

Mineralogical nomenclature: pseudorutile revalidated and neotype given

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Abstract

Pseudorutile, $\text{Fe}_2^{3+}\text{Ti}_3\text{O}_9$, has recently been revalidated as a mineral species, and the neotype locality is now South Neptune Island, South Australia. Powder X-ray diffraction data are given on a hexagonal primitive unit cell with $a = 2.8667(5)$ and $c = 4.5985(9)$ Å. Leucoxene, arizonite and proarizonite are considered to be mixtures. Kleberite is considered to be a hydroxylated pseudorutile, $\text{Fe}_{2-x}^{3+}\text{Ti}_3\text{O}_{9-3x}(\text{OH})_{3x}$.

KEYWORDS: pseudorutile, arizonite, proarizonite, leucoxene, kleberite, type specimen, type locality

Introduction

THE name pseudorutile was introduced into the literature by Teufer and Temple (1966), who chemically analysed alteration products of ilmenite from Florida and New Jersey, USA; Quilon, India; and Brazil. The name was given to the phase with a composition corresponding approximately to $\text{Fe}_2^{3+}\text{Ti}_3\text{O}_9$. None of the specimens investigated were nominated as a type specimen. X-ray powder diffraction gave a pattern with sharp reflections that were indexed on a hexagonal unit cell with $a = 2.872$ and $c = 4.594$ Å, and five diffuse reflections that may be poorly indexed on a superstructure with $a = 4.8a$. Temple (1966) was able to index fully the powder patterns of commercial ilmenite concentrates from various countries, in terms of the three minerals: ilmenite, rutile and pseudorutile. Further powder X-ray diffraction data of pseudorutile have been published by Larrett and Spencer (1971), and Frost *et al.* (1986).

The natural alteration product of ilmenite has also been called leucoxene (Gümbel, 1874). The name leucoxene has been loosely applied to alteration products high in titanium and has

been found to consist of rutile, anatase or titanite (Palache *et al.*, 1944). In current usage (Frost *et al.*, 1983), leucoxene generally refers to a commercial concentrate with about 90 wt.% TiO_2 and is a mixture of pseudorutile and rutile. Arizonite, an alteration product of ilmenite named by Palmer (1909), has been shown to be a mixture of hematite, anatase and rutile (Overholt *et al.*, 1950). Proarizonite was named by Bykov (1964) for an intermediate product between ilmenite and arizonite; however, proarizonite was discredited by the CNMMN (Commission of New Minerals and Mineral Names of the International Mineralogical Association) in 1968.

Description of pseudorutile

The colour of pseudorutile varies from black to intermediate shades of brown, red and grey. The mineral is opaque and magnetic with a specific gravity of ~ 3.8 . Pseudorutile generally occurs as a fine-grained alteration product of ilmenite, although single crystals of a size suitable for single-crystal diffraction analysis have been found. The crystal structure of pseudorutile was determined by Grey and Reid (1975) on a specimen

TABLE 1. X-ray powder diffraction data of pseudorutile

<i>d</i>	<i>I</i>	<i>hkl</i>
3.897	15d	s
2.784	20d	s
2.481	80	100
2.2993	8	002
2.1830	70	101
1.8625	1d	s
1.6860	100	102
1.6253	6d	s
1.5005	3d	s
1.4324	25	110
1.3831	6d	s
1.3049	4	103
1.2415	2	200
1.2160	1	112
1.1988	2	201
1.1497	3	004
1.0927	5	202
1.0430	3	104

s: reflection from incommensurate super-structure

d: defuse reflection

from an unspecified locality in Indonesia. Refinement of the crystal structure was done in space group *P322* on a hexagonal unit cell with $a = 14.375$ and $c = 4.615$ Å. The substructure is a hexagonal close-packed oxygen framework. The Ti and Fe atoms have two thirds occupancy over half the available octahedral sites with random distribution and are fully ordered over the other half of the octahedral sites. The sharpness of the non-substructure reflections indicates the degree of Ti and Fe ordering.

A specimen in a clay horizon from South Neptune Island, South Australia, which was described by Larrett and Spencer (1971), is

shown to be pure, with reflections from rutile and ilmenite absent. Powder X-ray diffraction data from this specimen are given in Table 1 and Fig. 1. The data were collected with $\text{Cu-K}\alpha_1$ radiation and a graphite monochromator ($\lambda = 1.540579$ Å) on a diffractometer between 10 and $100^\circ 2\theta$. Silicon was used as an external standard in order not to contaminate the specimen, which was required for deposition in a museum. Peak heights have been used for reflection intensities. The hexagonal dimensions with a primitive lattice for the substructure calculated from the sharp reflections on the X-ray powder diffraction pattern are $a = 2.8667(5)$ and $c = 4.5985(9)$ Å; whereas the six diffuse asymmetrical reflections did not index satisfactorily within a superstructure. Therefore, the Fe and Ti atoms are poorly ordered.

Ilmenite FeTiO_3 (47.3 FeO and 52.7 wt.% TiO_2) with oxidization and loss of soluble Fe^{2+} by $[3\text{Fe}^{2+}\text{TiO}_3 = \text{Fe}_2^{3+}\text{Ti}_3\text{O}_9 + \text{Fe}^{2+}]$ will transform to pseudorutile (40.0 Fe_2O_3 and 60.0 wt.% TiO_2) without disturbing the oxygen framework; however, experimentally it is difficult to differentiate between $\text{Fe}_2^{3+}\text{Ti}_3\text{O}_9$ and $\text{Fe}_2^{3+}\text{Ti}_3(\text{OH})_2$. Synthetic Fe-rich pseudorutiles were prepared from hydrothermal synthesis by Grey *et al.* (1983) with a composition range of $0.3 < \text{Ti}/(\text{Ti} + \text{Fe}) < 0.6$ [$\text{Fe}_2(\text{Ti}_{1.5}\text{Fe}_{1.5})\text{O}_9 - \text{Fe}_2\text{Ti}_3\text{O}_9$]. Dyadchenko and Khatuntseva (1960) described a titanium-rich product of weathered ilmenite, which they called arizonite but can be regarded as hydroxylan pseudorutile. The composition range was expressed by the formula $\text{Fe}_2\text{O}_3 \cdot n\text{TiO}_2 \cdot m\text{H}_2\text{O}$ with $3 < n < 5$ and $1 < m < 2$. With $n = 5$ and 9 anions, the formula is $\text{Fe}_{1.2}^{3+}\text{Ti}_3\text{O}_{6.6}(\text{OH})_{2.4}$; whereas with $m = 2$ and 9 anions, the formula is $\text{Fe}_{0.67}^{3+}\text{Ti}_3\text{O}_5(\text{OH})_4$. That is hydroxylan pseudorutile with $x = 0.8$ and 1.33 respectively.

The weathering process appears to involve the removal of the soluble Fe^{2+} rather than the

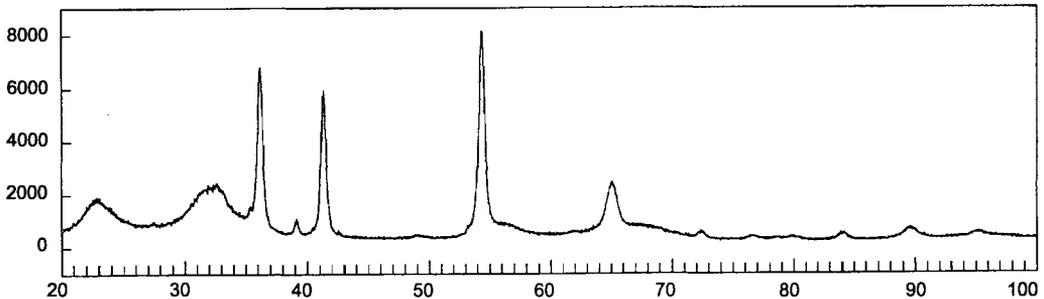


FIG. 1. X-ray powder diffraction data of pseudorutile.

oxidation of Fe^{2+} to Fe^{3+} and the removal of the insoluble Fe^{3+} . With the removal of Fe^{2+} , the electrostatic charge balance is maintained by oxidation of the remaining iron to Fe^{3+} and/or the addition of H^+ . If the Fe atoms are removed in any regular pattern, then the pseudorutile will show ordering.

Pseudorutile may be an oxyhydroxide mineral with an extended range of homogeneity (Frost *et al.*, 1983) due to replacement of Fe^{3+} by 3H^+ , giving the general formula $\text{Fe}_{2-x}^{3+}\text{Ti}_3\text{O}_{9-3x}(\text{OH})_{3x}$. The chemical formula of the pseudorutile from South Australia reported by Grey and Reid (1975) from electron probe analysis and the water from weight loss on heating with the Mn oxidation state chosen to balance the formula was given as $\text{Fe}_{1.81}^{3+}\text{Fe}_{0.07}^{2+}\text{Mn}_{0.03}^{3+}\text{Ti}_{3.08}^{4+}\text{O}_9 \cdot 0.75\text{H}_2\text{O}$. If the water in the chemical analysis is taken as hydroxide and the total number of anions is taken as 9, the chemical formula can be expressed as $\text{Fe}_{1.67}^{3+}\text{Fe}_{0.07}^{2+}\text{Mn}_{0.03}^{3+}\text{Ti}_{2.84}^{4+}\text{O}_{7.6}(\text{OH})_{1.4}$.

Discussion

Pseudorutile was rejected as a valid mineral species by the CNMMN (1968) before the mineral was adequately characterized. Based upon a well defined description, pseudorutile has been used in the literature by numerous authors and compilations such as Fleischer (1987), Nickel and Nichols (1990), and Clark (1993).

Arizonite was named by Palmer (1909), from a chemical analysis, as $\text{Fe}_2\text{Ti}_3\text{O}_9$ with an axial ratio of $a:b:c = 1.88:1:2.37$ and $\beta = 125^\circ$. X-ray diffraction data (PDF 29-1494) of the only extant specimen (Smithsonian Institute, Washington D.C., 86,973) by Overholt *et al.* (1950) showed that arizonite is an impure mixture of hematite, ilmenite, anatase and rutile. Discussions by Lynd (1960), Flinter (1960), and Golding (1961) show a similar lack of agreement. An attempt to index partially the X-ray diffraction data of Overholt *et al.* (1950) on the pseudorutile subcell was unsuccessful. Under hydrothermal conditions, Karkhanavala and Momin (1959) produced synthetic arizonite, $\text{Fe}_2\text{Ti}_3\text{O}_9$, documented by X-ray powder diffraction data (PDF 13-326); however, an attempt to index the data on the pseudorutile subcell was unsuccessful. Therefore, arizonite is considered to be a mixture.

Although the names leucoxene and arizonite have historical priority, neither has been adequately defined, and both have been shown to be mixtures.

It has not been possible to obtain any specimen of pseudorutile described by Teufer and Temple (1966) for study. Requests to the Harvard

University Mineralogical Museum, the Field Museum of Natural History in Chicago, the American Museum of Natural History in New York, the Natural History Museum of Los Angeles County, and the National Museum of Natural History (Smithsonian Institution) in Washington all proved fruitless.

Therefore, it is proposed to reinstate pseudorutile as a valid species and to designate the locality of South Neptune Island, South Australia, described by Larrett and Spencer (1971), as a neotype. The choice was based upon an exact locality, a pure specimen, and evidence that the disordered state is the most common. A specimen used for the single crystal study by Grey and Reid (1975) has been deposited at the Museum of Victoria in Melbourne, Victoria, Australia, as specimen number M42789. This proposal has been approved by the CNMMN.

Kleberite, without CNMMN approval, was described by Bautsch *et al.* (1978) and the crystal structure given by Zedler *et al.* (1978); however, Fleischer (1979) describes these as a 'thoroughly unsatisfactory description'. The unindexed powder diffraction data were indexed upon the hexagonal substructure of pseudorutile with $a = 2.8348(14)$ and $c = 4.579(9)\text{\AA}$ and no superstructure reflections were observed. The chemical formula based upon 9 anions and ferric iron from the chemical analysis (Bautsch *et al.*, 1978) may be expressed as $(\text{Fe}_{0.54}^{3+}\text{Si}_{0.15}\text{Al}_{0.08}\text{Ca}_{0.05}\text{Ba}_{0.03}\text{P}_{0.02})\text{Ti}_{3.07}\text{O}_{6.01}(\text{OH})_{2.99}$, which is similar to the chemical formula of hydroxylan pseudorutile by Dyadchenko and Khatuntseva (1960). Therefore kleberite, which has a similar crystal structure and chemical formula to pseudorutile, is considered to be a hydroxylan pseudorutile.

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