

## NEW DATA ON TITANIUM-RICH BIOTITE: A PROBLEM OF "WODANITE"

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Titanium-rich mica of the biotite series ("wodanite") was found in tefrite of paleovolcano Rothenberg, Eifel, Germany, and studied by combining of electron microprobe analysis, IR spectroscopy and single-crystal structure analysis. The mineral is monoclinic, space group  $C2/m$ ; unit-cell parameters are:  $a = 5.3165(1)$ ,  $b = 9.2000(2)$ ,  $c = 10.0602(2)$  Å,  $\beta = 100.354(2)$ . The presence of Ti results in strong distortion of the octahedron  $M(2)$ . IR spectrum demonstrates the absence of detectable amounts of OH groups. The empirical formula of Ti-rich biotite is:  $(K_{0.74}Na_{0.15}Ca_{0.05})_{\Sigma 0.94}(Mg_{1.60}Ti_{0.74}Fe^{2+}_{0.62}Cr_{0.04})_{\Sigma 3.00}[(Si_{2.61}Al_{1.29}Fe^{3+}_{0.10})_{\Sigma 4.00}O_{10}](O_{1.17}F_{0.71})$ . Regularities of isomorphous substitutions, as well as genesis of Ti-rich micas of the biotite series are discussed. The idealized formula of the magnesium-titanium end member of this series is:  $K(Mg_2Ti)(Si_3AlO_{10})O_2$ . 5 tables, 4 figures, 26 references.

Keywords: wodanite, titanium biotite, oxybiotite, paleovolcano Rothenberg.

### Introduction

The name "wodanite" was first mentioned in a manuscript by G. Lattermann as applied to titanium-bearing biotite-type mica from syenite dykes of the paleovolcano Katzenbuckel located near Odenwald, Baden-Württemberg, Germany. Later Lattermann's original manuscript was lost, but it is referred in the book (Rosenbusch, 1910). The mineral is named from the Teutonic deity Wodan (variants: Wotan, Woden, Odin). The rock with "wodanite" was uncovered by the basalt quarry Michelsberg that functioned up to 1974. The content of  $TiO_2$  in "wodanite" from Katzenbuckel reaches 12.56 wt. % (Rosenbusch, 1910; Hallimond, 1927; see also Freudenberg, 1920).

Later high-titanium trioctahedral micas have been repeatedly detected in different magmatic and metamorphic rocks including phlogopite-leucite lamproite from Western Australia (phlogopite with 8.97 wt. %  $TiO_2$ ; Prider, 1939), lamprophyric dyke from Ilha da Trindade, Brazil (mica with  $TiO_2$  up to 12.71 wt. % and BaO up to 7.11 wt. %; Greenwood, 1998), gabbro from Ontario, Canada (mica with  $TiO_2$  up to 7.11 wt. % and BaO up to 6.1 wt. %; Shaw, Penczak, 1996), basaltoid rocks of

Mongolia (mica with  $TiO_2$  up to 12.49 wt. %; Koval *et al.*, 1988), nephelinites from Oahu, Hawaii (barian biotite with  $TiO_2$  up to 14 wt. %; Mansker *et al.*, 1979), carbonatites from Anti-Atlas, Morocco (mica with  $TiO_2$  up to 13.85 wt. % and BaO up to 21.46 wt. %; Ibhi *et al.*, 2005), high-grade gneisses from West Greenland (biotite with Ti content up to 0.3 atoms per formula unit; Dymek, 1983), corundum-bearing gneisses from Kyushu Island, Japan ( $TiO_2$  up to 17 wt. %; Ushakova, 1971).

In first publications concerning "wodanite" (Rosenbusch, 1910; Hallimond, 1927), it was noted that this mineral is remarkable for very low water content of 0.76 wt. % (for comparison: theoretical content of  $H_2O$  is 4.32 wt. % for phlogopite and 3.52 wt. % for annite). In most cases, the calculation of empirical formulae of titanium-rich micas indicates the presence of additional O atoms substituting OH groups in free vertices of octahedral (the site X). The composition of this site is:  $(OH)_{1.25}O_{0.65}F_{0.10}$  in a phlogopite sample investigated in detail and containing 3 wt. %  $TiO_2$  (Scordari *et al.*, 2006);  $(OH)_{0.93}O_{0.92}F_{0.15}$  in mica with 8.97 wt. %  $TiO_2$  (Prider, 1939);  $O_{1.20}(OH)_{0.41}F_{0.39}$  in phlogopite containing 10.85 wt. %  $TiO_2$  (Cruciani, Zanazzi, 1994).



Fig. 1. Crystals of titaniferous biotite in nepheline tephrite. Photo: A.V. Kasatkin.

For trioctahedral mica with 12.57 wt. %  $\text{TiO}_2$ , charge-balance empirical formula shows the prevalence of O over OH and F in the X site (even under assumption that all iron is  $\text{Fe}^{2+}$ , the composition of this site is  $\text{O}_{1.04}(\text{OH},\text{F})_{0.96}$ ; Greenwood, 1998).

These examples demonstrate the existence of O-dominant micas belonging to the biotite series (i. e. trioctahedral micas with potassium as the main interlayer cation). It should be noted that the names like "oxybiotite", "oxyannite", "ferrixyannite" have been used rather widely though in different sense (see Ohta *et al.*, 1982; Koval *et al.*, 1988; Rancourt *et al.*, 2001). Owing to the uncertainty of the term "oxybiotite", this name was descredited with the comment "oxybiotite = oxidized biotite?" (Burke, 2006). However recently Ba-dominant and Ti-rich oxy-mica oxykinoshitalite,  $\text{Ba}(\text{Mg}_2\text{Ti})(\text{Si}_2\text{Al}_2\text{O}_{10})\text{O}_2$ , was approved by the IMA CNMNC as new mineral species (Kogarko *et al.*, 2005). At the same time, O-dominant analogues of phlogopite-annite series minerals are absent in the accepted nomenclature of micas (Rieder *et al.*, 1998).

The present work is devoted to the mineralogical and the structural investigation of Ti-rich trioctahedral oxy-mica from the paleovolcano Rothenberg located in the effusive complex Eifel.

### Occurrence, properties and chemical composition

Specimens of cavernous tephrite with high-titanium mica have been collected in the basalt quarry on the Mt. Rothenberg. Nepheline, plagioclase and augite are the main rock-forming minerals. Among accessory minerals, titanium-rich magnetite is most abundant. Mica forms dark brown to black scales and prismatic crystals up to 1 mm length crowing on the walls of cavities (Fig. 1) and in the rock near the vugs. Twins of feldspars (sanidine and plagioclase), crystals of diopside and magnetite are present in close association with mica.

Although mica was obviously formed later than the main minerals of tephrite, the temperatures of its crystallization were probably rather high: experimental data for lherzolite demonstrate the growth of the ratio  $\text{Ti} : \text{K}$  in phlogopite with growing temperature (up to  $\text{Ti} : \text{K} = 0.4$  at 1150-1250°C – Thibault *et al.*, 1992). High activity of oxygen also promotes the formation of oxy-micas. For example, unusually high oxygen fugacity (0.5 – 1.9 logarithmic units above the FMQ buffer) was recorded for the rocks of Katzenbuckel, where "wodanite" was first described (Mann *et al.*, 2006), autometasomatic stage being characterized by even higher oxygen fugacity.

As compared with common biotite, high-titanium mica is more brittle. IR

Table 1. Chemical composition of Ti-rich biotite

Component	Content, wt. %	Ranges	Probe Standard
Na <sub>2</sub> O	1.05	0.97–1.15	Albite
K <sub>2</sub> O	7.69	7.60–7.84	Microcline
CaO	0.64	0.52–0.70	Wollastinite
MgO	14.21	14.12–14.26	Diopside
FeO	11.47	11.35–11.61	Fe
Al <sub>2</sub> O <sub>3</sub>	14.48	14.35–14.66	Al <sub>2</sub> O <sub>3</sub>
Cr <sub>2</sub> O <sub>3</sub>	0.71	0.67–0.75	Cr
TiO <sub>2</sub>	13.08	12.95–13.28	Ti
SiO <sub>2</sub>	34.62	34.49–34.71	SiO <sub>2</sub>
F	2.99	2.64–3.16	CaF <sub>2</sub>
-O=F <sub>2</sub>	-1.26		
Total	99.68		

Table 2. Atomic coordinates, equivalent atom displacements, site multiplicities (Q) and site occupancy factors (q)

Atom	x/a	y/b	z/c	Q	q	B <sub>eq</sub> , Å <sup>2</sup>
M(1)	0	0	0.5	2	1	1.20(1)
M(2)	0	0.3441(1)	0.5	4	1	1.03(1)
T	0.742(1)	0.1675(1)	0.2218(1)	8	1	0.80(1)
K	0	0.5	0	2	1	1.11(2)
O(1)	0.0181(5)	0	0.1653(2)	4	1	1.60(8)
O(2)	0.3218(3)	0.2320(2)	0.1621(1)	8	1	1.59(6)
O(3)	0.1325(2)	0.1702(1)	0.3902(2)	8	1	1.02(6)
X	0.1285(3)	0.5	0.4009(1)	4	1	1.11(7)

Table 3. Characteristics of coordination polyhedra

Site	Composition (Z=2)	Coordination			The distance cation – anion, Å		
		number	Minimum	Maximum	Mean		
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 <sup>3+</sup>	4	1.6509(9)	1.666(1)	1.655		
K	0.7K+0.3Na	12	2.944(1)	3.295(2)	3.110		

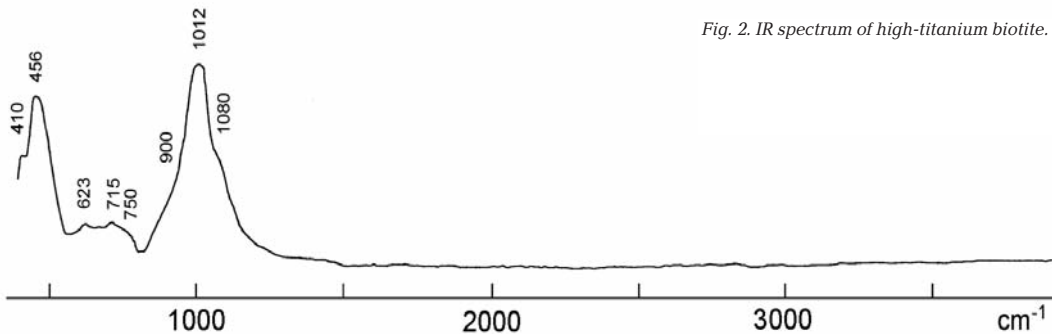


Fig. 2. IR spectrum of high-titanium biotite.

spectrum of the sample from Rothenberg differs from the spectra of other biotite-series micas by the absence of the bands of O-H stretching vibrations (the range 3300–3750 cm<sup>-1</sup>, Fig. 2). The absence of hydroxyl groups can be connected with the combined influence of different genetic and crystal-chemical factors including magma outgassing, high temperature of crystallization, high activity of oxygen, as well as the presence of Ti<sup>4+</sup> that favours the compensation of high positive charge of octahedral cations by a mechanism like (Mg,Fe) + (OH,F) Ti + O.

The chemical composition of high-titanium biotite from Rothenberg was investigated by the EDS-mode electron microprobe (Table 1). The empirical formula calculated on 7 layer cations (including octahedral and tetrahedral ones) is: (K<sub>0.74</sub>Na<sub>0.15</sub>Ca<sub>0.05</sub>)<sub>Σ0.94</sub>(Mg<sub>1.60</sub>Ti<sub>0.74</sub>Fe<sup>2+</sup><sub>0.62</sub>Cr<sub>0.04</sub>)<sub>Σ3.00</sub>[(Si<sub>2.61</sub>Al<sub>1.29</sub>Fe<sup>3+</sup><sub>0.10</sub>)<sub>Σ4.00</sub>O<sub>10</sub>](O<sub>1.17</sub>F<sub>0.71</sub>). The basis of the formula calculation was chosen taking into account that structural data show the absence of vacancies in the TOT layer. Some deficiency of X-anions (1.88 instead of 2) can result from the assumption that all iron in octahedral sites is Fe<sup>2+</sup>. Taking into account oxidative conditions of mineral formation, the presence of Fe<sup>3+</sup> in octahedral sites seems very likely. Full occupancy of the X site (i. e. O<sub>1.29</sub>F<sub>0.71</sub>) would correspond the following

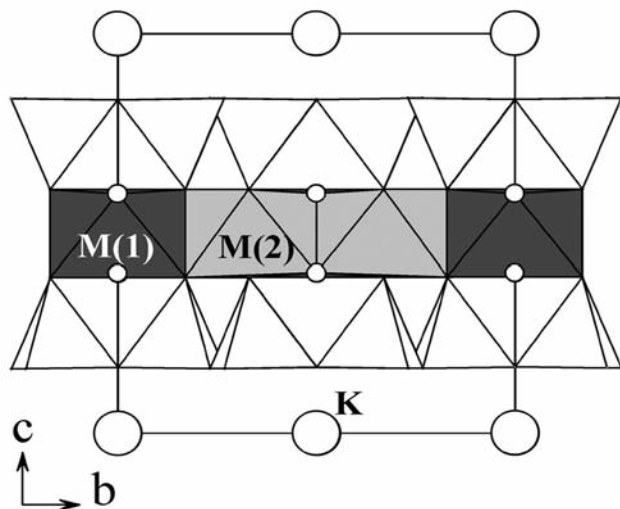


Fig. 3. Crystal structure of high-titanium biotite: *bc*-projection. The X site is denoted by small rings.

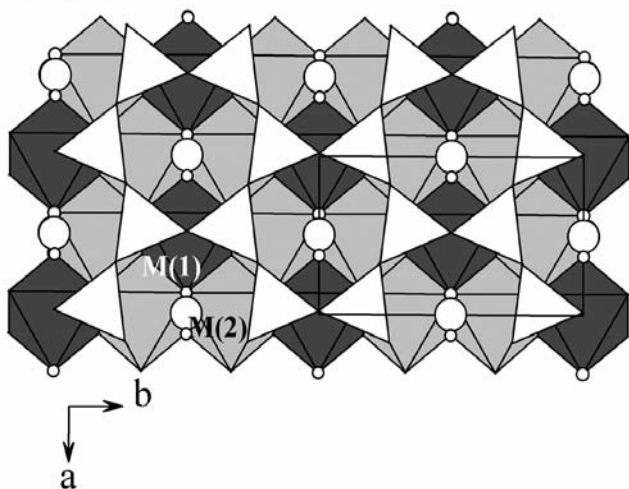


Fig. 4. Crystal structure of high-titanium biotite: *ab*-projection.

composition of the octahedral sheet:  
 $\text{Mg}_{1.60}\text{Ti}_{0.74}\text{Fe}^{2+}_{0.38}\text{Fe}^{3+}_{0.24}\text{Cr}_{0.04}$ .

### Crystal structure

For the structural investigation of Ti-rich biotite, a crystal with the dimensions 0.1 0.2 0.3 mm was used. Single-crystal diffraction data have been obtained using the Xcalibur CCD diffractometer with MoK radiation. In the range with  $\max = 54$  ( $-10 < h < 12$ ,  $-20 < k < 20$ ,  $-22 < l < 20$ ) 1642 independent reflections were obtained with  $F > 5(F)$ . R-factor of averaging of the equivalent reflections is 0.025; R-factor of anisotropic refinement is 0.047; the structure refinement was carried out using the program AREN (Andrianov, 1988); the program DIFABS (Walker, Stuart, 1983) was used for the absorption correction.

The mineral is monoclinic, space group  $C2/m$ , unit cell parameters are:  $a = 5.3165(1)$ ,  $b = 9.2000(2)$ ,  $c = 10.0602(2)$  Å,  $\beta = 100.354(2)$ ,  $V = 484.05$  Å<sup>3</sup>,  $Z = 2$ .

Atomic coordinates, equivalent atom displacements, site multiplicities and site occupancy factors are given in Table 2; for the characteristics of coordination polyhedra see Table 3.

The crystal structure of high-titanium biotite (Figs. 3, 4), as well as that of other trioctahedral micas, contains triple TOT layers where T is the sheet of the tetrahedra  $(\text{Si,Al,Fe}^{3+})\text{O}_4$  sharing common edges, and O is the sheet of the octahedra  $(\text{Mg,Ti,Fe,Cr})(\text{O,F})_6$  sharing common vertices. The TOT layers are connected to each other via interlayer cations (K, Na, Ca).

**Table 4. Variants of the distribution of cations over octahedral sites M(1) and M(2)**

№	Composition of the M(1) site	The number of electrons - in M(1)	Composition of the M(2) site	The number of electrons - in M(2)
1	Mg <sub>0.6</sub> Fe <sub>0.4</sub>	17.6	Mg <sub>1.0</sub> Ti <sub>0.74</sub> Fe <sub>0.22</sub> Cr <sub>0.04</sub>	17.48
2	Ti <sub>0.55</sub> Mg <sub>0.45</sub>	17.5	Mg <sub>1.15</sub> Fe <sub>0.62</sub> Ti <sub>0.19</sub> Cr <sub>0.04</sub>	17.53
3	Mg <sub>0.6</sub> Fe <sub>0.2</sub> Ti <sub>0.2</sub>	16.8	Mg <sub>1.0</sub> Fe <sub>0.42</sub> Ti <sub>0.54</sub> Cr <sub>0.04</sub>	17.88

**Table 5. Local valence balance for the X anion**

Site	Composition	Валентное усилие	Total
M(1)	Mg <sub>0.6</sub> Fe <sub>0.4</sub>	0.41	1.61
M(2)	Mg <sub>1.0</sub> Ti <sub>0.74</sub> Fe <sub>0.22</sub> Cr <sub>0.04</sub>	1.20=0.6 x 2	
M(1)	Fe <sub>1</sub> <sup>2+</sup>	0.57	1.59
M(2)	Mg <sub>2</sub>	1.02=0.51 x 2	
M(1)	Fe <sub>1</sub> <sup>2+</sup>	0.43	1.87
M(2)	Ti <sub>2</sub>	1.44=0.72 x 2	
M(1)	Mg <sub>1</sub>	0.39	1.53
M(2)	Fe <sub>2</sub> <sup>3+</sup>	1.14=0.57 x 2	
M(1)	Ti <sub>1</sub>	0.54	1.98
M(2)	Ti <sub>2</sub>	1.44=0.72 x 2	
M(1)	Mg <sub>1</sub>	0.39	1.41
M(2)	Mg <sub>2</sub>	1.02=0.51 x 2	
M(1)	Fe <sub>1</sub> <sup>3+</sup>	0.46	1.68
M(2)	Fe <sub>2</sub> <sup>3+</sup>	1.22=0.61 x 2	
M(1)	Fe <sub>1</sub> <sup>2+</sup>	0.43	1.57
M(2)	Fe <sub>2</sub> <sup>3+</sup>	1.14=0.57 x 2	

The site partitioning of Mg, Fe, Ti and Cr was determined taking into account the sizes of octahedral, the values of thermal parameters and R factor. The octahedral sheet of high-titanium biotite contains two types of octahedral, M(1)(O,F)<sub>6</sub> and M(2)(O,F)<sub>6</sub> (Table 3). The latter is smaller and more distorted than the M(1)-centered octahedron. For this reason, the presence of titanium in the site M(2) is more probable than in the site M(1). The refinement of the crystal structure of Ti-rich biotite under the assumption that titanium is present only in the site M(2) results in the following crystal-chemical formula: (K<sub>0.7</sub>Na<sub>0.3</sub>)<sub>Σ=1</sub>(Mg<sub>0.6</sub>Fe<sub>0.4</sub>)<sub>Σ=1</sub>(Mg<sub>1.0</sub>Ti<sub>0.74</sub>Fe<sub>0.22</sub>Cr<sub>0.04</sub>)<sub>Σ=2</sub>[(Si<sub>2.6</sub>Al<sub>1.3</sub>Fe<sub>0.1</sub>)<sub>Σ=4</sub>O<sub>10</sub>](O,F)<sub>2</sub>. The refined numbers of electrons in the sites M(1) and M(2) are respectively 17.60 and 17.48 that corresponds to the full (without vacancies) occupancy of both sites. This site population is in good agreement with the values of equivalent atom displacements (Table 2). The dependence of the R-factor on the site partitioning of Mg, Fe, Ti and Cr is weak.

The mechanisms of isomorphous substitution and cation ordering in biotite-series micas have been discussed in numerous publications. According to M.F. Brigatti with coauthors (Brigatti *et al.*, 1991; Brigatti, Poppi, 1993), the cations Mg, Fe and Ti can be present simultaneously in both M(1) and M(2) sites, although in different proportions. However it was shown (Hazen, Burnham, 1973) that of eight possible cation configurations involving Ti and Fe in trioctahedral micas, only three (Fe<sub>3</sub>Si, TiFe<sub>2</sub>Al and TiFe Si) are close to the ideal net charge contribution of <sup>2+</sup> for oxygen. The supposition that the presence of Ti in octahedral sites of micas can be accompanied by the formation of vacancies in octahedral (in accordance with the scheme of isomorphism Ti<sup>4+</sup> + 2R<sup>2+</sup>) was adduced in some other publications (Dymek, 1983; Mineraly, 1992).

In the basic work (Cruciani, Zanazzi, 1994), crystal structures of 24 phlogopite samples (space group C2/m) were investigated. It was shown that the cations Ti<sup>4+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup> and Cr<sup>3+</sup> concentrate in the site M(2). The preferential partitioning of high-charge cations in M(2) results in the distortion of the M(2)-centered octahedron. In particular, the off-center shift of the cation within the M(2) site correlates with the total content of titanium in mica and changes from a practically zero shift for low-titanium samples to 0.08 – 0.09 Å for the samples with Ti<sub>0.59–0.65</sub>. In the sample investigated in the present work, off-center shift of the M(2) cation is (2.133 – 1.939):2 = 0.097 Å where 1.939 Å is the distance between M(2) and X. According to (Cruciani, Zanazzi, 1994), the shortening of the bond M(2)-X can be due to the substitution of OH for O.

The results of bond valence calculations for different statistical combinations of octahedral cations coordinating the site X are given in Table 5. The value of 1.61 valence units calculated for X with average compositions of the octahedra M(1) and M(2) indicates that the affinity of the site X with respect to O is better than that with respect to OH of F. Among different local situations around X, only the variant M<sup>2+</sup>M<sub>2</sub><sup>2+</sup> (M = Mg or Fe) agrees with a monovalent anion (F<sup>-</sup> or OH<sup>-</sup>) whereas other variants, especially MTi<sub>2</sub> and TiTi<sub>2</sub>, agree better with O.

On the basis of available chemical and structural data, it was concluded (Cruciani, Zanazzi, 1994) that in Ti-bearing phlogopite

the following scheme of isomorphic substitutions is realized:  ${}^{[6]}R^{2+} + 2OH^{-} \rightarrow {}^{[6]}Ti^{4+} + 2O^{2-}$ . Thus the idealized formula of Ti-rich "oxyphlogopite" can be written as follows:  $K(Mg_2Ti)(Si_3AlO_{10})O_2$ .

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