

MANNARDITE FROM VANADIUM-BEARING SCHISTS OF KAZAKHSTAN AND CENTRAL ASIA

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Mannardite $\text{Ba}(\text{H}_2\text{O})(\text{Ti}_6\text{V}_2)\text{O}_{16}$ is found in carbonaceous-siliceous schists of the Karatau Ridge (areas Balacauskandyk and Kurumsak), Kazakhstan, and in the Kara-Chagyr and Kara-Tangi, Southern Kyrgyzstan. At Kara-Tangi, it is present as rare grains 10 micron or less in size in assemblages with quartz, pyrite, chalcocopyrite, sphalerite, fluorapatite, nickelalumite, and kyrgyzstanite. At Kara-Chagyr, mannardite occurs as small grains under 10 micron in size in quartz veinlets with pyrite, Ce-phosphate, Ba-V-bearing muscovite, nickelalumite, and ankinovichite. In the Balacauskandyk and Kurumsak areas, it forms grains up to 50 micron and aggregates up to 100 micron and larger in size being present in quartz veinlets with Ba-V-bearing muscovite, chernykhite (Kurumsak), V-bearing rutile, Nd, La, and Y phosphates, barite, and hematite. Mannardite from Balacauskandyk is studied in most detail. The mineral has black colour, deep brown in thin scales, and metallic luster. Micro-hardness measurements (from 5 repeated tests) are averaged at 628 kg/mm². Density is determined at 4.34(3) g/cm³, by measurement and 4.40 g/cm³ by calculation. Mannardite is anisotropic in reflected light, showing dark-gray color. Unit cell parameters are: $a = 14.37(1)$, $c = 5.922(6)\text{\AA}$, $V = 1223(2)\text{\AA}^3$. Intensive X-ray powder diffraction peaks are as follows: (d , \AA ; l ; hkl): 3.590(4)(400); 3.211(10)(420); 2.844(3)(112); 2.476(7)(312); 2.276(4)(620); 2.227(5)(332); 1.892(5)(352); 1.690(4)(660); 1.592(5)(732). Chemical composition (average by 19 microprobe analyses, wt.%): BaO 20.58; TiO₂ 58.10; V₂O₅ 18.07; Cr₂O₃ 0.40; H₂O(calc.) 1.98; Total 99.13. Empirical formula: $\text{Ba}_{1.10}(\text{Ti}_{5.94}\text{V}_{1.97}\text{Cr}_{0.04})\text{O}_{16} \cdot 0.90\text{H}_2\text{O}$. Mannardite from Kara-Tangi contains up to 2.4 wt.% of Cr₂O₃. Along with micas and sulvanite, mannardite is one of early concentrators of vanadium in these rocks. The majority of mannardite is associated with netted quartz veins, which belong to the type of alpine veins. This article discusses the mechanism of formation of these veins during the regional metamorphism of sediments.

2 tables, 6 figures, 33 references.

Key words: mannardite, cryptomelane group, vanadium-bearing schist, Kara-Tau, Kara-Chagyr.

Introduction

Mannardite $\text{Ba}(\text{H}_2\text{O})(\text{Ti}_6\text{V}_2)\text{O}_{16}$ a rare complex titanate, was first described in quartz-carbonate veins crosscutting shales and sandstones in Rough Claims (British Columbia) and in the Brunswick polymetallic deposit (Scott and Peatfield, 1986). A mineral of similar composition, but containing no H₂O, was found at the same time in the Kantsi silver deposit in China (Scott and Peatfield, 1986). Later on, mannardite was found in the Upper Silurian and Lower Devoian schists of the Turkestan Ridge, Kyrgyzstan (Pautov, 1994). We found mannardite while studying carbonaceous-siliceous schists in a number of locations: the Kara-Tangi uranium-vanadium deposit, Kara-Chagyr vanadium locality (South Kyrgyzstan), and the Balacauskandyk and Kurumsak vanadium deposits, North-Western Karatau, Kazakhstan.

Along with several minerals close in composition and structure – redlegite $\text{Ba}(\text{H}_2\text{O})(\text{Ti}_6\text{Cr}_2)\text{O}_{16}$, ankangite $\text{Ba}(\text{Ti}_6\text{V}_2)\text{O}_{16}$, priderite $\text{K}_2(\text{Ti}_6\text{Fe}_2^+)\text{O}_{16}$, and henrymeyerite $\text{Ba}(\text{Ti}_7\text{Fe}^{+2})\text{O}_{16}$ – mannardite belongs to the hollandite structure type ($AB_8\text{O}_{16}$). All these minerals crys-

tallize with tetragonal symmetry. They often contain superstructures associated with different types of ordering of the tunnel A-cations (Ba, K, Na), which results in an increase of the c -dimension and causes a slight deviation from the original hollandite structure (Dmitrieva *et al.*, 1992; Mitchell *et al.*, 2000).

Titanates with the hollandite structure occur in very diverse geological settings – hydrothermal veins of ore deposits (Scott and Peatfield, 1986; Xiong *et al.*, 1989; Ivanov *et al.*, 1996; Biagioni *et al.*, 2009), carbonaceous-siliceous schists (Pautov, 1994; Karpenko, 2010), metamorphic rocks of carbonate-silicate composition (Reznitskii *et al.*, 2007), carbonatites (Zhuravleva *et al.*, 1978; Mitchell *et al.*, 2000), kimberlites and lamproites (Mitchell and Meyer, 1989), and mantle hartzburgite and lherzolite xenoliths (Kogarko *et al.*, 2007). Interest in this group of minerals has grown over the past few decades, in part due to the experimental studies showing transformation of feldspar structures into hollandite-type structures under high pressure (Zhang *et al.*, 1993). In a practical sense, compounds of this type act as adsorbents in water treatment, especially for streams contaminated with

heavy metals and radionuclides (Zhang *et al.*, 1993; Foley *et al.*, 1997; Mitchell *et al.*, 2000).

Occurrence

Vanadium-bearing carbonaceous-siliceous-argilliferous rocks with roscoelite were first noticed at the Karatau Ridge (Kazakhstan) by N.A. Kozlov and V.A. Sokolov in the early 1940s. That set the ground for the discovery and development of the Karatau uranium-vanadium deposits (Kozlov and Sokolov, 1944). The geology and mineralogy of the Karatau vanadium-bearing schists were further described in numerous works by S.G. Ankinovich and E.A. Ankinovich (Ankinovich and Ankinovich, 1954; Ankinovich, 1964; Ankinovich *et al.*, 1979; etc.). The geochemistry of the schists was studied by V.M. Kholodov (1968), G.K. Bekenova (2007), and V.Yu. Karpenko (2010) who obtained new mineralogical data and reviewed the available information on the Karatau schists. These rocks belong to the Lower Cambrian vanadium-bearing carbonaceous-siliceous schist formation, which is represented in Southern Kazakhstan by the Kurumsak Suite. It includes a vanadium-rich horizon 7 to 12 m in thickness (so-called "ore horizon"), which has vanadium contents (by metal) up to 2.5 wt.% (Ankinovich *et al.*, 1979). This ore zone consists mainly of phthanites rhythmically alternating with carbonaceous-quartz-argillaceous schists which form the bulk of the horizon. This ore horizon also shows increased contents of Mo, Re, Cu, Zn, Ni, Pb, U and carbonaceous matter (up to 10–15 wt.% in phthanites), and is exceptionally uniform in lithological and chemical composition over vast areas of the Lower Paleozoic section (Geology..., 1986). The mineralogy of these schists is notably rich, featuring more than 160 mineral species, including 12 new minerals (Bekenova, 2007; Karpenko, 2010). The best-studied deposits (areas) are Bala-sauskandyk, Kurumsak and Ran. The early vanadium and vanadium-bearing minerals in the Karatau carbonaceous-siliceous schists are represented by mica group: barium-vanadium-bearing muscovite (phengite) (Ankinovich *et al.*, 1992) and vanadium micas – roscoelite and chernykhite (Ankinovich *et al.*, 1997; 2001).

Carbonaceous-siliceous schists of Southern Kirgystan were described by D.I. Mushketov and V.N. Weber as early as 1909–1913 while compiling geological maps of this region (Belov *et al.*, 1989). The Radium Expedition

(Shcherbakov, 1924) and the Tadjik-Pamir Expedition also made significant contributions to geological and mineralogical studies of these schists. " ... Over 200 km by latitude along the Altai and Turkestan Ridges, there is a remarkable zone of siliceous and carbon-rich schists, which contains, among the products of intense thermal alteration, special formations rich in V_2O_5 , NiO, CuO and some other elements" – this brief description was given by A.E. Fersman to this region, which has quite a complicated geological and tectonic structure (Fersman, 1928). The carbonaceous-siliceous schists form olistoliths in the Lower and Middle Carboniferous Malyaran mǎlange complex. The size of the blocks ranges from several meters to tens and even hundreds of meters.

Slickenside surfaces are common in these strata. The stratigraphic affiliation of the olistolith blocks is not always clear; most likely, they are residual blocks of Cambrian-Silurian formations (Belov *et al.*, 1989). These schists are characterized by elevated contents of V, Ni, Zn, Cu, Mo and U. The carbonaceous-siliceous schists of the Kara-Chagyr and Kara-Tangi are most notable in this respect. Their outcrops show fairly confined but rich vanadium mineralization, represented by the nickelalumite-group minerals (ankinovichite, alvanite, nickelalumite, kyrgyzstanite), kurumsakite and related minerals, Zn-bearing folborite, vanadium-bearing minerals of the alunite group, carnotite, tuyamunite, a variety of Zn-Ni-V phases (united under the common name "kolovratites") (Karpenko, 2010).

Micas are less widespread in Southern Kirgystan than at Karatau. Our studies showed that mannardite is another efficient concentrator of vanadium in the carbonaceous-siliceous schists of the Karatau Ridge.

Mineral assemblages

At Kara-Tangi, mannardite was found in carbonaceous-siliceous schists from the dumps of the uranium mine, which was developed in the early 1970s (personal communication, V.M. Rogovoi). The "black" schists are composed of quartz and argillaceous-carbonaceous matter which forms lenticular nodules up to 1 mm. Quartz is present as micro-granular aggregates (grain size 0.05–0.50 mm, mean size 0.08–0.10 mm). The rock is penetrated by numerous quartz veinlets which can contain cavities encrusted with quartz crystals and lamellar crystals of later minerals – nickelalumite $(Ni,Zn)Al_4(SO_4)(OH)_{12} \cdot 3H_2O$, kyrgyzs-

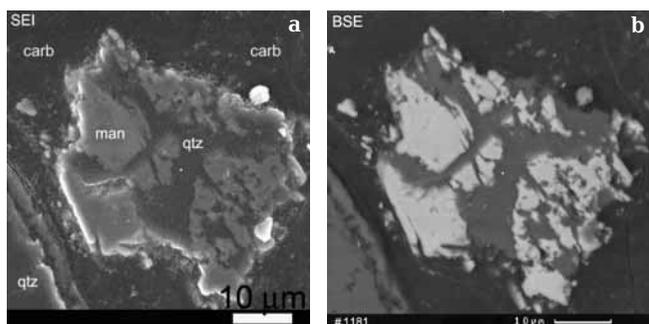


Fig. 1. Micrograins of mannardite (*man*) in quartz (*qtz*) among the carbonaceous matter (*carb*), Kara-Tangi. Scale marker 10 micron; secondary electron (SEI), back-scattered electrons (BSE) images; characteristic X-ray maps of the specified elements.

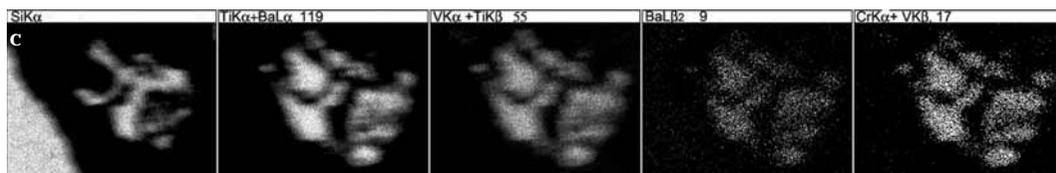


Fig. 2. A typical "quartz net" specimen with mannardite; Karatau Ridge, Kazakhstan.

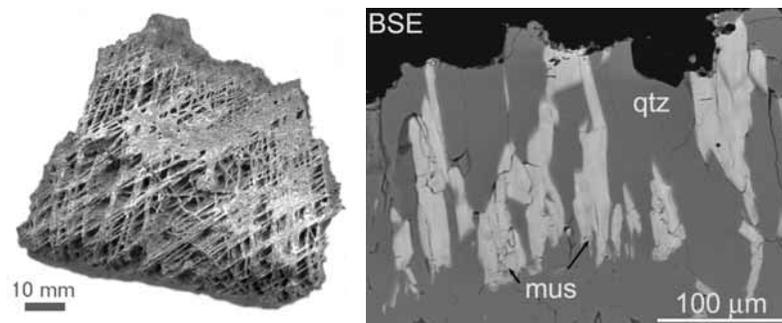


Fig. 3. A fragment of a selvad veinlet (*qtz*) with in-growing (or possibly co-growing) lamellar grains of Ba-V-bearing muscovite (sericite) (*mus*), Balasauskandyk, Karatau. BSE image.

tanite $(\text{Zn,Ni})\text{Al}_4(\text{SO}_4)(\text{OH})_{12}\cdot 3\text{H}_2\text{O}$ and Al-hydroxide forming after the former two minerals. Rare grains (10–20 micron in size) of pyrite, chalcopyrite, cadmium-bearing sphaerite (1.44 wt.% Cd), fluorapatite and mannardite are occasionally present. Mannardite occurs as rare and quite uniformly distributed spots 10 micron and less in size (Fig. 1). The mannardite from Kara-Tangi contains up to 2.4 wt.% Cr_2O_3 (Table 1).

At Kara-Chagyry, mannardite was found in quartz veinlets in a carbonaceous-siliceous matrix, where it is associated with pyrite, a non-identified cerium phosphate, and rare grains of barium-vanadium-bearing muscovite (8.6 wt.% V_2O_5). Aggregates of lamellar crystals of ankinovchite, $(\text{Ni,Zn})\text{Al}_4(\text{VO}_3)_2(\text{OH})_{12}\cdot 2\text{H}_2\text{O}$ and silicon-bearing nickelalumite (up to 6.8% SiO_2) are often present in cavities in the largest veinlets. The size of the mannardite grains here is no more than 10 microns. The composition of Kara-Chagyry mannardite is given in Table 1; it is almost completely free of chromium, unlike Kara-Tangi mannardite.

At Balasauskandyk, mannardite was found during analysis of a specimen of so-called "quartz-roscoelite net" (Fig. 2), which appears as a net aggregate formed by intersecting veinlets. These veinlets are composed of parallel rods of quartz and barium-vanadium-bearing muscovite (7.9–8.2 wt.% V_2O_5 , 6.9–8.3 wt.% BaO) (Fig. 3). Unlike localities of S. Fergana, mannardite is more abundant here, with its grain size ranging from 15 to 50 micron, while aggregates can reach more than 100 micron in size.

In polished section it can be often seen as square cross sections of single crystals. In some cases, chains of mannardite grains are observed, which trace along the axial lines or casing of veinlets of rod-shaped quartz. In some cases mannardite grains are visible to the naked eye, as they give a grayish tint to quartz. In addition to vanadium-bearing muscovite, which is closely intergrown with quartz, mannardite is associated with a number of phosphates of Ce, La, Nd, and Y* (Fig. 4), vanadium-bearing rutile (1.25 wt.% V)

* – in phosphates the ratio $(\text{REE}+\text{Y})/\text{P}$ (*apfu*) = 1; X-ray pattern obtained for the Nd-dominant phosphate is quite close to churche-Nd (Podporina *et al.*, 1983).

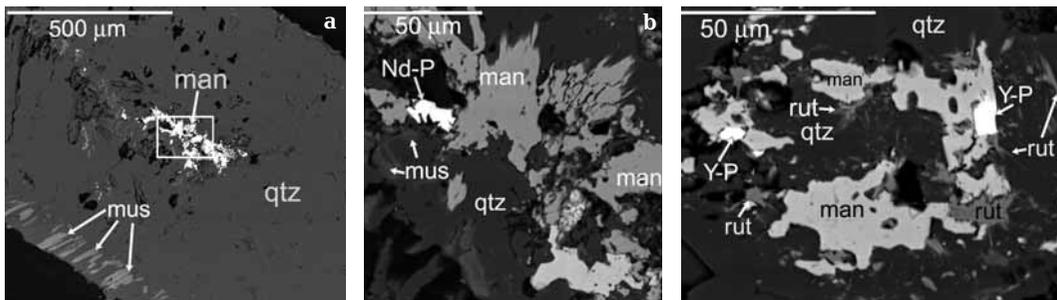


Fig. 4. Mannardite in a veinlet of parallel-rod quartz: (a) mannardite (man) with Nd-phosphates (Nd-P) in quartz (qtz) with V-bearing muscovite (mus); (b) fragments marked on Fig. 4a; rut – V-bearing rutile; Balasauskandyk, Kazakhstan. BSE image.

Fig. 5. Mannardite grain (man) in aggregate with V-bearing rutile (rut), Y-phosphate (Y-P) in a quartz (qtz) veinlet. Balasauskandyk. BSE image.

(Fig. 4 and 5), strontium-bearing barite (1.17–1.30 wt.% SrO), and hematite. Only traces of chromium were found in the mannardite from Balasauskandyk (Table 1).

We also found mannardite in the specimens of netted quartz aggregates from a mine dumps at Kurumsak, together with chernykhite, barium-vanadium-bearing muscovite and barite. In general, mannardite was observed in almost all specimens of quartz net, collected from various area of Kurumsak and Balasauskandyk.

Physical properties

A fraction (-250 micron) significantly enriched in mannardite was extracted by bromoform treatment from a grounded specimen of a quartz net aggregate from Balasauskandyk. Several tens of mannardite grains (30–100 microns in size) from this fraction were placed on electrically conductive carbon tape, and their composition was measured under the scanning electron microscope equipped with an energy-dispersion spectrometer (SEM-EDS). Several grains, free of inclusions of other minerals were removed from the tape and used for studying the physical, optical, and X-ray properties of this mineral.

Mannardite is black with metallic luster; it is opaque, brittle, and its micro-hardness, measured by PMT-3 (calibrated by NaCl) under 100 g load, is $VHN = 628 \text{ kg/mm}^2$ (mean value of 5 measurements ranging from 463 to 732 kg/mm^2). The density of mannardite was determined by suspending three grains in Clerichi liquid solution; the value obtained was $4.34(3) \text{ g/cm}^3$, and the calculated density is 4.40 g/cm^3 (using the average composition, Table 1, an. 4). In transmitted light, only the thinnest edges of the mineral

are translucent, exhibiting deep brown color. In reflected light, mannardite is anisotropic, dark gray, with reflectivity lower than that of redledgeite, which is similar to mannardite in properties and structure (some grains of redledgeite were included in the thin section for comparison). This observation is consistent with the measurements of other authors (Ivanov *et al.*, 1996; Scott and Peatfield, 1986).

Chemical composition

Mannardite was analyzed using a Cam-Scan-4D scanning electron microscope with a Link ISIS energy-dispersion spectrometer (20 kV, specimen current 4 nA on metallic cobalt). Standards used are as follows: barite (Ba), ilmenite USNM 96189 (Ti, Fe), V_2O_5 (V), Cr_2O_3 (Cr), and benitoite (USNM 86539) as control sample. The composition of mannardite is given in Table 1 (an. 1–4), together with analyses of redledgeite from Saranovskoe deposit (Urals) for comparison. A characteristic feature of Kara-Tangi mannardite is the presence of chromium (up to 2.4 wt.%). Fig. 6 shows the correlation between V and sum of trivalent cations (Cr+Fe) for vanadium and vanadium-bearing titanates with the hollandite structure (mannardite, redledgeite, ankanite, and several non-identified phases). In general, the data corresponding to mannardite are confined to the line connecting the idealized compositions $Ba(Ti_6(Cr^{+3}, Fe^{+3})_2)O_{16}$ and $Ba(Ti_6V_2^{+3})O_{16}$, but do not always coincide with it, as neither do the data points of other phases. The reason for this deviation is that the mineral compositions correspond to the formula $Ba_x(Ti_{8-2x}Me_{2x}^{+3})O_{16}$ ($x \sim 1.0-1.3$), as a consequence of the structural vacancies in hollandite type phases (Gatthouse *et al.*, 1986; Xiong *et al.*, 1989, Dmitrieva *et al.*, 1992; Foley *et al.*, 1997). In this

Table 1. Chemical compositions of mannardite (1–9) and redledgeite (10) (wt.%)

Components	1	2	3	4	5	6	7	8	9	10
BaO	18.32	18.37	16.84	20.58 (19.12-21.58)	18.96 (17.72-19.49)	18.22	19.27	19.4	19.8	20.29
TiO ₂	58.54	58.95	59.18	58.10 (56.46-59.00)	57.49 (56.35-58.60)	59.37	58.69	60.1	60.2	60.00
V ₂ O ₃	16.25	16.27	19.53	18.07 (17.51-18.39)	18.59 (17.98-19.11)	18.98	18.43	16.3	12.2	1.12
Cr ₂ O ₃	2.29	2.46	–	0.40 (0.00-1.03)	–	0.83	1.78	1.9	1.9	12.45
Fe ₂ O ₃	0.20	–	–	–	–	0.00	0.00	–	3.7	2.80
H ₂ O (calc.)	2.20	2.24	2.42	1.99	2.10	2.31	2.18	2.15	2.10	2.03
Total	97.80	98.28	97.97	99.14	97.52*	99.73**	100.35	99.85	99.90	99.33***
Amounts in unit formula (per O = 16 atoms)										
Ba ⁺²	0.98	0.97	0.89	1.10	1.02	0.95	1.01	1.02	1.04	1.07
Ti ⁺⁴	5.98	5.99	5.98	5.94	5.95	5.94	5.88	6.03	6.07	6.09
V ⁺³	1.77	1.76	2.10	1.97	2.05	2.02	1.97	1.75	1.32	0.12
Cr ⁺³	0.25	0.26	0.00	0.04	0.00	0.09	0.19	0.20	0.20	1.33
Fe ⁺³	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.38	0.28
Al ⁺³	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10
H ₂ O	1.02	1.03	1.11	0.90	0.98	1.05	0.99	0.98	0.96	0.93

Note: calculation for H₂O was done taking into account the theoretical concentration of the water molecules in channels H₂O = (2-Ba, apfu). The analysis sums include: * – 0.38 wt. % SiO₂; ** – 0.02 wt. % K₂O; *** – 0.65 wt. % Al₂O₃. An. 1–9 – mannardite: 1, 2 – carbonaceous-siliceous quartz from mine dumps, Kara-Tangi, Kyrgyzstan; 3 – carbonaceous-siliceous schist from the cleaning tails, Kara-Chagyr, Kyrgyzstan; 4, 5 – quartz-roscoelite “net”, Balasauskandyk, Kazakhstan (4 – average of 19 analyses, scatter of values is shown in parenthesis; 5 – specimen of G.K. Bekenova, average of 7 analyses, scatter of values is shown in parenthesis); 6, 7 – South Kyrgyzstan (materials of the Daudinskaya crew, South Kyrgyz Geological Survey Expedition, Osh, Kyrgyzstan; analyst I.M. Kulikova (Pautov, 1994)); 8 – Rough Claims, British Columbia, Canada; grain used for decoding the mineral structure (Scott, Peatfield, 1986); 9 – Brunswick No.12 (ore body), Bathurst, New Brunswick, Canada (Scott, Peatfield, 1986); 10 – redledgeite, Saranovskoe Deposit, Central Urals (M.M. Moiseev sample).

Analytical parameters: 1–4, 9, 10 – CamScan-4D, EDS Link ISIS, 20 kV, 4 nA. Analyst V.Yu. Karpenko; 5 – Jeol Superprobe 733, EDS Inca. Analysts P.E. Kotelnikov and V.L. Levin. Dash denotes values under the detection limit.

graph, there are strong deviations of the compositions of niobium-bearing K-Ba titanates from the Star Mine kimberlites (South Africa) from the correlation line. This is probably due to the presence of Nb⁵⁺ at an octahedral site and the presence of K⁺ as a channel cation (Mitchell and Meyer, 1989). The presence of H₂O in Balasauskandyk mannardite was confirmed by infrared spectroscopy: absorption bands at 1597, 3460 and 3518 cm⁻¹ (the spectra were obtained using a Hyperion 2000 FT-IR microscope with ATR-objective of Brucker; analyst A. Cherevan, A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences). An indirect indicator of the presence of H₂O in mannardite is the low totals in the microprobe analyses.

X-ray Data

The X-ray powder-diffraction pattern was obtained for Balasauskandyk mannardite by photographic techniques (URS-50, FeK α -radiation, Mn-filter, camera RKD-57.3, cylinder dia. 0.15 mm, internal standard: quartz, Table 2). The pattern is similar to those of other titanates of the hollandite structure

type (for example, redledgeite). The main difference between these X-ray data and that of other mannardites known to date (Scott and Peatfield, 1986; Pautov, 1994) is the presence of a weak peak at $d = 5.04\text{\AA}$ (220) and indexed in the $I4_1/a$, space group of mannardite (Szymanski, 1986). The units cell parameter of Balasauskandyk mannardite are: $a = 14.37(1)$, $c = 5.922(6)\text{\AA}$, $V = 1223(2)\text{\AA}^3$.

Many researchers (Mitchell and Meyer, 1989; Biagioni *et al.*, 2009) have noted the need for a better nomenclature for this group. We also encountered difficulties in the nomenclature of the hollandite group, which is not in accord with IMA nomenclature criteria.

The hollandite structure type is based on a rutile-like framework, with tunnels occupied by large atoms (Ba, K, Pb, Sr) and H₂O groups. This framework is formed by M -octahedra, which are occupied in titanates by Ti⁺⁴, V⁺³, Cr⁺³, Fe⁺³, Fe⁺², Al⁺³, Nb⁺⁵. The dominating constituent is Ti, its content ranging from 5.8 to 7.0 apfu, while the sum of cations in this site is 8.0. Hence, formally following the conventional nomenclature rules, redledgeite Ba(Ti₆Cr₂)O₁₆, henrymeyerite Ba(Ti₇Fe⁺²)O₁₆ and ankangite Ba(Ti₆V₂)O₁₆

Table 2. X-Ray powder diffraction data for mannardite and redledgeite

1		2		3		
I	d/n, Å	I	d/n, Å	I	d/n, Å	hkl
		—	—	20	7.10	200
2	5.04	—	—	5	5.05	220
4	3.590	20	3.587	50	3.570	400
10	3.211	100	3.201	100	3.195	420
3	2.844	10	2.836	30	2.831	112
		—	—	10	2.536	440
7	2.476	70	2.473	60	2.470	312
4	2.276	30	2.264	30	2.257	620
5	2.227	50	2.224	40	2.217	332
		10	2.031	30	2.033	152
2	1.992	20	1.985	30	1.985	460
5	1.892	70	1.887	50	1.885	352
2	1.800	5	1.792	20	1.788	800
1	1.745	5	1.737	20	1.735	820
4	1.690	50	1.690	40	1.685	660
5	1.592	80	1.586	60	1.583	732
3	1.480	20	1.475	30	1.474	004
2	1.456	5	1.452	20	1.448	572
5	1.400	40	1.394	50	1.393	192
3	1.348	20br	1.341	20	1.339	424,392
1	1.337	20br	1.332	20	1.325	10.4.0, 772
1	1.240	—	—	10	1.234	624
<1	1.202	10	1.192	10	1.193	12.0.0
1	1.162	10	1.156	10	1.154	11.3.2, 972
		10	1.139	—	—	804
2	1.117	10	1.119	20	1.117	10.8.0
		20	1.111	20	1.109	664
		10br	1.070	—	—	12.6.0
2br	1.0332	10	1.030	20	1.027	13.1.2, 7.11.2
2br	1.0129	10	1.010	10	1.007	3.13.2
2br	0.9917	—	—	—	—	10. 4 4

Note: reflections used for calculation of the cell parameters are shown in bold.

1 — mannardite, Balasaukandyk, FeK α -radiation, Mn-filter. URS-50; analyst V.Yu. Karpenko; 2 — mannardite (holotype), Rough Claims, British Columbia, Canada, (Scott and Peatfield, 1986); 3 — redledgeite (holotype), Red Ledge, California, USA (USNM 95846) (Scott, Peatfield, 1986).

from Monte Arsiccio (Italy) (Biagioni *et al.*, 2009), which belong to the $I4/m$, space group, should have been considered as one mineral species, as neither Cr, nor Fe nor V in these minerals are dominant. However, dominance of one or another cation at the (2+) or (3+) valent octahedral position (which compensates the excess charge of the tunnel cations) in the minerals of the hollandite structure type was taken as sufficient reason to recognize it as a distinct species.

Another typical feature of this group is the variation in symmetry, even in specimens from the same locality. For example, redledgeite from its original locality Red Ledge (California, USA) proposed, has been assigned the following space groups: $I4_1/a$ (Szymanski, 1986); $I2/m$ (Gatehouse *et al.*, 1986); $I4/m$ (Foley *et al.*, 1997).

Genesis and discussion of results

As mentioned above, mannardite is associated with the quartz-roscoelite netted formations (Fig. 2), which were described in detail by Ankinovich and Ankinovich (1954). These rocks are typical of the Karatau schists and South Fergana occurrences. The "delicate quartz web" in carbonaceous-siliceous schists of Kara-Chagyr drew the attention of Fersman (1928). Such netted aggregates appear as framework of cells, formed by a system of quartz veinlets (fractions of millimeter to 20 mm in thickness) oriented in three intersecting directions: fractures of tear, fractures of shear, and break fractures. The quartz veinlets are composed of parallel-rod aggregates (Fig. 3). In the weathered zones, frameworks with almost hollow cells are found. These structures are so typical of the carbonaceous-siliceous schists that the geologists working at the Karatau Ridge deposits came up with the terms "quartz-roscoelite net" and "netted ores", because these formations contain the majority of vanadium-concentrating minerals — micas, sylvanite and now mannardite. The quartz netted structures occur uniformly over a "vast territory of the bituminous schists, from Talassky Ridge to Ulutau" (Ankinovich and Ankinovich, 1954), without any signs of strengthening or weakening of quartz formation, and localized strictly within the ore horizon. This fact suggests that such quartz net are not formed by action of hydrothermal solutions associated with some deep intrusion. Ankinovich and Ankinovich (1954) explain the origin of these frameworks by "pseudohydrothermal effects" as a result of

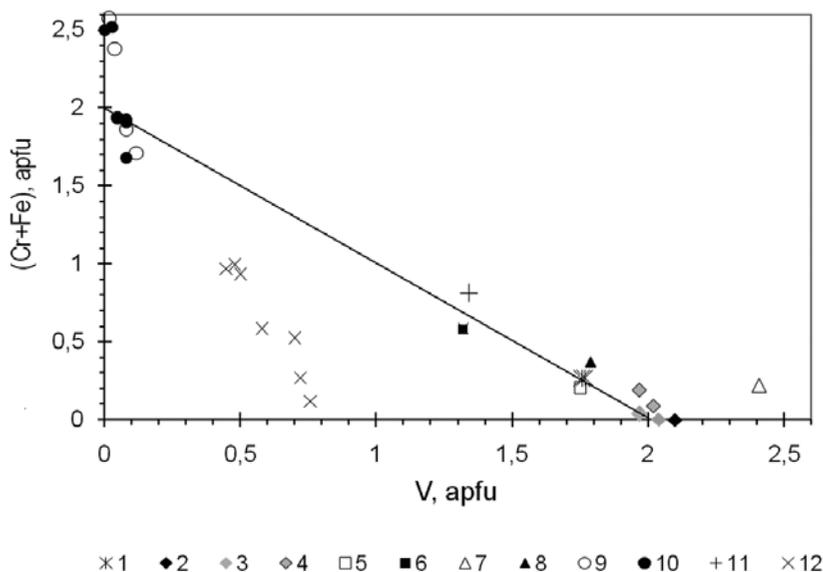


Fig. 6. Variation in V versus (Cr+Fe) for vanadium and vanadium-bearing natural phases of the hollandite structure type.

1–6 – mannardite (1 – Kara-Tangi, Kyrgyzstan; 2 – Kara-Chagyr, Kyrgyzstan; 3 – Balasauskandyk, Kazakhstan; 4 – northern slope of the Turkestan Ridge, Kyrgyzstan; 5 – Rough Claim, Canada; 6 – Brunswick, Canada); 7, 8 – ankangite (7 – Shiti, China; 8 – Monte Arsiccio, Italy); 9, 10 – redlegite (9 – Saranovskoye Deposit, Central Urals, Russia; 10 – Red Ledge, California, USA); 11 – “Ba-Ti-V-hollandite”, Tuvish pipe, Southern Tien-Shan; 12 – niobium-bearing K-Ba-V-titanates, Star Mine, South Africa. 1–3 – this study; 4 – Pautov, 1994; 5, 6 – Scott and Peatfield, 1986; 7 – Xiong *et al.*, 1989; 8 – Biagioni *et al.*, 2009; 9 – Ivanov *et al.*, 1996; 10 – Scott, Peatfield, 1986; Gatehouse *et al.*, 1986; Foley *et al.*, 1997; 11 – Dmitrieva *et al.*, 1992; 12 – Mitchell and Meyer, 1989.

regional metamorphic alteration of the sediment discharged along one or several impermeable barriers. The mechanism of the formation of these nets, according to later studies (Fyfe *et al.*, 1981; Spiridonov *et al.*, 2000), involve in filling of the hydraulic-fracture systems with silica from sediment and release of pore solutions with low-grade metamorphism. The vertical distribution of the netted structures within the ore horizon is related to the various degree of plasticity of the parent rocks (Ankinovich and Ankinovich, 1954). The vanadium-bearing horizon at Karatau consists of alternating layers of bituminous and siliceous schists. Of these two types of rocks, bituminous schists are more brittle and become more susceptible to disintegration and fracture. Some quartz nets strongly resemble the theoretically simulated fracture systems developing in a block of rock under a constant static stress (Fyfe *et al.*, 1981).

Metamorphic pore solutions caused leaching of many elements from the schists and their re-deposition in the quartz-net zones. These quartz veins and veinlets are similar to Alpine-type veins. In the Karatau veins of that type Ankinovich and Ankinovich (1954) found calcite, fluorapatite, rutile, pyrite,

sphalerite, roscoelite, dolomite, orthite, clinzoisite, epidote, tremolite, sericite (barium-vanadium-bearing muscovite), barite, tetrahedrite, chalcopyrite, clinocllore, zircon, albite, titanite, sulvanite, galenite, molybdenite, patronite, breithauptite and native gold. Later, Ankinovich and co-authors (1972; 1997) found chernykhite, and we have discovered mannardite and rare-earth phosphates.

The presence of mannardite in the schists of the South Fergana and in similar rocks of Karatau suggests that common processes occurred during the formation of the vanadium-bearing strata in those regions.

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