

Oxyphlogopite $K(\text{Mg}, \text{Ti}, \text{Fe})_3[(\text{Si}, \text{Al})_4\text{O}_{10}](\text{O}, \text{F})_2$: A New Mineral Species of the Mica Group¹

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Abstract—Oxyphlogopite is a new mica-group mineral with the idealized formula $K(\text{Mg}, \text{Ti}, \text{Fe})_3[(\text{Si}, \text{Al})_4\text{O}_{10}](\text{O}, \text{F})_2$. The holotype material came from a basalt quarry at Mount Rothenberg near Mendig at the Eifel volcanic complex in Rhineland-Palatinate, Germany. The mineral occurs as crystals up to $4 \times 4 \times 0.2$ mm in size encrusting cavity walls in alkali basalt. The associated minerals are nepheline, plagioclase, sanidine, augite, diopside, and magnetite. Its color is dark brown, its streak is brown, and its luster is vitreous. $D_{\text{meas}} = 3.06(1)$ g/cm³ (flotation in heavy liquids), and $D_{\text{calc}} = 3.086$ g/cm³. The IR spectrum does not contain bands of OH groups. Oxyphlogopite is biaxial (negative); $\alpha = 1.625(3)$, $\beta = 1.668(1)$, and $\gamma = 1.669(1)$; and $2V_{\text{meas}} = 16(2)^\circ$ and $2V_{\text{calc}} = 17^\circ$. The dispersion is strong; $r < v$. The pleochroism is medium; $X > Y > Z$ (brown to dark brown). The chemical composition is as follows (electron microprobe, mean of 5 point analyses, wt %; the ranges are given in parentheses; the H₂O was determined using the Almarin method; the Fe²⁺/Fe³⁺ was determined with X-ray emission spectroscopy): Na₂O 0.99 (0.89–1.12), K₂O 7.52 (7.44–7.58), MgO 14.65 (14.48–14.80), CaO 0.27 ((0.17–0.51), FeO 4.73, Fe₂O₃ 7.25 (the range of the total iron in the form of FeO is 11.09–11.38), Al₂O₃ 14.32 (14.06–14.64), Cr₂O₃ 0.60 (0.45–0.69), SiO₂ 34.41 (34.03–34.66), TiO₂ 12.93 (12.69–13.13), F 3.06 (2.59–3.44), H₂O 0.14; O=F₂ –1.29; 99/58 in total. The empirical formula is $(\text{K}_{0.72}\text{Na}_{0.14}\text{Ca}_{0.02})(\text{Mg}_{1.64}\text{Ti}_{0.73}\text{Fe}_{0.30}^{2+}\text{Fe}_{0.27}^{3+}\text{Cr}_{0.04})_{\Sigma 2.98}(\text{Si}_{2.59}\text{Al}_{1.27}\text{Fe}_{0.14}^{3+}\text{O}_{10}\text{O}_{1.20}\text{F}_{0.73}(\text{OH})_{0.07})$. The crystal structure was refined on a single crystal. Oxyphlogopite is monoclinic with space group $C2/m$; the unit-cell parameters are as follows: $a = 5.3165(1)$, $b = 9.2000(2)$, $c = 10.0602(2)$ Å, $\beta = 100.354(2)^\circ$. The presence of Ti results in the strong distortion of octahedron $M(2)$. The strongest lines of the X-ray powder diffraction pattern [d , Å (I , %) $[hkl]$] are as follows: 9.91(32) [001], 4.53(11) [110], 3.300(100) [003], 3.090(12) [112], 1.895(21) [005], 1.659(12) [–135], 1.527(16) [–206, 060]. The type specimens of oxyphlogopite are deposited at the Fersman Mineralogical Museum in Moscow, Russia; the registration numbers are 3884/2 (holotype) and 3884/1 (cotype).

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INTRODUCTION

Chemical substitutions in the mica-group minerals are characteristic of both the cation and anion sites of the crystal structure. In particular, the calculated formulas of Ti-bearing trioctahedral micas, as a rule, indicate additional oxygen atoms substituting for OH

groups in the free apices of the octahedral layer. For example, in thoroughly examined phlogopite containing 3 wt % TiO₂, the composition of this site is $(\text{OH})_{1.25}\text{O}_{0.65}\text{F}_{0.10}$ (Scordari et al., 2006); in phlogopite with 8.97 wt % TiO₂, it is $(\text{OH})_{0.93}\text{O}_{0.92}\text{F}_{0.15}$ (Prider, 1939); and in phlogopite with 10.85 wt % TiO₂, it is $\text{O}_{1.20}(\text{OH})_{0.41}\text{F}_{0.39}$ (Cruciani, Zanazzi, 1994). In trioctahedral mica with 12.57 wt % TiO₂ (Greenwood, 1998), the formula calculated even under the assumption that the total Fe in the octahedral sites is divalent displays predominant oxygen in the free apices of the octahedra $(\text{O}_{1.04}(\text{OH}, \text{F})_{0.96})$. Recently, oxykinoshitalite $(\text{Ba}(\text{Mg}_2\text{Ti})(\text{Si}_2\text{Al}_2\text{O}_{10})\text{O}_2)$ Ba-dominant trioctahedral oxymica was approved as a new mineral

¹ A new mineral oxyphlogopite and its name were recommended by the Commission on New Minerals and Mineral Names of the Russian Mineralogical Society on October 10, 2009 and approved by the Commission on New Minerals, Nomenclature, and Classification of the International Mineralogical Association on November 5, 2009 (IMA no. 2009-069).

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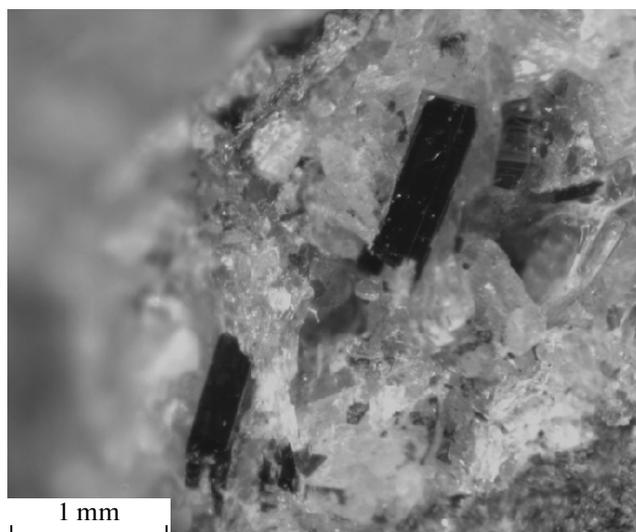


Fig. 1. Crystals of oxyphlogopite.

(Kogarko et al., 2005). At the same time, no oxygen-dominant counterparts of the phlogopite–annite series are included into the nomenclature of micas (Rieder et al., 1998).

The results of the comprehensive mineralogical and crystallochemical investigation of K-dominant trioctahedral magnesian oxymica from the Rothenberg paleovolcano located 4.5 km NW of Mendig in Rhieland-Palatinate, Germany are presented in this paper.

The mineral was named oxyphlogopite. The type material is deposited at the Fersman Mineralogical Museum of the Russian Academy of Sciences in Moscow, Russia (registration nos. 3884/1 (cotype) and 3884/2 (holotype)).

MODE OF OCCURRENCE

Oxyphlogopite is pneumatolitic in origin. It occurs as crystals lining the walls of large (up to 10 cm) cavities in cavernous alkali basalt and growing into the rock near the caverns (Fig. 1). The alkali basalt is composed largely of plagioclase, nepheline, and augite. In addition to mica, the late pneumatolitic assemblage

consists of nepheline, plagioclase, sanidine, diopside, and magnetite encrusting cavity walls in basalt.

Despite the phlogopite being formed obviously later than the host rock, the temperature of its crystallization was rather high. The formation of Ti-rich oxymica is facilitated by a combination of factors, including high oxygen fugacity, magma degassing, and crystallochemical factors related to the compensation of the high positive charge of the trioctahedral layer with a high content of ^{VI}Ti and $^{VI}\text{Fe}^{3+}$ (Thibault et al., 1992; Mann et al., 2006; Chukanov et al., 2008).

PHYSICAL PROPERTIES

Oxyphlogopite occurs as imperfect prismatic (up to 1.5 mm long) and thin lamellar (up to $4 \times 4 \times 0.2$ mm in size) dark brown to almost black crystals with brown streaks. The Mohs hardness is 3; the cleavage is perfect parallel to (001). In comparison with minerals of the phlogopite–annite series, it is brittle, but the thin cleavage lamellae are flexible. The density measured with equilibration in heavy liquids is $3.06(1)$ g/cm³; the calculated density is 3.086 g/cm³.

The IR spectrum of oxyphlogopite is close to that of biotite, but bands of O–H stretching vibrations (region of 3300 – 3750 cm⁻¹) are absent (Fig. 2).

The new mineral is biaxial, negative, $\alpha = 1.625(3)$, $\beta = 1.668(1)$, $\gamma = 1.669(1)$, and $2V_{\text{meas}} = 17^\circ$. Axis X is perpendicular to the cleavage plane. The dispersion is strong: $r < v$. The new mineral is pleochroic in brown color: $X > Y > Z$.

The relative integral intensity of the last line ($\text{Fe}_{K\beta_5}$) of the X-ray emission spectrum of Fe was used to determine the iron valence. The intensity of the $\text{Fe}_{K\beta_5}$ line depends on both the iron valence and the content of Fe in the mineral. Thus, having normalized the intensity of the $\text{Fe}_{K\beta_5}$ to the intensity of $\text{Fe}_{K\beta_1}$, the analytical signal depending only on the iron species in the mineral is obtained. A similar approach was substantiated by Kupriyanova et al. (2003) for the determination of the As valence.

The X-ray emission spectra in the region of the $\text{Fe}_{K\beta_1}$ and $\text{Fe}_{K\beta_5}$ lines were recorded with a Tescan

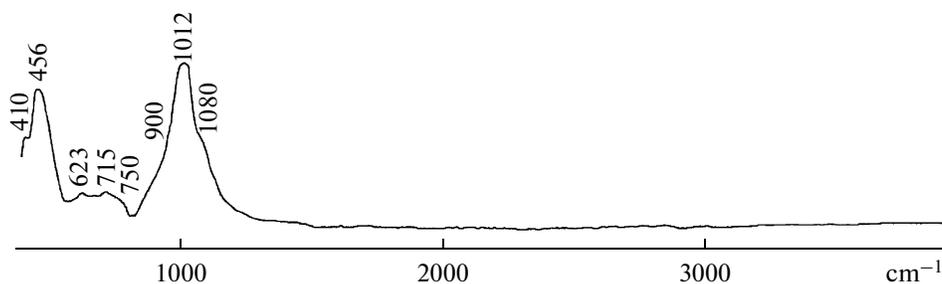


Fig. 2. IR spectrum of oxyphlogopite

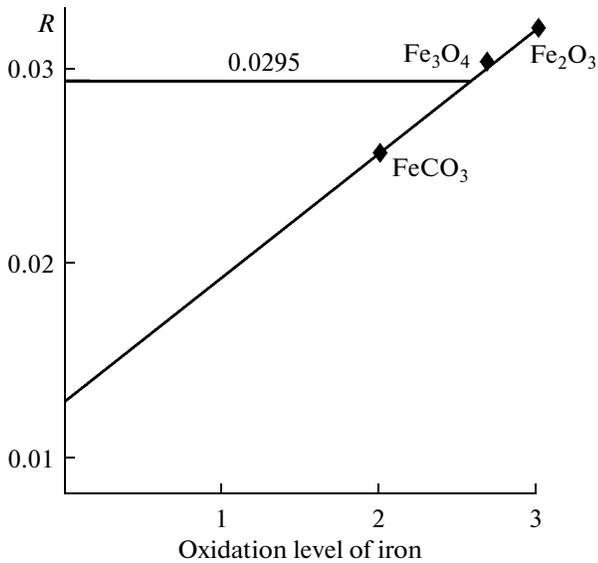


Fig. 3. $R = I(\text{Fe}_{K\beta_5})/I(\text{Fe}_{K\beta_1})$ versus the oxidation level of Fe in the holotype sample of oxyphlogopite. The horizontal line at $R = 0.0295$ corresponds to oxyphlogopite.

Vega IIXMU SEM equipped with an INCA 700 WDS operating at an accelerating voltage of 20 kV, a current of the absorbed electrons on the Faraday cup of 200 nA, and with an LiF crystal detector. Siderite, magnetite, and hematite (the average oxidation level is 2.0, 2.67, and 3.0, respectively) were used as standards. The average oxidation level of Fe in the holotype sample of oxyphlogopite determined from the corresponding correlation is 2.58. A similar procedure applied to cotype gave an oxidation level of about 2.8.

CHEMICAL COMPOSITION

The chemical composition of oxyphlogopite was determined with a Tescan Vega II XMU SEM equipped with an INCAx-sight EDS operating at an accelerating voltage on a tungsten cathode of 20 kV, the current of the absorbed electrons on Co of 0.3 nA, the angle of selection of the X-ray radiation of 35° , and the distance between the sample and the detector of 25 mm.

The chemical composition of the holotype sample (average of 5 point analyses; the $\text{Fe}^{2+}/\text{Fe}^{3+}$ determined with X-ray emission spectroscopy; the water determined using the Alimarin method) is as follows, wt % (the range of the contents is given in parentheses): 0.99 (0.89–1.12) Na_2O , 7.52 (7.44–7.58) K_2O , 14.65 (14.48–14.80) MgO , 0.27 (0.17–0.51) CaO , 4.73 FeO , 7.25 Fe_2O_3 (the range of the total iron in the form of FeO is 11.09–11.38), 14.32 (14.06–14.64) Al_2O_3 , 0.60 (0.45–0.69) Cr_2O_3 , 34.41 (34.03–34.66) SiO_2 , 12.93 (12.69–13.13) TiO_2 , 3.06 (2.59–3.44) F , 0.14 H_2O , $-1.29 \text{ O} = \text{F}_2$; the total is 99.58. The Cl, V,

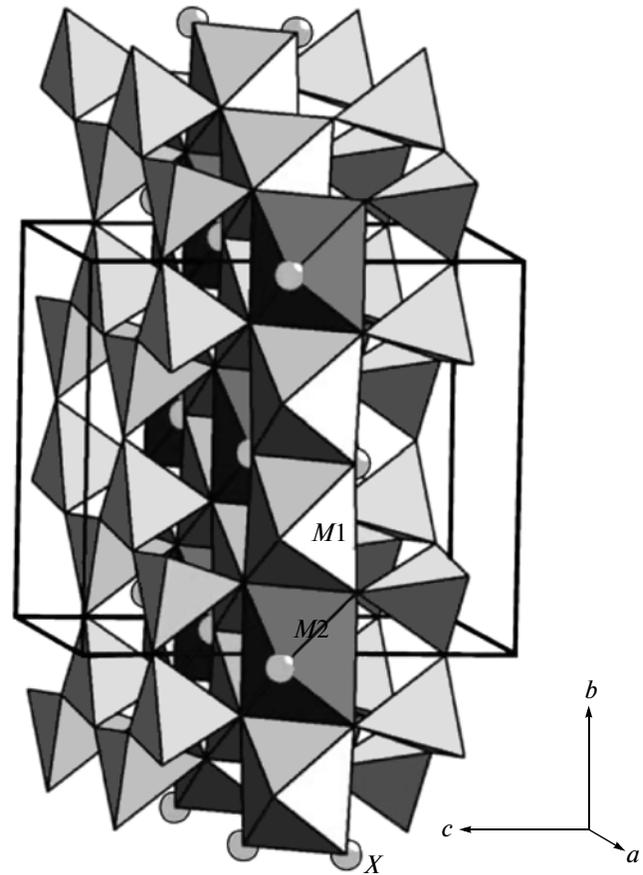
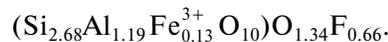


Fig. 4. Crystal structure of oxyphlogopite

Mn, Zn, Co, and Ni contents are below the detection limit. The empirical formula based on 12 (O + F) atoms is



$(\text{Si}_{2.59}\text{Al}_{1.27}\text{Fe}_{0.14}^{3+}\text{O}_{10})\text{O}_{1.20}\text{F}_{0.73}(\text{OH})_{0.07}$. The chemical composition of the cotype is as follows, wt %: Na_2O 1.42, K_2O 8.26, MgO 16.64, CaO 0.17, FeO 10.54, Al_2O_3 13.66, SiO_2 36.38, TiO_2 11.14, F 2.86, $1.20 - \text{O} = \text{F}_2$; the total is 99.87. Taking into account $\text{Fe}^{2+}/\text{Fe}^{3+} = 1/4$ (according to the X-ray emission spectroscopy), the empirical formula of the oxyphlogopite cotype can be written as



X-RAY CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

The X-ray powder diffraction pattern of the holotype sample was recorded with a Rigaku D/MAX-2200 diffractometer with $\text{CuK}\alpha_1$ radiation.

The X-ray powder diffraction pattern of the cotype sample was obtained using the Gandolfi method on a

Table 1. X-ray powder diffraction data of oxyphlogopite

Holotype			Cotype			<i>h</i>	<i>k</i>	<i>l</i>
<i>I</i> , %	<i>d</i> _{meas} , Å	<i>d</i> _{calc} , Å	<i>I</i> , %	<i>d</i> _{meas} , Å	<i>d</i> _{calc} , Å			
32	9.91	9.90	79	9.99	10.03	0	0	1
2	4.93	4.85	3	4.94	5.02	0	0	2
			17	4.58	4.59	0	2	0
11	4.53	4.55	7	4.40	4.55	1	1	0
					4.40	$\bar{1}$	1	1
10	4.14	4.16	2	4.19	4.18	0	2	1
			18	3.91	3.93	1	1	1
8	3.60	3.65	46	3.66	3.65	$\bar{1}$	1	2
100	3.30	3.30	60	3.36	3.35	0	0	3
12	3.09	3.11	77	3.14	3.15	1	1	2
8	2.892	2.899	28	2.908	2.910	$\bar{1}$	1	3
5	2.673	2.677				$\bar{2}$	0	1
			100	2.625	2.619	2	0	0
10	2.610	2.611			2.613	$\bar{1}$	3	1
					2.619	2	0	0
10	2.483	2.491	11	2.500	2.503	1	3	1
		2.475			2.509	0	0	4
					2.505	$\bar{2}$	0	2
5	2.421	2.423	57	2.431	2.427	$\bar{1}$	3	2
					2.434	2	0	1
0.5	2.334	2.335				$\bar{1}$	1	4
2	2.277	2.277	23	2.266	2.275	2	2	0
1	2.246	2.245			2.259	1	3	2
					2.259	$\bar{2}$	0	3
9	2.162	2.161	55	2.164	2.173	2	0	2
		2.160			2.167	$\bar{1}$	3	3
			3	2.102	2.151	2	2	1
					2.088	0	4	2
21	1.985	1.980	25	1.987	2.007	0	0	5
					1.992	1	3	3
					1.991	$\bar{2}$	0	4
10	1.980	1.980	8	1.898	1.904	$\bar{1}$	3	4
1	1.892	1.892			1.909	2	0	3
0.5	1.874	1.881			1.893	0	4	3
			1	1.839	1.839	0	2	5
			1	1.826	1.826	$\bar{2}$	2	4
			4	1.742	1.746	1	3	4
					1.744	$\bar{2}$	0	5

Table 1. (Contd.)

Holotype			Cotype			<i>h</i>	<i>k</i>	<i>l</i>
<i>I</i> , %	<i>d</i> _{meas} , Å	<i>d</i> _{calc} , Å	<i>I</i> , %	<i>d</i> _{meas} , Å	<i>d</i> _{calc} , Å			
					1.743	1	1	5
					1.734	1	5	0
3	1.747	1.749				2	2	3
		1.747			1.740	$\bar{3}$	1	1
12	1.659	1.659	39	1.662	1.670	$\bar{1}$	3	5
					1.674	2	0	4
					1.652	$\bar{1}$	1	6
1	1.607	1.611	10	1.615	1.611	$\bar{2}$	4	3
		1.603			1.611	1	5	2
2	1.576	1.575				$\bar{3}$	2	3
			8	1.578	1.576	$\bar{1}$	5	3
1	1.573	1.572			1.579	2	4	2
		1.571				$\bar{1}$	5	3
					1.572	0	2	6
			58	1.533	1.536	1	3	5
9	1.537	1.537			1.534	$\bar{3}$	3	1
16	1.527	1.528			1.534	$\bar{2}$	0	6
		1.527				0	6	0
1	1.501		5	1.467				
1	1.483		2	1.419				
1	1.457		4	1.393				
1	1.444							
4	1.416							

Stoe IPDS II diffractometer with an image plate detector, MoK_α radiation, an accelerating voltage of 50 kV, and a current of 40 mA. To obtain the X-ray powder diffraction pattern, several crystals of oxyphlogopite were pasted on a glass fiber so that their relative orientation was significantly different. The sample was measured with rotation around two axes (ω and ϕ), the sample–detector distance was 200 mm, and the measurement time was 60 min.

Both X-ray powder diffraction patterns (Table 1) are well indexed in a monoclinic unit cell (space group $C2/m$) with the dimensions refined by the least squares method of $a = 5.338(1)$ and $5.317(12)$ Å, $b = 9.161(2)$ and $9.186(17)$ Å, $c = 10.069(2)$ and $10.185(13)$ Å, $\beta = 100.53(6)$ and $99.9(1)^\circ$, and $V = 484.1(2)$ and $490(2)$ Å³, respectively; $Z = 2$.

The X-ray single-crystal data were collected with an Xcalibur CCD diffractometer using MoK_α radiation. In the region of the collection ($\theta_{\text{max}} = 54^\circ$; $-10 <$

$h < 12$, $-20 < k < 20$, $-22 < l < 20$), 1642 unique reflections with $F > 5\sigma(F)$ were obtained. The R factor of the anisotropic refinement is 0.047. The structure was refined with the AREN program (Andrianov, 1988); the DIFABS program (Walker and Stuart, 1983) was used to take the absorption into account.

According to the X-ray single crystal data, oxyphlogopite is monoclinic with space group $C2/m$; the unit-cell dimensions are $a = 5.3165(1)$, $b = 9.2000(2)$, $c = 10.0602(2)$ Å, $\beta = 100.354(2)^\circ$, $V = 484.05(1)$ Å³, and $Z = 2$. As other trioctahedral mica (Fig. 4), the crystal structure of this mineral contains triple-layer TOT packets, where T is the layer of $(\text{Si,Al,Fe}^{3+})\text{O}_4$ apex-shared tetrahedra, and O is the layer of $(\text{Mg,Ti,Fe,Cr})(\text{O,F})_6$ edge-shared octahedra. The TOT packets are linked by interlayer cations (K, Na, Ca). Two octahedron types are distinguished in the trioctahedral layer, $M(1)(\text{O,F})_6$ and $M(2)(\text{O,F})_6$; the latter is smaller and more distorted than $M(1)$ -centered

Table 2. Comparative data on oxyphlogopite and related mica-group minerals (all monoclinic, $C2/m$, $Z = 2$)

Parameter	Oxyphlogopite	Phlogopite	Fluorphlogopite	Oxykinoshitalite
Simplified formula	$K(Mg, Ti, Fe)_3 \cdot [(SiAl)_4O_{10}](O, F)_2$	$KMg_3(Si, AlO_{10})(OH)_2$	$KMg_3(Si_3AlO_{10})F_2$	$BaMg_2Ti(Si_2Al_2O_{10})O_2$
a , Å	5.3165	5.31—5.32	5.3094	5.3516
b , Å	9.2000	9.19—9.20	9.1933	9.2817
c , Å	10.0602	10.15—10.30	10.1437	10.0475
β , °	100.354	99.9—100.1	100.062	100.337
Strong reflections in the X-ray powder diffraction pattern, d , Å, ($I\%$)	9.91(32)	9.97(100)	9.99 (80)	3.646 (70)
	4.53(11)	3.389(20)	3.369(100)	3.383 (60)
	3.302(100)	3.348(100)	3.324(100)	3.130(70)
	3.09(12)	2.614(30)	3.121(80)	2.902 (50)
	1.985(21)	2.515(15)	2.610(80)	2.637(100)
	1.659(12)	2.430(15)	2.426 (80)	2.435(50)
	1.527(16)	2.17(15)	1.663 (8)	2.172(90)
		2.012(30)		1.988(50)
Optical parameters				
α	1.625	1.53—1.57	1.543	1.708
β	1.668	1.58—1.62	1.568	1.710
γ	1.669	1.58—1.62	1.569	1.719
Optical sign, $2V$	−16	−3—−14	−17	+56
Density, g/cm ³	3.083 (calc), 3.06 (meas)	2.79 (calc), 2.73—2.94 (meas)	2.83 (calc)	3.45 (calc), 3.3 (meas)
Source	This study	Hazen, Burnham, 1973; Bailey, 1980; Mineralogy, 1992	Gianfagna et al., 2007	Kogarko et al., 2005

Table 3. Parameters of the coordination polyhedra

Site	Composition ($Z = 2$)	Coordination number	Cation–anion distance, Å		
			minimum	maximum	average
$M(1)$	0.60Mg + 0.40Fe	6	2.046(1)	2.109(1)	2.088
$M(2)$	1.0Mg + 0.74Ti + 0.22Fe + 0.04Cr	6	1.939(1)	2.133(1)	2.047
T	2.6Si + 0.33Al + 0.1Fe ³⁺	4	1.6509(9)	1.666(1)	1.655
K	0.7K + 0.3Na	12	2.944(1)	3.295(2)	3.110

octahedron. The parameters of the coordination polyhedra are given in Tables 2 and 3. Chukanov et al. (2008) have described the crystal structure of oxyphlogopite in more detail.

The crystallochemical formula of oxyphlogopite derived from the refined crystal structure is $(K_{0.7}Na_{0.3})_{\Sigma=1}(Mg_{0.6}Fe_{0.4})_{\Sigma=1}(Mg_{1.0}Ti_{0.74}Fe_{0.22}Cr_{0.04})_{\Sigma=2}[(Si_{2.6}Al_{1.3}Fe_{0.1})_{\Sigma=4}O_{10}](O, F)_2$.

DISCUSSION

The Ti-rich (4–17 wt % TiO₂) trioctahedral micas are usual minerals of alkali basalt and some metamorphic rocks (Prider, 1939; Ushakova, 1971; Mansker et al., 1979; Dymek, 1983; Koval et al., 1988; Shaw and Penczak, 1996; Greenwood, 1998; Ibhi et al., 2005; Chukanov et al., 2008). Rosenbusch (1910) mentioned Ti-rich biotite (wodanite) for the first time

when referring to an unpublished manuscript by G. Latterman. "Wodanite" described from syenite dykes of the Katzenbuckel volcano in southwestern Germany (Katzenbuckel, Odenwald, Baden-Württemberg) contains 12.56 wt % TiO_2 and only 0.76 wt % H_2O (Rosenbusch, 1910; Freudenberg, 1920; Hallimond, 1927) and apparently is oxyphlogopite. In all likelihood, most samples of trioctahedral potassic micas from alkali basalts with TiO_2 higher than 9–10 wt % and Ti-poor micas a high content of Fe^{3+} in octahedral sites are attributed to this mineral species.

The structural examination of 24 samples of phlogopite has shown that high-charge cations (Ti^{4+} , Al^{3+} , Fe^{3+} , Cr^{3+}) selectively concentrate in site $M(2)$ changing the size of the $M(2)$ -centered octahedron and distorting it (Cruciani, Zanazzi, 1994). The off-center shift of the $M(2)$ site of this octahedron is correlated with the total Ti content in the sample (increasing from nearly zero in Ti-poor mica to 0.08–0.09 Å in the samples with 0.59–0.65 apfu Ti). In this case, the parameters of the $M(1)$ -centered octahedron change insignificantly.

In the oxyphlogopite examined in this study, the distortion is $(2.133 - 1.939) : 2 = 0.097 \text{ \AA}$, where 1.939 Å is the distance between the $M(2)$ and X sites. According to Cruciani and Zanazzi (1994), the shortening of the $M(2)$ – X bond can be caused by the substitution of OH for O in site X as a result of the substitution of $^{6l}\text{R}^{2+} + 2\text{OH} \leftrightarrow ^{6l}\text{Ti}^{4+} + 2\text{O}^{2-}$. The mean valence force of 1.61 calculated taking into account the complete composition of the $M(1)$ and $M(2)$ octahedra indicates that the affinity of site X to O is closer than to OH or F. Thus, the assumption that Mg, Fe, and Ti cations occur in both the trioctahedral sites $M(1)$ and $M(2)$ simultaneously (Brigatti et al., 1991; Brigatti, Poppi, 1993) is invalid. The assumption that the incorporation of Ti the trioctahedral sites of the micas is related to the formation of vacancies in the octahedra ($\text{Ti}^{4+} + \square \leftrightarrow 2\text{R}^{2+}$) (Hazen, Burnham, 1973; Dymek, 1983; Mineralogy, 1992) also did not find its substantiation.

Thus, the idealized formula of oxyphlogopite can be written as $K(\text{Mg}_2\text{Ti})(\text{Si}_3\text{AlO}_{10})\text{O}_2$.

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