Ferri-obertiite from the Rothenberg quarry, Eifel volcanic complex, Germany: mineral data and crystal chemistry of a new amphibole end-member

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ABSTRACT

Pink-orange crystals of a composition within the ferri-obertiite compositional space were found in vesicles in a pale beige silicate vein found from a basalt quarry at Mount Rothenberg. Eifel district, Germany. Associated minerals are potassic feldspar, alpha quartz paramorphic after beta quartz, eifelite (the second occurrence after the Caspar quarry at Bellerberg volcano, Eifel region), tridymite, rutile, roedderite and other amphiboles. The ideal formula of ferri-obertiite is ^ANa^BNa₂^C(Mg₃Fe³⁺Ti)^TSi₈O₂₂^WO₂; the empirical formula derived for the holotype specimen from Mount Rothenberg from the results of electron-microprobe $\begin{array}{l} \text{analysis} \quad \text{and} \quad \text{single-crystal} \quad \text{structure} \quad \text{refinement} \quad \text{is} \quad {}^{A}(\text{Na}_{0.76}\text{K}_{0.22})_{\Sigma 0.98} {}^{B}(\text{Na}_{1.61}\text{Ca}_{0.35}\text{Mn}_{0.04}^{2+})_{\Sigma 2.00} \\ {}^{C}(\text{Mg}_{3.58}\text{Mn}_{0.11}^{2+}\text{Fe}_{0.62}^{3+}\text{Ti}_{0.66}^{4+}\text{Cr}_{0.01}^{3+}\text{Zn}_{0.01}\text{Ni}_{0.01})_{\Sigma 5.00} \quad {}^{T}(\text{Si}_{7.82}\text{Ti}_{0.12}^{4+}\text{Al}_{0.06})_{\Sigma 8.00}\text{O}_{22} \quad {}^{W}[\text{O}_{1.26}\text{F}_{0.55}(\text{OH})_{0.19}]_{\Sigma 2.00} \\ \end{array}$ The unit-cell dimensions are a = 9.7901(7), b = 17.9354(13), c = 5.2892(4) Å, $\beta = 104.142(2)^{\circ}$, $V = 104.142(2)^{\circ}$ 900.58 (11) Å³. The space group is $C^{2/m}$, Z = 2. Ferri-obertiite is biaxial (+), with $\alpha = 1.664$, $\beta = 1.680$, $\gamma =$ 1.722, all ± 0.002 and 2V (meas.) = 66.4(3)°, 2V (calc.) = 64.7°. The strongest eight reflections in the powder X-ray pattern [d values (in Å), I, (hkl)] are: 2.704, 100, (151); 3.116, 76, (310); 3.388, 72, (131); 8.931, 72, (110); 2.529, 67, (202); 2.583, 39, (061); 2.160, 38, (261); 3.260, 37, (240). Both the mineral and the name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2015-079); the rock specimen has been deposited at the Museo di Mineralogia, Dipartimento di Scienze della Terra e dell'Ambiente, Università degli Studi di Pavia, under the code 2015-02.

Keywords: ferri-obertiite, amphibole, oxo component, electron-microprobe analysis, crystal-structure refinement, Eifel district, Germany.

Introduction

THE name obertiite, presently assigned to the ideal composition ${}^{A}Na{}^{B}Na{}_{2}{}^{C}(Mg_{3}AITi){}^{T}Si_{8}O_{22}{}^{W}O_{2}$, is a relatively young rootname within amphibole compositional space, specifically within the oxoamphibole group. It was first proposed by Hawthorne *et al.* (2000) for a sample of

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composition ^A(Na_{0.84} K_{0.18})^B(Na_{1.86}Ca_{0.08}Fe²⁺_{0.06}) ^C(Mg_{3.09}Fe²⁺_{0.41}Zn_{0.01}Fe³⁺_{0.29}Mn³⁺_{0.37}Al_{0.03}Ti⁴⁺_{0.86}Li_{0.03}) ^TSi_{8.00}O₂₂^W[O_{1.54}F_{0.26}(OH)_{0.20}], occurring in vugs in volcanic rocks at the Bellerberg quarry, Laacher See district, Eifel, Germany. These authors proposed that rootname obertiite should be applied (with no prefix) to ferri-dominant compositions. This decision was later reversed according to the rules introduced for the nomenclature and classification of the amphibole supergroup (Hawthorne *et al.*, 2012). These authors assigned a rootname to ^CMg- and ^CAl- dominant compositions (with very few exceptions where the terminology is wellembedded in the petrological literature). Hence, the sample described by Hawthorne *et al.* (2000) has now to be named mangani-obertiite because its Mn^{3+} content is higher than that of Fe^{3+} (Williams *et al.*, 2014). Analogously, the sample described as ferro-obertiite in Hawthorne *et al.* (2010), with composition ^A(Na_{0.72}K_{0.29})^B(Na_{1.85}Ca_{0.15}) ^C(Mg_{1.30}Fe²⁺_{2.35}Mn²⁺_{0.02}Fe³⁺_{0.32}Al_{0.01}Ti_{0.75}Li_{0.10})

^T(Si_{7,99}Al_{0.01})O₂₂^W[O_{1.16}(OH)_{0.59}F_{0.25}], has now to be named ferro-ferri-obertiite. This latter sample is from Coyote Peak, Humboldt County, California, and was found in inclusions of lithic-wacke sandstones in an alkali-rich ultramafic diatreme (Hawthorne *et al.*, 1998).

As a part of our systematic work on clarifying the end-members and crystal chemistry of the oxo amphiboles, we invited mineral collectors to provide samples of nominal obertiite. One of these samples has a chemical composition suitable for the recognition of ferri-obertiite, ideally ^ANa ^BNa₂^C(Mg₃Fe³⁺Ti) ^TSi₈O₂₂^WO₂, and also showed interesting and unusual crystal-chemical features. Both the mineral description of ferri-obertiite and a discussion of its crystalchemical peculiarities are reported in this work.

Occurrence and paragenesis

Ferri-obertiite was found in vesicles in pale beige silicate veins within a green-yellow scoria found

from a basalt quarry at Rothenberg volcano near Bell/Mendig in the Eifel volcanic complex (Rhineland-Palatinate, Germany). The Rothenberg quarry has coordinates: $50^{\circ}24'16''$ N, $7^{\circ}13'56''$ E. Mount Rothenberg is a scoria cone with lavas of basanitic and tephritic composition. The Rothenberg quarry is the type locality of oxyphlogopite (Chukanov *et al.*, 2010) and the second occurrence of eifelite (after the Caspar quarry, Bellerberg volcano, Eifel district; Abraham *et al.*, 1983). More details on the mineralogy of Rothenberg volcano can be found in Schüller (2013).

The holotype specimen of ferri-obertiite comes from the mineral collection of one of the authors (GB); the part studied in this work is shown in Fig. 1a. More than 90% of the greenish-yellow porous slag consists of a groundmass of tiny anhedral yellow pyroxene aggregates with sporadic large, olive-brown pyroxene crystals. Voids (0.5-2 mm in diameter) may contain very small black metallic-looking spheres of hematite. The embedded pale beige matrix consist mainly of slightly foliated feldspar (classified as potassic feldspar by powder X-ray diffraction) and minor quartz, with some alpha quartz paramorphic after beta quartz. Small acicular to lamellar ferri-obertiite crystals occur in voids (2-20 mm in diameter) within the pale-beige part of the specimen. Other associated minerals are rare clinopyroxene (colourless to pale



FIG. 1. (*a*) The rock specimen containing holotype ferri-obertiite (scale in cm); (*b*) pink ferri-obertiite crystals with thin tabular sanidine crystals and alpha quartz paramorphic after beta quartz in an analogous rock specimen from the same quarry (courtesy of Marko Burkhardt; collection: Marko Burkhardt; field of view: 1.5 mm).

9./901(/)	Crystal size (mm)	$0.25 \times 0.04 \times 0.03$
17.9354(13)	Crystal colour	Pink orange
5.2892(4)	Total no. of reflections	6970
104.142(2)	No. unique reflections	1365
900.58(11)	No. observed reflections $(I > 3 \sigma_I)$	1138
C2/m	θ range (°)	2-30
2	R_{marga} (%)	2.1
3.145	R_{obs} (%)	3.0
21.4	$R_{\rm all}^{\rm obs}$ (%)	3.7
	17.9354(13) 5.2892(4) 104.142(2) 900.58(11) <i>C2/m</i> 2 3.145 21.4	$17.9354(13)$ Crystal colour $5.2892(4)$ Total no. of reflections $104.142(2)$ No. unique reflections $900.58(11)$ No. observed reflections $(I > 3 \sigma_I)$ $C2/m$ θ range (°)2 R_{merge} (%) 3.145 R_{obs} (%) 21.4 R_{all} (%)

TABLE 1. Miscellaneous information for holotype ferri-obertiite (crystal 1262).

green, a = 9.6872(11), b = 8.8399(10), c = 5.2836(6) Å, $\beta = 106.928(2)^\circ$, V = 432.85(14) Å³, space group C2/c; estimated as aegirine₅₅ jadeite₁₅diopside₃₀ based on a structure refinement converging to $R_{all} = 2.9\%$), tridymite, rutile, roedderite, eifelite (as hexagonal lamellar-to-platy colourless crystals).

The new mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2015-079), and the rock specimen shown in Fig. 1*a* has been deposited at the Museo di Mineralogia of the Dipartimento di Scienze della Terra e dell'Ambiente of the Università degli Studi di Pavia under the code 2015-02. The refined and analysed crystal of this work has the code 1262 in the amphibole database of the CNR-IGG Pavia.

Appearance, physical and optical properties

Crystals of ferri-obertiite (Fig. 1b) are acicular in shape and pink orange in colour. Their typical size is $\sim 40 \ \mu\text{m} \times 40 \ \mu\text{m} \times 300 \ \mu\text{m}$. Ferri-obertiite has a vitreous lustre; crystals are transparent and do not fluoresce. Single crystals are brittle and show perfect cleavage parallel to {110}. The density calculated from the empirical formula and unit-cell dimensions is 3.145 g cm⁻³. A spindle stage was used to orient a crystal for measurement of the indices of refraction 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, ferri-obertiite is pleochroic, X = pale pink (minimum), Y = pinkish orange (moderate), Z = orange brown (maximum), $X \parallel b$, $Y \wedge c = 17.8^{\circ}$ (β obtuse), $Z \wedge a = 3.5^{\circ}$ (in β acute). It is biaxial (+), with indices of refraction α = 1.664, β = 1.680, γ = 1.722 (all ± 0.002) measured with gel-filtered Na light (λ = 589.9 nm); $<math>2V_{obs} = 66.4(3), 2V_{calc} = 64.7^{\circ}.$

X-ray diffraction and crystal-structure refinement

The crystal selected for data collection and structure refinement was $\sim 250 \ \mu\text{m} \times 40 \ \mu\text{m} \times 30 \ \mu\text{m}$ in size. Data collection was done on a Bruker-AXS Smart-Apex CCD-based diffractometer with graphite-monochromatized MoKa X-radiation $(\lambda = 0.7107 \text{ Å})$. 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. Accurate unit-cell dimensions were calculated by least-squares refinement of the positions of 2268 reflections with $I > 10 \sigma_I$ in the 20 range 2–60°. The *a:b:c* ratio calculated from the unit-cell parameters is 0.546:1:0.295. A total of 6970 collected reflections was reduced to 1365 unique reflections (mean redundancy = 5, R_{int} 2.1%). Of these, 1138 reflections with I > 3 σ_I were considered as observed during unweighted full-matrix leastsquares refinement on F carried out with a program written locally to handle complex solidsolutions (Cannillo et al., 1983). 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)]. Full-matrix least-squares refinement on $I > 3 \sigma_I$ converged at $R_{obs} = 3.0\%$ and $R_{\rm all} = 3.7\%$. The unit-cell dimensions and details of the crystallographic study are reported in Table 1. In

TABLE 2. Refined site-scattering values (ss, electrons per formula unit.), fractional atom coordinates and atom-displacement parameters (B_{eq} , Å²; $\beta^{ij} \times 10^4$) for holotype ferri-obertiite (crystal 1262).

Site	SS	x/a	y/b	z/c	B _{eq}	β^{11}	β^{22}	β^{33}	β^{12}	β^{13}	β^{23}
O(1)		0.11351(16)	0.08588(9)	0.21916(31)	0.78(3)	20	7	72	-1	9	-2
O(2)		0.11684(17)	0.16561(9)	0.72383(32)	0.93(4)	25	8	85	0	13	0
O(3)	16.59(10)	0.10417(24)	0	0.70598(45)	1.16(6)	31	11	92	_	10	_
O(4)		0.35831(18)	0.25044(10)	0.79933(34)	1.18(4)	43	7	96	-4	13	0
O(5)		0.34938(17)	0.12815(10)	0.08317(33)	1.08(4)	26	11	95	-1	18	9
O(6)		0.34658(17)	0.11993(10)	0.58350(32)	1.08(4)	27	11	80	0	10	-8
O(7)		0.34265(25)	0	0.29968(50)	1.13(5)	26	6	154	_	8	_
T(1)		0.28353(6)	0.08522(3)	0.29551(12)	0.71(1)	21	6	65	0	10	-1
T(2)		0.28740(6)	0.17101(3)	0.79937(12)	0.67(1)	19	6	57	-2	8	-1
M(1)	36.73(14)	0	0.08059(4)	1/2	1.07(2)	23	14	65	_	13	_
M(2)	31.98(14)	0	0.18114(5)	0	0.86(2)	24	8	72	_	13	_
M(3)	12.48(4)	0	0	0	0.81(4)	24	7	56	_	8	_
M(4)	24.70(18)	0	0.27393(7)	1/2	1.56(4)	49	11	179	_	56	_
A	3.58(3)	0	1/2	0	2.4(2)	36	40	121	-	53	_
A(m)	8.84(11)	0.0436(5)	1/2	0.0920(8)	2.8(1)	75	27	243	_	75	_

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614(2) 620(2) 622(2) 633(1) 622 33	T(2)-O(2) T(2)-O(4) T(2)-O(5) T(2)-O(6) < T(2)-O> T(2)-O> T(2)-O> T(2)-O> T(2)-O> T(2)-O> T(2)-O> T(2)-O> T(2)-O(2) T(2)-O(2) T(2)-O(2) T(2)-O(3) T(2)-O(4) T(2)-O(4) T(2)-O(5) T(2)-O(5) T(2)-O(6) T(2)-O(6) T(2)-O(6) T(2)-O(7) T	$1.622(2) \\ 1.585(2) \\ 1.663(2) \\ 1.674(2) \\ 1.636$	$M(4)-O(2) \times 2 M(4)-O(4) \times 2 M(4)-O(5) \times 2 M(4)-O(6) \times 2 (1)(4)-O(6) \times 2 \\(1)(4)-O(6) $	2.413(2) 2.386(2) 2.921(2) 2.530(2)
0021	IAV TQE	25.38 1.0059	< <u>M(4)–U></u>	2.562
063(2) 1 1991(2) 1 142(2) 1 132 1 36 1 113 1	$M(2)-O(1) \times 2 M(2)-O(2) \times 2 M(2)-O(4) \times 2 OAV OQE$	2.206(2) 2.082(2) <u>1.959(2)</u> 2.083 58.38 1.0191	M(3)–O(1) ×4 M(3)–O(3) ×2 <m(3)–o> OAV OQE</m(3)–o>	2.079(2) 2.058(2) 2.072 49.17 1.0152
223(2) 81(2) 995 201(1)	$\begin{array}{l} A(m)-O(5) \times 2\\ A(m)-O(5) \times 2\\ A(m)-O(6) \times 2\\ A(m)-O(7)\\ A(m)-O(7)\\ A(m)-O(7)\\ A(m)-O(7)\\ < A(m)-O> \end{array}$	2.976(4) 2.777(3) 2.798(5) 2.477(3) 3.137(8) 2.580(5) 2.811	T(1)-O(5)-T(2) T(1)-O(6)-T(2) T(1)-O(7)-T(1) O(5)-O(6)-O(5) O(6)-O(7)-O(6)	136.6(1) 137.3(1) 138.8(1) 173.5(1) 110.5(1)
.3 12 28 6 9 20	6 13 33(2) 41(2) 5 46(3) 5 41(1)	$\begin{array}{cccc} 6 & OAV \\ 13 & OQE \\ 3(2) & A(m)-O(5) \times 2 \\ 4(m)-O(5) \times 2 \\ 6(3) & A(m)-O(6) \times 2 \\ 5 & A(m)-O(7) \\ A(m)-O(7) \\ 11(1) & A(m)-O(7) \\ \\ \end{array}$	6 OAV 58.38 13 OQE 1.0191 (3(2)) $A(m)$ -O(5) ×2 2.976(4) (31(2)) $A(m)$ -O(5) ×2 2.777(3) (6(3)) $A(m)$ -O(6) ×2 2.798(5) (5) $A(m)$ -O(7) 2.477(3) $A(m)$ -O(7) 3.137(8) (11) $A(m)$ -O(7) 2.580(5) <a(m)-o> 2.811</a(m)-o>	6 OAV 58.38 OQE 13 OQE 1.0191 OQE 33(2) $A(m)$ -O(5) ×2 2.976(4) $T(1)$ -O(5)- $T(2)$ 41(2) $A(m)$ -O(5) ×2 2.777(3) $T(1)$ -O(6)- $T(2)$ 6(3) $A(m)$ -O(6) ×2 2.798(5) $T(1)$ -O(7)- $T(1)$ 5 $A(m)$ -O(7) 2.477(3) $A(m)$ -O(7) 3.137(8) O(5)-O(6)-O(5) $A(m)$ -O(7) $2.580(5)$ O(6)-O(7)-O(6) $-O> \overline{2.811} O(5)-O(6)$

TABLE 3. Selected interatomic distances (Å) and angles (°), tetrahedral and octahedral angle variances (°²) and quadratic elongations (Robinson *et al.*, 1971) in holotype ferri-obertiite (crystal 1262).

Table 2, we report atom coordinates and anisotropicdisplacement parameters, and in Table 3 we list selected interatomic distances and geometrical parameters relevant to the crystal-chemistry of this composition. The crystallographic information file with embedded structure factors has been deposited with the Principal Editors of *Mineralogical Magazine* and is available from http://www. minersoc.org/pages/e_journals/dep_mat.html

Powder X-ray diffraction data (CuK α , $\lambda = 1.54178$ Å) were obtained using the *XPREP* utility of *SAINT* (©Bruker, 2003), which generates a 2D powder diffractogram (Debye-Scherrer technique) starting from the F_{obs} collected on the single crystal and taking into account solely the information concerning the unit-cell dimensions and the Laue symmetry. No Lorentz and polarization correction was applied. Data are given in Table 4.

Chemical composition

The crystal of ferri-obertiite used for the crystallographic study was embedded in epoxy and analysed by electron microprobe using a Cameca SX-100 operating in wavelength-dispersive mode with excitation voltage 15 kV, specimen current 10 nA, beam diameter 5 µm, peak count-time 20 s and background count time 10 s. The following standards and crystals were used for Ka X-ray lines: Si: diopside, TAP; Ca: diopside, LPET; Ti: titanite, LPET; Fe: fayalite, LLiF; Mn: spessartine, LLiF; Cr: chromite, LPET; Mg: forsterite, LTAP; Al, andalusite, TAP; K: orthoclase, LPET; Na: albite, TAP; F: fluoro-riebeckite, LTAP; Zn: gahnite, LLiF; Ni: pentlandite (LLiF). Data reduction was undertaken using the $\varphi(\rho Z)$ procedure of Pouchou and Pichoir (1985). Vanadium was below the detection limit. The average of 10 analytical points is given in Table 5, together with a formula based on stoichiometric constraints and results from the single-crystal refinement (e.g. occupancy of the A-group sites, comparison between the observed and calculated values of the site-scattering (Hawthorne et al., 1995), and mean bond lengths at the M sites; see below for more details). The amount of H₂O used in the calculation is the minimum amount required to allow non-negative values of Fe^{2+} and (F + OH + Cl + O) = 2 atoms per formula unit (apfu). The resulting oxo-component (1.26 apfu) is coherent with the trend of the M(1)-M(2) distance vs. the oxo-component observed in other obertiite samples where H2O was analysed by

$I_{\rm rel}$	d(calc)	h k l	$I_{\rm rel}$	d(calc)	h k l	I_{rel}	d(calc)	h k l	I_{rel}	d(calc)	h k l
72.09	8.391	110	100.00	2.704	151	38.52	2.160	261	10.71	1.854	<u>1</u> 91
32.30	4.483	0 4 0	39.03	2.583	0 6 1	10.86	2.134	<u>3</u> 3 2	5.07	1.793	$0 \ 10 \ 0$
16.82	4.008	111	67.06	2.529	$\overline{2}$ 0 2	16.37	2.056	202			191
14.05	3.862	<u>1</u> 3 1	5.12	2.474	170	11.14	2.017	351	7.16	1.735	<u>5</u> 12
72.16	3.388	131	7.42	2.373	350	10.53	2.003	$\overline{4} 0 2$	9.77	1.687	<u>1</u> 33
37.50	3.260	2 4 0	28.91	2.322	$\overline{3}$ 5 1	8.29	1.950	1 9 0	12.64	1.678	$\frac{2}{2}$ 8 2
76.19	3.116	$3 \ 1 \ 0$	16.94	2.308	$\overline{4}$ 2 1	7.74	1.930	421	28.94	1.649	461
10.76	3.003	<u>3</u> 11	18.22	2.286	$\overline{1}$ 7 1			<u>3</u> 52	11.24	1.630	480
25.01	2.950	221	24.61	2.266	312	6.25	1.888	510	9.07	1.607	1 11 0
10.94	2.928	$\overline{1}$ 5 1	9.35	2.203	$\overline{2}$ 4 2	8.27	1.867	242	22.65	1.580	<u>1</u> 53
17.06	2.797	3 3 0	16.24	2.174	171			$\overline{4} 6 1$	6.16	1.562	402

TABLE 4. Powder X-ray data for holotype ferri-obertiite. The strongest eight lines are in bold.

 $\begin{array}{l} SIMS \mbox{ (Hawthorne $et al., 2000; 2010). The empirical unit-formula of our sample (crystal 1262) is: $$^A(Na_{0.76}K_{0.22})_{\Sigma0.98}{}^B(Na_{1.61}Ca_{0.35}Mn_{0.04}^{2+})_{\Sigma2.00}{}^C(Mg_{3.58}Mn_{0.11}^{2+}Fe_{0.62}^{3+}Ti_{0.66}^{4+}Cr_{0.01}^{3+}Zn_{0.01}Ni_{0.01})_{\Sigma5.00}{}^T(Si_{7.82}Ti_{0.12}^{4+}Al_{0.06})_{\Sigma8.00}O_{22}{}^W[O_{1.26}F_{0.55}(OH)_{0.19}]_{\Sigma2.00}. \\ The end-member formula of ferri-obertiite, $$^ANa^BNa_2{}^C(Mg_3Fe^{3+}Ti)^TSi_8O_{22}{}^WO_2$, requires SiO_2 56.27, TiO_2 9.35, MgO 14.15, Fe_2O_3 9.35 Na_2O 10.88, total 100.00 wt.%. The compatibility index $$[1-(K_p/K_c)]$ is 0.018 (superior). \\ \end{array}$

Site populations and crystal chemistry of ferri-obertiite

In Table 6 we report the site populations obtained from the electron-microprobe analysis and the results of the structure refinement. As far as the A- and B-group cations are concerned, the refined site-scattering values are in close agreement with those calculated from the proposed unit-formula, confirming that the assumptions used in the calculation of the unit formula are substantially correct. For the T-group cations, Al³⁺ was assigned to the T(1) site, and Ti⁴⁺ to the T(2) site based on present knowledge of amphibole crystal chemistry (Oberti *et al.*, 2007). The $T^{(2)}$ Ti⁴⁺ content (0.12 apfu) is significant and unusual in sodium amphiboles. $T^{(2)}$ Ti⁴⁺ contents (up to 0.35 apfu) has been, so far, observed solely in potassic-richterite from lamproites, and are associated with high T(800-1000°C) and low P (1-2 kbar) conditions of crystallization from K-, F- and Ti-rich peralkaline melts (Oberti et al., 1992). This suggestion was later confirmed by experimental studies (Della Ventura et al., 1993; Konzett, 1997). Interestingly, potassic-richterite from lamproites commonly has a significant amount of the oxo component.

In [4]-coordination, Ti^{4+} is significantly larger than Si⁴⁺ (the ionic radii tabulated by Shannon (1976) are 0.42 and 0.26 Å, respectively). In potassic-richterite, ideally ${}^{A}K^{B}(NaCa){}^{C}Mg_{5}{}^{T}Si_{8}$ $O_{22}{}^{W}(OH)_{2}$, the strip of large octahedra coexists with a double chain of small tetrahedra occupied by Si. However, the M(2) octahedron is always relaxed, i.e. larger than expected based on the aggregate ionic radius of the constituent cations. Therefore, richterite rarely incorporates (smaller) ${}^{C}R^{3+}$ cations. Indeed, the incorporation of Ti^{4+} at the T(2) site enlarges the T(2) tetrahedron and allows a better fit of the structural units. According to Oberti *et al.* (1992), the crystallographic indications of the presence of Ti^{4+} at the T(2) site

ferri-	FERRI-OBEF
apfu	RTIIT
$ \begin{array}{r} 0.04 \\ 1.61 \\ \underline{0.35} \\ 2.00 \end{array} $	E FROM THE
0.76 0.22 0.98	ROTHENBI
$ \begin{array}{r} 1.26 \\ 0.55 \\ \underline{0.19} \\ 2.00 \end{array} $	ERG QUARRY, EIFEL

TABLE 5. Chemical composition (10 analytical points) and unit formula (atoms per formula unit, apfu) calculated based on 24 (O, OH, F) apfu for holotype ferriobertiite (crystal 1262).

Oxide	Wt.%	Range	Oxide	Wt.%	Range		apfu		apfu
SiO ₂	55.32(24)	55.04-55.54	Na ₂ O	8.62(7)	8.53-8.81	Si	7.82	Mn ²⁺	0.04
TiO ₂	7.31(7)	6.76-7.96	K ₂ O	1.24(4)	1.22-1.29	Al	0.06	Na	1.61
$Al_2 \tilde{O}_3$	0.34(2)	0.27-0.39	H ₂ O*	0.20		Ti ⁴⁺	0.12	Са	0.35
Cr_2O_3	0.12(2)	0.05-0.26	F	1.22(31)	0.84-1.70	Sum T	8.00	Sum B	2.00
Fe ₂ O ₃ *	5.81		Cl	0.01(1)	0.00-0.02				
FeO	0.04		O = F	-0.52		Ti ⁴⁺	0.66	Na	0.76
[FeO] _{tot}	[5.27(14)]	5.03-5.80	Total	100.43		Cr^{3+}	0.01	K	0.22
MnO	1.32(8)	1.07-1.49				Fe ³⁺	0.62	Sum A	0.98
MgO	17.00(8)	15.96-17.59				Mg	3.58		
ZnO	0.05(3)	0.01-0.07				Mn ²⁺	0.11	O^{2-}	1.26
NiO	0.04(5)	0.00-0.05				Zn	0.01	F^{-}	0.55
CaO	2.31(4)	1.98-2.48				Ni	0.01	$(OH)^{-}$	0.19
						Sum C	5.00	Sum W	2.00

*calculated based on single-crystal structure-refinement results and with the constraints of non-negative Fe^{2+} values and W(O, OH, F) = 2 apfu.

are: (i) a value of B_{eq} smaller than that of the *T*(1) site, indicating a higher value of *Z* than that at *T*(1); (ii) a mean bond length longer than expected from the bulk composition (1.640 Å for ~0.19 $T^{(2)}$ Ti apfu and 1.648 Å for 0.35 $T^{(2)}$ Ti apfu in potassic richterite); and (iii) a high value of TAV (tetrahedral angular variance; Robinson *et al.*, 1971). All these features are evident in the results of Tables 3 and 4.

Ferri-obertiite is completely different in composition from potassic-richterite; however, the refined < T(2)-O> distance (1.636 Å) fits well with the proposed T(2)Ti content and the trend observed in specimens of potassic-richterite from lamproites. This first evidence for the presence of Ti at the T(2)site in a sodium oxo-amphibole could be related to the high ^BR²⁺ content in the present sample (0.39 apfu), and perhaps to relaxation at the M(2)octahedron (cf. Table 3 and the discussion below), which does not favour further incorporation of Ti4+ at this site. As shown in Table 7, T(2)Ti should not be present in the other samples of obertiite so far reported (which both have ${}^{B}R^{2+}$ contents \approx 0.15 apfu). It is true that in mangani-obertiite, the < T(2)-O> distance is 1.637 Å, but the values of the atomic displacement parameters refined at the T(1)and T(2) sites are equal, and the TAV value at the T(2) tetrahedron is low (Hawthorne *et al.*, 2000).

Site populations for the C-group cations were calculated by assigning the cations so as to obtain the best fit between the refined values of the sitescattering and the mean bond lengths, with the constraint that ^CR^{3,4+} cations balancing deprotonation must be ordered at the M(1) and M(3) sites. Indeed, our results indicate quite clearly that CR^{3,4+} cations balancing deprotonation occur solely at the M(1) site. Although a prevalent order of $^{\rm C}R^{3,4+}$ cations related to deprotonation has been observed recently in other oxo-amphiboles (cf. oxo-manganileakeite, Oberti et al., 2016a and synthetic 'oxoferro-richterite', Oberti et al., 2016b), this is a further peculiarity of this amphibole composition. Complete Mg occupancy at the M(3) site has been reported also for mangani-obertiite based on the refined site-scattering (12.0 electrons per formula unit); in that case however, the < M(3) - O > distance is far shorter than that in ferri-obertiite (2.066 vs. 2.072 Å). The case of ferro-ferri-obertiite (Hawthorne et al., 2010) is somewhat different because it has a significant Li content (0.10 apfu), which orders at the M(3) site. It is also worth noting that ferri-obertiite shows relaxation of the M(2)octahedron typical of potassic-richterite, confirming that the mechanism for Ti incorporation proposed for richterite crystallizing from lamproitic melts can also be invoked for specimens of obertiites sensu lato.

A comparison of the optical and crystallographic properties of the three amphiboles related to the rootname obertiite is provided in Table 7.

Two other compositions related to the rootname obertiite have been reported in the literature. Robinson *et al.* (2008) analysed zoned amphiboles

		SS	(epfu)	m.t	o.l. (Å)
Site	Site population (apfu)	Refined	Calculated	Refined	Calculated
T(1)	3.94 Si + 0.06 Al			1.622	1.621
T(2)	3.88 Si+0.12 Ti ⁴⁺				
M(1)	$1.16 \text{ Mg} + 0.42 \text{ Fe}^{3+} + 0.42 \text{ Ti}^{4+}$	36.73	34.08	2.032	2.035
<i>M</i> (2)	$1.42 \text{ Mg} + 0.11 \text{ Mn}^{2+} + 0.01 \text{ Zn} + 0.20 \text{ Fe}^{3+} + 0.24 \text{ Ti}^{4+} + 0.01 \text{ Ni} + 0.01 \text{ Cr}^{3+}$	31.98	31.09	2.083	2.064
<i>M</i> (3)	1.00 Mg	12.48	12.00	2.072	2.071
C cations	C C	81.19	77.17		
B cations	1.61 Na+0.35 Ca+0.04 Mn ²⁺	24.70	25.71		
A cations	0.76 Na+0.22 K	12.41	12.54		
W anions	1.26 O ²⁻ +0.19 (OH) ⁻ +0.55 F ⁻	16.59	16.55		

TABLE 6. Site populations for holotype ferri-obertiite (crystal 1262). There is good agreement between the refined values of site-scattering (ss, epfu) and mean bond lengths (m.b.l., Å) and those calculated based on the proposed site populations.

epfu - electrons per formula unit

	Mangani-obertiite	Ferri-obertiite	Ferro-ferri-obertiite
Locality	Bellerberg quarry, Eifel, Germany	Rothenberg quarry, Eifel, Germany	Humboldt County, California, USA
Colour	Pale pink	Pink orange	Black
Optical class	Biaxial (-)	Biaxial (+)	Biaxial (-)
Pleochroism	Pink to red-orange	$\alpha =$ pale pink, $\beta =$ pinkish orange, $\gamma =$ orange-brown	Dark brown to dark grey
Orientation	$X^{\wedge} a = 2^{\circ} (\beta \text{ obtuse})$	X // b	$X^{\wedge} a = 77.3^{\circ} (\beta acute)$
	Z // b	$Y \wedge c = 17.8$ (B obtuse)	Y // b
	$Y^{\wedge} c = 12^{\circ}$ (ß obtuse)	$Z^{\wedge} a = 3.5^{\circ}$ (β acute)	$Z^{\wedge} c = 91.2^{\circ}$ (B obtuse)
α	1.643(1)	1.664(2)	1.671(1)
β	1.657(1)	1.680(2)	1.674(1)
γ	1.670(3)	1.722(5)	1.675(1)
2V _{meas} (°)	81	66.4 (3)	60 (3)
a (Å)	9.776(2)	9.7901(7)	9.845(4)
$b(\mathbf{A})$	17.919(3)	17.9354(13)	18.018(8)
c (Å)	5.292(1)	5.2892(4)	5.296(3)
β (°)	104.05(2)	104.142(2)	103.86(3)
$V(Å^3)$	899.3(3)	900.58(11)	912.1(4)
< T(1) - O > (Å)	1.620	1.622	1.621
< T(2) - O > (Å)	1.637	1.636	1.633
< <i>M</i> (1)–O> (Å)	2.035	2.032	2.062
< <i>M</i> (2)–O> (Å)	2.081	2.083	2.080
< <i>M</i> (3)–O> (Å)	2.066	2.072	2.104
< <i>M</i> (4)–O> (Å)	2.567	2.562	2.572
M(1) - M(2) (Å)	3.225 M(1A)-3.105 M(1)	3.201	3.178
TAV T(2) (°)	18.90	25.38*	20.90
Reference	Hawthorne et al. (2000)	This work	Hawthorne <i>et al.</i> (1998); Hawthorne <i>et al.</i> (2010)

TABLE 7. A comparison of the optical and crystallographic properties reported for the three known end-members related to rootname obertiite.

*The TAV value measured at the T(2) site in richterite 537 (R(5) in Oberti *et al.*, 1992) with 0.19 T(2) Ti apfu is 28.98°.

from silica-rich lamproites from the Xixano region, northeastern Mozambique, and reported - especially in the core region - chemical analyses referable to F-rich 'oxo-potassic-magnesio-arfvedsonite' with ^CTi up to 0.49 apfu, thus falling at the borders of the 'potassic-obertiite' compositional space. Quote marks are used here because the two rootnames (determined based on chemical composition according to Hawthorne et al., 2012), have not yet been recognized by the International Mineralogical Association - Commission on New Minerals, Nomenclature and Classification due to the lack of a complete mineral description. Indeed, neither structure refinement nor physical properties could be obtained from those samples, so that we do not have reliable information on cation order or crystal-chemical features. However, structural and crystal-chemical studies of a suite of amphiboles from Mozambique provided by P. Robinson led to the description of fluoro-potassic-magnesioarfvedsonite with 12% Ti-related oxo-component (Oberti *et al.*, 2010), where Ti orders at the M(1)site.

Kullerud *et al.* (2013) reported on sodium amphiboles from a high-silica phlogopite lamproite from Kvaloya, northen Norway, and used 'composition A' (^{A,B}(K_{1.01}Na_{1.99})^C(Na_{0.26}Mg_{1.58} Mn_{0.03} Fe³⁺_{0.91}Fe³⁺_{1.6}Ti_{0.47} $\square_{0.13}$)^TSi₈O₂₂^W[F_{0.97} O_{1.03}], referred to as '^CNa-rich variety of potassic-obertiite'), as one of the three limiting compositions describing the system. Notwithstanding the anomalies in the calculated unit-formulae (i.e. the significant amounts of Na and vacancy present among C cations, two features that have never been proven satisfactorily in amphiboles), we may conclude that amphibole compositions tending towards 'potassic-obertiite' are likely to be found in lamproites crystallized at highly oxidizing conditions. Further investigation of these and similar geological environments should provide more insights into the occurrence and stability of 'potassic-obertiite'.

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