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FERRO-OBERTIITE, Na Na_2 (Fe^{2+}_3 Fe^{3+}Ti) Si_8 $O_{22}O_2$, A NEW MINERAL SPECIES OF THE AMPHIBOLE GROUP FROM COYOTE PEAK, HUMBOLDT COUNTY, CALIFORNIA

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ABSTRACT

Ferro-obertiite, Na Na_2 (Fe^{2+}_3 Fe^{3+}Ti) Si_8 $O_{22}O_2$, is a new mineral species of the amphibole group from Coyote Peak, Humboldt County, California, U.S.A., associated with inclusions of lithic-wacke sandstone in an alkali-rich ultramafic diatreme. Ferro-obertiite occurs as euhedral to subhedral crystals up to 1.25 mm across in a matrix of aegirine and feldspar. Crystals are black with a grey streak. Ferro-obertiite is brittle, has a Mohs hardness of 6, and a splintery fracture; it is non-fluorescent, with perfect {110} cleavage, no observable parting, and has a calculated density of 3.330 g cm^{-3}. In plane-polarized light, it is pleochroic, *X* dark brown, *Y* brown, *Z* dark grey; $X \wedge a = 77.3°$ (in β acute), $Y \parallel b$, $Z \wedge c = 91.2°$ (in β obtuse). Ferro-obertiite is biaxial negative, α 1.671(1), β 1.674(1), γ 1.675(1); $2V$(obs.) = 60(3)°, $2V$(calc.) = 59.9°. It is monoclinic, space group *C*2/*m*, *a* 9.845(4), *b* 18.018(8), *c* 5.296(3) Å, β 103.86(3)°, *V* 912.1(4) $Å^3$, *Z* = 2. The strongest ten X-ray-diffraction lines in the powder pattern [*d* in Å(*I*)(*hkl*)] are: 2.722(100)($\bar{3}$31,151), 8.448(80)(110), 3.407(60)(131, 041), 3.144(50)(201, 310), 2.596(50)(061), 2.533(40)($\bar{2}$02), 2.178(30)(261), 4.514(20)(040, 021), 3.283(20)(240) and 2.332(20)($\bar{3}$51). Analysis by a combination of electron microprobe and crystal-structure refinement gave SiO_2 52.47, Al_2O_3 0.09, TiO_2 6.51, Fe_2O_3 4.54, FeO 18.43, MgO 5.74, MnO 0.15, CaO 0.90, Na_2O 8.70, K_2O 1.51, Li_2O 0.17, F 0.51, H_2O 0.58, sum 100.09 wt%. The formula unit, calculated on the basis of 24 (O, OH, F), is $^A(Na_{0.72}K_{0.29})$ $(Na_{1.85}Ca_{0.15})$ $(Mg_{1.30}Fe^{2+}_{2.35}Mn^{2+}_{0.02}Fe^{3+}_{0.52}Al_{0.01}Ti_{0.75}Li_{0.10})$ $(Si_{7.99}Al_{0.01})$ O_{22} $(O_{1.16}F_{0.25}OH_{0.59})$. The crystal-structure refinement shows Ti to be strongly ordered at the *M*(1) site. Ferro-obertiite, ideally Na Na_2 (Fe^{2+}_3 Fe^{3+}Ti) Si_8 $O_{22}O_2$, is related to obertiite, Na Na_2 (Mg_3 Fe^{3+}Ti) Si_8 $O_{22}O_2$, by the substitution $Fe^{2+} \rightarrow Mg$.

Keywords: ferro-obertiite, new amphibole species, electron-microprobe analysis, optical properties, Coyote Peak, Humboldt County, California, U.S.A.

SOMMAIRE

Nous décrivons la ferro-obertiite, Na Na_2 (Fe^{2+}_3 Fe^{3+}Ti) Si_8 $O_{22}O_2$, nouvelle espèce minérale du groupe des amphiboles provenant de Coyote Peak, comté de Humboldt, en Californie, associée à des enclaves de grès de type wacke lithique prises dans un diatrème ultramafique enrichi en alcalins. La ferro-obertiite se présente en cristaux idiomorphes à subidiomorphes atteignant 1.25 mm dans une matrice d'aegyrine et de feldspath. Les cristaux sont noirs avec une rayure grise. Le minéral est cassant, possède une dureté de Mohs de 6, et une fracture esquilleuse; il est non fluorescent, avec un clivage {110} parfait, aucun plan de séparation observable, et une densité calculée de 3.330 g cm^{-3}. En lumière transmise, il est pléochroïque, *X* brun foncé, *Y* brun, *Z* gris foncé; $X \wedge a = 77.3°$ (β aigu), $Y \parallel b$, $Z \wedge c = 91.2°$ (β obtus). La ferro-obertiite est biaxe négative, α 1.671(1), β 1.674(1), γ 1.675(1); $2V$(obs.) = 60(3)°, $2V$(calc.) = 59.9°. Elle est monoclinique, groupe spatial *C*2/*m*, *a* 9.845(4), *b* 18.018(8), *c* 5.296(3) Å, β 103.86(3)°, *V* 912.1(4) $Å^3$, *Z* = 2. Les dix raies les plus intenses du spectre de diffraction, méthode des poudres [*d* en Å(*I*) (*hkl*)] sont: 2.722(100)($\bar{3}$31,151), 8.448(80)(110), 3.407(60)(131, 041), 3.144(50)(201, 310), 2.596(50)(061), 2.533(40)($\bar{2}$02), 2.178(30)(261), 4.514(20)(040, 021), 3.283(20)(240) et 2.332(20)($\bar{3}$51). L'analyse, effectuée avec une microsonde électronique et complétée par les résultats de l'analyse structurale, a donné SiO_2 52.47, Al_2O_3 0.09, TiO_2 6.51, Fe_2O_3 4.54, FeO 18.43, MgO 5.74, MnO 0.15, CaO 0.90, Na_2O 8.70, K_2O 1.51, Li_2O 0.17, F 0.51, H_2O 0.58, pour un total de 100.09% (poids). La formule unitaire, calculée sur une base de 24(O, OH, F), est $^A(Na_{0.72}K_{0.29})$ $(Na_{1.85}Ca_{0.15})$ $(Mg_{1.30}Fe^{2+}_{2.35}Mn^{2+}_{0.02}Fe^{3+}_{0.52}Al_{0.01}Ti_{0.75}Li_{0.10})$ $(Si_{7.99}Al_{0.01})$ O_{22} $(O_{1.16}F_{0.25}OH_{0.59})$. L'affinement de la structure cristalline montre que le Ti est fortement ordonné sur le site *M*(1).

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La ferro-obertiite, dont la composition idéale est Na Na_2 (Fe^{2+}_3 Fe^{3+}Ti) Si_8 $O_{22}O_2$, est liée à l'obertiite, Na Na_2 (Mg_3 Fe^{3+}Ti) Si_8 $O_{22}O_2$, par la substitution $Fe^{2+} \rightarrow$ Mg.

(Traduit par la Rédaction)

Mots-clés: ferro-obertiite, nouvelle espèce d'amphibole, données de microsonde électronique, propriétés optiques, Coyote Peak, comté de Humboldt, Californie.

Introduction

Prior to the solution of the crystal structure of tremolite (Warren 1929), amphiboles were generally considered to be anhydrous minerals. Using Pauling's second rule (Pauling 1929), Warren (1929) showed that the O(3) site in tremolite is occupied by (OH), and Warren (1930) also assigned F to the O(3) site in amphiboles. Subsequent analytical work on a wide variety of amphiboles showed that they can contain major amounts of (OH), F and Cl, and that the amount of monovalent cations in the structure is not fixed at 2 *apfu*. Leake (1968) showed that there is a negative correlation between the [(OH) + F + Cl] and Ti contents in amphiboles characterized by Engel & Engel (1962). Saxena & Ekström (1970) showed that there is, in general, a negative correlation between the [(OH) + F + Cl] and Ti contents in amphiboles. Kitamura & Tokonami (1971), Hawthorne & Grundy (1973), Kitamura *et al*. (1975), Jirak *et al*. (1986) and Pechar *et al*. (1989) showed that Ti can occur at the *M*(1) site, locally associated with O^{2-} at O(3). Oberti *et al*. (1992) proposed that this association of Ti at *M*(1) with O^{2-} at O(3) is short range, and further work has been done by Tiepolo *et al*. (1999) and Della Ventura *et al*. (2007). Popp *et al*. (1995a, b) and King *et al*. (1999, 2000) examined the effect of Fe^{2+} and Fe^{3+} on the content of monovalent anions in amphiboles. All of this work (except that of Oberti *et al*. 1992) focused on calcic amphiboles. In the last 15 years, several new oxo-amphiboles [amphiboles with O^{2-} as the dominant anion at O(3)] have been described (Table 1), and these have all been sodic amphiboles: ungarettiite, obertiite and dellaventuraite. They are characterized by the occurrence of high-valence cations (Ti^{4+}) at the *M*(1) site [with the exception of ungarettiite which has *M*(1) = *M*(3) = Mn^{3+}, *M*(2) = Mn^{2+}].

Hawthorne *et al*. (1998) described a suite of sodic–calcic and sodic amphiboles from lithic-wacke sandstone inclusions in an alkali diatreme at Coyote Peak, Humboldt County, California. These amphiboles contain minor to major contents of O^{2-} at the O(3) site that correlate with the amount of Ti in the structure. One of these amphiboles (sample CYP 52, crystal 745) has an $^{O(3)}O^{2-}$ content of 1.16 *apfu* and a Ti content of 0.746 *apfu*. This amphibole is a new species, and a formal description is given here. The new species and new name, ferro-obertiite, have been approved by the International Mineralogical Association Commission on New Minerals and Mineral Classification (2009–034). Holotype material is deposited at the Department of Natural History, Royal Ontario Museum, Toronto, Ontario, Canada, specimen number M54035.

Occurrence

Ferro-obertiite occurs in an alkali diatreme that penetrates a lithic-wacke sandstone sequence of the Franciscan assemblage 20 km southeast of Orick, California, U.S.A. Detailed descriptions of the rocks are given by Morgan *et al*. (1985), and Czamanske & Atkin (1985) described the metasomatism and crystal growth associated with the fragments of lithic-wacke sandstone entrained in the host ultramafic rocks. The degree of metasomatism of the fragments is very uneven; small fragments are totally recrystallized to microcline, aegirine and calcic–sodic and sodic amphibole, whereas large fragments show strong core-to-rim zonation and contain abundant unreacted albite, quartz and clay. As a consequence, the amphibole exhibits conspicuous intergrain heterogeneity, and compositions can vary widely on a centimeter scale. Czamanske & Atkin (1985) proposed the following mechanism of reaction for metasomatism of the fragments of lithic-wacke sandstone: (1) loss of Si from the fragment, (2) influx of K, which reacted with the original albite to produce microcline and caused the release of Na, (3) combination of Na with Ti and Fe to form Ti-rich aegirine and large strongly zoned crystals of (inclusion-free) amphibole, and (4) crystallization of late-stage zeolite(s). The sequence and compositional variation of pyroxene and amphibole were ascribed to decreasing $f(O_2)$ and T as the xenoliths reacted with the rapidly cooling reduced ultramafic melt.

TABLE 1. LIST OF OXO-AMPHIBOLES

Name	End-member formula	Ref.
Obertiite	Na Na_2 ($Mg_3Fe^{3+}Ti^{4+}$) Si_8 O_{22} O_2	(1)
Ferro-obertiite	Na Na_2 ($Fe^{2+}_3Fe^{3+}Ti^{4+}$) Si_8 O_{22} O_2	(2)
Dellaventuraite	Na Na_2 ($MgMn^{3+}_2Ti^{4+}Li$) Si_8 O_{22} O_2	(3)
Ungarettiite	Na Na ($Mn^{2+}_2Mn^{3+}_3$) Si_8 O_{22} O_2	(4)
Kaersutite	Na Ca_2 (Mg_4AlTi^{4+}) Si_8 O_{22} O_2	(5)
Ferrokaersutite	Na Ca_2 ($Fe^{2+}_4AlTi^{4+}$) Si_8 O_{22} O_2	(5)

References: (1) Hawthorne *et al*. 2000, (2) this work, (3) Tait *et al*. 2005, (4) Hawthorne *et al*. 1995, (5) Hawthorne & Oberti (2007b).

Hawthorne *et al*. (1998) showed that these amphiboles contain minor to major amounts of O^{2-} at the O(3) site and that the amount of $^{O(3)}O^{2-}$ is positively correlated with the amount of Ti in the amphibole (Fig. 1). As indicated in Figure 1, most of the amphiboles in this paragenesis are (OH + F + Cl)-dominant; however, one sample (CYP 52, crystal 745) has O^{2-} dominant at O(3) and hence is an oxo-amphibole (Hawthorne & Oberti 2007b).

Physical and Optical Properties

Ferro-obertiite is black with a grey streak. It has a vitreous luster and shows no fluorescence under long-wave or short-wave ultraviolet light. Grains are euhedral to subhedral, prismatic to acicular on [001] and are bounded by {110} cleavage faces. Ferro-obertiite has a Mohs hardness of ~6 and is brittle with a splintery fracture; it has the characteristic perfect {110} cleavage of monoclinic amphiboles, intersecting at ~56°. The calculated density is 3.330 g.cm^{-3}.

A spindle stage was used to orient a crystal for measurement of indices of refraction and 2*V* 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, ferro-obertiite is pleochroic with *X* dark brown, *Y* brown, *Z* dark grey; $X \wedge a = 12.8°$ (in β obtuse), $Z \parallel b$, $Y \wedge c = 1.2°$ (in β obtuse). It is biaxial negative, $\alpha = 1.671(1)$, $\beta = 1.674(1)$, $\gamma = 1.675(1)$; $2V$(obs.) = 60(3)°, $2V$(calc.) = 59.9°.

Chemical Composition

Ferro-obertiite was analyzed primarily by electron microprobe, as reported by Hawthorne *et al*. (1998), using a Cameca SX–100 operating in the wavelength-dispersive mode with an excitation voltage of 15 kV, a specimen current of 10 nA, a beam diameter of 5 μm, a peak-count time of 20 s and a background count-time of 10 s, with the standards listed by Oberti *et al*. (1992). Data reduction was done using the φ(ρZ) procedure of Pouchou & Pichoir (1985). The amount of Li was derived by SREF, and the Fe^{3+} content was derived from the observed <*M*(2)–O> distance and the mean-bond-length – aggregate-cation-radius relation of Hawthorne (1983; Hawthorne *et al*. 1998). The average result of 10 analyses on a single grain is given in Table 2. The end-member formula of ferro-obertiite is $Na\ Na_2 (Fe^{2+}{}_3Fe^{3+}Ti)\ Si_8\ O_{22}\ O_2$, which corresponds to Na_2O 9.80, FeO 22.72, Fe_2O_3 8.41, TiO_2 8.42, SiO_2 50.65, for a total of 100.00 wt.%.

X-Ray Powder-Diffraction Pattern

A simulated powder-diffraction pattern was recorded from a small fragment on a Debye–Scherrer camera with a Gandolfi attachment and Fe-filtered Cu*K*α X-radiation. Cell dimensions were refined from the measured *d* values; the indexed powder pattern and refined unit-cell dimensions are given in Table 3. Peak intensities reported in Table 3 are those estimated by eye from the darkening on the film. The possible space-groups are *C*2/*m*, *C*2 and *Cm*; our crystal-structure

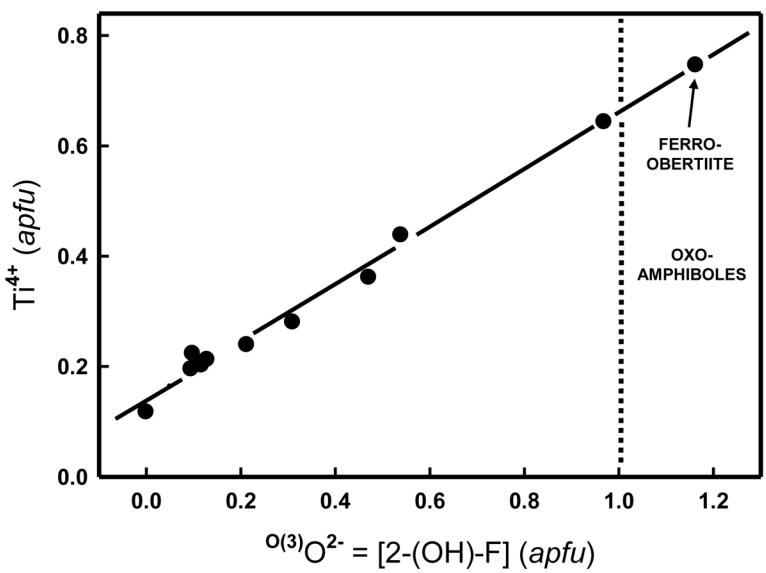

FIG. 1. Variation in Ti^{4+} as a function of O^{2-} content of the O(3) site in amphiboles from Coyote Peak. Modified from Hawthorne *et al*. (1998).

refinement (Hawthorne *et al*. 1998) confirmed the space group *C*2/*m*. For convenience, a table of structure factors is available from the Depository of Unpublished Data on the MAC website [document Ferro-obertiite CM48_301].

Discussion

The crystal structure of ferro-obertiite was reported by Hawthorne *et al*. (1998) as sample CYP 52, crystal 745. The structure was refined to an R_1 value of 1.7% for 774 observed reflections. Assigned site-populations are given in Table 4 and are in close accord with the refined site-scattering values reported by Hawthorne *et al*. (1998). The key features of ferro-obertiite are the presence of >1.00 O^{2-} at the O(3) site and >0.50 Ti *apfu* at the *M*(1) site; the local bond-valence requirements that underlie the relation between these variables (Fig. 1) have been discussed in detail by Hawthorne & Oberti (2007a) and Hawthorne & Della Ventura (2007). Ferro-obertiite has the end-member formula $Na\ Na_2(Fe^{2+}{}_2Fe^{3+}Ti)\ Si_8\ O_{22}\ O_2$. This may be derived from obertiite, $Na\ Na_2(Mg_2Fe^{3+}Ti)\ Si_8\ O_{22}\ O_2$, by the homovalent substitution $^{C}Fe^{2+} \rightarrow {}^{C}Mg$. Selected properties of obertiite and ferro-obertiite are compared in Table 5.

TABLE 2. CHEMICAL COMPOSITION AND UNIT FORMULA OF FERRO-OBERTIITE*

SiO_2 wt.%	52.47	Si *apfu*	7.99
TiO_2	6.51	Al	0.01
Al_2O_3	0.09	**Sum T**	8.00
Fe_2O_3	4.54		
FeO	18.43	Al	0.01
MnO	0.15	Ti^{4+}	0.75
MgO	5.74	Mg	1.30
CaO	0.90	Fe^{3+}	0.52
Na_2O	8.70	Fe^{2+}	2.35
K_2O	1.51	Mn	0.02
Li_2O	0.17	Li	0.10
H_2O	0.58	**Sum C**	5.05
F	0.51		
-O=F	-0.21	Ca	0.15
		Na	1.85
Total	**100.09**	**Sum B**	2.00
		Na	0.72
		K	0.29
		Sum A	1.01
		O	1.16
		F	0.25
		OH	0.59
		Sum W	2.00

* from Hawthorne *et al.* (1998).

TABLE 3. X-RAY POWDER-DIFFRACTION PATTERN OF FERRO-OBERTIITE

I_{est}	d_{meas} (Å)	d_{calc} (Å)	*h*	*k*	*l*	I_{est}	d_{meas} (Å)	d_{calc} (Å)	*h*	*k*	*l*
80	8.515	8.448	1	1	0	50	2.596	2.599	1	5	1
20	4.514	4.515	0	4	0	40	2.533	2.536	$\bar{2}$	0	2
〃	〃	4.478	0	2	1	20	2.332	2.333	$\bar{3}$	5	1
<5	4.045	4.039	1	1	1	15	2.275	2.271	$\bar{3}$	1	2
<5	3.885	3.879	$\bar{1}$	3	1	30	2.178	2.176	2	6	1
60	3.407	3.413	1	3	1	<5	2.073	2.072	2	0	2
〃	3.407	3.397	0	4	1	<5	2.027	2.034	3	5	1
20	3.283	3.282	2	4	0	<5	1.687	1.695	$\bar{1}$	3	3*
50	3.144	3.150	2	0	1	10	1.660	1.662	4	6	1
〃	3.144	3.138	3	1	0	〃	1.660	1.660	5	1	1
15	2.979	2.975	2	2	1	<5	1.619	1.618	1	11	0
10	2.813	2.816	3	3	0	〃	1.619	1.619	1	1	3
100	2.722	2.725	$\bar{3}$	1	1	<5	1.586	1.587	$\bar{4}$	0	3
〃	2.722	2.723	0	6	1	〃	1.586	1.587	$\bar{1}$	5	3

114.6 mm Debye–Scherrer powder camera with Gandolfi attachment, using Ni-filtered Cu radiation; (λ Cu*K*α = 1.54178 Å). Intensities estimated visually. Not corrected for shrinkage, and no internal standard was used. Indexed on a cell having *a* 9.844(8), *b* 18.058(12), *c* 5.310(3) Å, β 103.81(5)°, *V* 916.7(7) Å^3. * Line omitted from unit-cell refinement.

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TABLE 4. SITE POPULATIONS FOR FERRO-OBERTIITE*

Site	Site population (*apfu*)
T(1)	0.01 Al + 3.99 Si
T(2)	4 Si
M(1)	0.44 Mg + 0.96 Fe^{2+} + 0.60 Ti
M(2)	0.59 Mg + 0.56 Fe^{2+} + 0.72 Fe^{3+} + 0.13 Ti
M(3)	0.36 Mg + 0.53 Fe^{2+} + 0.11 Li
M(4)	1.85 Na + 0.15 Ca
A sites	0.71 Na + 0.29 K
W site	1.20 O + 0.24 F + 0.56 OH

* from Hawthorne *et al.* (1998).

TABLE 5. COMPARISON OF SELECTED PHYSICAL PROPERTIES OF FERRO-OBERTIITE AND OBERTIITE

	Ferro-obertiite	Obertiite
a (Å)	9.845(4)	9.776(2)
b	18.018(8)	17.919(3)
c	5.296(3)	5.292(1)
β (°)	103.86(3)	104.05(2)
V (Å^3)	912.1(4)	899.3(3)
Space group	*C*2/*m*	*C*2/*m*
Optic sign	Biaxial –	Biaxial –
α	1.671	1.657
β	1.674	1.670
γ	1.675	1.681
$2V_{obs}$ (°)	60	81
Color	Black	Pale pink
Pleochroism	Dark brown to dark grey	Pink to red-orange
Reference	(1)	(2)

(1) this work and Hawthorne *et al.* (1998); (2) Hawthorne *et al.* (2000).

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