

Schreyerite, $V_2Ti_3O_9$: New occurrence and crystal structure

NICOLA DÖBELIN,^{1,*} LEONID Z. REZNITSKY,² EVGENY V. SKLYAROV,² THOMAS ARMBRUSTER,¹
AND OLAF MEDENBACH³

¹Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

²Institute of the Earth's Crust, Siberian Branch of the Russian Academy of Science, Irkutsk 664033, Russia

³Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität, D-44780 Bochum, Germany

ABSTRACT

A new occurrence of schreyerite, $V_2Ti_3O_9$, has recently been found in metamorphic rocks of the Sludyanka complex at the southern shore of Lake Baikal, Russia. In contrast to previously known schreyerite lamellae, which are intergrown with rutile, crystals from the Sludyanka complex occur as isolated single crystals associated with titanite, allowing single-crystal X-ray diffraction experiments. The chemical composition was determined with an electron microprobe giving the composition $(V_{1.785}Cr_{0.157}Fe_{0.036})(Ti_{2.536}V_{0.468})O_9$. A peculiarity of this schreyerite sample is the partial substitution of V^{4+} for Ti^{4+} . The crystal structure was determined by single-crystal X-ray diffraction and was refined in the monoclinic space group $C2/c$ [$a = 17.102(2)$, $b = 5.0253(5)$, $c = 7.0579(8)$ Å, $\beta = 106.636(10)^\circ$] to $R_1 = 2.84\%$. The structure is in agreement with the qualitative model of Grey et al. (1973) determined on the basis of electron diffraction and X-ray powder data for synthetic $(Fe,Cr)_2Ti_3O_9$. Reinvestigation of schreyerite from the type locality indicates that this sample has cell dimensions and symmetry corresponding to the Sludyanka sample. The structure of schreyerite may be considered as a 1:1 polysome composed of slabs of berdesinskiite, V_2TiO_5 , and Ti_2O_4 (a high-pressure phase of TiO_2 with α - PbO_2 structure).

Keywords: Schreyerite, polysomatism, crystal structure, oxide

INTRODUCTION

Schreyerite, $V_2Ti_3O_9$, was first discovered in metamorphic rocks of the Kwale district, Kenya (Medenbach and Schmetzer 1978; Bernhardt et al. 1983). It also occurs in a pyrite deposit at Sartra, Sweden (Zakrzewski et al. 1982), in a Pb–Zn ore deposit at Rampura Agucha, India (Höller and Stumpfl 1995), and in metamorphic rocks of the Ol'khon complex on the western shore of Lake Baikal, Russia (Boronikhin et al. 1990). Schreyerite usually occurs as polysynthetically twinned exsolution lamellae in rutile, and until now, single-crystal X-ray structure solution has not been possible. Recently, schreyerite was found in metamorphic rocks of the Sludyanka complex at the southern shore of Lake Baikal, Russia. Instead of the usual intergrowths with rutile, single crystals of schreyerite were found, associated with titanite.

Phase equilibria in the system V_2O_3 – TiO_2 at 1200 °C (Brach et al. 1977) yielded the intermediate phases V_2TiO_5 (berdesinskiite), $V_2Ti_2O_7$, and $V_2Ti_4O_{11}$. $V_2Ti_3O_9$ was also found, but it was interpreted to be a metastable phase at this temperature with a free energy slightly larger than those of the adjacent phases $V_2Ti_2O_7$ and $V_2Ti_4O_{11}$. Both the vanadium and titanium end-members $V^{3+}_2V^{4+}_3O_9$ and $Ti^{3+}_2Ti^{4+}_3O_9$ can be prepared easily (Brach et al. 1977), but these homologues have a triclinic structure of different topology (LePage et al. 1991; Marezio et al. 1977) compared to monoclinic $V_2Ti_3O_9$ (schreyerite). It is not clear which structure type is represented by metastable $V_2Ti_3O_9$ (Brach et al. 1977).

Attempts to synthesize and to derive a structural model of the M_5O_9 compound in the system $(Cr,Fe)_2Ti_{n-2}O_{2n-1}$ began with Grey and Reid (1972). Oxidation of ilmenite at 770 °C yielded the reaction: $6 FeTiO_3 + 3O \rightarrow 2 Fe_2Ti_3O_9 + Fe_2O_3$. Above 800 °C, $Fe_2Ti_3O_9$ decomposed to pseudobrookite and rutile. Between 1050 and 1250 °C, predominantly single-phase $(Fe,Cr)_2Ti_3O_9$ was obtained, and electron diffraction confirmed the unit-cell dimensions previously derived from X-ray powder data for $Fe_2Ti_3O_9$.

The structures of $(Cr,Fe)_2Ti_{n-2}O_{2n-1}$, with $n = 6, 7, 8$, and 9 , are closely related to that of rutile and may be derived from it by crystallographic shear (Magneli-Andersson phases). Grey and Reid (1972) recognized that the members with $n = 3, 4$, and 5 are closely related to the high-pressure modification of TiO_2 with the structure of α - PbO_2 , and may also be derived from it by crystallographic shear. Subsequently, they depicted (their Fig. 5) an inferred structure for $(Fe,Cr)_2Ti_3O_9$ (monoclinic with $a = 7.1$, $b = 4.9$, $c = 18.6$ Å, $\beta = 119.7^\circ$). However, this model proved to be incorrect and was revised by Grey et al. (1973). As will be shown in this paper, the new improved model is the correct structure of schreyerite. When schreyerite $V_2Ti_3O_9$ was described as a new mineral, Medenbach and Schmetzer (1978) noticed the similarity of its powder-diffraction pattern to $(Fe,Cr)_2Ti_3O_9$, and they indexed their powder data with the settings of both Grey and Reid (1972) and Grey et al. (1973).

The aim of the present study is to provide structural details of schreyerite from a new locality at the Baikal region (Russia) and to show that this schreyerite with slightly modified chemical composition has the same structure as schreyerite from the type locality described by Medenbach and Schmetzer (1978)

* E-mail: ndoebelin@gmx.ch

and Bernhardt et al. (1983). In addition, the excellent study by Grey et al. (1973) provides the basis for a description of the schreyerite structure as a 1:1 member of a polysomatic series composed of alternating slabs of berdesinskiite V_2TiO_5 (Bernhardt et al. 1983) and Ti_2O_4 (high-pressure phase of TiO_2 with the α - PbO_2 structure).

GEOLOGICAL SETTING AND OCCURRENCE OF SCHREYERITE

The Sludyanka complex belongs to one of the metamorphic terranes of the Central Asian fold belt. The terrain is situated to the south of Lake Baikal near the boundary with the Siberian craton. The Sludyanka complex includes folded supracrustal series of intercalated mafic granulite, gneiss, marble, and carbonate-silicate rocks metamorphosed in granulite facies. Metamorphism of the Sludyanka group corresponds to granulite facies of moderate pressure (maximum P,T -conditions: $T = 800$ – 830 °C, $P = 6$ – 8 kbar). The age of metamorphism and syn- and late metamorphic magmatic and metasomatic processes is Early Paleozoic (460–490 Ma); the age of the protolith is unknown and is thought to be Early Paleozoic or Proterozoic.

One of the most typical types of metasedimentary rocks in the Sludyanka complex consists of diopside, quartz, and calcite, indicating siliceous-dolomite sediments as the protolith. These rocks are usually referred to as quartz-diopside rocks and include several assemblages according to the content of the principal minerals: diopsidite, diopside-quartz, diopside-calcite rocks, calciphire, diopside-bearing quartzite (up to 80–90% quartz). Apatite can be relatively abundant (1–3 up to 50 wt%), particularly in metaphosphorites. Thin layers and lenses, characterized by relatively high contents of Cr and V (0.1–0.7 wt% $Cr_2O_3 + V_2O_5$, with Cr/V ratio from 15:1 to 1:6) and various Cr-V minerals, occur in this type of rock (Reznitsky and Sklyarov 1996). The most diverse assemblages of chromium and vanadium minerals (as well as Cr-V-bearing minerals, mostly in trace amounts) usually occur in high-silica (80–95 wt%) lenses and thin layers in diopside-calcite rocks and marbles. Studying the new mineral vanadiumdravite of the tourmaline group from such high-silica lenses with high V/Cr ratio, we have found two unknown Ti-V oxides (Reznitsky et al. 2001) and later, after careful investigations of the heavy fraction, other ore minerals including schreyerite.

Cr-V mineral associations in investigated samples are similar, differing only in detail. They include, in association with quartz, (Cr-V)-bearing diopside, tremolite, di- and trioctahedral micas, Cr-bearing tourmalines of the dravite-vanadiumdravite series, Cr-bearing goldmanite, eskolaite-karelianite, V-bearing chromite and titanite, and barite. Sporadically occurring ilmenite, magnetite, and anatase also contain vanadium. Together with schreyerite and berdesinskiite, unknown Ti-V oxides and two Ba-Ti-V oxides (one of the mannardite-ankangite type and another unknown oxide belonging to the derbylite group) are present.

In all V-Ti and Ba-V-Ti oxides of this association, a combination of microprobe and structure data indicates the presence of V^{4+} and V^{3+} and the isomorphic substitution $V^{4+} \rightarrow Ti^{4+}$. Therefore, an extensive solid-solution of the form $V_3O_5(V_2^{3+}V^{4+}O_5)-V_2TiO_5$ (berdesinskiite) is possible.

Schreyerite from Sludyanka forms anhedral and rarely sub-

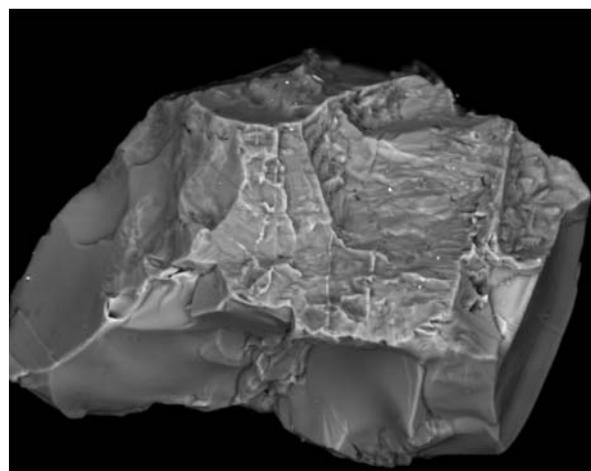


FIGURE 1. Scanning electron-microscopic image of schreyerite crystal studied by single-crystal X-ray diffraction. The width of the picture is 0.14 mm.

hedral grains (Fig. 1), sometimes as inclusions in quartz, but usually intergrown with silicates and opaque Cr-V minerals. The maximum size of the grains is 100–150 μm .

EXPERIMENTAL METHODS

Chemical analysis

After crushing the rock sample to grain sizes of 0.2–0.3 mm, opaque minerals were extracted by electromagnetic separation using pure Clerichi solution. These grains were pressed into plastic, polished, and analyzed with a JXA-733 electron microprobe at the Institute of Geochemistry, Irkutsk, as well as with a modified MAR-3 microprobe at the Geological Institute of Ulan-Ude. Both devices were operated at 15 kV acceleration voltage and 20 nA beam current using a fine-focused beam (2 and 10 μm). Raw data were reduced and converted into oxide weight percentages using the ZAF and PAP (Pouchou and Pichoir 1991) programs. The following standards were used: synthetic V_2O_5 (V), chromite UV-126, 79/12, and Cr-spinel (Cr, Fe, Al), rutile and ilmenite (Ti), blue diopside (Si, Mg), and spessartine (Mn). For additional control, some grains were analyzed with an ABT-55 electron microscope equipped with a LINK AN-1000/S85 device, using pure metals (Ti, V, Cr, Mn, Fe) and oxides (SiO_2 , MgO , Al_2O_3) as standards. The results of the analyses using different instruments gave almost the same element concentrations. Grains for X-ray analysis were selected after semi-quantitative analysis with a LEO electron microscope to check for uniform compositions.

Structure determination

The structure of a schreyerite crystal (ca. $0.10 \times 0.07 \times 0.05$ mm) was studied by single-crystal X-ray diffraction using an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated $MoK\alpha$ X-radiation. Cell dimensions were obtained from high-angle data ($\theta > 20^\circ$), giving a C-centered monoclinic lattice with $a = 17.102(2)$, $b = 5.0253(5)$, $c = 7.0579(8)$ Å, $\beta = 106.636(10)^\circ$, $V = 581.20(12)$ Å³. A total of 1432 reflections was measured, of which 1277 were unique. Data reduction, including background, Lorentz and polarization corrections, and an empirical absorption correction based on ψ scans, was done using the SDP program library (Enraf-Nonius 1983). As indicated by systematic absences, the structure was solved in space group $C2/c$ by direct methods and refined using the program SHELX-97 (Sheldrick 1997), converging at $R_1 = 2.84\%$. Refinements were done with anisotropic displacement parameters for all sites. The refined chemical composition was constrained to the ideal composition of schreyerite ($V_2Ti_3O_9$) because the scattering factors of Ti^{4+} , V^{3+} , V^{4+} , and Cr^{3+} are very similar.

In addition, single-crystal X-ray data were collected for the same (twinned) schreyerite crystal intergrown with rutile used by Bernhardt et al. (1983) for the improved X-ray powder data from type-locality schreyerite from Kenya. Our recollected data showed that the diffraction pattern can be indexed in space group $C2/c$ with $a = 17.023(9)$, $b = 5.012(2)$, $c = 7.058(5)$ Å, $\beta = 106.20(4)^\circ$, $V = 578.3(6)$ Å³.

This confirms our suggestion that type-locality schreyerite and the crystal from the Baikal region have the same structure.

RESULTS

Chemical composition

According to electron-microprobe analysis, the main components of the mineral are Ti and V, with minor amounts of Cr and Fe (Table 1). The ratio $Ti:R^{3+}$ (Cr, V, Fe, Al) is nearly 1:1, which is not consistent with the refined ratio $R^{4+}:R^{3+} = 3:2$. This can be explained by the fact that Ti^{4+} is partly replaced by V^{4+} . The $V^{4+}:V^{3+}$ ratio was calculated to maintain charge balance and to be consistent with the refined composition (Table 2). Usual substitutions are $Ti^{4+} \leftarrow V^{4+}$ and $V^{3+} \leftarrow Cr^{3+}$ (up to 5.2 wt% Cr_2O_3 , or up to 0.27 a.f.u.), and minor Fe^{3+} (up to 1.13 wt% Fe_2O_3 , or 0.05 a.f.u.). Contents of other analyzed elements (Si, Al, Mn, Mg) are insignificant or not detected. The grain selected for X-ray investigation is relatively uniform in composition (three determinations, mean composition TiO_2 : 51.83, V_2O_5 : 44.41, Cr_2O_3 : 3.04 wt%) and corresponds to the average composition of schreyerite as determined by electron-microprobe analysis.

Crystal structure

Details of the diffraction experiment and structure refinement are given in Table 3. Atom coordinate sites, occupancies, and anisotropic displacement parameters of the refined structure are given in Table 4. The three cation sites Ti1, Ti2, and V3 are each coordinated by six oxygen atoms within rather similar bond distances: $Ti1-O = 1.987-2.025$, $Ti2-O = 1.913-2.070$, $V3-O = 1.851-2.191$ Å (Table 5). The oxygen atoms bonding to Ti1 form an almost perfect octahedron with bond angles close to 180° and 90° , respectively, whereas the Ti2 and V3 octahedra are slightly distorted. These octahedra are connected to two different types of chains of edge-sharing octahedra usually referred to as a berdesinskiite-type chain and α - PbO_2 -type chain. As shown

in Figure 2, these chains are connected to staircase-like sheets, which alternate to form a framework.

There are two distinct tetravalent sites and one trivalent site, leading to an ionic ratio $R^{4+}:R^{3+} = 3:2$. As electron-microprobe analysis shows that all three sites are occupied by elements with similar scattering factors (Ti, V, Cr), one cannot clearly assign each element to a particular position. In addition, EMP analysis indicates that vanadium occurs in both trivalent and tetravalent oxidation states, and partly replaces Ti^{4+} . However, as the structure contains one face-sharing octahedron (V3), one can assume that this site is occupied by the trivalent cation to minimize

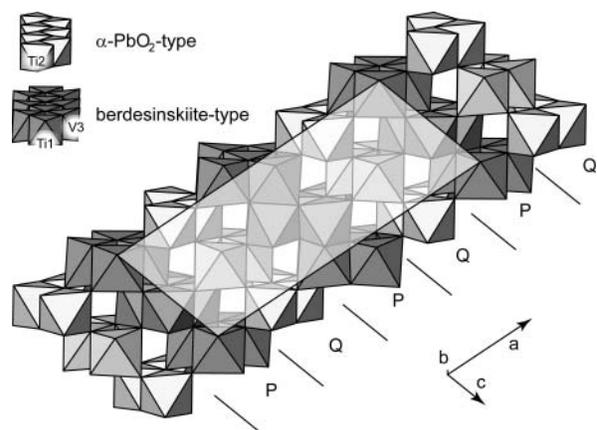


FIGURE 2. A polyhedral representation of the schreyerite structure projected approximately along $[010]$. Two types of chains can be distinguished: the dark polyhedra form berdesinskiite-type (V_3O_5 -type) chains of edge-sharing octahedra, whereas the light polyhedra form α - PbO_2 -type chains of edge-sharing octahedra. The chains are interconnected to staircase-like layers (P and Q slabs). Different stacking sequences of P and Q slabs are possible. Schreyerite shows maximum alternation, also expressed as P_1Q_1 .

TABLE 1. Representative chemical analyses and average composition of schreyerite from the Sludyanka complex, Russia

	1	2	3	4	5	6	7
SiO_2	0.00	0.00	0.00	0.26	0.00	0.22	0.12 (0.00–0.34)
TiO_2	51.47	51.93	51.78	53.46	53.3	52.8	51.91 (49.89–53.46)
Al_2O_3	0.00	0.00	0.00	0.14	0.00	0.00	0.04 (0.00–0.21)
Cr_2O_3	4.11	4.15	5.20	2.86	3.93	3.63	3.06 (0.79–5.20)
$V_2O_5^*$	42.57	41.72	41.57	42.74	41.14	41.35	43.26 (41.72–45.11)
Fe_2O_3	0.97	0.95	0.60	0.19	0.82	0.75	0.75 (0.00–1.13)
MnO	0.00	0.00	0.00	0.00	0.00	0.32	0.11 (0.00–0.32)
MgO	0.00	0.06	0.00	0.00	0.00	–	0.04 (0.00–0.24)
Total	99.12	98.81	99.09	99.65	99.19	99.07	99.30 (96.58–100.55)
VO_3^\dagger	10.19	9.66	9.84	8.17	8.27	8.86	9.94 (8.17–11.45)
$V_2O_3^\dagger$	33.36	32.99	32.62	35.36	33.67	33.35	34.28 (32.13–35.76)
Total	100.1	99.74	100.04	100.44	99.99	99.93	100.26 (97.57–101.54)

Notes: 1–6 = analyses of individual grains; 7 = average composition of schreyerite (17 analyses), maximal and minimal values in parentheses.

* All vanadium as V_2O_5 .

† V^{3+} and V^{4+} calculated according to the ideal formula.

TABLE 2. Unit formulae (9 O atoms and 5 cations) for schreyerite based on the results in Table 1

	1	2	3	4	5	6	7
Si	–	–	–	0.017	–	0.014	0.006 (0.000–0.022)
Ti	2.519	2.549	2.536	2.600	2.610	2.586	2.536 (2.475–2.610)
V^{4+}	0.481	0.457	0.464	0.383	0.390	0.418	0.468 (0.390–0.536)
Al	–	–	–	0.011	–	–	0.003 (0.000–0.016)
V^{3+}	1.741	1.727	1.703	1.834	1.758	1.741	1.785 (1.665–1.880)
Cr^{3+}	0.212	0.214	0.268	0.146	0.202	0.187	0.157 (0.040–0.268)
Fe^{3+}	0.047	0.047	0.029	0.009	0.040	0.037	0.036 (0.009–0.054)
Mn	–	–	–	–	–	0.018	0.005 (0.000–0.018)
Mg	–	0.006	–	–	–	–	0.004 (0.000–0.023)

repulsion between central cations. The Ti1 and Ti2 octahedra are connected by edge- and corner-sharing, which leads to a greater separation between central cations and less repulsion in the case of high positive charge.

DISCUSSION

In the Cr₂Ti_{n-2}O_{2n-1} system the mixed oxides with $n = 6, 7, 8,$ and 9 are isomorphous with the homologous series Ti_nO_{2n-1} and V_nO_{2n-1} (Andersson et al. 1959). The first attempts to describe the crystal structure of Me₂³⁺Ti_{n-2}O_{2n-1}-like phases with $n < 6$ from X-ray powder patterns and electron diffraction were published by Grey and Reid (1972). According to the nomenclature used by Grey et al. (1973), the structure-building sheets are referred to as *P* slabs (V₃O₅, berdesinskiite-type) and *Q* slabs (α-PbO₂-type, Ti₂O₄), respectively. Grey and Reid (1972) described the structure of a high temperature phase, $n = 5$, of composition (Cr,Fe)₂Ti₃O₉ as a *P*₂*Q*₂ polysome with stacking sequence *PPQQ*... Later, that structure was revised by the same authors (Grey et al. 1973) and described as a *PQPQ*... sequence, because the new structural model was most compatible with the observed electron-diffraction pattern. This is in perfect agreement with the fact that polysomes with maximum alternation of *P* and *Q* slabs are the most abundant in Nature. Periodic intergrowths of the corresponding structural slabs can be expressed as *pM*₃O₅^{*q*}Ti₂O₄ or *P_pQ_q*. This approach also allows derivation of phases with non-integer values of n . The unit cell Grey et al. (1973) used to describe the revised structure is illustrative in that the monoclinic angle describes

the “slope” of the *P* and *Q* slabs (Fig. 3). However, their cell ($a = 7.06, b = 5.01, c = 25.06 \text{ \AA}, \beta = 139^\circ$) has a rather obtuse monoclinic angle and is *A*-centered, and can be transformed (by 201, 010, $\bar{1}00$) to a reduced *C*-centered setting, as used in the present study. The original setting by Grey and Reid (1972), $a = 7.06, b = 5.01, c = 18.74 \text{ \AA}, \beta = 119^\circ$, is also *A*-centered and can be transformed (201, 010, $\bar{1}00$) to the standard setting for space group *C2/c*. The various settings are summarized in Table 6 and Figure 3.

The end-member phase berdesinskiite V₂TiO₅ (*P* slab) of the polysomatic series was described by Bernhardt et al. (1983) as a mineral. However, the structure has not been published for a crystal of composition V₂TiO₅, but it has been assumed to be analogous to Fe₂TiO₅ (Drofenik et al. 1981), based on corresponding unit-cell dimensions and symmetry (Fig. 4). Our own structure refinements of berdesinskiite (from the same Baikal locality as schreyerite) confirm this assumption.

To our knowledge, the *P*₁*Q*₁ schreyerite structure is the only polysome of this series in the system V₂O₃-TiO₂ that has been

TABLE 3. X-ray data collection and refinement parameters for schreyerite

Sample	IV8-13
Crystal size (mm)	0.10 × 0.07 × 0.05
Chemical composition	(V _{1.785} Cr _{0.157} Fe _{0.036} (Ti _{2.536} V _{0.468})O ₉)
Diffractometer	Enraf Nonius CAD4
X-ray radiation	fine focus sealed tube, MoK α
X-ray power	50 kV, 40 mA
Temperature	293 K
Space group	<i>C2/c</i>
Z	4
Cell dimensions <i>a, b, c</i> (Å)	17.102(2), 5.0253(5), 7.0579(8)
β (°)	106.636(10)
Cell volume (Å ³)	581.20(12)
Absorption correction	Empirical ψ scans
Maximum 2 θ	69.83°
Measured reflection	1432
Index range	0 ≤ <i>h</i> ≤ 27; 0 ≤ <i>k</i> ≤ 8; -11 ≤ <i>l</i> ≤ 10
Unique reflections	1277
Reflections > 4 σ <i>I</i>	727
<i>R</i> _{int}	0.0195
<i>R</i> _s	0.0572
Number of l.s. parameters	67
Goof	0.999
<i>R</i> ₁ , <i>F</i> _o > 4 σ (<i>F</i> _o)	0.0284
<i>R</i> ₁ , all data	0.0775
<i>wR</i> ₂ (on <i>F</i> _o ²)	0.0923

TABLE 4. Atom positional parameters, occupancies, and anisotropic displacement parameters for schreyerite from the Sludyanka complex, Russia

Atom	Occupancies	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Ti1	1	0	0	0	0.233(7)	0.0035(2)	0.0021(2)	0.0032(2)	0.0003(3)	0.0009(2)	0.0000(3)
Ti2	1	-0.21608(2)	0.0067(1)	-0.07227(6)	0.560(6)	0.0072(2)	0.0058(2)	0.0074(2)	0.0007(2)	0.0007(1)	-0.0011(3)
V3	1	-0.07555(3)	-0.5010(1)	0.10036(6)	0.612(6)	0.0101(2)	0.0068(2)	0.0053(2)	-0.0011(2)	0.0005(1)	0.0003(2)
O1	1	-0.1085(1)	0.1585(4)	-0.0203(3)	0.47(3)	0.0040(7)	0.0049(8)	0.0089(7)	-0.0005(6)	0.0017(6)	-0.0008(6)
O2	1	-0.1742(1)	-0.3316(4)	0.0731(3)	0.50(2)	0.0055(7)	0.0051(7)	0.0091(7)	0.0005(7)	0.0034(6)	0.0004(6)
O3	1	-0.0474(1)	-0.3463(4)	-0.1300(3)	0.40(2)	0.0061(8)	0.0041(7)	0.0051(7)	-0.0004(6)	0.0016(6)	-0.0006(6)
O4	1	-0.2262(1)	-0.1679(4)	-0.3190(3)	0.52(2)	0.0081(7)	0.0063(8)	0.0058(7)	-0.0016(7)	0.0025(6)	-0.0005(6)
O5	1	0	0.1965(5)	-0.25	0.37(3)	0.007(1)	0.003(1)	0.0039(9)	0	0.0018(8)	0

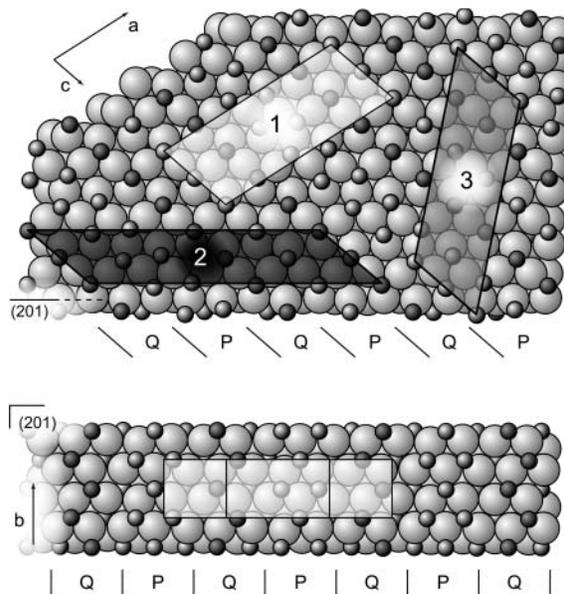


FIGURE 3. The schreyerite structure shown as a closest oxygen-packing representation projected normal to (010) (**top**) and (201) (**bottom**). The large light spheres represent oxygen atoms and the small dark spheres represent octahedrally coordinated cations. Three different monoclinic unit cells are shown: (1) the unit cell presented in this study, (2) the unit cell reported by Grey et al. (1973), and (3) the unit cell reported by Grey and Reid (1972). Axis labels and indices apply to unit cell 1.

TABLE 5. Interatomic distances (Å) and angles (°) for the refined schreyerite structure

Ti1 -	Distance	Angles				
O1	1.989(2)					
O1	1.989(2)	180.0(1)				
O5	2.024(1)	91.45(7)	88.55(7)			
O5	2.024(1)	88.55(7)	91.45(7)	180		
O3	2.027(2)	93.87(8)	86.13(8)	82.87(8)	97.13(8)	
O3	2.027(2)	86.13(8)	93.87(8)	97.13(8)	82.87(8)	180.0(2)
Ti1 -	O1	O1	O5	O5	O3	
Ti2 -	Distance	Angles				
O4	1.915(2)					
O1	1.929(2)	100.78(9)				
O4	1.953(2)	97.05(5)	95.23(9)			
O2	2.011(2)	90.18(9)	93.27(8)	167.62(9)		
O4	2.017(2)	169.7(1)	89.52(8)	81.36(8)	89.73(8)	
O2	2.073(2)	87.55(8)	169.57(8)	89.93(8)	80.32(8)	82.28(9)
Ti2 -	O4	O1	O4	O2	O4	
V3 -	Distance	Angles				
O2	1.852(2)					
O1	1.924(2)	102.72(8)				
O3	1.981(2)	103.99(8)	92.35(9)			
O3	1.984(2)	99.39(9)	95.43(8)	153.1(1)		
O5	2.086(2)	97.45(8)	159.80(7)	81.52(7)	82.35(6)	
O3	2.193(2)	173.07(8)	83.25(8)	79.04(9)	76.33(8)	76.71(6)
V3 -	O2	O1	O3	O3	O5	

TABLE 6. An overview of the different unit cells mentioned in this study

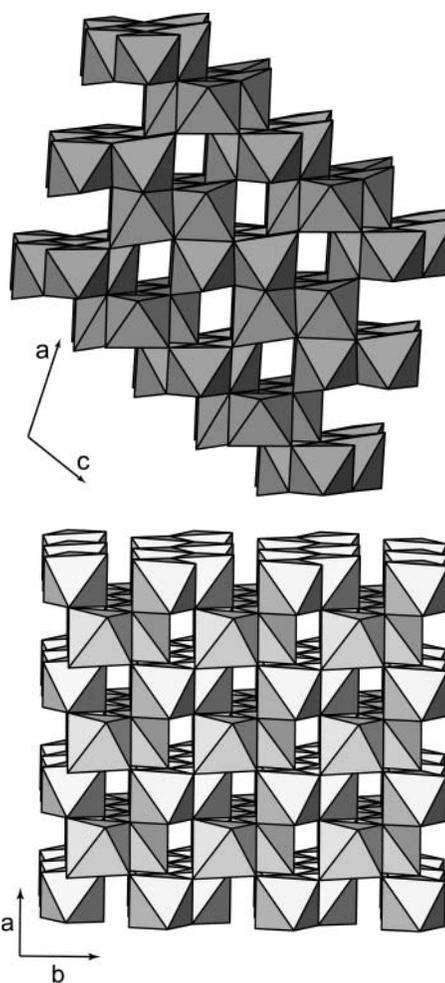
	A	B	C	D
a (Å)	18.74	25.06	17.023(9)	17.102(2)
b (Å)	5.01	5.01	5.012(2)	5.0253(5)
c (Å)	7.06	7.06	7.058(5)	7.0579(8)
β (°)	119.4	139.35	106.20(4)	106.636(10)
V (Å ³)	577.48	577.43	578.3(6)	581.20(12)

Note: A: The cell published by Grey and Ried (1972). B: The revised cell published by Grey et al. (1973). C: Schreyerite from Kenia, reinvestigated in this study. The original data were published by Bernhardt et al. (1983). D: Schreyerite from Sludyanka complex described in the present study.

found to date. The synthetic phases $V_2Ti_2O_7$, $V_2Ti_4O_{11}$, and $V_2Ti_8O_{15}$ (Brach et al. 1977) in the system $V_2Ti_{n-2}O_{2n-1}$ at 1200 °C, corresponding to $n = 4, 6,$ and $8,$ are isomorphous with members of the homologous series Ti_nO_{2n-1} and V_nO_{2n-1} , and are thus not composed of P and Q slabs. At high temperature ($T > 1200$ °C) in the more complex system Cr_2O_3 - Fe_2O_3 - TiO_2 - ZrO_2 , several phases occur which are assembled of P and Q slabs (Grey et al. 1973); for $n = 4$ the sequence $QPP..$, for $n = 6$ $QPQQP..$, and for $n = 8$ $PQQPQPQQ..$ These n values are the same as those found in $V_2Ti_{n-2}O_{2n-1}$, indicating the possibility of polymorphism. If additional $V_2Ti_{n-2}O_{2n-1}$ phases with a structure composed of berdesinskiite (V_2TiO_5) and Ti_2O_4 (α - PbO_2 structure) slabs are discovered, they should be regarded as schreyerite polysomes, adopting the rules for a polysomatic series.

The only polysome of the general $pM_3O_5qM_2O_4$ series (except schreyerite) for which a crystal-structure refinement is available is the $n = 4$ member $CrFeTi_2O_7$ (Grey and Mumme 1972), which has the stacking sequence P_2Q_1 (Fig. 5). The structure of most other (P, Q) polysomes have not been solved from single-crystal X-ray data but are derived as “models” from systematic features in electron-diffraction patterns (Grey et al. 1973).

Peculiar to schreyerite from the Baikal region is the partial V^{4+} for Ti^{4+} substitution indicating highly oxidizing conditions. Similar substitutions have also been observed for berdesinskiite

**FIGURE 4.** The end-members of the polysomatic series P_pQ_q are the structures of berdesinskiite (top, V_2TiO_5) (Drofenik et al. 1981; Bernhardt et al. 1983) and α - PbO_2 (bottom).

from the same locality (to be published). The occurrence of both V^{4+} and V^{3+} is rare in minerals. We are only aware of one other example, the new mineral zoltaite $Ba(V^{4+},Ti)_2(V^{3+},Ti,F^{2+},Cr,Mg)_{12}(Si,Al)_2O_{27}$ (Bartholomew et al. 2005).

According to a recent personal communication with W. Schreyer, experiments were done at Bochum some 15 years ago to synthesize schreyerite (and perhaps berdesinskiite) under hydrothermal conditions. At 3 kbar and 700 °C a mixture of V_2O_3 and TiO_2 in the stoichiometric ratio of 1:3 reacted to single-phase schreyerite after 3 days at the oxygen fugacity of the wustite-magnetite buffer and in the presence of water. However, the addition of as much as 30 wt% excess V_2O_3 relative to that in $V_2Ti_3O_9$ did not produce any additional berdesinskiite, only schreyerite. This indicates solid solution in schreyerite, with V^{4+} replacing Ti^{4+} as well. In addition, Kosuge and Kachi (1975) presented a phase diagram of the system TiO_2 - VO_2 - Ti_2O_3 - V_2O_3 and emphasized complete solid-solution in the pseudo-binary system V_nO_{2n-1} - $V_2Ti_{n-2}O_{2n-1}$ ($3 \leq n \leq 7$). Unfortunately, their reference for this part of the phase diagram (Okinaka, H., Makino, T., Kosuge, K., Kachi, S., to be published) could not be located.

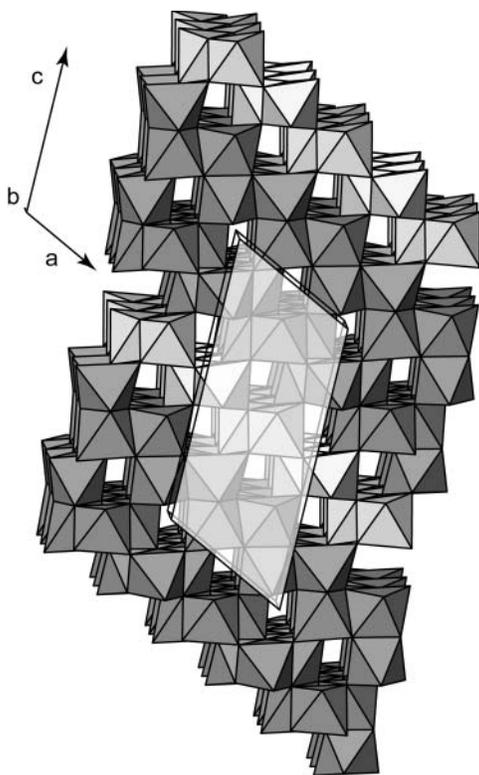


FIGURE 5. The structure of $(CrFe)Ti_2O_7$ (Grey and Mumme 1972) represents another polysome of the $pM_3O_5 \cdot qM_2O_4$ series with the stacking sequence P_2Q_1 .

Their complete solid-solution between V_5O_9 and $V_2Ti_3O_9$ suggests that their $V_2Ti_3O_9$ phase is not isotypic with schreyerite, but is related to triclinic V_5O_9 (LePage et al. 1991).

There are still several unanswered questions concerning the binary system V_2O_3 - TiO_2 , particularly under geologically relevant P and T conditions. Smyslova et al. (1982) reported a monoclinic dimorph of schreyerite, named kyzylkumite, with $a = 33.80$, $b = 4.578$, $c = 19.99$ Å, $\beta = 93.4^\circ$ (as determined by Laue and oscillation photographs). This mineral was found in fine veins cutting siliceous schists, associated with chlorite, pyrite, and rutile. The crystal structure of this dimorph could not be investigated due to complex twinning and low crystal quality. Nevertheless, the cell dimensions and X-ray powder data are significantly different from those of triclinic V_5O_9 and monoclinic schreyerite $V_2Ti_3O_9$. The periodicity of 4.578 Å along b emphasizes that kyzylkumite represents a structure composed of two octahedral layers where each layer is ca. 2.3 Å thick. Kyzylkumite is thus not structurally related to the polysomatic series derived from V_2TiO_5 and Ti_2O_4 (with α - PbO_2 structure). Most probably, kyzylkumite has some structural relation to tivanite $TiVO_3(OH)$ (Grey and Nickel 1981) and carmichaelite $(Ti,Cr,Fe)_2O_3(OH)$ (Wang et al. 2000), both of which have in common an octahedral two-layer structure and a periodicity of 4.56 Å along b .

Olkhonskite $(Cr,V)_2Ti_3O_9$ (Koneva et al. 1996) is isotypic with schreyerite. An important step toward understanding the stability of phases in the Cr_2O_3 - Fe_2O_3 - TiO_2 system was taken

by Pownceby et al. (2001) who explored the ternary phase diagram between 1000 and 1300 °C. At 1200 °C, the ternary phases $(Cr,Fe)_2TiO_5$ (berdesinskiite type), $(Cr,Fe)_2Ti_2O_7$ (P_2Q polysome, Grey and Mumme 1972), $(Cr,Fe)_6Ti_7O_{23}$ ($PQPQPQPQP$ polysome, Grey et al. 1973), $(Cr,Fe)_4Ti_5O_{16}$ ($QPQPQP$ polysome, Grey et al. 1973), and $(Cr,Fe)_2Ti_3O_9$ ($PQPQ$ polysome, olkhonskite) were analyzed. At 1100 and 1000 °C, no ternary phase between $(Cr,Fe)_2TiO_5$ (berdesinskiite type) and $(Cr,Fe)_2Ti_3O_9$ ($PQPQ$ polysome, olkhonskite) was found. This also agrees with the predominant occurrence of olkhonskite $(Cr,V)_2Ti_3O_9$ as lamellae in rutile and $(Cr,Fe)_2TiO_5$ (berdesinskiite type) as rims around olkhonskite, as described by Koneva (2002) for the Cr-V-Ti oxide minerals of the Olkhon series of the Lake Baikal area. Surprisingly, Koneva (2002) also analyzed (by electron microprobe) a few tiny inclusions of $(Cr,V)_2Ti_4O_{11}$ and $(Cr,V)_2Ti_2O_7$ in rutile. In particular, $(Cr,V)_2Ti_2O_7$ should not be found in rutile if olkhonskite is a stable phase in this assemblage. However, as shown in this study, a $(Cr,V,Fe)/Ti$ ratio of 1:1 does not necessarily indicate a phase of $(Cr,V)_2Ti_2O_7$ composition. If vanadium occurs as V^{4+} and V^{3+} , the latter inclusions could also be interpreted as schreyerite-olkhonskite with partial substitution of Ti^{4+} by V^{4+} .

ACKNOWLEDGMENTS

The study of mineral composition was partly supported by Russian Foundation of Basic Research (project 05-05-64200). We are grateful to N. Karmanov, L. Suvorova, and E. Galuskin for help with the microprobe and electron-microscope investigations. N.D. and T.A. acknowledge support from the Swiss Science Foundation. The authors acknowledge comments and corrections by W. Schreyer and H.-J. Bernhardt.

REFERENCES CITED

- Andersson, S., Sundholm, A., and Magnéli, A. (1959) A homologous series of mixed titanium chromium oxides $Ti_{n-2}Cr_2O_{2n-1}$ isomorphous with the series Ti_nO_{2n-1} and V_nO_{2n-1} . *Acta Chemica Scandinavica*, 13, 989–997.
- Bartholomew, P.R., Mancini, F., Cahil, C., Harlow, G.E., and Bernhardt, H.-J. (2005) Zoltaiite, a new barium-vanadium neosubstituted mineral from British Columbia: Description and crystal structure. *American Mineralogist*, 90, 1655–1660.
- Bernhardt, H.-J., Schmetzer, K., and Medenbach, O. (1983) Berdesinskiite, V_2TiO_5 , a new mineral from Kenya and additional data for schreyerite, $V_2Ti_3O_9$. *Neues Jahrbuch für Mineralogie Monatshefte*, 1983, 110–118.
- Boronikhin, V.A., Dmitrieva, M.T., Koneva, A.A., and Korikovskii, S.P. (1990) Chromian schreyerite and chromium-vanadium-manganese-iron-zinc spinel in sillimanite-cordierite quartzitic schists in of the Olkhon region, southwestern Baikal. *Doklady Akademii Nauk SSSR*, 314, 447–451.
- Brach, B., Grey, I.E., and Li, C. (1977) Phase equilibria in the vanadium(3+) oxide-titanium(3+) oxide-titanium(4+) oxide system. *Journal of Solid State Chemistry*, 20, 29–41.
- Drofenik, M., Golič, L., Hanžel, D., Kraševc, V., Prodan, A., Bakker, M., and Kolar, D. (1981) A new monoclinic phase in the Fe_2O_3 - TiO_2 system. I. Structure determination and Mössbauer spectroscopy. *Journal of Solid State Chemistry*, 40, 47–51.
- Enraf-Nonius (1983) Structure determination package (SDP). Enraf-Nonius, Delft, The Netherlands, (computer program).
- Grey, I.E. and Mumme, W.G. (1972) The structure of $CrFeTi_2O_7$. *Journal of Solid State Chemistry*, 5, 168–173.
- Grey, I.E. and Nickel, E.H. (1981) Tivanite, a new oxyhydroxide mineral from Western Australia, and its structural relationship to rutile and diasporite. *American Mineralogist*, 66, 866–871.
- Grey, I.E. and Reid, A.F. (1972) Shear structure compounds $(Cr,Fe)_2Ti_{n-2}O_{2n-1}$ derived from the α - PbO_2 structural type. *Journal of Solid State Chemistry*, 4, 186–194.
- Grey, I.E., Reid, A.F., and Allpress, J.G. (1973) Compounds in the system Cr_2O_3 - Fe_2O_3 - TiO_2 - ZrO_2 based on intergrowth of the α - PbO_2 and V_5O_9 structural types. *Journal of Solid State Chemistry*, 8, 86–99.
- Höller, W. and Stumpf, E.F. (1995) Cr-V oxides from the Rampura-Agucha Pb-Zn (Ag) deposit, Rajasthan, India. *Canadian Mineralogist*, 33, 745–752.
- Koneva, A.A. (2002) Cr-V oxides in metamorphic rocks, Lake Baikal, Russia. *Neues Jahrbuch für Mineralogie Monatshefte*, 2002, 541–550.

- Koneva, A.A., Piskunova, L.F., Ushchapovskaya, Z.F., and Konev, A.A. (1996) Olkhonskite $(Cr,V)_2Ti_3O_9$ —A new mineral from the Priolkhon'ye (Abstract). *American Mineralogist*, 81, 251–252.
- Kosuge, K. and Kachi, S. (1975) Electron-diffraction and electron-microscopic observation of the pseudo binary TiO_2 - V_2O_5 system. *Chemica Scripta*, 8, 70–83.
- LePage, Y., Bordet, P., and Marezio, M. (1991) Valence ordering in V_5O_9 below 120 K. *Journal of Solid State Chemistry*, 92, 380–385.
- Marezio, M., Tranqui, D., Lakkis, S., and Schlenker, C. (1977) Phase transitions in Ti_3O_9 single crystals: Electrical conductivity, magnetic susceptibility, specific heat, electron paramagnetic resonance, and structural aspects. *Physical Review B*, 16, 2811–2821.
- Medenbach, O. and Schmetzer, K. (1978) Schreyerite, $V_2Ti_3O_9$, a new mineral. *American Mineralogist*, 63, 1182–1186.
- Pouchou, J.L. and Pichoir, F. (1991) Quantitative analysis of homogeneous or stratified microvolumes applying the model "PAP". In K.F.J. Heinrich and D.E. Newbury, Eds., *Electron Probe Quantitation*, p. 31–75. Plenum Press, New York.
- Pownceby, M.I., Fisher-White, M.J., and Swamy, V. (2001) Phase relations in the system $Fe_2O_3 + Cr_2O_3 + TiO_2$ between 1000 and 1300 °C and the stability of $(Cr,Fe)_2Ti_{n-2}O_{2n-1}$ crystallographic shear structure compounds. *Journal of Solid State Chemistry*, 161, 45–56.
- Reznitsky, L.Z. and Sklyarov, E.V. (1996) Unique Cr-V mineral association in metacarbonate rocks of the Sludyanka, Russia. *Proceedings of the 30th International Geological Congress, Beijing, China*, 446.
- Reznitsky, L.Z., Sklyarov, E.V., Ushchapovskaya, Z.F., Nartova, N.V., Kashaev, A.A., Karmanov, N.S., Kanakin, S.V., Smolin, A.S., and Nekrasova, E.A. (2001) Vanadiumdravite $NaMg_3V_4[Si_6O_{18}][BO_3]_2(OH)_4$, a new mineral of the tourmaline group. *Proceedings Russian Mineralogical Society*, 130, 59–72.
- Sheldrick, G.M. (1997) SHELX-97. University of Göttingen, Germany (computer program).
- Smyslova, I.G., Komkov, A.I., Pavshukov, V.V., and Kuznetsova, N.V. (1982) Kyzylkumite, $V_2Ti_3O_9$, a new mineral of vanadium and titanium of a group of complex oxides (Abstract). *American Mineralogist*, 67, 855–856.
- Wang, L., Rouse, R.C., Essene, E.J., Peacor, D.R., and Zhang, Y. (2000) Carmichaelite, a new hydroxyl-bearing titanate from Garnet Ridge, Arizona. *American Mineralogist*, 85, 792–800.
- Zakrzewski, M.A., Burke, E.A.J., and Lustenhouwer, W.J. (1982) Vuorelainenite, a new spinel, and associated minerals from the Satra (Doverstorp) pyrite deposit, central Sweden. *Canadian Mineralogist*, 20, 281–290.

MANUSCRIPT RECEIVED JANUARY 4, 2005

MANUSCRIPT ACCEPTED MAY 2, 2005

MANUSCRIPT HANDLED BY GEORGE LAGER