorporated into rutile and anatase. Since most Al and Si is actually present as discrete clay minerals and gibbsite, they may therefore be removed by caustic leaching procedures that do not dissolve the titanium oxides.\*

The West Australian mineral sand deposits

\* Dr Grey has now kindly supplied sub-samples of altered ilmenite specimens YE-90 and YE-150 described in Frost *et al.* (1983). Both specimens were examined using the procedures described in this communication and were found to contain gibbsite, kaolinite, and halloysite.

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are soils which have developed on ancient strand lines and it is reasonable to suppose that similar soil-forming processes (e.g. clay mineral and gibbsite crystallization) should operate here and in the lateritic pallid zone. However, the weathering environment is not identical in both soils since anatase and rutile are the major alteration products in pallid zones and beach sands respectively. This difference may be a consequence of a difference in the height of the water table and its effect on Eh and the mobility of Fe and other ions. For example, Schossberger (1942) has shown that the presence of SO<sub>3</sub> favours the formation of anatase instead of rutile.

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## Note on cell parameters of zaheerite

THE *hkl*-indices for the X-ray diffraction spectrum of zaheerite was recently calculated for material from Pofadder, South Africa (Beukes *et al.*, Table II, 1984), using the method of Appleman *et al.* (1972). The authors have now become aware that the calculated cell volume is about 30% too small. This becomes apparent when a formula is employed

which relates volume and density to the cation cell content (D. Peacor, pers. comm. 1984). We have now been successful in obtaining more refined indices (Table I) which are in agreement with the predicted cell volume. The revised cell parameters, with the standard errors given in parentheses, are:  $a = 18.475$  (0.942),  $b = 19.454$  (0.591),  $c = 3.771$