

Leakeite, $\text{NaNa}_2(\text{Mg}_2\text{Fe}^{3+}\text{Li})\text{Si}_8\text{O}_{22}(\text{OH})_2$, a new alkali amphibole from the Kajlidongri manganese mine, Jhabua district, Madhya Pradesh, India

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ABSTRACT

Leakeite is a new amphibole species from the Kajlidongri manganese mine, Jhabua district, Madhya Pradesh, India; it occurs in an amphibole-albite-braunite-bixbyite rock from the manganese metasediments. It forms deep red prisms, elongated along *c* and up to 1 mm long. It is brittle, $H = 6$, $D_{\text{meas}} = 3.11 \text{ g/cm}^3$, $D_{\text{calc}} = 3.107 \text{ g/cm}^3$. In plane-polarized transmitted light, it is strongly pleochroic $X \sim Y = \text{dark mauve-red}$, $Z = \text{light pink-red}$; $X \wedge c = 10^\circ$ (in β obtuse), $Y \wedge a = 4^\circ$, $Z = b$, with absorption $X \sim Y > Z$. Leakeite is biaxial negative, $\alpha = 1.667(1)$, $\beta = 1.675(1)$, $\gamma = 1.691(1)$; $2V = 59\text{--}71^\circ$, dispersion strong $r \ll v$.

It is monoclinic, space group $C2/m$, $a = 9.822(3)$, $b = 17.836(6)$, $c = 5.286(2) \text{ \AA}$, $\beta = 104.37(3)^\circ$, $V = 897.1(5) \text{ \AA}^3$, $Z = 2$. The strongest ten X-ray diffraction lines in the powder pattern [d in $\text{\AA}(I)(hkl)$] are 3.122(100)(201), 8.399(56)(110), 2.798(48)(330), 3.254(20)(240), 3.383(18)(131), 2.696(15)(151), 4.461(13)(040), 1.431(10)(4101), 2.154(9)(201), 1.891(9)(510). Analysis by a combination of electron microprobe, atomic absorption, and crystal structure refinement gave SiO_2 55.80 wt%, Al_2O_3 1.27, TiO_2 0.03, Fe_2O_3 12.23, Mn_2O_3 3.86, MgO 10.96, CaO 0.50, Na_2O 9.69, K_2O 1.12, F 1.08, Li_2O (by AA ~ 2 wt%, calc. = 1.42 wt%), $\text{H}_2\text{O}_{\text{calc}}$ 1.63, sum 99.14 wt%. The formula unit (23 Ox calc.) is $^{(K_{0.20}Na_{0.75})}^{(Na_{1.92}Ca_{0.08})}^{(Mg_{2.32}Fe_{1.31}^{3+}Mn_{0.42}^{3+}Al_{0.14}Li_{0.81})}^{(Si_{7.93}Al_{0.07})}O_{22}([OH]_{1.49}F_{0.51})$ with the ideal end-member formula $\text{NaNa}_2\text{Mg}_2\text{Fe}_2^{3+}\text{LiSi}_8\text{O}_{22}(\text{OH})_2$. Crystal structure refinement shows Li to be completely ordered at the M3 site; thus leakeite can be derived from ferri-eckermannite [$\text{NaNa}_2\text{Mg}_4\text{Fe}^{3+}\text{Si}_8\text{O}_{22}(\text{OH})_2$] by the substitution $\text{Fe}^{3+} + {}^{\text{M3}}\text{Li} = \text{Mg} + {}^{\text{M3}}\text{Mg}$.

INTRODUCTION

The manganese metasediments of the Kajlidongri area, Jhabua district, Madhya Pradesh, India, contain a fascinating assemblage of amphiboles and other manganese silicate and oxide minerals. Syngenetic bands of manganese silicates and oxides associated with quartzites are interbedded with the phyllites and schists of the Aravalli Group, a series of Precambrian metasediments. The regional metamorphism is chlorite or low-biotite zone (Lahiri, 1971; Leake et al., 1981), but the complexities of the silicate mineral relations are associated with later epigenetic veining. Details of the regional and local geology are given by Lahiri (1971).

There have been extensive investigations of the amphiboles from this region. It is the type locality for winchite, originally reported by Fermor (1904, 1909). Several subsequent investigations (Nayak and Leake, 1975; Leake et al., 1981; Ghose et al., 1986) showed that a wide variety of Mn-rich alkali amphiboles occur in this region. In particular, Leake et al. (1981) reported some very unusual analyses of amphiboles from the Kajlidongri area.

Specifically, the C-group cation sums of the formula unit are significantly less than 5.0 apfu, the number of available M1, M2, and M3 sites in the structure. This does tend to be a characteristic of compositions of alkali amphiboles with filled A sites (Hawthorne, 1976), and the fact that the C-group totals for some of the Kajlidongri amphiboles were so low (down to 4.3 apfu) provided an excellent opportunity for more detailed crystal structure work to examine the stereochemical details of this apparent vacancy.

Structure refinement of several crystals of this amphibole showed the M3 site to have very little X-ray scattering power (down to 4.5 electrons). This result is compatible with the presence of vacancies or first-row cations at M3. Of the first-row cations, only Li is normally found in octahedral coordination (as is the case for the M3 site), and analysis for Li showed it to be present in significant amounts, with the M3 site nearly filled by Li. When ${}^{\text{M3}}\text{Li} > 0.5$ apfu, this constitutes a new amphibole species, and the formal description is given here.

Leakeite is named in honor of Bernard E. Leake, Pro-

TABLE 1. Chemical analysis and formula unit* for leakeite

SiO ₂	55.80 wt%	Si	7.93	Ca	0.08
Al ₂ O ₃	1.27	Al	0.07	Na	1.92
TiO ₂	0.03	Sum	8.00	Sum	2.00
Fe ₂ O ₃	12.23				
Mn ₂ O ₃	3.86	Al	0.14	Na	0.75
MgO	10.96	Fe ³⁺	1.31	K	0.20
CaO	0.50	Mn ³⁺	0.42	Sum	0.95
Na ₂ O	9.69	Mg	2.32		
K ₂ O	1.12	Li	0.81	F	0.49
Li ₂ O	(1.42)	Sum	5.00	OH	(1.51)
F	1.08				
O = F	-0.45				
H ₂ O*	1.63				
Sum	99.11				

* Calculated assuming (OH + F) = 2 in formula unit.

fessor of Geology, Glasgow University, Scotland, in recognition of his work on the chemistry of amphiboles. The new species and the new name have been approved by the International Mineralogical Association Commission on New Minerals and Mineral Names. Holotype material is deposited in the Canadian Museum of Nature, Ottawa.

OCCURRENCE

Leakeite occurs in association with albite (Ab₁₀₀) and manganese oxides (braunite, bixbyite) in a dark red rock with a semimetallic appearance from the manganiferous metasediments of the Kajlidongri manganese mine, Jhabua district, Madhya Pradesh, India. The mineral content of these rocks has been described by Lahiri (1971), and Leake et al. (1981) have reported on a variety of amphiboles from this locality. According to Lahiri (1971), the manganese silicate minerals are associated with crosscutting epigenetic veins that have reacted with the regionally metamorphic manganese minerals (braunite, bixbyite, jacobsonite, spessartine, alurgite) to produce a variety of manganiferous silicates (pyroxenes, amphiboles, piemontite, manganophyllite).

PHYSICAL AND OPTICAL PROPERTIES

Leakeite is deep red and translucent with a vitreous luster; it has a very pale pink streak and shows no fluorescence under long-wave or short-wave ultraviolet light. When separated from a coarse crush of the rock, grains are prismatic on [001] and are bounded by {110} cleavage faces with the prism direction terminated by irregular fractures. Leakeite has a Mohs hardness of ~6 and is brittle. It has the characteristic perfect {110} cleavage of monoclinic amphiboles, intersecting at ~56°. The density, measured by flotation, is 3.11 g/cm³, compared with the calculated density of 3.107 g/cm³.

A spindle stage was used to orient five crystals for refractive index measurements and determination of 2*V* by extinction curves. The optical orientation was determined by transferring crystals from the spindle stage to a precession camera and determining the relative axial relationships by X-ray diffraction. The data given below are for the (compositionally homogeneous) crystal that was used for the electron microprobe work. In transmit-

TABLE 2. Indexed powder pattern for leakeite

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{calc} Å	<i>d</i> _{obs} Å	<i>I</i>
0	2	0	8.925	8.926	4
1	1	0	8.392	8.399	56
1	3	0	5.044	5.049	6
2	0	0	4.754	4.759	5
0	4	0	4.462	4.461	13
2	0	1	4.012	4.006	4
1	1	1	4.006		
1	3	1	3.382	3.383	18
2	4	0	3.254	3.254	20
2	0	1	3.124	3.122	100
2	2	1	2.949	2.949	6
3	3	0	2.797	2.798	48
1	5	1	2.695	2.696	15
0	6	1	2.573	2.573	5
2	0	2	2.531	2.531	5
3	5	0	2.370	2.369	6
1	7	1	2.277	2.274	4
3	1	2	2.268		
2	6	1	2.154	2.154	9
2	0	2	2.055	2.055	3
3	5	1	2.015	2.013	3
5	1	0	1.891	1.891	9
4	10	1	1.431	1.431	10
4	10	1	1.431	1.431	10
2	12	2	1.282	1.282	5

Note: Cell: *a* = 9.808(2), *b* = 17.850(4), *c* = 5.289(1) Å, β = 104.22(2)°.

ted light, leakeite is strongly pleochroic with *X* ~ *Y* = dark mauve-red, *Z* = light pink-red, *X* ∩ *c* = 10° (in β obtuse), *Y* ∩ *a* = 4°, *Z* = *b* with absorption *X* ~ *Y* > *Z*. It is biaxial negative with indices of refraction α = 1.667(1), β = 1.675(1), γ = 1.691(1) measured with gel-filtered Na light (λ = 589.9 nm). The 2*V*_{*x*} varies considerably (59–71°) because of zoning within crystals and compositional variations from crystal to crystal; 2*V*_{*x*calc} = 72(10)°. Dispersion is strong, *r* ≪ *v*.

CHEMICAL COMPOSITION

Leakeite was analyzed primarily by electron microprobe using a Cameca SX-50 operating in the wavelength dispersive mode with the following conditions: excitation voltage 15 kV, specimen current 20 nA, peak count time 20 s, background count time 10 s. The following standards and crystals were used for *K*α X-ray lines: Si = diopside, PET; Al = hornblende, TAP; Ti = titanite, LiF; Fe = arfvedsonite, LiF; Mn = Mn₂SiO₄, LiF; Mg = olivine, TAP; Ca = diopside, PET; Na = albite, TAP; K = orthoclase, PET; F = fluor-riebeckite, TAP. Data reduction was done using the φ(ρ*Z*) procedure of Pouchou and Pichoir (1984, 1985). Several different grains were analyzed. There was significant zoning in most of the crystals, primarily involving Mg, Fe, Mn, and perhaps Li, but some fairly homogeneous grains were found; there were also significant compositional differences between grains. Both of these observations are consistent with previous optical (Lahiri, 1971) and microprobe (Leake et al., 1981) work on amphiboles from the Kajlidongri mine. A typical average analysis is given in Table 1; this represents the average of six analyses from a fairly homogeneous grain on which the optical properties were measured.

TABLE 3. Crystal structure refinement data for leakeite

<i>a</i> (Å)	9.822(3)	radiation	MoK α
<i>b</i> (Å)	17.836(6)	scan mode	ω
<i>c</i> (Å)	5.286(2)	scanwidth	1.6°
β (°)	104.37(3)	θ range	2–30°
<i>V</i> (Å ³)	897.1(1)	total reflections	2630
Sp. gr.	<i>C2/m</i>	unique reflections	1359
		obs. reflections	1072
<i>R</i> _{sym} (%)	1.8		
<i>R</i> _{obs}	1.5		
<i>R</i> _{int}	2.8		

Leakeite was separated from the rock using a Frantz magnetic separator, followed by hand-picking; it is probable that the final separate (~500 mg), although appearing clean, was slightly contaminated by manganese oxide minerals, as opaque inclusions in the amphibole were observed in transmitted light. However, in the amounts estimated to be present ($\ll 1\%$), these will have had negligible effect on the subsequent analysis and cell content. Li was analyzed by atomic absorption. A value of ~2 wt% Li₂O was obtained. However, this value is judged to be not very accurate, as the standardization used was not adequate for this level of concentration (we were not expecting this large amount to be present). Recalculation of the formula assuming that Li brings the C-group cation sum to 5.0 apfu gives a value of 0.81 Li apfu and 1.42 wt% Li₂O. This is in agreement with several crystal structure refinements of these crystals which indicate Li occupancies of up to 0.83 at the M3 site. An example of such a refinement is given below. Determination of light-element contents of minerals by site-occupancy refinement is now a well-established technique (Hawthorne and Grice, 1990). In addition, the refinement results allowed the characterization of the valence state of both Mn and Fe. Using the site occupancies together with the curves of Hawthorne (1983) for the relationships between the

mean bond lengths and the constituent ionic radii for the M1 and M2 sites shows that Fe and Mn must be in the trivalent state at these two sites.

There was insufficient material for both Li₂O and H₂O analyses, and the former initially was judged to be more important for this specific amphibole. The F content is quite variable (0.3–1.3 apfu). Preliminary details of the structures of several crystals indicate that the O3 anion position is completely occupied by monovalent anions, and hence the H content of the crystals should vary inversely with the F values. Ion microprobe work is planned to test this conjecture.

X-RAY CRYSTALLOGRAPHY

X-ray precession photographs with Zr-filtered MoK α X-radiation were compatible with Laue symmetry *2/m*, and the condition for reflections to be present $h + k = 2n$ showed that the lattice is C centered. Long-exposure photographs (80 h) showed no sign of any violating reflections, and thus the possible space groups are *C2/m*, *C2*, and *Cm*. Crystal structure refinement confirmed space group *C2/m*.

The powder diffraction pattern for a bulk sample was recorded on a Philips PW 1710 diffractometer with graphite monochromatized CuK α X-radiation. Peak positions were measured by fitting a five-point parabolic curve to the top of the diffraction peaks, followed by correction for α_1 - α_2 splitting; NBS Si was used as a standard. Cell dimensions were refined from the corrected *d* values using the program Celref (Appleman and Evans, 1973); the indexed powder pattern and refined cell dimensions are given in Table 2.

Several crystals were examined in detail by single-crystal structure refinement. The details of the ⁶Li substitution in the amphibole structure will be examined elsewhere, and we report here only the results of the most Li-rich crystal (Li = 0.83 apfu). Crystals were selected on

TABLE 4. Final parameters for the crystal structure refinement of leakeite

	<i>x</i>	<i>y</i>	<i>z</i>	m.a.n.*	<i>B</i> _{eq} **	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O1	0.1100	0.0905	0.2154		0.71	13	6	81	-1	5	-1
O2	0.1184	0.1685	0.7284		0.76	16	6	83	1	6	4
O3	0.1110	0	0.6985	8.2	0.91	23	5	111	-4	5	-1
O4	0.3623	0.2504	0.8027		0.89	33	4	96	-3	17	0
O5	0.3486	0.1281	0.0850		0.74	14	8	68	1	6	7
O6	0.3436	0.1193	0.5854		0.74	16	8	59	0	5	-6
O7	0.3338	0	0.2983		0.94	21	3	149	0	7	0
T1	0.2780	0.0862	0.2944	14.0	0.46	13	3	48	0	4	-1
T2	0.2883	0.1712	0.8018	14.0	0.45	11	3	50	-1	5	0
M1	0	0.0848	1/2	15.9	0.70	17	7	61	0	12	0
M2	0	0.1796	0	22.1	0.50	13	3	56	0	6	0
M3	0	0	0	4.5	0.69	23	3	65	0	-2	0
M4	0	0.2763	1/2	11.2	1.21	37	7	160	0	45	0
A	0	1/2	0	4.7	4.51	201	9	771	0	384	0
Am	0.0399	1/2	0.0930	4.1	2.81	108	16	337	0	149	0
A2	0	0.4766	0	0.5	4.14						
H	0.1845	0	0.7705								

Note: Standard deviations are 1 or 2 in the last significant figure.

* The abbreviation m.a.n. = mean atomic number = refined scattering power at site in electrons; site occupancies are as follows: M1 0.72 Mg + 0.28 (Fe + Mn); M2 0.28 Mg + 0.72 (Fe + Mn); M3 0.83 Li + 0.17 Mg; M4 0.98 Na + 0.02 Ca; A ~ 0.85 Na.

** The $\beta_{ij} = \beta_{ij} \times 10^4$.

TABLE 5. Selected interatomic distances (Å) in leakeite (esd = 0.001 Å)

T1-O1	1.600	T2-O2	1.618
T1-O5	1.627	T2-O4	1.588
T1-O6	1.624	T2-O5	1.656
T1-O7	1.631	T2-O6	1.664
(T1-O)	1.621	(T2-O)	1.631
M1-O1 × 2	2.061	M2-O1 × 2	2.093
M1-O2 × 2	2.084	M2-O2 × 2	2.069
M1-O3 × 2	2.001	M2-O4 × 2	1.943
(M1-O)	2.049	(M2-O)	2.035
M3-O1 × 4	2.111	M4-O2 × 2	2.409
M3-O3 × 2	2.147	M4-O4 × 2	2.385
(M3-O)	2.123	M4-O5 × 2	2.883
		M4-O6 × 2	2.525
(A-O)	2.903	(M4-O)	2.551
(Am-O)	2.823	(A2-O)	2.656

the basis of optical clarity and freedom from inclusions. X-ray data measurement and refinement were done as described by Oberti et al. (1992). For the M3 site, the scattering curves for Li^+ and Mg^{2+} were used. Selected data relevant to data measurement and structure refinement are given in Tables 3–5. Both the scattering observed at the M3 site (mean atomic number = number of electrons ~ 4.5) and the geometrical details of the octahedral strip (to be published) indicate complete ordering of Li at the M3 site.

DISCUSSION

Ideal end-member leakeite has the formula $\text{NaNa}_2(\text{Mg}_2\text{Fe}_3^+\text{Li})\text{Si}_8\text{O}_{22}(\text{OH})_2$. This may be derived from end-member ferri-eckermannite by the substitution $\text{Fe}^{3+} + \text{M}^3\text{Li} = \text{Mg} + \text{M}^3\text{Mg}$. This is a heterovalent cation substitution taking place completely within the octahedral strip, that is, completely within the C group of cations; this is the first example of this sort of cation substitution in amphiboles. Alternatively, leakeite may be considered to be derived from end-member magnesioriebeckite by the substitution $^A\text{Na} + \text{M}^3\text{Li} = ^A\text{□} + \text{M}^3\text{Mg}$.

Hawthorne et al. (unpublished data) show that both substitutions are common in alkali amphiboles from granitic rocks (cf. Hawthorne, 1978; Ungaretti et al., 1978), although the limited data currently available suggest that the series ferri-eckermannite-leakeite is more common. The occurrence of this substitution in metamorphic rocks as well (Ghose et al., 1986; this study) suggests that the presence of Li at M1, M2, and M3 sites in amphiboles may be a lot more common than has hitherto been realized, and more work in Li-enriched environments may reveal other occurrences of Li-bearing amphiboles. It should also be noted that the occurrence of Li at the M1, M2, and M3 sites could account for the apparently low

C-group cation sums in alkali amphiboles (Hawthorne, 1976; Czamanske and Dillet, 1988) and could also have a considerable effect on (real and apparent) chemical variations in magmatic alkali amphiboles from granitic rocks.

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REFERENCES CITED

- Appleman, D.E., and Evans, H.T., Jr. (1973) Job 9214: Indexing and least-squares refinement of powder diffraction data. U.S. National Technical Information Service, Document PB 216 188.
- Czamanske, G.K., and Dillet, D. (1988) Alkali amphibole, tetrasilicic mica, and sodic pyroxene in peralkaline siliceous rocks, Questa Caldera, New Mexico. *American Journal of Science*, 288-A, 358–392.
- Fermor, L.L. (1904) A new form of blue amphibole from Central India. *Records of the Geological Survey of India*, 31, 235–236.
- (1909) The manganese ore deposits of India. *Memoirs of the Geological Survey of India*, 37, 1294 p.
- Ghose, S., Kersten, M., Langer, K., Rossi, G., and Ungaretti, L. (1986) Crystal field spectra and Jahn Teller effect of Mn^{3+} in clinopyroxene and clinopyroxenes from India. *Physics and Chemistry of Minerals*, 13, 291–305.
- Hawthorne, F.C. (1976) The crystal chemistry of the amphiboles. V. The structure and chemistry of arfvedsonite. *Canadian Mineralogist*, 14, 346–365.
- (1978) The crystal chemistry of the amphiboles. IX. The crystal structure and site chemistry of fluor-riebeckite. *Canadian Mineralogist*, 14, 187–194.
- (1983) The crystal chemistry of the amphiboles. *Canadian Mineralogist*, 21, 173–480.
- Hawthorne, F.C., and Grice, J.D. (1990) Crystal structure refinement as a chemical analytical method: Application to light elements. *Canadian Mineralogist*, 28, 693–702.
- Lahiri, D. (1971) Mineralogy and genesis of the manganese oxide and silicate rocks in Kajlidongri and surrounding areas, Jhabua district, Madhya Pradesh, India. *Economic Geology*, 66, 1176–1185.
- Leake, B.E., Farrow, C.M., and Nayak, V.K. (1981) Further studies on winchite from the type locality. *American Mineralogist*, 66, 625–631.
- Nayak, V.K., and Leake, B.E. (1975) On 'winchite' from the original locality at Kajlidongri, India. *Mineralogical Magazine*, 40, 395–399.
- Oberti, R., Ungaretti, L., Cannillo, E., and Hawthorne, F.C. (1992) The behaviour of Ti in amphiboles: I. Four- and six-coordinate Ti in richterites. *European Journal of Mineralogy*, in press.
- Pouchou, J.L., and Pichoir, F. (1984) A new model for quantitative analysis: Part I. Application to the analysis of homogeneous samples. *La Recherche Aérospatiale*, 3, 13–38.
- (1985) 'PAP' $\phi(\rho Z)$ procedure for improved quantitative microanalysis, p. 104–106. *Microbeam analysis—1985*. San Francisco Press, San Francisco.
- Ungaretti, L., Mazzi, F., Rossi, G., and Dal Negro, A. (1978) Crystal-chemical characterization of blue amphiboles. *Proceedings of the Eleventh General Meeting of the International Mineralogical Association, Rock-forming minerals*, p. 82–110. Nauka, Moscow.

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