

Schreyerite, $V_2Ti_3O_9$, a new mineral

OLAF MEDENBACH

*Institut für Mineralogie, Ruhr-Universität
D-4630 Bochum, West Germany*

AND KARL SCHMETZER

*Institut für Mineralogie, Rupprecht-Karl-Universität
D-6900 Heidelberg, West Germany*

Abstract

Schreyerite, a new vanadium titanium oxide with the composition $(V_{0.93}Cr_{0.06}Al_{0.01})_2Ti_3O_9$ giving idealized $V_2Ti_3O_9$, is described from the Kwale District, south of Voi, Kenya. The ore mineral occurs as exsolution lamellae and particles in rutile coexisting with kyanite, sillimanite, tourmaline, and kornepurine in a highly metamorphosed gneiss. The reflectivity of schreyerite is 21 percent, and the microhardness after Knoop is 1100-1200 kp/mm². The d values of 4.075 (m), 3.381 (m), 2.874 (s), 2.737 (vs), and 2.432 (w) suggest a direct analogy to an Andersson phase $(Cr_{0.86}Fe_{0.16})_2Ti_3O_9$ with a monoclinic unit cell.

The investigation of a deposit of green vanadium-bearing kornepurine from Kenya (Schmetzer *et al.*, 1974) has revealed the presence of a new vanadium mineral through observations in reflected light. The mineral is called schreyerite in honour of Professor Dr. Werner Schreyer, Professor of Mineralogy at Ruhr University, Bochum (F.R. Germany), distinguished for his mineralogical and petrological work on kornepurine- and sapphirine-bearing rocks. The mineral and its name have been approved by the Commission of New Minerals and Mineral Names of the IMA. Type material is deposited in the Institute of Mineralogy and Petrology, University of Heidelberg, D-6900 Heidelberg (F.R. Germany).

Occurrence and paragenesis

Around 1970 emerald-green kornepurine crystals of gem quality were discovered 6km southeast of Lasamba Hill (4°12'S, 38°40'E) in the Kwale District, south of Voi, Kenya. The kornepurine came from a deeply weathered layer about 2m thick, which was systematically searched for material of gem quality. Exploratory excavations showed that the host rock consists of alternating layers of gneiss and quartzite. Further information on the geology and petrology of this particular area is not available. The samples of schreyerite-bearing country rock and the

overlying weathered zone were collected by Dr. H. Krupp, Heidelberg, who visited the mine in 1974. The strongly weathered, highly metamorphosed gneiss contains quartz, biotite, tourmaline, diopside, and epidote. The most abundant opaque minerals are graphite and rutile, although traces of pyrrhotite, chalcopyrite, and pentlandite are also found. Schreyerite always occurs in intergrowth with rutile. The rutile grains in the gneiss reach a diameter of up to 0.5mm and are partly idiomorphic. The ratio of schreyerite to rutile is strongly variable. In one section, rutile crystals devoid of schreyerite coexist with others containing predominantly schreyerite. Intergrowths of the latter range from finest exsolution lamellae (Figs. 1 and 2) through coarser lamellae to prominent compact sections (Figs. 3a and 3b). Even the finest lamellae show strong polysynthetic twinning. In some cases the intergrowth has a definite orientation to the rutile. In the cyclic rutile twin shown in Figure 2, two exsolution lamellae of schreyerite oriented parallel to the rutile twin plane {101} or {301} may be observed. From this and other observations in different sections (for example Fig. 1), one can argue that parts of the oriented intergrowths are parallel to {101} in rutile. In the more strongly weathered parts of the gneiss, schreyerite is altered to a spotty, inhomogeneous substance with lower reflectivity (Figs. 3a and 3b, phase x).

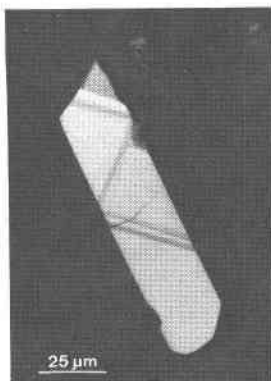


Fig. 1. Euhedral rutile crystal elongated parallel to the *c* axis with fine exsolution lamellae of schreyerite. Reflected light, oil immersion.

Physical properties

The reflectivity of schreyerite is only slightly lower than that of rutile; the color is reddish-brown. There is a weak pleochroism from yellow-brown to reddish-brown. With oil immersion the contrasts between rutile and schreyerite become clearer, and the reddish-brown color is more intense. With crossed polarizers a moderate anisotropism becomes evident, so that the very fine lamellar twinning is very distinct (Fig. 3). Internal reflections were never observed, a fact that points to an opaque behaviour of schreyerite. This was confirmed by investigating polished thin sections in transmitted light. The sections were covered by a thin aluminum foil with a small hole directly above the rutile grains rich in schreyerite that had been selected for investigation. The foil effectively blocks transmitted light from the surrounding silicates. The reflectivity was measured with a Leitz Orthoplan Pol together with an MPV2. Owing to the

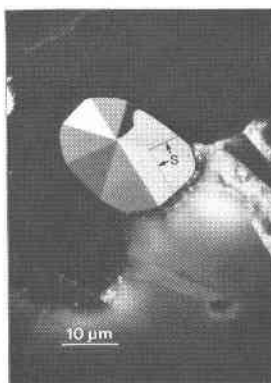


Fig. 2. Cyclic twin of rutile with oriented exsolution lamellae of schreyerite (S) parallel to the rutile twin plane {101} or {301}. Reflected light, oil immersion.

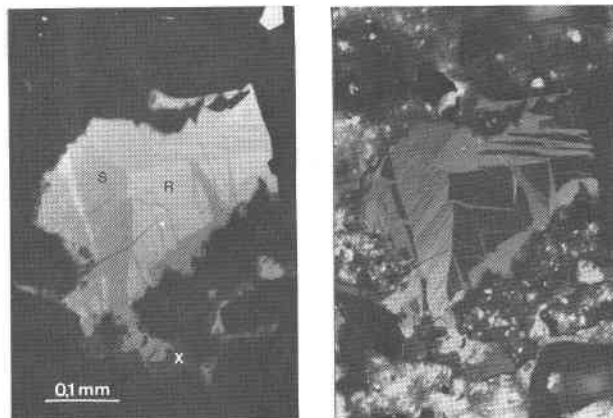


Fig. 3. Rutile intergrowth with schreyerite which is partly altered into an unknown phase *x*. The unusually coarse appearance is due to an orientation effect. Reflected light, oil immersion; (a) in plane polarized light, rutile (R) (white), schreyerite (S) (bright grey), alteration product (X) (dark grey); (b) under crossed polarizers showing anisotropy and twinning of schreyerite.

small size of the untwinned areas, no reproducible measurements of the spectral reflectivity could be obtained. The mean value for 546 nm (Na light) is 21 percent. From this, neglecting absorption, an index of refraction of 2.7 can be calculated. Microhardness is slightly higher than that of rutile and gives Knoop hardness numbers between 1100 and 1200 kp/mm². Solubility tests with inorganic acids were negative.

Chemical composition

Chemical analyses were made with an ARL-EMX microprobe. The standards used were synthetic Nb and Ta oxide for Nb and Ta respectively, synthetic rutile for Ti, analysed chromite for Al, Cr, Mg, and Fe, analysed pyroxmangite for Mn, and analysed vanadinite for V. Six representative analyses (Nos. 1–6) are shown in Table 1. The mean composition yields the formula $(V_{0.93}Cr_{0.06}Al_{0.01})_2Ti_3O_9$, giving idealized $V_2Ti_3O_9$, which corresponds to 61.53 weight percent TiO_2 and 38.47 weight percent V_2O_5 . The coexisting rutile is vanadium-bearing. Three rutile analyses (Nos. 7–9) are also given in Table 1. Quantitative analyses of the alteration product (phase *x*) could not be made because of the high content of volatile elements (H_2O ?) and the rapid decomposition under the electron beam. Energy-dispersive analyses with a Si(Li) detector gave as main elements Ti, V, Al, and Cr. Figure 4 compares the energy-dispersive spectra of the unknown phase *x*, schreyerite, and the coexisting vanadium-bearing rutile.

Table 1. Microprobe analysis of schreyerite (anal. nos. 1-6) and coexisting rutile (anal. nos. 7-9)

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	$V_2Ti_3O_9$ calcul.	No. 7	No. 8	No. 9
Nb ₂ O ₅	n.d.†	n.d.	n.d.	n.d.	n.d.	n.d.		0.03	0.06	0.09
Ta ₂ O ₅	0.02	0.01	n.d.	0.04	0.03	n.d.		n.d.	n.d.	n.d.
TiO ₂	60.4	62.0	61.5	60.9	61.7	59.9	61.53	99.1	97.0	98.0
Al ₂ O ₃	0.40	0.56	0.41	0.52	0.43	0.26		n.d.	n.d.	n.d.
V ₂ O ₃	35.9	35.9	36.5	35.6	35.3	36.4	38.47	1.67	1.90	1.79
Cr ₂ O ₃	2.28	2.28	2.22	2.48	1.95	2.16		0.07	0.08	0.08
MgO	0.14	0.14	0.13	0.14	0.07	0.06		n.d.	n.d.	n.d.
MnO	0.03	0.03	0.01	n.d.	n.d.	n.d.		n.d.	0.02	n.d.
FeO	0.09	0.10	0.06	0.05	0.18	0.15		0.01	n.d.	0.05
Sum	99.26	101.02	100.83	99.73	99.66	98.93	100.00	100.88	99.06	100.01
	Cations based on 9 oxygens							Cations based on 2 oxygens		
Ti	2.966	2.987	2.972	2.976	3.014	2.954	3.000	0.986	0.984	0.984
Al	0.031	0.041	0.030	0.040	0.032	0.019		0.000	0.000	0.000
V	1.882	1.844	1.881	1.854	1.838	1.915	2.000	0.017	0.020	0.019
Cr	0.117	0.114	0.112	0.127	0.100	0.111		0.001	0.001	0.001
Mg	0.012	0.011	0.011	0.014	0.007	0.005		0.000	0.000	0.000
Fe	0.004	0.004	0.002	0.001	0.010	0.007		0.000	0.000	0.000
Sum	5.012	5.001	5.008	5.012	5.001	5.011	5.000	1.004	1.005	1.004
M ₁ ⁺⁺	2.030	1.999	2.023	2.021	1.970	2.045				
M ₂ ⁺⁺⁺	2.982	3.002	2.985	2.991	3.031	2.966				

† not detected
 ++ V+Cr+Al
 +++ Ti+Mg+Mn+Fe

X-ray crystallography

Due to the intergrowth with rutile and the limited amount of material available, neither single crystals nor concentrates of schreyerite could be separated for X-ray investigations. Rutile grains with a high schreyerite content were picked out of the polished sections and cleaned from silicates with HF. The d values measured on these powdered grains with a Debye-Scherrer camera (114.6mm diameter, FeK α) were controlled by further films of single grains made with a Gandolfi camera (57.3mm diameter). All investigated grains similar to the one in Figure 3 show predominantly rutile in the powder patterns, thus implying that the coarse appearance of the schreyerite is due to the subparallel orientation of thin lamellae to the plane of the section. All films gave identical X-ray patterns *without any additional lines* except for rutile. The d values of schreyerite (with rutile lines eliminated) are listed in Table 2. A comparison of these values with those of oxides with the general formula M_5O_9 from the literature shows a very good correlation of d values and intensities with

the synthetic phases $Fe_2Ti_3O_9$ and $(Cr_{0.85}Fe_{0.15})_2Ti_3O_9$. The latter are members of the Andersson phases with the general formula $M_2M_{(n-2)}O_{(2n-1)}$ (Grey and Reid, 1972). From the similarity of the chemical formula and the d values between schreyerite and those Andersson phases with $n = 5$, we assume that the crystal structures are the same. The structures of the Andersson phases can be clearly derived by means of crystallographic shear from the rutile structure, or as oriented intergrowths of V_2O_5 and PbO_2 structure types. A detailed discussion of these shear structure compounds is given in Grey and Reid (1972), Grey *et al.* (1973), Hyde *et al.* (1974), and others. Electron diffraction patterns show that the primitive unit cell which Grey and Reid (1972) derived for $Fe_2Ti_3O_9$ may also be described as a body centered unit cell with a crystallographic shear plane (132) (Grey *et al.*, 1973). The two alternative indexing schemes as well as the lattice constants of $Fe_2Ti_3O_9$ and schreyerite are given in Tables 2 and 3 (see the discussion in Hyde *et al.*, 1974). We conclude therefore that schreyerite is the first natural Andersson phase with shear plane structure.

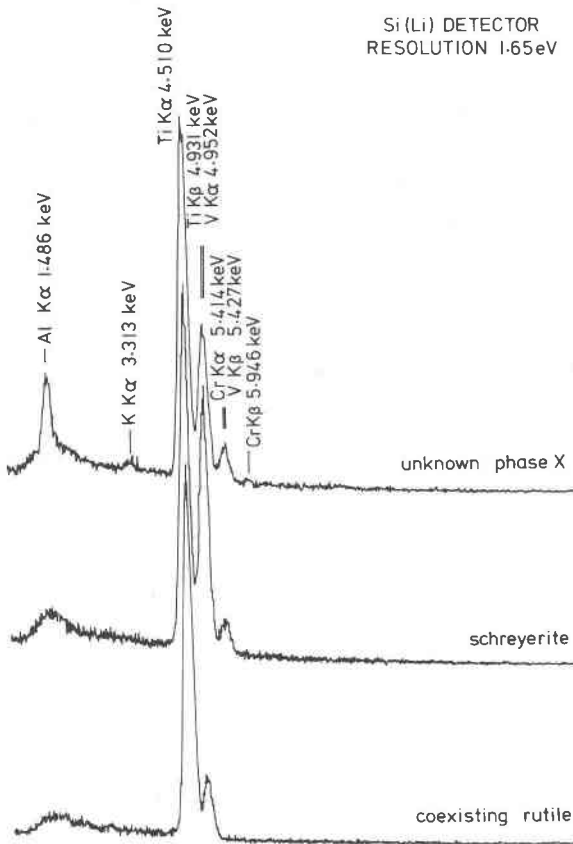


Fig. 4. Energy-dispersive X-ray spectra of V-bearing rutile, schreyerite, and its alteration product (phase x).

Discussion

Microprobe analyses of some silicates from Voi show an unusually high V₂O₅ content, e.g. kornerupine 0.22 weight percent (Schmetzer *et al.*, 1974), tourmaline 4.03 weight percent, and kyanite 0.72 weight percent (Schmetzer, 1978). Vanadium enrichment in bituminous sediments is common, but these values imply an unusually high vanadium content of

Table 2. *d* values of synthetic Fe₂Ti₃O₉ and schreyerite

Fe ₂ Ti ₃ O ₉	schreyerite	I	h k l	
		++++	+	++
4.101	4.075	m	004	004
3.382	3.381	m	204	204
2.877	2.874	s	213	215
2.738	2.737	vs	015	015
2.497	++		020	020
2.432	2.432	w	211	219

+ indexed by GREY and REID (1972), primitive unit cell
 ++ indexed after GREY *et al.* (1973), body centered unit cell
 +++ line superimposed by d=2.487 (101) of rutile
 +++ intensities for both, Fe₂Ti₃O₉ and schreyerite

Table 3. Lattice parameters of synthetic (Cr_{0.85}Fe_{0.15})₂Ti₃O₉, synthetic Fe₂Ti₃O₉, and schreyerite

	(Cr _{0.85} Fe _{0.15}) ₂ Ti ₃ O ₉		Fe ₂ Ti ₃ O ₉		schreyerite	
	A†		A	B††	A	B
a ₀ (Å)	7.031		7.071	7.071	7.06	7.06
b ₀ (Å)	4.974		4.997	4.997	5.01	5.01
c ₀ (Å)	18.788		18.862	25.08	18.74	25.06
β	119.72°		119.56°	139.15°	119.4°	139.35°
v (Å ³)	570.78		579.69	579.63	577.48	577.43

† calculated as primitive unit cell after GREY and REID (1972)
 †† calculated as body-centered unit cell after GREY *et al.* (1973)

the gneiss. Unfortunately no fresh material for a whole-rock analysis was available.

The presence of sillimanite, kyanite, and kornerupine shows that pressure and temperature during metamorphism were high. Seifert (1975) determined that the stability field of boron-free kornerupine lies above 4.5 kbar and 700°C. The stability of boron-bearing kornerupine can be somewhat lower (Werdning, personal communication), but the presence of kyanite and sillimanite gives minimum conditions of more than 5kbar and 600°C (Richardson *et al.*, 1969). The microscopic features show that schreyerite has been exsolved from a homogeneous phase (see Figs. 1 and 2), indicating that at these pressures and temperatures a titanium-vanadium-oxide of a composition intermediate between schreyerite and rutile must exist.

Investigations on the stability of titanium-vanadium-oxides, especially in the pseudobinary TiO₂-V₂O₅ system, are rare. Kosuge and Kachi (1975) synthesized a series of Andersson phases Ti_{n-2}V₂O_{2n-1} (where *n* equals the integers 20, 30, 40, 50, 100, 200) at 1200°C. In addition, they found a series of solid solutions between Ti_{n-2}V₂O_{2n-1} and V_nO_{2n-1} for 3 ≤ *n* ≤ 7. Schreyerite represents the endmember of one such series Ti₃⁴⁺V₂³⁺O₉-V₃⁴⁺V₂³⁺O₉ with *n* = 5. Nothing is known on the stability of these shear plane structures at lower temperatures.

In the Fe₂O₃-TiO₂ system, Andersson phases have also been synthesized at high temperatures. These decompose at lower temperatures eutectoidally to rutile + pseudobrookite. Nevertheless, at still lower temperatures, a phase Fe₂Ti₃O₉ with *n* = 5 and the same shear vector as schreyerite exists (Bursill, 1974). The excellent analogy between this phase and schreyerite yields a very probable explanation for the existence of the latter as a discrete phase: at high temperatures, a V³⁺-bearing rutile was formed because of the high vanadium supply in the rock. The valence deficiency in the crystal is compensated by

crystallographic shear leading to an Andersson phase with the general formula $Ti_{n-2}V_2O_{2n-1}$ with $n > 5$. With decreasing temperature, this phase becomes unstable and decomposes to rutile and schreyerite.

Another conceivable mode of formation is based on the variable valence state of vanadium. The vanadium could be incorporated as $V^{4+}O_2$ in solid solution in the rutile (VO_2 has a structure comparable to that of rutile). During metamorphism, the decreasing O_2 fugacity in the graphite-rich gneiss could have caused a change from V^{4+} to V^{3+} , thus initiating reduction exsolution of schreyerite from rutile. In any case, at low temperatures schreyerite seems to be the only stable Andersson phase in the compositional region $Ti_{n-2}V_2O_{2n-1}$ with $n \geq 5$.

Acknowledgments

We are indebted to Professor Dr. P. Ramdohr for comments and help during the microscopic investigations and Dr. Th. Armbruster for discussions on the Andersson phases. The reflectivity measurements were carried out with the kind support of Dr. K. Medenbach in the laboratories of Fa. Leitz-Wetzlar GmbH. We appreciate critical comments on the manuscript and assistance in the preparation of the English text from Dr. W. V. Maresch.

References

Bursill, L. A. (1974) An electron microscope study of the $FeO-Fe_2O_3-TiO_2$ system and of the nature of iron doped rutile. *J. Solid State Chem.*, 10, 72-94.

- Grey, I. E. and A. F. Reid (1972) Shear structure compounds $(Cr,Fe)_2Ti_{n-2}O_{2n-1}$ derived from the $\alpha-PbO_2$ structural type. *J. Solid State Chem.*, 4, 186-194.
- , ——— and J. G. Allpress (1973) Compounds in the system $Cr_2O_3-Fe_2O_3-TiO_2-ZrO_2$, based on intergrowth of the $\alpha-PbO_2$ and V_2O_5 structural types. *J. Solid State Chem.*, 8, 86-99.
- Hyde, B. G., A. N. Bagshaw, S. Andersson and M. O'Keeffe (1974) Some defect structures in crystalline solids. *Ann. Rev. Mat. Sci.*, 4, 43-92.
- Kosuge, K. and S. Kachi (1975) Electron-diffraction and electron-microscopic observation of the pseudo binary $TiO_2-V_2O_5$ system. *Chemica Scripta*, 8, 70-83.
- Richardson, S. W., M. C. Gilbert and P. M. Bell (1969) Experimental determination of kyanite-andalusite and andalusite-sillimanite equilibria; the aluminum silicate triple point. *Am. J. Sci.*, 267, 259-272.
- Schmetzer, K. (1978) *Vanadium III als Farbträger bei natürlichen Silikaten und Oxiden—ein Beitrag zur Kristallchemie des Vanadiums*. Ph.D. Thesis, University of Heidelberg.
- , O. Medenbach and H. Krupp (1974) Das Mineral Kornerupin unter besonderer Berücksichtigung eines neuen Vorkommens im Kwale Distrikt, Kenya. *Z. Dtsch. Gemmol. Ges.*, 23, 258-278.
- Seifert, F. (1975) Boron-free kornerupine: a high pressure phase. *Am. J. Sci.*, 275, 57-87.

Manuscript received, March 13, 1978; accepted for publication, June 22, 1978.