FERROKINOSHITALITE, A NEW SPECIES OF BRITTLE MICA FROM THE BROKEN HILL MINE, SOUTH AFRICA: STRUCTURAL AND MINERALOGICAL CHARACTERIZATION

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ABSTRACT

Ferrokinoshitalite, ideally $BaFe^{2+}_3(Si_2Al_2)O_{10}(OH)_2$, is the iron-rich analogue of kinoshitalite, and thus a new species of the brittle mica group. Samples commonly have considerable chemical substitutions, with large cations (*e.g.*, K, Na) for Ba, medium-size cations (*e.g.*, Mg, Mn, Ti, Al, Fe^{3+}) in octahedral sites, and F for OH. The color is dark green, the luster is vitreous, thin grains are translucent, the streak is green, the Mohs hardness is 3, the density is 3.69(8) g/cm^3 (measured) and 3.59 g/cm^3 (calculated), and it has perfect (001) cleavage. From single-crystal determinations, ferrokinoshitalite is monoclinic, space group $C2/m$, with unit-cell parameters a 5.389(1), b 9.337(2), c 10.054(2) Å, β 100.53(2)°. The polytype is $1M$, and Z is equal to 2. The strongest five powder X-ray diffraction lines [d in Å(I)] are: 2.651(100), 2.176(40), 1.551(30), 1.659(25), and 1.529(25). The mean index of refraction, as determined from the Gladstone–Dale relationship, is 1.6939. The mineral is biaxial negative, and strongly pleochroic. Thermal gravimetric analysis shows a net gain in weight of ~2.4 wt% from 400 to 1000°C, after a small loss in weight of ~0.2% from 24 to 400°C. The weight gain is attributed to iron oxidation, which produces hematite. The crystal structure of ferrokinoshitalite was refined to an agreement factor $R = 0.032$ and $wR = 0.036$ using 750 unique observed reflections on a sample with a structural formula of $(Ba_{0.47}K_{0.33}Na_{0.04})(Fe^{2+}_{1.72}Mg_{0.74}Mn_{0.08}Fe^{3+}_{0.15}Ti_{0.17})(Si_{2.44}Al_{1.56})O_{10}(OH_{1.35}F_{0.65})$. The two independent octahedral sites are marginally different in size ($M1$: 2.120 *versus* $M2$: 2.106 Å). The effect of Fe content on the structures of Ba-rich micas is discussed. The tetrahedral rotation angle, α, is small at 3.95°, owing to the relatively large size of Fe^{2+} and Ba. Ferrokinoshitalite occurs in massive Pb–Zn–Cu–Ag sulfide orebodies at the Broken Hill mine, northern Cape Province, South Africa, in a mineral assemblage containing quartz + magnetite + spessartine-rich garnet + apatite ± sillimanite ± ferroan gahnite ± sulfides, with Mn-rich grunerite (in places, manganogrunerite), manganoan fayalite and Mn-rich pyroxferroite also present in amphibole-rich layers. On the basis of previous studies, ferrokinoshitalite is believed to have formed at or near the peak of metamorphism (at 670 ± 20°C and 4.5 ± 1.0 kbar).

Keywords: banded iron-formation, brittle mica, ferrokinoshitalite, new mineral species, structure determination, sulfide deposits, Broken Hill mine, Cape Province, South Africa.

SOMMAIRE

La ferrokinoshitalite, de composition idéale $BaFe^{2+}_3(Si_2Al_2)O_{10}(OH)_2$, est l'analogue riche en fer de la kinoshitalite, et ainsi une nouvelle espèce minérale du groupe des micas cassants. Les échantillons font preuve de substitutions importantes dans les sites, impliquant des cations assez gros, par exemple K et Na, dans le site du Ba, des cations de taille moyenne, par exemple Mg, Mn, Ti, Al et Fe^{3+}, dans les sites octaédriques, et F pour OH dans les sites anioniques. C'est un minéral vert foncé à éclat vitreux; les grains les plus minces sont translucides, la rayure est verte, la dureté (échelle de Mohs), 3, la densité, 3.69(8) (mesurée) et 3.59 g/cm^3 (calculée), et le clivage (001), parfait. A la lumière des déterminations sur cristaux uniques, la ferrokinoshitalite est monoclinique, groupe spatial $C2/m$, avec paramètres réticulaires a 5.389(1), b 9.337(2), c 10.054(2) Å, et β 100.53(2)°. Le polytype est $1M$, et Z est égal à 2. Les cinq raies les plus intenses du spectre de diffraction (méthode des poudres) [d en Å(I)] sont: 2.651(100), 2.176(40), 1.551(30), 1.659(25), et 1.529(25). L'indice de réfraction moyen, déterminé selon la relation de Gladstone et Dale, est 1.6939. La ferrokinoshitalite est biaxe négative, et fortement pléochroïque. Une analyse thermogravimétrique révèle un gain en poids d'environ 2.4% de 400 à 1000°C, suite à une légère perte en poids d'environ 0.2% de 24 à 400°C. Le gain serait dû à l'oxydation du fer, qui mène à la formation de l'hématite. La structure cristalline a été affinée jusqu'à un résidu R de 0.032 ($wR = 0.036$) en utilisant 750 réflexions uniques observées sur un échantillon dont la formule structurale est $(Ba_{0.47}K_{0.33}Na_{0.04})$

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$(Fe^{2+}_{1.72}Mg_{0.74}Mn_{0.08}Fe^{3+}_{0.15}Ti_{0.17})$ $(Si_{2.44}Al_{1.56})O_{10}$ $(OH_{1.35}F_{0.65})$. Les deux sites octaédriques indépendants diffèrent très légèrement dans leurs dimensions: ($M1$: 2.120 *versus* $M2$: 2.106 Å). Nous évaluons l'effet de la teneur en fer sur les structures des micas riches en Ba. L'angle de rotation des anneaux de tétraèdres, α, est petit, 3.95°, vue la dimension relativement importante des ions Fe^{2+} et Ba. On trouve la ferrokinoshitalite dans des amas de sulfures Pb–Zn–Cu–Ag massifs à la mine Broken Hill, secteur nord de la province du Cap, en Afrique du Sud, dans un assemblage contenant quartz + magnétite + grenat riche en spessartine + apatite ± sillimanite ± gahnite ferreuse ± sulfures, avec grunerite manganifère (localement, manganogrunerite), fayalite et pyroxferroïte manganifères aussi présentes dans des niveaux riches en amphibole. D'après les résultats d'études antérieures, la ferrokinoshitalite se serait formée aux conditions du paroxysme métamorphique, 670 ± 20°C, 4.5 ± 1.0 kbar, ou près de celles-ci.

(Traduit par la Rédaction)

Mots-clés: formation de fer rubanée, mica cassant, ferrokinoshitalite, nouvelle espèce minérale, détermination de la structure, amas de sulfures, mine de Broken Hill, province du Cap, Afrique du Sud.

INTRODUCTION

Kinoshitalite, found as both $1M$ and $2M_1$ polytypes, was defined by Yoshii *et al.* (1973) as the Ba- and Mg-rich brittle mica. Kinoshitalite differs from the Ba mica, anandite, primarily because anandite is S-rich and enriched in Fe and Si relative to kinoshitalite (Table 2 of Rieder *et al.* 1998). Initially, the kinoshitalite-$1M$ polytype was refined structurally by Kato *et al.* (1979) in space group $C2/m$, and refined further and examined in subgroup symmetries by Guggenheim & Kato (1984). The latter study showed that kinoshitalite does not show additional order of cations either in the tetrahedral or octahedral sites in subgroup symmetries; the material is properly described in space group $C2/m$. Unfortunately, the poor precision of the data, attributed to the inferior quality of the material, left the possibility open that twinning could account for the apparent disorder of cations in the higher-order space group (Guggenheim & Kato 1984).

Ba-bearing trioctahedral micas occur in metamorphic and igneous rocks; references to many petrological studies are given in Brigatti & Poppi (1993) and Guggenheim (1984). Bigi *et al.* (1993) examined Ba-bearing biotite from layered gabbroic and calc-alkaline rocks and related the observed variations in crystal chemistry to the genesis of the rocks. By single-crystal X-ray study, Brigatti & Poppi (1993) studied ten Ba-bearing igneous and metamorphic micas to determine the exchange vectors (cation substitutions) that balance the excess positive charge caused by the substitution of Ba for K in the mica structure. They also presented several graphs to show the relationships among chemical and structural parameters.

An Fe-rich analogue of kinoshitalite was first identified by Frimmel *et al.* (1995) from high-grade metamorphosed banded iron-formations enclosing massive sulfide orebodies at the Broken Hill mine near Aggeneys, northern Cape Province, South Africa. This Fe-analogue of kinoshitalite constitutes a new mineral, named ferrokinoshitalite. In this paper, we examine in detail the crystal chemistry of this mineral and discuss

its relationship to the trends established by Brigatti & Poppi (1993) for the more Mg-rich, Ba-bearing micas. The mineral species and its name were approved by the IMA Commission on New Minerals and Mineral Names (no. 99-026). Cotype material is preserved in the collection of the Department of Geological Sciences, University of Cape Town, South Africa.

DESCRIPTION AND OCCURRENCE

The massive Pb–Zn–Cu–Ag sulfide orebodies at the Broken Hill mine near Aggeneys in the northern Cape Province of South Africa (latitude 29°14'S, longitude 18°48'E) consist of pyrrhotite, galena, sphalerite, chalcopyrite, and pyrite, and they are interpreted as representing sedex-type deposits of Mid-Proterozoic age (Ryan *et al.* 1986). They are enclosed in a banded iron-formation in which a magnetite-rich oxide facies is distinguished from a garnet- and amphibole-rich manganiferous silicate facies. Within the latter facies, ferrokinoshitalite occurs in the form of very small, tabular, individual crystals to 0.2 mm across. The mineral assemblages containing the ferrokinoshitalite are quartz + magnetite + spessartine-rich garnet + apatite ± sillimanite ± ferroan gahnite ± sulfides, with Mn-rich grunerite (in places, manganogrunerite), manganoan fayalite and Mn-rich pyroxferroite also present in amphibole-rich layers. Despite high-grade metamorphism, reaching the upper-amphibolite-facies pressure–temperature (P–T) conditions, constrained at 670 ± 20°C and 4.5 ± 1.0 kbar (Frimmel *et al.* 1995, Waters 1989), steep geochemical gradients are preserved on a millimeter scale between the iron formation and sulfide bands (Frimmel *et al.* 1993), suggesting little post-depositional modification of the compositions. Derivation of the silicate-rich bands from chemical precipitates near hydrothermal vents on the seafloor was suggested by Hoffmann (1994).

Textural equilibrium between the ferrokinoshitalite and the associated minerals indicates mica formation at or near the peak of metamorphism. The age of the mica is indirectly constrained by Ar–Ar data obtained on less

Ba-rich biotite in associated metapelites (Frimmel & Frank 1998); that age, 1006 ± 4 Ma, suggests cooling below ~300°C by then.

PHYSICAL AND OPTICAL PROPERTIES

The color of ferrokinoshitalite is dark green, its luster is vitreous, and the Mohs hardness is 3. Crushed material (streak) is green. Even very small and thin crystals are not transparent, but are translucent, which prevented a complete detailed determination of the optical properties. Ferrokinoshitalite is brittle, displays no fracture, and has a perfect (001) cleavage. No fluorescence is observed in either long- or short-wave ultraviolet radiation, and no cathodoluminescence is observed. Ferrokinoshitalite is soluble in sulfuric acid and hydrofluoric acid, but not in hydrochloric acid. The density could not be determined accurately because of lack of material, but preliminary results [3.69(8) g/cm³] using very little material and employing heavy-liquid techniques are in reasonable agreement with the calculated density, 3.59 g/cm³.

Grain samples immersed in index of refraction (Cargille) oils were not sufficiently transparent to determine the indices, but β was estimated to be 1.680. The mean index of refraction calculated from the Gladstone–Dale relationship is 1.6939. Ferrokinoshitalite is biaxial negative, with $2V_\alpha$ estimated to be ~20° (from extinction curves). The mineral is strongly pleochroic (X = grass green, Y = dark brown green, Z = dark greenish gray-brown); absorption is X << Z < Y.
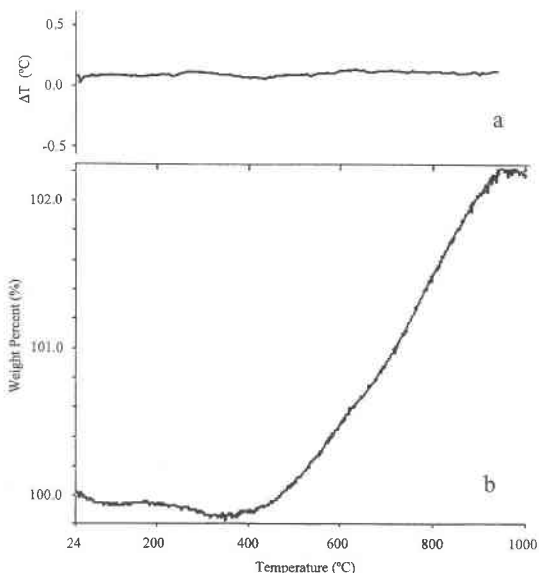

FIG. 1.   Thermal analytical data for ferrokinoshitalite: (a) DTA and (b) TG. See text for details.

THERMAL ANALYSIS

A Perkin–Elmer 7 series thermal analysis system was used to obtain a differential thermal analysis (DTA) and thermal gravimetric (TG) analysis (Fig. 1). Aluminum crucibles with a Pt/Pt13%Rh thermal couple were used. To try to maintain non-oxidizing conditions, N_2 gas with a flow rate of 20 cm³/min was maintained. A heating rate of 10°C/min was applied, and the DTA experiment used α-alumina powder as a reference. The DTA curves show no evidence of a reaction, and the TG curve indicates that weight loss was ~0.2 wt% from 24 to 400°C and a weight gain of ~2.4 wt% occurred from 400 to 1000°C. The product after heating sample HFN43 was dark brown in color, and X-ray analysis indicated that hematite was present, as well as unidentified product phases. Thus, oxidation of the iron in ferrokinoshitalite had occurred, although the amount of weight gain, which is less than expected for oxidation to hematite, may indicate that some weight loss by dehydroxylation had occurred also.

CHEMICAL COMPOSITION

An electron microprobe (Cameca CAMEBAX, 15 kV, 40 nA, beam diameter of 5 μm) was employed for chemical analyses. The standards used were Kakahui hornblende (Si, Al, Fe, Mg, Na, K), rutile (Ti), rhodonite (Mn), fluorite (F) and synthetic Ba silicate (Ba, Sr). The composition of seven grains from sample HFN43, on which all physical, thermal, optical and crystallographic data were obtained, is given in Table 1. The standard deviation of the mean composition reported in Table 1 does not necessarily reflect analytical uncertainties. The small amount of material available prohibited direct determination of H_2O. Furthermore, the thermogravimetric analysis cannot be used to determine H_2O content (see above).

A ZAF procedure was used for data reduction. This procedure, based on our experience, consistently yields totals that are 1–2 wt% high for samples with >18 wt% FeO, probably because of an imperfect absorption coefficient for Fe used by the ZAF program, which leads to an overestimation of the SiO_2 and Al_2O_3 contents. This overestimation prevents the approximation of H_2O by difference, which would produce low values for H_2O. Thus, the amount of OH in the formulae was obtained by taking the difference of F from two atoms per formula unit (*apfu*), the amount of F,OH present in the ideal formula.

The chemical formula of ferrokinoshitalite was calculated on the basis of 11 atoms of oxygen. The formula involves a correction for the oxygen equivalent for the fluorine atoms present. The tetrahedral sites are assumed to be completely filled with Si and Al and, in some cases, very small amounts of Fe^{3+}. The bulk of Fe^{3+}, as well as all the Ti, Fe^{2+}, Mg, and Mn, were assigned to the octahedral sites. These sites are never com-

pletely filled, but occupancy of the octahedral sites is, on average, 2.87 ± 0.03 *apfu*. Similarly, the sum of the interlayer cations (Ba, Sr, K, Na) is less than ideal, on average 0.85 ± 0.01 *apfu*. Substitution of OH by F occurs, with some samples containing up to 4.0 wt% F (Frimmel *et al.* 1995). The structural formula thus derived from results of seven analyses is written as $(Ba_{0.49}K_{0.34}Na_{0.04})_{\Sigma 0.85}$ $(Fe^{2+}_{1.72}Mg_{0.74}Mn_{0.08}Fe^{3+}_{0.15}Ti_{0.17})_{\Sigma 2.87}$ $(Si_{2.44}Al_{1.56})_{\Sigma 4.00}$ $O_{10}(OH_{1.35}F_{0.65})_{\Sigma 2.00}$ or, ideally, $BaFe^{2+}_3Al_2Si_2O_{10}(OH)_2$. On the basis of structural data obtained (see below) and the mean chemical composition, a molecular weight of 537.72 was calculated.

Ferrokinoshitalite is characterized by high Ba contents (up to 17.1 wt% BaO), with a ratio Ba/(Ba + K + Na) as high as 0.73, which is similar to that found in kinoshitalite (Yoshii *et al.* 1973). In contrast to kinoshitalite, the Fe/(Fe + Mg) value is >0.5, with recorded values to 0.72 (Frimmel *et al.* 1995). As revealed by high-performance ion-chromatography analyses of the same study, on average, 8% of the total Fe is present as Fe^{3+}. Ferrokinoshitalite is not only more enriched in ferrous iron, but with Al:Si = 0.6, it is also less aluminous than kinoshitalite (Al:Si = 1.0). Thus it also resembles the essentially Al-free, Ba,Fe-rich silicate anandite (Pattiaratchi *et al.* 1967)

X-Ray Diffraction

The ferrokinoshitalite studied is specimen number HFN43. The crystal chosen for the structural determination was $0.35 \times 0.35 \times 0.05$ mm in size and showed sharp reflections with little mosaic spread, on the basis of Buerger precession photographs. Examination of zero- and upper-level photographs indicated the presence of reflections of type $h + k = 2n$, which define a C-centered cell. On the basis of an apparent two-fold axis and m plane and cell geometry, space group $C2/m$ was assumed. This is consistent with the $1M$ polytype.

Cell parameters were refined ($MoK\alpha_1 = 0.70930$ Å) from 12 high-angle ($47 < 2\theta < 55°$) reflections, each measured in eight octants, to produce 96 independent measurements to yield a 5.389(1), b 9.337(2), c 10.054(2) Å, β 100.53(2)°. Approximately 1,630 reflections were measured over the 2θ range 4–60° in the $2\theta{:}\theta$ scan mode at a scan rate of 1°/min, a background time equal to the scan time for the reflection, and with a 2.0° scan window adjusted by adding the increment of $0.75\tan\theta$. Reflections were measured in one-half of the limiting sphere, with indices varying along $\bar{8} < h < 8$, $0 < k < 14$, and $\overline{15} < l < 15$. Three standard reflections were measured every 50 reflections to check for crystal and electronic stability. If I was greater than 3σ, then reflections were considered observed, where $(I) = [CT + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$, and CT is the total integrated count in time t_c, B_1 and B_2 are the background counts in time t_b, and p (the estimate of the standard error) is equal to 0.03.

After Lorentz–polarization corrections, absorption corrections were made empirically on the basis of the 040 reflection taken at psi increments of 10°. Reflections were symmetry-averaged according to Laue group $2/m$. This resulted in 773 unique nonzero reflections. Twenty-three reflections were removed from the dataset near the final stages of refinement according to the equation $|F_0 - F_c| > 2[(F_o - F_c)^2/M - N]^{1/2}$, where M represents the number of reflections, and N, the number of parameters.

The crystallographic least-squares program SDPWIN (Frenz 1995) was used with initial values for the scattering factors from Cromer & Mann (1968), based on the site occupancies derived from the structural formula. All atoms were considered half-ionized, and reflections

TABLE 1. REPRESENTATIVE COMPOSITIONS OF
FERROKINOSHITALITE FROM AGGENEYS, SOUTH AFRICA,
AND RESULTING FORMULAE

	Sample HFN43							mean	s.d.
SiO_2 wt.%	28.72	28.37	28.77	28.65	28.68	28.88	29.98	28.86	0.52
TiO_2	2.43	2.67	2.86	2.37	2.68	3.44	2.34	2.68	0.38
Al_2O_3	15.32	15.85	15.99	16.28	16.09	15.85	15.24	15.80	0.39
$Fe_2O_3^*$	2.32	2.32	2.35	2.40	2.34	2.39	2.31	2.35	0.04
FeO^*	23.96	24.01	24.34	24.79	24.23	24.72	23.86	24.27	0.37
MnO	1.09	1.08	1.18	1.13	1.18	1.18	1.16	1.14	0.04
MgO	6.34	5.89	5.60	5.27	5.82	5.35	6.59	5.84	0.49
BaO	13.73	15.46	14.82	14.13	14.59	13.58	12.66	14.14	0.92
SrO	0.00	0.00	0.17	0.16	0.16	0.00	0.00	0.07	0.09
Na_2O	0.23	0.28	0.32	0.27	0.25	0.30	0.20	0.26	0.04
K_2O	3.45	2.71	2.83	3.09	2.93	3.40	3.87	3.18	0.41
F	2.19	2.94	2.32	2.42	2.33	2.33	2.45	2.43	0.24
Total**	98.86	100.34	100.57	99.94	100.30	100.44	99.63	100.01	0.60
Formula based on 11 oxygen atoms									
Si *apfu*	2.45	2.41	2.43	2.43	2.42	2.42	2.51	2.44	0.03
Al	1.54	1.59	1.57	1.57	1.58	1.57	1.49	1.56	0.04
Fe^{3+}	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Tetrahedral site	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	0.00
Al	0.00	0.00	0.02	0.06	0.02	0.00	0.01	0.01	0.00
Ti^{4+}	0.16	0.17	0.18	0.15	0.17	0.22	0.15	0.17	0.02
Fe^{3+}	0.14	0.15	0.15	0.15	0.15	0.14	0.15	0.15	0.00
Fe^{2+}	1.71	1.71	1.72	1.76	1.71	1.73	1.67	1.72	0.02
Mn	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.00
Mg	0.81	0.75	0.70	0.67	0.73	0.67	0.82	0.74	0.06
Octahedral site	2.90	2.86	2.85	2.86	2.86	2.84	2.88	2.87	0.03
Ba	0.46	0.52	0.49	0.47	0.48	0.45	0.42	0.47	0.03
Sr	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00
K	0.38	0.29	0.30	0.33	0.32	0.36	0.41	0.34	0.04
Na	0.04	0.05	0.05	0.04	0.04	0.05	0.03	0.04	0.01
Interlayer site	0.88	0.86	0.85	0.85	0.85	0.86	0.86	0.85	0.01
F	0.59	0.79	0.62	0.65	0.62	0.62	0.65	0.65	0.06

* Fe^{2+}/Fe^{3+} derived from high-performance ion chromatography (Frimmel *et al.* 1995). ** Totals corrected for F = O equivalent. s.d.: standard deviation.
The compositions were derived from electron-microprobe data. The amounts of Ca and Cl are below detection limits.

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS
FOR FERROKINOSHITALITE

Atom	x	y	z	*β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba	0.0	0.5	0.0	**0.0140(2)	0.00386(6)	0.00671(7)	0.00	0.0038(2)	0.00
M1	0.0	0.0	0.5	0.0070(3)	0.0013(1)	0.0034(1)	0.00	0.0028(3)	0.00
M2	0.0	0.3331(1)	0.5	0.0055(2)	0.00202(8)	0.00324(7)	0.00	0.0012(2)	0.00
T	0.0745(2)	0.1664(1)	0.2199(1)	0.0076(3)	0.00193(9)	0.00303(8)	−0.0000(3)	0.0017(2)	−0.0002(2)
O1	0.0333(9)	0.0	0.1578(4)	0.027(2)	0.0034(4)	0.0027(3)	0.00	0.001(1)	0.00
O2	0.3134(6)	0.2400(4)	0.1586(3)	0.0160(9)	0.0064(3)	0.0039(2)	−0.008(1)	0.0028(7)	−0.0010(5)
O3	0.1319(5)	0.1659(3)	0.3883(3)	0.0099(7)	0.0030(2)	0.0036(2)	−0.0000(8)	0.0026(6)	−0.0005(4)
OH	0.1229(7)	0.5	0.3871(4)	0.010(1)	0.0028(3)	0.0063(4)	0.00	0.004(1)	0.00

* The form of the anisotropic displacement parameter is:
exp[−0.25{$h^2a^{*2}\beta(1,1) + k^2b^{*2}\beta(2,2) + l^2c^{*2}\beta(3,3) + 2hka^*b^*\beta(1,2) + 2hla^*c^*\beta(1,3) + 2klb^*c^*\beta(2,3)$}]

** Values in parentheses represent estimated standard deviations (esd) in terms of the least units cited for the values to the immediate left, thus 0.0140(2) indicates an esd of 0.0002.

TABLE 3. SELECTED INTERATOMIC DISTANCES AND BOND ANGLES
IN FERROKINOSHITALITE

Bond	Distance	Bond	Distance	Linkage	Angle
			Octahedra		
M1 site		O–O shared (M1 and M2)		O3–M1–O3' × 2	94.4(1)
M1–O3 × 4	2.111(3)	O3–O3' × 2	2.869(4)	–O3" × 2	85.6(1)
–OH × 2	2.139(3)	–OH × 4	2.856(4)	–OH × 4	95.58(9)
Mean	2.120	O–O unshared (triads)		–OH' × 4	84.42(9)
		O3–O3' × 2	3.098(4)	Mean	90.00
		–OH × 4	3.148(4)		
		Mean O–O	2.996		
M2 site		O–O shared (M1 and M2)		O3–M2–O3'	85.2(1)
M2–O3 × 2	2.093(2)	O3–O3'	2.869(4)	–O3" × 2	84.9(1)
–O3' × 2	2.120(3)	–OH × 4	2.856(4)	–O3' × 2	95.5(1)
–OH × 2	2.105(3)	O–O shared (M2 and M2)		–OH × 2	85.7(1)
Mean	2.106	O3–O3' × 2	2.844(4)	–OH' × 2	95.2(1)
		OH–OH'	2.830(5)	–OH" × 2	93.9(1)
		O–O unshared (triads)		OH–M2–OH'	84.5(1)
		O3–O3' × 2	3.119(3)	Mean	90.0
		–OH × 2	3.120(3)		
		O3'–OH × 2	3.068(4)		
		Mean O–O	2.976		
		Tetrahedron			
T–O1	1.674(2)	O1–O2	2.701(4)	O1–T–O2	107.6(2)
–O2	1.673(3)	–O2'	2.702(4)	–O2'	107.6(2)
–O2'	1.675(3)	–O3	2.757(4)	–O3	111.4(2)
–O3*	1.665(3)	O2–O2'	2.701(4)	O2–T–O2'	107.5(2)
Mean	1.672	–O3	2.756(4)	–O3	111.3(1)
		O2'–O3	2.757(4)	O2'–T–O3	111.3(1)
		Mean	2.729	Mean	109.5
		Interlayer			
	Inner	Outer			
Ba–O1 × 2	3.018(4)	3.210(4)			
–O2 × 4	3.027(3)	3.210(3)			
Mean	3.024	3.210			

Notes: ', " indicates symmetry-equivalent; * indicates apical oxygen atom.

were assigned unit weights with a single scale-factor. The scale factor was initially varied, followed by atomic coordinates and isotropic temperature-factors in succeeding cycles. Site-occupancy factors were allowed to vary at this stage to check for variations in assigned occupancy, but adjustments were not necessary. Site-occupancy factors were then fixed. The R factors for the isotropic refinement along with an extinction correction were $R = 0.069$ and $wR = 0.070$, where $wR = [w(|F_o| − |F_c|)^2/w|F_o|^2]^{1/2}$. Anisotropic temperature-factors were then allowed to vary. Final R factors are $R = 0.032$ and $wR = 0.036$. There were a total of 59 varied parameters. Final atomic coordinates and displacement parameters are given in Table 2, Table 3 gives bond lengths and angles, and Table 4 gives calculated structural parameters. Reflection data and structure factors are on deposit at the Depository of Unpublished Data, Canada Institute for Scientific and Technical Information, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

TABLE 4. CALCULATED STRUCTURAL PARAMETERS
FOR FERROKINOSHITALITE

Parameter		Value	Parameter	Value
α(°)*		3.95	Sheet thickness†	
ψ(°)**	M1:	58.49	Octahedral (Å)	2.216
	M2:	58.26	Tetrahedral (Å)	2.270
τ(°)***		111.3	Interlayer separation (Å)	3.129
Δz_ave (Å)†		0.008		
β_ideal (°)‡		100.29		

* Tetrahedral rotation angle, $\alpha = \frac{1}{2}[120° − \text{mean } O_b – O_b – O_b \text{ angle}]$
** $\psi = \cos^{-1}[\text{oct. thickness}/2(M–O,OH)]$
*** $\tau = \text{mean } O_b – T – O_a$
¶ Tetrahedral thickness includes OH
† Δz_{ave} = corrugation of plane of basal oxygen atoms
‡ $\beta_{ideal} = 180° − \cos^{-1}[a/3c]$

Powder X-ray-diffraction data (Table 5) were obtained with a Gandolfi camera (Fe$K\alpha$ = 1.93736 Å, diameter = 114.6 mm) using multiple crystals of near-equal size of about $0.07 \times 0.07 \times 0.002$ mm, which were obtained by lightly crushing several larger crystals. Diffraction lines were measured using an optical scanner and programs FilmScan and Jade (MDI, Livermore, CA). The resulting digitized data allowed nearly superposed lines to be distinguished. Thus, Table 5 includes d-values as observed from the digitized data. However, nearly superposed lines that cannot be resolved visually are grouped together. Intensities were determined visually. Least-squares refinement was performed using LCLSQ (Burnham 1991). Within the estimated errors, the resultant unit-cell parameters are consistent with the derived parameters from the single-crystal data.

DISCUSSION

Chemical composition

The DTA curve suggests that no apparent reactions occur in ferrokinoshitalite upon heating to 1000°C, but DTA requires a dynamic thermal response, and weight changes by TG analysis take place over a range of 600°C, from 400 to 1000°C. The weight gain as indicated by the TG curves and the presence of hematite in the product after thermal analysis indicates oxidation. Dehydroxylation involving weight loss at these elevated temperatures, however, may be masked by the oxidation reaction. These results highlight the dangers involved in attributing weight loss to dehydroxylation

alone when obtaining thermal analytical data for iron-bearing phases.

Thus, obtaining the amount of OH present in the sample is problematic. Determining OH by difference assumes that associated errors in the analysis of each component cancel, which is highly unlikely, especially for minerals containing high amounts of iron. We have obtained the amount of OH by taking the difference of F from 2 *apfu*, the amount of F,OH present in the ideal formula. This approach is also not precise because it assumes that the quantities of associated elements (*e.g.*, fluorine) are accurately known.

X-ray diffraction

The low R value resulting from refinement in $C2/m$ symmetry suggests that the space group is correct. This is consistent with the results of Guggenheim & Kato (1984), in which they examined possible schemes of cation ordering in kinoshitalite in subgroup symmetry involving $C2$. In the latter study, kinoshitalite was found to show disorder of octahedrally coordinated cations of $M2$, and $M3$ (the site related by mirror symmetry in the parent space-group) became equivalent as the refinement process proceeded to completion in $C2$ symmetry, even after the two sites were initially modeled as unequal. Twinning, which is both difficult to detect in single-crystal X-ray experiments and common in many phyllosilicates, and the poor precision of the data, can account for the apparent disorder. However, the high precision of the ferrokinoshitalite refinement and low R value (0.032) suggest that twinning is very unlikely, and that the mirror plane truly exists (and thus $C2/m$ is appropriate). Note, however, in Table 3 that bond lengths $M1$–O differs slightly in size from $M2$–O ($M1$: 2.120 Å, $M2$: 2.106 Å), suggesting that either small differences in occupancy may exist between these two octahedral sites or that the occupancies of $M1$ and $M2$ are identical and that the different site-geometries affect these average bond-lengths.

The ferrokinoshitalite sample studied here departs significantly from end-member ferrokinoshitalite of composition $BaFe_3Al_2Si_2O_{10}(OH)_2$, with considerable substitution of K for Ba and of Si for Al. The lower-than-ideal Si/Al ratio of 1:1 would suggest that disorder of tetrahedral cations occurs, as indicated also by the successful refinement in $C2/m$ symmetry. Complete order of tetrahedral cations in subgroup symmetry $C\bar{1}$ was also considered earlier (Guggenheim & Kato 1984), but no order was observed. Guggenheim (1984, p. 81) attributed lack of order among tetrahedral cations in kinoshitalite to the large interlayer separation caused by the Ba cation propping the layers apart, thereby reducing any T–T electrostatic interactions between the layers. Ferrokinoshitalite, which has considerable substitution of K for Ba in the sample studied here, has an interlayer separation of 3.129 Å, which is smaller than that in kinoshitalite (3.328 Å, Guggenheim & Kato

TABLE 5. POWDER X-RAY-DIFFRACTION DATA
FOR FERROKINOSHITALITE

hkl	d(calc),Å	d(obs),Å	I	hkl	d(calc),Å	d(obs),Å	I
001	9.886	9.95	10	13$\bar{3}$	2.181	2.182	40
002	4.943	4.95	5	202	2.167	2.170	
111	3.931	3.95	5	20$\bar{4}$	1.998	2.001	
11$\bar{2}$	3.673	3.655	15	133	1.989	1.993	10
022	3.392	3.408	10	005	1.977	1.982	
003	3.295	3.278	10	13$\bar{5}$	1.667	1.669	
112	3.123	3.121	10	31$\bar{3}$	1.661	1.665	
11$\bar{3}$	2.909	2.914	10	204	1.657	1.659	25
023	2.691	2.693	10	311	1.653	1.653	
13$\bar{1}$	2.649	2.662	100*	006	1.648	1.648	
200	2.639	2.640		060	1.554	1.554	30
004	2.472	2.465	12	33$\bar{1}$	1.552	1.547	
13$\bar{2}$	2.454	2.453	15	20$\bar{6}$	1.531	1.529	25
201	2.440	2.440		135	1.524	1.520	15
040	2.331	2.331	2				
22$\bar{1}$	2.321	2.313	2				
220	2.297	2.297	2				

* Intensities referring to more than one d(obs) value indicate that these peaks cannot be resolved visually (see text). Thus this line visually has a d(obs) value (average) of 2.651 Å at 100% intensity. Other average values and associated intensities are: 2.447 Å (15), 2.176 Å (40), 1.992 Å (10), 1.659 Å (25), and 1.551 Å (30).
Refined parameters: a 5.372(5), b 9.325(9), c 10.060(8) Å, β 100.67(8)°, Fe$K\alpha$ radiation, 1.93736 Å; Gandolfi camera, 114.6 mm.

1984), synthetic Ba-rich fluormica (3.172 Å, McCauley & Newnham 1973), Ba-rich phlogopite (3.380 Å, Guggenheim & Kato 1984), and all the Ba-bearing micas reported by Brigatti & Poppi (1993) [3.281–3.427 Å], but larger than Ba micas that show tetrahedral order [*e.g.*, anandite, 3.078 Å (Filut *et al.* 1985); 3.041 Å, Giuseppetti & Tadini (1972)].

Brigatti & Poppi (1993) used a series of plots to define exchange reactions of the Ba-rich micas they studied. Ferrokinoshitalite has an interlayer-cation site containing $(Ba_{0.47}K_{0.34}Na_{0.04})$, very close to that of their sample #26 $(Ba_{0.48}K_{0.41}Na_{0.04}Ca_{0.01})$. Although very iron-rich micas were not included in their analyses, it is nonetheless useful to compare how iron content may affect the trends established previously, especially since Ba content is not a variable.

The most notable deviations from established trends in Brigatti & Poppi (1993) are associated with plots involving the tetrahedral rotation angle, α. The tetrahedral rotation angle is a measure of the rotation of adjacent tetrahedra in opposite directions in the (001) plane. A deviation from $0°$ is an indication primarily of the amount of misfit between the octahedral and tetrahedral sheets. In ferrrokinoshitalite, the relatively large size of Fe in the octahedra allows a better fit to the Al-rich tetrahedral sheet, which accounts for the small tetrahedral rotation angle ($\alpha = 3.95°$). In contrast, the samples of Brigatti & Poppi (1993) have smaller average octahedra (containing Mg, Al, Ti) and various compositions of the tetrahedral sheet. Consequently, α varies from 4.8 to 11.5°, with sample #26 at 11.5°. Less rotation of the tetrahedra implies a larger size of the silicate ring, which allows the Ba to fit well within the ring. Thus, the interlayer separation of ferrokinoshitalite is smaller (3.129 Å) than for sample #26 (3.285 Å), although the Ba content of the two samples is similar. As noted by Brigatti & Poppi (1993), deviations in chemistry from an Mg-rich octahedral sheet cannot be ignored, and contribute at least in part to the scatter on the plots involving α (Figs. 4 and 7 of Brigatti & Poppi).

Guidotti *et al.* (1975) showed the dangers of inferring crystallochemical relations in solid solutions using data from samples from too diverse a group of rocks. For example, biotite saturated in Al at the time of formation will produce little variation of ^{IV}Al or ^{VI}Al occupancy owing to differences in bulk composition. In contrast, Al-undersaturated biotite will show much different results. Much of the scatter in the diagrams of Brigatti & Poppi (1993) may also be related to the diversity of the metamorphic and igneous rocks sampled, where there is little or no control over the bulk composition.

ACKNOWLEDGEMENTS

REFERENCES

BIGI, S., BRIGATTI, M.F., MAZZUCCHELLI, M. & RIVALENTI, G. (1993): Crystal chemical variations in Ba-rich biotites from gabbroic rocks of lower crust (Ivrea Zone, NW Italy). *Contrib. Mineral. Petrol.* **113**, 87-99.

BRIGATTI, M.F. & POPPI, L. (1993): Crystal chemistry of Ba-rich trioctahedral micas-1*M*. *Eur. J. Mineral.* **5**, 857-871.

BURNHAM, C.W. (1991): LCLSQ: lattice parameter refinement using correction terms for systematic errors. *Am. Mineral.* **76**, 663-664.

CROMER, D.T. & MANN, J.B. (1968): X-ray scattering factors computed from numerical Hartree–Fock wave functions. *Acta Crystallogr.* **A24**, 321-324.

FILUT, M.A., RULE, A.C. & BAILEY, S.W. (1985): Crystal structure refinement of anandite-2*Or*, a barium- and sulfur-bearing trioctahedral mica. *Am. Mineral.* **70**, 1298-1308.

FRENZ, B.A. (1995): *SDP for Windows*. B.A. Frenz & Associates, Inc., College Station, Texas.

FRIMMEL, H.E. & FRANK, W. (1998): Neoproterozoic tectonothermal evolution of the Gariep Belt and its basement, Namibia and South Africa. *Precamb. Res.* **90**, 1-28.

_____, HOFFMANN, D. & MOORE, J.M. (1993): Preservation of syn-depositional geochemical characteristics of the Broken Hill massive sulphide deposits, South Africa, during upper amphibolite facies metamorphism. *In* Current Research in Geology Applied to Ore Deposits (P. Fenoch Hach-Alí, J. Torres-Ruiz & F. Gervilla, eds.).University of Granada, Granada, Spain (303-306).

_____, _____, WATKINS, R.T. & MOORE, J.M. (1995): An Fe analogue of kinoshitalite from the Broken Hill massive sulfide deposit in the Namaqualand Metamorphic Complex, South Africa. *Am. Mineral.* **80**, 833-840.

GIUSEPPETTI, G. & TADINI, C. (1972): The crystal structure of 2*O* brittle mica: anandite. *Tschermaks Mineral. Petrogr. Mitt.* **18**, 169-184.

GUGGENHEIM, S. (1984): The brittle micas. *In* The Micas (S.W. Bailey, ed.). *Rev. Mineral.* **13**, 61- 104.

_____ & KATO, T. (1984): Kinoshitalite and Mn phlogopites: trial refinements in subgroup symmetry and further refinement in ideal symmetry. *Mineral. J. (Japan)* **12**, 1-5.

GUIDOTTI, C.V., CHENEY, J.T. & CONATORE, P.D. (1975): Interrelationship between Mg/Fe ratio and octahedral Al content in biotite. *Am. Mineral.* **60**, 849-853.

HOFFMANN, D. (1994): Geochemistry and genesis of manganiferous silicate-rich iron formation bands in the Broken Hill deposit, Aggeneys, South Africa. *Explor. Mining Geol.* **3**, 407-417.

KATO, T., MIÚRA, Y., YOSHII, M. & MAEDA, K. (1979): The crystal structures of 1*M*-kinoshitalite, a new barium brittle mica, and 1*M*-manganese trioctahedral micas. *Mineral. J.* (*Japan*) **9**, 392-408.

MCCAULEY, J.W. & NEWNHAM, R.E. (1973): Structure refinement of a barium mica. *Z. Kristallogr.* **137**, 360-367.

PATTIARATCHI, D.B., SARI, E. & SAHAMA, T.G. (1967): Anandite, a new barium iron silicate from Wilagedera, North Western Province, Ceylon. *Mineral. Mag.* **36**, 1-4.

RIEDER, M., CAVAZZINI, G., D'YAKONOV, Y.S., FRANK-KAMENETSKII, V.A., GOTTARDI, G., GUGGENHEIM, S., KOVAL, P.V., MÜLLER, G., NEIVA, A.M.R., RADOSLOVICH, E.W., ROBERT, J.-L., SASSI, F.P., TAKEDA, H., WEISS, Z. & WONES, D.R. (1998): Nomenclature of the micas. *Can. Mineral.* **36**, 905-912.

RYAN, P.J., LAWRENCE, A.L., LIPSON, R.D., MOORE, J.M., PATERSON, A., STEDMAN, D.P. & VAN ZYL, D. (1986): The Aggeneys base metal sulphide deposits, Namaqualand district. *In* Mineral Deposits of Southern Africa **2** (C.R. Anhaeusser & S. Maske, eds.). Geological Society of South Africa, Johannesburg, South Africa (1447-1474).

WATERS, D.J. (1989): Metamorphic evidence for the heating and cooling path of Namaqualand granulites. *In* Evolution of Metamorphic Belts (J.S. Daly, R.A. Cliff & B.W.D. Yardley, eds.). *Geol. Soc., Spec. Pap.* **43**, 357-363.

YOSHII, M., MAEDA, K., KATO, T., WATANABE, T., YUI, S., KATO, A. & NAGASHIMA, K. (1973): Kinoshitalite, a new mineral from the Noda-Tamagawa mine, Iwaté Prefecture, *Chigaku Kenkyu* **24**, 181-190.