

Eckermannite revised: The new holotype from the Jade Mine Tract, Myanmar—crystal structure, mineral data, and hints on the reasons for the rarity of eckermannite

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ABSTRACT

Following the characterization of the new amphibole species fluoro-leakeite, ideally ${}^A\text{Na} {}^B\text{Na}_2 {}^C(\text{Mg}_2\text{Al}_2\text{Li}) {}^T\text{Si}_8 \text{O}_{22} {}^W\text{F}_2$, at Norra Kärr (Sweden), so far considered the type locality of eckermannite, re-examination of the holotype material of eckermannite deposited at the Museum of Natural History in London (BM 1949.151) and of the original sample analyzed by Törnebohm (1906) confirmed that they both are actually fluoro-leakeite. A survey of literature data showed that the only analysis reported for eckermannite is that of sample AMNH 108401 from the Jade Mine Tract, Myanmar. Complete characterization of that sample has led to the approval of a new holotype for eckermannite (IMA-CNMNC 2013-136), ideally ${}^A\text{Na} {}^B\text{Na}_2 {}^C(\text{Mg}_4\text{Al}) {}^T\text{Si}_8 \text{O}_{22} {}^W(\text{OH})_2$, which is described in this work.

Holotype eckermannite from Myanmar has the empirical unit formula ${}^A(\text{Na}_{0.87}\text{K}_{0.06})_{\Sigma=0.93} {}^B(\text{Na}_{1.89}\text{Ca}_{0.11})_{\Sigma=2.00} {}^C(\text{Mg}_{3.87}\text{Fe}_{0.09}^{2+}\text{Mn}_{0.01}\text{Fe}_{0.38}^{3+}\text{Al}_{0.62})_{\Sigma=4.97} {}^T\text{Si}_{8.00} \text{O}_{22} {}^W(\text{F}_{0.03}\text{OH}_{1.97})_{\Sigma=2.00}$. It is monoclinic, $C2/m$, with $a = 9.8087(7)$, $b = 17.8448(13)$, $c = 5.2905(4)$ Å, $\beta = 103.660(1)$, $V = 899.8(1)$ Å³; $Z = 2$, $D_{\text{calc}} = 3.02$ g/cm³. Optics: biaxial (–); $\alpha = 1.605$, $\beta = 1.630$, $\gamma = 1.634$ all ± 0.002 ($\lambda = 590$ nm). The 10 strongest reflections in the X-ray powder pattern [d values (in Å), I , (hkl)] are: 2.702, 100, [(331) (151)]; 3.395, 59, (131); 3.128, 56, (310); 2.525, 56, ($\bar{2}02$); 8.407, 42, (110); 2.574, 36, [(061) (002)]; 3.257, 34, (240); 2.161, 33, (261); 2.966, 33, (060); 4.460, 30, (040).

The reason for the rarity of eckermannite compositions are examined and discussed based on considerations on the short-range order of A cations and W anions.

Keywords: Eckermannite, new holotype, amphibole, chemical analysis, crystal structure, Myanmar

INTRODUCTION

Eckermannite is a “grandfathered” amphibole end-member with ideal formula ${}^A\text{Na} {}^B\text{Na}_2 {}^C(\text{Mg}_4\text{Al}) {}^T\text{Si}_8 \text{O}_{22} {}^W(\text{OH})_2$, which was named after the Swedish petrologist Claes V.H. (Harry) von Eckermann (1886–1969). The name was proposed by Adamson (1942) based on the study of rock samples from Norra Kärr, Gränna, Jönköping, Småland, Sweden. According to Holtstam (1998), the Norra Kärr locality (58°06'N, 14°40'E) is a small oval Proterozoic alkaline intrusion, composed mainly of fine-grained schistose agpaitic nepheline-syenite (grennaite). Petrological and genetic aspects of Norra Kärr have been described extensively by Adamson (1944), von Eckermann (1968), Blaxland (1977), and Kramm and Koark (1988). Adamson (1942) re-calculated the analyses of R. Mauzelius reported (together with optical properties) in Törnebohm (1906), and recognized that this was a new amphibole species. It should be noted that a significant amount of Li (1.15 wt% Li₂O, corresponding to 0.65 atoms per formula unit, apfu) was later reported in amphiboles from Norra Kärr by Sundius (1945), who raised doubts on the composition of eckermannite.

However, this did not result in re-examination of the sample.

A few years ago, the study of a specimen from Norra Kärr in the collection of Renato and Adriana Pagano showed the occurrence of a Li- and F-rich amphibole that was subsequently described as fluoro-alumino-leakeite (IMA-CNMNC 2009-012; Oberti et al. 2009), and became fluoro-leakeite after Hawthorne et al. (2012). Based on the similarity of the published optical properties of holotype eckermannite, that paper suggested that eckermannite did not occur at Norra Kärr. Re-examination of the holotype specimen deposited at the Natural History Museum in London (BM 1949.151) and of the original material analyzed by Törnebohm (1906) (NRM 570725; courtesy of Ulf Hålenius, Stockholm) later confirmed this hypothesis, and showed that those samples are also fluoro-leakeite.

Eckermannite is quite rare, and most of the available analyses of natural or synthetic samples actually refer either to ferro-eckermannite or to fluoro-eckermannite (note that presently both these species have the status of named amphiboles, so that their complete mineral descriptions have never been reported). However, the rootname eckermannite was used by Hawthorne et al. (2012) to redefine kozulite (IMA 1968-028; Nambu et al. 1969; formerly assigned by Leake et al. 1997) to mangano-ferri-eckermannite

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based on the newly approved rules for amphibole classification and nomenclature. Hence, it was not possible to discredit the root-name eckermannite. Instead of simply discrediting the holotype material, we started a systematic characterization of the “eckermannite” samples published in the literature. We found a specimen related to the ideal eckermannite composition only in the sample from the collection of the American Museum of Natural History described in this work. After the approval of IMA-CNMNC (vote 2013-136), the rock sample AMNH H108401 must be considered as the holotype sample of eckermannite.

MINERAL DATA

Occurrence and paragenesis

The sample was extracted from a jadeitite-amphibole fels rock catalogued as AMNH H108401 in the mineral collection of the American Museum of Natural History, acquired in Myanmar by one of us (G.E.H.) in 2000. The rock consists of a boundary layer between mixed white and emerald green jadeitite and a black amphibole fels, a sharp boundary separating the two parts. The rock was mined in the Jade Mine Tract, Kachin Province, Myanmar. It is not known whether the rock comes from a tectonic block in serpentinite or as part of a boulder extracted from the Uru River conglomerates (Hughes et al. 2000). Associated minerals are jadeite and albite. All of the amphibole in this sample falls within eckermannite-dominant compositions with $Mg/(Mg+Fe^{2+})$ between 0.84 and 1.

Amphibole fels adjacent to jadeitite from the Jade Mine Tract in Myanmar have been ascribed to reactions between hydrous fluids that crystallized jadeitite and hosting serpentinitized ultramafic mantle wedge during subduction, but timing (whether jadeitite or fels formed first) is uncertain (Shi et al. 2003, 2012). Conditions of formation in this high-pressure–low-temperature regime are not well constrained, but are somewhere in the blueschist facies of metabasites, probably $300 < T < 400$ °C and $5 < P < 15$ kbar.

Appearance, physical and optical properties

The amphibole fels is gray with white veins (Fig. 1) and grains of eckermannite are intergrown prisms generally less than 1 mm in maximum dimension. They are colorless to gray in color, transparent, vitreous, and non-fluorescent. The tenacity is brittle and single crystals show a perfect cleavage according {110}. The density calculated from the unit formula and cell dimensions is 3.02 g/cm^3 .

A spindle stage was used to orient a crystal for measurement of refractive indices and $2V$ by extinction curves (Bartelmehs et al. 1992). The optical orientation was determined by transferring the crystal from the spindle stage to a single-crystal diffractometer and measuring the relative axial relations by X-ray diffraction. In transmitted light, eckermannite is biaxial negative with indices of refraction $\alpha = 1.605$, $\beta = 1.630$, $\gamma = 1.634$ (all ± 0.002), measured with gel-filtered Na light ($\lambda = 589.9 \text{ nm}$); $2V_{\text{obs}} = 43.0(5)$, $2V_{\text{calc}} = 43^\circ$. Orientation is $X \wedge a = 23.8^\circ$ (in β obtuse), $Y \parallel b$, $Z \wedge c = 10.1^\circ$ (in β acute), and pleochroism is as follows: $X =$ medium gray (strongest), $Y =$ pale gray to colorless (weakest), $Z =$ light gray (medium).

Crystallography

For samples AMNH H108401 (single crystal $120 \times 60 \times 40 \text{ }\mu\text{m}$ in size) and NMR 570725 (single crystal $200 \times 160 \times 60 \text{ }\mu\text{m}$ in

size), diffraction data were collected in the 2θ range $2\text{--}60^\circ$ with a Bruker-AXS CCD diffractometer with graphite-monochromatized $\text{MoK}\alpha$ X-radiation ($\lambda = 0.7107 \text{ \AA}$). For both crystals, omega-rotation frames (scan width 0.3° , scan time 20 s, sample-to-detector distance 50 mm) were processed with the SAINT software (Bruker 2003) and intensities were corrected for Lorentz and polarization effects; absorption effects were empirically evaluated by the SADABS software (Sheldrick 1996) and an absorption correction was applied to the data.

A total of 6891 reflections collected for sample AMNH H108401 was reduced to 1377 unique reflections (mean redundancy = 5, $R_{\text{int}} = 2.3\%$), and accurate unit-cell dimensions were calculated by least-squares refinement of the positions of 1998 reflections with $I_o > 10 \sigma I$ in the θ range $2\text{--}30^\circ$. For sample NMR 570725, 6580 collected reflections were reduced to 1321 unique reflections (mean redundancy = 5, $R_{\text{int}} = 1.3\%$), and accurate unit-cell dimensions were calculated by least-squares refinement of the positions of 4074 measured reflections with $I_o > 10 \sigma I$ in the θ range $2\text{--}30^\circ$.

For samples BM 1949.151, XRD analysis was done with a Philips PW1100 4-circle diffractometer ($\lambda = \text{MoK}\alpha$). Two monoclinic equivalents were collected in the 2θ range $4\text{--}70^\circ$; corrections for absorption and L_p were applied and 3960 collected data were merged to 2017 unique reflections ($R_{\text{int}} = 2.2\%$). Unit-cell parameters were calculated from least-squares refinement of the d^* values obtained for 60 rows of the reciprocal lattice by measuring the center of gravity of each reflection and of its antireflection in the 2θ range -70 to 70° .

For all samples, only the reflections with $I_o > 3 \sigma I$ were considered as observed during unweighted full-matrix least-squares refinement on F done with a program locally written to handle complex solid-solutions. Scattering curves for fully ionized chemical species were used at sites where chemical substitutions occur; neutral vs. ionized scattering curves were used at the T and anion sites [except O(3)]. More details on the refinement procedure and on the terminology used are given in Oberti et al. (1992) and in Hawthorne et al. (1995). The $A(m)$ and $A(2)$ sites were inserted into the model to better account for the irregular shape of the electron density within the A cavity, and testify to the presence



FIGURE 1. Jadeitite-amphibole fels rock catalogued as AMNH H108401 in the mineral collection of the American Museum of Natural History. (Color online.)

of significant ordering of the A cations. The absence of residual electron-density along the *b* direction at around 0.40 Å from the *M*(4) site [i.e., at the *M*(4') site] indicates the absence of significant amounts of smaller B cations (e.g., Li⁺, Fe²⁺, Mg²⁺).

The final values of R_{obs} and R_{all} are 2.9 and 4.0% for AMNH H108401, 1.6 and 2.6% for BM 1949.151, and 2.1 and 2.3% for NMR 570725. Refined coordinates, atomic displacement parameters, site occupancies, and selected bond lengths and angles are given in Tables 1 and 2. Measured structure factors have been deposited with the CIF¹.

X-ray powder-diffraction data (CuK α , $\lambda = 1.54178$ Å) for eck-

ermannite AMNH H108401 were obtained from the single-crystal data using the XPREP utility of SAINT (Bruker 2003). No Lorentz and polarization correction was applied. Data are given in Table 3.

EMP analysis

Chemical analysis of the refined crystal of eckermannite (10 point analyses) was done with a CAMECA SX-100 electron microprobe (WDS mode, 15 kV, 10 nA, 5 μ m beam diameter). The following standards were used for K α X-ray lines: Si: diopside, TAP; Ca: diopside, LPET; Ti: titanite, LLiF; Fe: fayalite, LLiF; Mn: spessartine, LLiF; Cr: chromite, LLiF; Mg: forsterite, LTAP; Al: andalusite, TAP; K: orthoclase, LPET; Na: albite, TAP; F: fluoro-riebeckite, LTAP. Zn, Cr, and Cl contents are below detection limits. H₂O was calculated from the unit formula to obtain 2 (OH+F) in the absence of dehydrogenation, as indicated by

¹ Deposit item AM-15-45132, CIF and structure factors. Deposit items are stored on the MSA web site and available via the *American Mineralogist* Table of Contents. Find the article in the table of contents at GSW (ammin.geoscienceworld.org) or MSA (www.minsocam.org), and then click on the deposit link.

TABLE 1. Refined site-scattering values (ss), atom coordinates, and displacement parameters ($\beta_{ii} \times 10^4$) for eckermannite AMNH H108401, fluoro-leakeite BM 1949.151 (former eckermannite holotype), and fluoro-leakeite NMR 570725

Atom	ss (epfu)	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	B_{eq} (Å ²)	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
AMNH H108401											
O(1)		0.11100(17)	0.08805(9)	0.21287(32)	0.85(3)	19	8	76	-2	9	-4
O(2)		0.11802(17)	0.16990(9)	0.73412(31)	0.94(4)	24	7	82	0	-4	-1
O(3)	16.49(6)	0.10828(24)	0	0.70978(46)	1.05(5)	25	9	101	-	7	-
O(4)		0.36274(19)	0.25079(10)	0.79757(34)	1.16(4)	43	7	103	-5	21	0
O(5)		0.34970(17)	0.12893(10)	0.08338(32)	1.03(4)	21	11	79	-1	3	8
O(6)		0.34156(17)	0.11827(10)	0.58486(32)	1.09(4)	27	11	73	0	4	-7
O(7)		0.33725(25)	0	0.28952(49)	1.15(6)	30	7	142	-	13	-
T(1)		0.27930(6)	0.08630(3)	0.29240(12)	0.67(1)	18	6	55	0	4	-1
T(2)		0.28706(6)	0.17250(3)	0.80083(12)	0.73(1)	21	6	59	-1	6	0
M(1)	25.72(14)	0	0.09002(6)	1/2	0.80(3)	23	7	66	-	8	-
M(2)	29.70(14)	0	0.18130(5)	0	0.81(2)	21	7	72	-	7	-
M(3)	12.95(4)	0	0	0	0.77(4)	24	6	58	-	4	-
M(4)	23.81(18)	0	0.27541(8)	1/2	1.51(4)	46	11	162	-	40	-
A	3.52(4)	0	1/2	0	1.6(2)	21	19	206	-	61	-
A(m)	3.03(11)	0.0259(16)	1/2	0.0717(25)	3.0(4)	80	26	245	-	10	-
A(2)	4.87(11)	0	0.4733(40)	0	3.1(2)	86	9	574	-	153	-
H	1.75(16)	0.204(5)	0	0.740(9)	1.0						
BM 1949.151											
O(1)		0.10796(9)	0.09295(5)	0.21081(17)	0.70(2)	15	7	64	-1	9	-2
O(2)		0.11774(9)	0.17108(5)	0.74128(18)	0.68(2)	16	6	70	0	8	1
O(3)	17.29(8)	0.11398(13)	0	0.69640(25)	0.99(3)	27	7	105	-	3	-
O(4)		0.36646(10)	0.25172(5)	0.80655(18)	0.80(2)	29	5	79	-4	20	-2
O(5)		0.35207(10)	0.12899(5)	0.08840(18)	0.73(2)	18	8	60	0	11	7
O(6)		0.34187(10)	0.12059(5)	0.58567(18)	0.76(2)	22	8	52	1	9	-7
O(7)		0.33211(15)	0	0.30121(28)	0.92(3)	30	4	115	-	14	-
T(1)		0.27745(3)	0.08705(2)	0.29475(7)	0.46(1)	14	4	41	-1	6	-1
T(2)		0.28951(3)	0.17255(2)	0.80684(6)	0.48(1)	15	4	40	-1	8	0
M(1)	28.83(8)	0	0.08757(3)	1/2	0.59(1)	20	5	48	-	13	-
M(2)	36.50(8)	0	0.17914(2)	0	0.51(1)	15	4	48	-	8	-
M(3)	4.90(4)	0	0.0000	0	0.83(6)	27	5	76	-	2	-
M(4)	22.06(5)	0	0.27668(5)	1/2	1.08(2)	37	7	121	-	40	-
A	1.79(19)	0	1/2	0	1.5(1)						
A(m)	12.56(8)	0.0425(2)	1/2	0.0888(4)	2.7(1)	100	16	322	-	133	-
H	0.49(10)	0.203(13)	0	0.734(24)	1.0						
NMR 570725											
O(1)		0.10827(10)	0.09276(6)	0.21145(19)	0.82(2)	22	9	61	-1	10	-2
O(2)		0.11782(11)	0.17085(6)	0.74050(19)	0.81(2)	23	7	68	-1	7	0
O(3)	17.29(4)	0.11319(15)	0	0.69597(27)	1.10(3)	33	7	106	-	6	-
O(4)		0.36628(11)	0.25151(6)	0.80595(20)	0.98(2)	39	6	80	-4	21	0
O(5)		0.35170(11)	0.12899(6)	0.08874(19)	0.85(2)	24	9	60	0	11	7
O(6)		0.34210(11)	0.12043(6)	0.58625(19)	0.88(2)	27	9	57	0	10	-6
O(7)		0.33217(17)	0	0.30097(31)	1.10(3)	38	5	120	-	12	-
T(1)		0.27760(4)	0.08704(2)	0.29523(7)	0.59(1)	21	5	45	-1	8	-1
T(2)		0.28923(4)	0.17251(2)	0.80668(7)	0.62(1)	22	5	44	-1	10	0
M(1)	28.28(6)	0	0.08783(3)	1/2	0.72(1)	25	6	52	-	14	-
M(2)	36.63(5)	0	0.17940(2)	0	0.68(1)	22	6	53	-	11	-
M(3)	6.14(2)	0	0.0000	0	0.89(5)	31	6	72	-	9	-
M(4)	22.08(5)	0	0.27654(5)	1/2	1.25(2)	43	9	129	-	43	-
A	1.72(4)	0	1/2	0	1.4(2)	32	21	87	-	50	-
A(m)	12.72(8)	0.04191(35)	1/2	0.08706(65)	2.9(1)	111	17	340	-	138	-
H	0.41(12)	0.208(5)	0	0.735(26)	1.0						

TABLE 2. Selected interatomic distances (Å) and angles (°) in eckermannite AMNH H108401 and fluoro-leakeite BM 1949.151 and NMR 570725

	AMNH H108401	BM 1949.151	NMR 570725		AMNH H108401	BM 1949.151	NMR 570725
T(1)–O(1)	1.605(2)	1.600(1)	1.599(1)	T(2)–O(2)	1.612(2)	1.619(1)	1.616(1)
T(1)–O(5)	1.624(2)	1.628(1)	1.625(1)	T(2)–O(4)	1.584(2)	1.591(1)	1.588(1)
T(1)–O(6)	1.627(2)	1.626(1)	1.624(1)	T(2)–O(5)	1.668(2)	1.656(1)	1.657(1)
T(1)–O(7)	1.643(1)	1.630(1)	1.630(1)	T(2)–O(6)	1.678(2)	1.662(1)	1.662(1)
<T(1)–O>	1.625	1.621	1.619	<T(2)–O>	1.636	1.632	1.631
M(1)–O(1) ×2	2.068(2)	2.054(1)	2.052(1)	M(2)–O(1) ×2	2.155(2)	2.027(1)	2.035(1)
M(1)–O(2) ×2	2.056(2)	2.102(1)	2.094(1)	M(2)–O(2) ×2	2.032(2)	1.988(1)	1.993(1)
M(1)–O(3) ×2	2.094(2)	2.039(1)	2.038(1)	M(2)–O(4) ×2	1.936(2)	1.894(1)	1.895(1)
<M(1)–O>	2.073	2.065	2.061	<M(2)–O>	2.041	1.970	1.974
M(3)–O(1) ×4	2.084(2)	2.119(1)	2.118(1)	M(4)–O(2) ×2	2.396(2)	2.394(1)	2.393(1)
M(3)–O(3) ×2	2.063(2)	2.159(1)	2.155(1)	M(4)–O(4) ×2	2.348(2)	2.362(1)	2.358(1)
<M(3)–O>	2.077	2.132	2.131	M(4)–O(5) ×2	2.900(2)	2.842(1)	2.842(1)
A–O(5) ×4	2.823(2)	2.800(1)	2.802(1)	M(4)–O(6) ×2	2.558(2)	2.493(1)	2.497(1)
A–O(6) ×4	3.175(2)	3.177(1)	3.172(2)	<M(4)–O>	2.551	2.523	2.523
A–O(7) ×2	2.460(3)	2.539(1)	2.537(2)	A(m)–O(5) ×2	2.887(2)	2.941(2)	2.941(2)
<A–O>	2.891	2.899	2.897	A(m)–O(5) ×2	2.816(2)	2.761(2)	2.761(2)
A(2)–O(5) ×2	2.450(2)	–	–	A(m)–O(6) ×2	2.886(2)	2.803(2)	2.804(3)
A(2)–O(6) ×2	2.880(2)	–	–	A(m)–O(7)	2.400(3)	2.558(2)	2.557(3)
A(2)–O(7) ×2	2.505(3)	–	–	A(m)–O(7)	3.329(3)	3.158(2)	3.166(4)
<A(2)–O>	2.612	–	–	A(m)–O(7)	2.582(3)	2.636(2)	2.629(3)
O(3)–H	0.91(1)	0.84(1)	0.89(1)	<A(m)–O>	2.832	2.818	2.818
M(1)–M(2)	3.107(1)	3.102(1)	3.100(1)	T(1)–O(5)–T(2)	134.6(1)	133.6(1)	133.8(1)
O(5)–O(6)–O(5)	171.1(1)	172.3(1)	172.4(1)	T(1)–O(6)–T(2)	137.9(1)	139.0(1)	138.7(1)
				T(1)–O(7)–T(1)	139.2(1)	142.5(1)	142.5(1)
				O(6)–O(7)–O(6)	107.3(1)	110.5(1)	110.3(1)

the single-crystal structure refinement. The total Fe content was first estimated as FeO; the ferrous and ferric populations were estimated later, imposing electroneutrality and crystal-chemical constraints obtained from structure refinement. The results are reported in Table 4. The empirical formula (based on 24 anions pfu) is $A(Na_{0.87}K_{0.06})_{\Sigma=0.93} B(Na_{1.89}Ca_{0.11})_{\Sigma=2.00} C(Mg_{3.87}Fe_{0.09}^{2+}Mn_{0.01}Fe_{0.38}^{3+}Al_{0.62})_{\Sigma=4.97} TSi_{8.00}O_{22} W(F_{0.03}OH_{1.97})_{\Sigma=2.00}$. The end-member formula is $A^1Na^1B^1Na^2C^1(Mg_4Al)^1Si_8O_{22}W(OH)_2$, which requires SiO_2 59.80, Al_2O_3 6.34, MgO 20.05, Na_2O 11.57, H_2O 2.24, total 100.00 wt%.

Compatibility

The final $1 - (K_p/K_c)$ index for eckermannite AMNH H108401 is 0.010 (superior).

Type material

Type material for eckermannite is deposited in the collections of the Department of Earth and Planetary Sciences, American Museum of Natural History, New York, U.S.A., specimen number AMNH H108401. The refined and analyzed crystal of this work has the code 1213 in the amphibole database of the CNR-IGG Pavia, where the refined fluoro-leakeite crystal from sample BM 1949.151 has the code 1161, and that from sample NMR 570725 has the code 1245.

DISCUSSION

A comparison of the new holotype eckermannite from the Jade Mine tract, Myanmar, holotype fluoro-leakeite from Norra Kärr, Sweden (Oberti et al. 2009), the former “holotype eckermannite” BM 1949.151, and the original material analyzed by Törnebohm (1906) (NMR 570725), is shown in Table 5. The three latter samples are nearly identical, both with regard to the geometrical (unit-cell parameters and refined site geometry) and crystal-chemical (refined site-scattering values) parameters, except for the higher site-scattering value refined at the M(3) site in NMR 570725, which indicates a slightly lower cLi content coupled with

TABLE 3. Powder X-ray data for eckermannite AMNH H108401

l_{rel}	d_{calc}	hkl	l_{rel}	d_{calc}	hkl	l_{rel}	d_{calc}	hkl	l_{rel}	d_{calc}	hkl
4	8.920	0 2 0	36	2.574	0 6 1	4	1.921	$\bar{3}$ 5 2	8	1.628	4 8 0
42	8.407	1 1 0			0 0 2	9	1.895	5 1 0	9	1.599	1 1 1 0
13	4.859	$\bar{1}$ 1 1	56	2.525	2 0 2	4	1.876	2 4 2	6	1.588	6 0 0
6	4.766	2 0 0	5	2.384	$\bar{2}$ 6 1	4	1.862	$\bar{4}$ 6 1	21	1.579	$\bar{1}$ 5 3
30	4.460	0 4 0	7	2.373	3 5 0	8	1.846	$\bar{1}$ 9 1	11	1.521	$\bar{6}$ 0 2
9	4.028	1 1 1	27	2.315	3 5 1	4	1.824	4 4 2	23	1.508	$\bar{2}$ 6 3
16	3.850	$\bar{1}$ 3 1	18	2.275	$\bar{1}$ 7 1	4	1.816	5 3 0	14	1.487	0 1 2 0
59	3.395	1 3 1	20	2.261	$\bar{3}$ 1 2	7	1.786	1 9 1	6	1.445	3 1 1 0
34	3.257	2 4 0	9	2.197	2 4 2			0 10 0	6	1.440	$\bar{6}$ 4 2
56	3.128	3 1 0	33	2.161	2 6 1	4	1.732	$\bar{5}$ 1 2	28	1.430	$\bar{6}$ 6 1
7	2.997	3 1 1	10	2.128	3 3 2	9	1.687	$\bar{1}$ 3 3	3	1.415	5 3 3
23	2.966	0 6 0	17	2.067	2 0 2			0 2 3	11	1.379	5 1 2
12	2.915	$\bar{1}$ 5 1	9	2.023	3 5 1	9	1.684	$\bar{1}$ 3 3	7	1.348	$\bar{5}$ 5 3
18	2.802	3 3 0	8	1.999	4 0 2			0 2 3			5 3 2
100	2.702	3 3 1	6	1.942	4 2 1	8	1.672	$\bar{2}$ 8 2			
		1 5 1			1 9 0	25	1.654	4 6 1			

Notes: The ten strongest line are in bold.

a slightly lower $^{M(2)}Fe^{3+}$ content (as shown by the longer <M(2)–O> distance). This confirms that samples BM 1949.151 and NMR 570725 are fluoro-leakeite, and hence that eckermannite has never been found at Norra Kärr.

In contrast, eckermannite can be easily distinguished from fluoro-leakeite by comparing either unit-cell parameters or optical properties or the details of the structure refinement.

Inspection of refined bond-lengths and site-scattering values allowed us to derive accurate site populations starting from the unit formula obtained by EMP analysis. They are reported in Table 6. As expected, trivalent cations are ordered at the M(2) site. For comparison, the site populations derived for the C cations in holotype fluoro-leakeite by Oberti et al. (2009) are: M(1): 1.76 Mg + 0.20 Fe²⁺ + 0.04 Zn, $d_{obs} = d_{cal} = 2.064$ Å; M(2): 1.13 Al + 0.75 Fe³⁺ + 0.09 Fe²⁺ + 0.03 Ti⁴⁺, $d_{obs} = 1.968$ Å, $d_{cal} = 1.972$ Å; M(3): 0.09 Mn²⁺ + 0.91 Li⁺, $d_{obs} = 2.133$ Å, $d_{cal} = 2.105$ Å [which by the way implies that the effect of $^{O(3)}F$ on the M(3) site geometry in cLi amphiboles is lower than observed in “standard” amphiboles]. From the crystal-chemical point of view, the two

amphibole compositions have the same charge arrangement for the A, B, C, T groups of cations and W anions, but differ by: (i) the coupled heterovalent exchange allowing the entrance of ^cLi into the amphibole structure, i.e., ^{M(2)}(Mg,Fe)²⁺ + ^{M(3)}(Mg,Fe)²⁺ → ^{M(2)}Fe³⁺ + ^{M(3)}Li⁺; (ii) the homovalent exchange ^{O(3)}(OH)⁻ → ^{O(3)}F⁻. Exchange (i) makes the refined site-scattering value at *M*(3) much lower and shortens the <*M*(2)-O> distances significantly,

TABLE 4. EMP analysis (10 points) and unit formula calculated based on 24 (O,OH,F,Cl) and 2 (OH,F,Cl) for the refined crystal of holotype eckermannite AMNH H108401 (1213 in the CNR-IGG-Pv database); ss = site scattering (electrons per formula unit, epfu); bdl = below detection limit

	wt%	e.s.d.		apfu
SiO ₂	59.30	0.24	Si	8.00
TiO ₂	0.03	0.02	Al	0.00
Al ₂ O ₃	3.89	0.61	ΣT	8.00
Cr ₂ O ₃	bdl		Ti	0.00
Fe ₂ O ₃	3.78		Al	0.62
FeO ^a	0.80		Fe ³⁺	0.38
MnO	0.07	0.02	Fe ²⁺	0.09
MgO	19.25	0.14	Mg	3.87
ZnO	bdl		Mn ²⁺	0.01
CaO	0.77	0.12	ΣC	4.97
Na ₂ O	10.56	0.18	Ca	0.11
K ₂ O	0.32	0.03	Na	1.89
F	0.06	0.04	ΣB	2.00
Cl	bdl		Na	0.87
O=F,Cl	0.03		K	0.06
(H ₂ O)cal	2.19		ΣA	0.93
			F	0.03
Total	101.00		OH	1.97
			ΣW	2.00
calculated ss				refined ss
ss C	67.08		ss C	68.37
ss B	23.00		ss B	23.81
ss A	10.35		ss A	11.42
Total	100.75		Total	103.60

^a e.s.d. for FeO(total) = 0.59.

notwithstanding the fact that the Fe content in fluoro-leakeite is much higher (29.70 vs. 37.00 electrons per formula unit, epfu). Exchange (ii) shortens the *M*(1,3)-O(3) distances significantly, and hence the <*M*(1,3)-O> distances; both these effects are evident from the structure refinements [note that the <*M*(3)-O> distance is much larger in fluoro-leakeite due to the presence of Li; <Li-O> = 2.119 Å and <Mg-O> = 2.078 Å for amphiboles]. Exchange (ii) also affects the ordering of A cations; as expected (according to the conclusions of Hawthorne et al. 1996), Na occurs at the *A*(*m*) and *A*(2) sites in eckermannite, but is ordered at *A*(*m*) in fluoro-leakeite.

There are other issues that require comment: why are eckermannite compositions so rare in Nature, and why are eckermannitic amphiboles often enriched in Fe (thus falling in the compositional field of magnesio-arfvedsonite and arfvedsonite) or in fluorine? Hawthorne (1997) examined the effect of OH-F substitution in arfvedsonite. In both arfvedsonite and fluoro-arfvedsonite, ^ΛNa is ordered at *A*(*m*). Where *M*(2) = Mg, the locally associated *A*(*m*) site is occupied by Na. Where *M*(2) = Al, the locally associated *A*(*m*) site is vacant; however, the *A* cavity still contains Na, but the Na occupies the *A*(*m*) site on the other side of the cavity, away from the *M*(2) site containing Al. In arfvedsonite, the separation

TABLE 6. Site occupancies proposed for eckermannite AMNH H108401 based on the results of the structure refinement

Site	Site population (apfu)	Site scattering (epfu)	
		refined	calculated
T(1)	4 Si		
T(2)	4 Si		
<i>M</i> (1)	1.90 Mg + 0.10 Fe ²⁺	25.72	25.40
<i>M</i> (2)	1.04 Mg + 0.62 Al + 0.34 Fe ³⁺	29.70	29.38
<i>M</i> (3)	0.96 Mg + 0.03 Fe ²⁺ + 0.01 Mn	12.95	12.55
ΣC cations		68.37	67.33
<i>M</i> (4) site	1.89 Na + 0.11 Ca	23.81	22.99
A sites	0.87 Na + 0.06 K	11.42	10.7

TABLE 5. Comparative data for holotype eckermannite AMNH H108401 (this work), holotype fluoro-leakeite (Oberti et al. 2009), the discredited holotype eckermannite kept at the Natural History Museum in London [with optical properties taken by the compilation in the Handbook of Mineralogy (Anthony et al. 2015) and marked with ^a], and sample NMR 570725 originally described in Törnebohm (1906)

	Eckermannite Jade Mine tract AMNH H108401	Fluoro-leakeite Norra Kärr	"Eckermannite" Norra Kärr BM 1949.151	"Eckermannite" Norra Kärr NMR 570725
<i>a</i> (Å)	9.8087(7)	9.7043(5)	9.7073(5)	9.7094(6)
<i>b</i>	17.8448(13)	17.7341(8)	17.7339(6)	17.7305(12)
<i>c</i>	5.2905(4)	5.2833(3)	5.2850(4)	5.2815(3)
β (°)	103.660(11)	104.067(4)	104.029(5)	104.040(1)
<i>V</i> (Å ³)	899.83(11)	881.97(8)	882.67(9)	882.06(10)
<i>a:b:c</i>	0.550:1:0.297	0.547:1:0.298	0.547:1:0.298	0.548:1:0.298
Space group	<i>C2/m</i>	<i>C2/m</i>	<i>C2/m</i>	<i>C2/m</i>
Optic sign	Biaxial (-)	Biaxial (-)	Biaxial (-) ^a	Biaxial (-)
α	1.605	1.632	1.610–1.640 ^a	1.636
β	1.630	1.638	1.625–1.650 ^a	1.644
γ	1.634	1.643	1.630–1.655 ^a	1.649
2 <i>V</i> (°)	43	98	15–80 ^a	74
Color	Pale gray	Pale greenish blue	Bluish green to dark green ^a	Bluish green to dark green ^a
Pleochroism	Pale gray to medium gray	Pale-green to dark-green	Pale green to dark green	Colorless to bluish green
< <i>T</i> (1)-O> (Å)	1.625	1.620	1.621	1.619
< <i>T</i> (2)-O> (Å)	1.636	1.631	1.632	1.631
< <i>M</i> (1)-O> (Å)	2.073	2.064	2.065	2.061
< <i>M</i> (2)-O> (Å)	2.041	1.968	1.970	1.974
< <i>M</i> (3)-O> (Å)	2.077	2.133	2.132	2.131
< <i>M</i> (4)-O> (Å)	2.551	2.523	2.523	2.523
ss <i>M</i> (1) (epfu)	25.72	28.86	28.83	28.28
ss <i>M</i> (2) (epfu)	29.70	37.00	36.50	36.63
ss <i>M</i> (3) (epfu)	12.95	4.81	4.90	6.14
ss <i>M</i> (4) (epfu)	23.81	22.30	22.06	22.08
ss <i>A</i> (epfu)	3.52	3.75	1.79	1.72
ss <i>A</i> (<i>m</i>) (epfu)	3.03	10.69	12.56	12.72
ss <i>A</i> (2) (epfu)	4.87	-	-	-

of the two locally associated (split) $A(m)$ sites is quite small as the Na at $A(m)$ has to minimize its interaction with the H atom of the OH group. In fluoro-arfvedsonite, the separation of the two locally associated (split) $A(m)$ sites is considerably larger (Hawthorne et al. 1996, their Fig. 8) as there is no H [i.e., OH at the O(3) site] to repel Na. These interactions will be increased in eckermannite as the octahedral strip contains Mg_4Al instead of $Fe_4^{2+}Fe^{3+}$ (as in arfvedsonite) and hence will be smaller, constraining the A cavity to be smaller than in arfvedsonite and making the Na-H interaction in eckermannite even more constraining than in arfvedsonite. These arguments suggest that arfvedsonite will be much more common than eckermannite, and that the fluoro-species should be more common than the OH species.

IMPLICATIONS

The results of this work emphasize that minerals with complex composition and crystal-chemistry should be carefully characterized using a combination of independent techniques. In particular, the occurrence of Li in amphiboles (either as a B or C cation, or both) should be carefully checked where the geochemistry of the system is compatible with Li. The analyses reported by Adamson (1942), but done by Törnebohm (1906), did not consider either F or Li; ironically, the presence of Li would have been easier to detect at a time where wet-chemical analysis was the only method to derive mineral composition. Indeed, Sundius (1945) reported the presence of Li in amphiboles from Norra Kärr, but did not consider re-examination and possibly re-definition of eckermannite. Admittedly, at this time, little was known about amphibole crystal-chemistry; however, it is strange that neither Adamson nor the other scientists studying the Norra Kärr locality (e.g., Adamson 1944; von Eckermann 1968; Blaxland 1977; Kramm and Koark 1988) re-considered the composition of “eckermannite.” It is worth noting in this regard that any attempt to do structure refinement data of “eckermannite” would have quickly shown deficiencies in the chemical characterization, confirming that SREF is a very powerful analytical technique.

Another conclusion to be drawn from the present work is that one must be cautious with regard to the use of older names in amphiboles (and in other groups or supergroups of rock-forming minerals) as names have been grandfathered without requiring proper characterization. Eckermannite and its ferro- (i.e., magnesio-arfvedsonite) and fluoro-counterparts, katophorite and kaersutite, have all had significant issues with regard to composition, and trivial names have been proposed after recognition solely of homovalent substitutions. We hope that the latest report on amphibole nomenclature (Hawthorne et al. 2012) has put some order in this matter and built a clear set of rules to be followed in the future. In this regard, we are presently checking and characterizing some grandfathered compositions.

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