

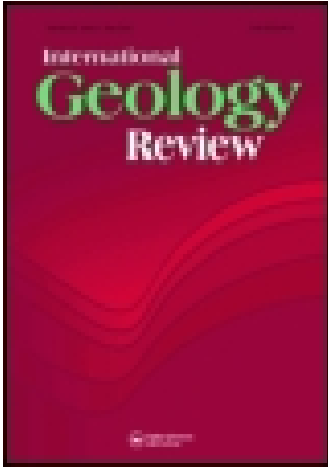
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Melkovite, a new phosphomolybdate from the oxidized zone

B.L. Yegorov, A.D. Dara and V.M. Senderova

In 1963, during mineralogical investigation of the oxidized zone of a molybdenum deposit in the Shunak Mountains of central Kazakhstan, we found extremely small crystals of a lemon-yellow mineral. It was established after a detailed study that the new mineral is a calcium-iron salt of phosphomolybdic acid, and it was named melkovite in honor of the noted Soviet mineralogist Professor Vyacheslav Gavrilovich Melkov.

The molybdenum mineralization is located in the immediate vicinity of contact between sedimentary and volcanic rocks and the Shunak alkali granite massif. The ore occurs in sandstones and quartz albitophyres overlain by Lower Devonian tuffites. The ore bodies in sandstones are localized in joints belonging to different systems of shear fissures, and are very rich but small (3-5 m across) equidimensional pockets containing fluorite, molydenite, and magnetite. The quartz albitophyres contain thin and sparsely mineralized fluorite-molybdenite veinlets localized in steeply dipping, often imbricated, distended fissures. Near the granite contacts the sandstones have been transformed into quartz-amphibole hornfels containing minerals characteristic of alkali metasomatism: albite, aegirine-augite, hornblende, actinolite, epidote, and zoisite. Albite is by far the most abundant

mineral in the hornfels and the rock contains up to 7.6 - 8% Na₂O (and only 0.18-0.20% K₂O). The ore minerals are magnetite and sulfides, with magnetite and molybdenite being strongly predominant.

The oxidation zone is of the linear type and only 8 to 10 m thick. The deposit lies in an area of high relief where the rate of erosion exceeds the rate of oxidation and prevents formation of the normal oxidation profile. As a result, unoxidized hypogene minerals occur in the oxidation zone together with such secondary minerals as powellite, iron montmorillonite, hydrous iron and manganese oxides, and less abundant irignite, autunite, ferrimolybdate, and jarosite. The new mineral, melkovite, occurs in the upper part of the oxidation zone in small branching veinlets cutting veinlets of molybdenite, fluorite, quartz-hematite, and supergene powellite. In the depressed parts of the oxidation zone melkovite is found in the weathered kaolinitic material, where together with ferrimolybdate and irignite, it forms coatings on fracture walls and on decomposed molybdenite. Many of the melkovite veinlets are not homogeneous; the material in contact with molybdenite is light-yellow, while the outer margins of the veinlets are brown, replaced by hydrous iron oxide.

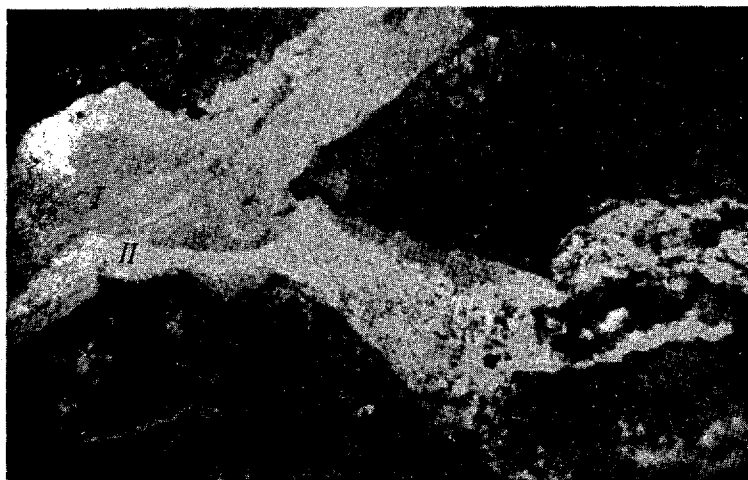


FIGURE 1. Veinlet of melkovite in hematitized sandstones.

Two generations of the mineral, differing in color, are distinctly seen. Polished section; x 10

Translated from Melkovit-novyy fosfato-molibdat iz zony okisleniya, Zap. Vses. Min. Obshch., 1969, no. 2, p. 207-213.

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The veinlets are small, not more than 3.5 mm thick and 20-30 cm long.

Two generations of melkovite, differing in time of crystallization and color have been distinguished. The first generation melkovite is brownish yellow and forms denser aggregates than the second generation melkovite. The latter is lemon yellow and cements fragments of the first generation melkovite aggregates which are frequently brecciated (fig. 1). Melkovite of both generations occurs in very fine-grained, powdery aggregates, composed of equidimensional, nearly hexagonal platy crystals. The crystals are very small, not more than 0.001 - 0.002 mm across, and can be seen only at very high magnification. An electron micrograph of a two-stage carbon replica of melkovite crystals is shown in Figure 2 (taken by Z.I. Zlomanova, electron microscopy laboratory, IGN Acad. Sci. Kazakh SSR).

Melkovite is a transparent mineral with dull, sometimes nearly waxy luster. Cleavage perfect. Brittle. Hardness of aggregate about 3. Specific gravity, determined by the hydrostatic method, varies from 2.969 to 2.973. Melkovite shows no luminescence in ultraviolet light. It swells in the blowpipe flame and fuses into a light-gray bead. Easily soluble in dilute inorganic acids. The pH of melkovite suspension is 5.0-5.1, as determined colorimetrically by V.N. Karyukina (VIMS). In transmitted polarized light melkovite exhibits characteristic greenish hue. It is weakly pleochroic, from colorless to light green, and exhibits anomalous

blue interference color. Extinction wavy in random sections, and nearly parallel in the direction normal to the cleavage. The average refractive index of melkovite, measured in phosphorus melts, is 1.838. Because of the very small size of the melkovite crystals it was not possible to determine its optical characteristics. A chemical analysis of the mineral, made by V. M. Senderova (IGEM, Akad. Nauk SSSR) is shown in Table 1.

TABLE 1. Chemical composition of melkovite

Components	Weight, %	Molecular proportions
K ₂ O	0.28	0.003
Na ₂ O	1.12	0.018
CaO	5.15	0.092
Fe ₂ O ₃	10.90	0.068
MoO ₃	57.17	0.396
P ₂ O ₅	7.86	0.056
ZrO ₂	0.97	0.007
H ₂ O	16.59	0.920
Sum	100.04	
Sp. G.	2.973	

Later investigation showed that zirconium is not a component of melkovite, and this element was disregarded in calculating the formula of the mineral.

The empirical formula of melkovite is:
 $0.92 \text{CaO} \cdot 0.21 (\text{Na}, \text{K})_2\text{O} \cdot 0.68 \text{Fe}_2\text{O}_3 \cdot 3.96$
 $\text{MoO}_3 \cdot 0.56 \text{P}_2\text{O}_5 \cdot 9.2 \text{H}_2\text{O}$
 or approximately,
 $\text{CaFeH}_6 (\text{MoO}_4)_4 (\text{PO}_4) \cdot 6\text{H}_2\text{O}$



FIGURE 2. Melkovite crystals under electron microscope
 x 20,000

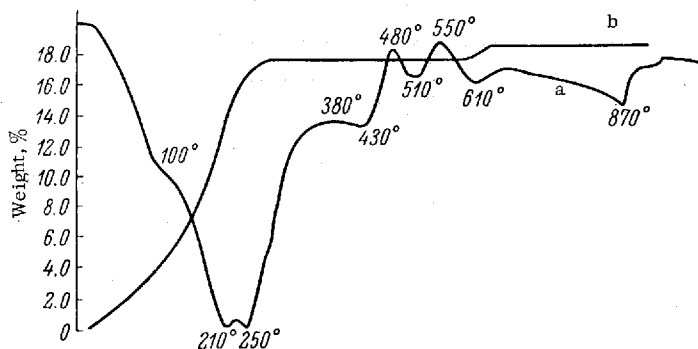


FIGURE 3. DTA curve (a) and loss of weight curve (b) of melkovite

Spectrographic analyses of melkovite showed $n \cdot 0.1\%$ Al, Ti, Si, and Mg; $n \cdot 0.01\%$ Ba, V, Ir, Pb, and Mn; and $n \cdot 0.001\%$ or less Cu, La, Ge, and Yb.

The DTA curve of melkovite (fig. 3a) shows an endothermic trough with two maxima at 210° and 250° C and an exothermic peak with maxima at 480° and 550° C. The weak endothermic effect at 870° C marks fusion of the mineral into a dark-gray bead. It may be concluded from the X-ray analyses of the products of heating and the loss of weight curve (table 2 and fig. 3b) that the first endothermic effect in the $30^\circ - 250^\circ$ C interval records loss of adsorbed ($\sim 4\%$) and crystallization ($\sim 13\%$) water. As can be seen from Table 2 the removal of adsorbed water at temperatures up to 100° C has no effect on the crystal structure of melkovite. The water of crystallization begins to separate at a temperature of 105° C and this is recorded by a flexure on the DTA curve. The dehydration of melkovite causes gradual destruction of its structure, and at $200 - 300^\circ$ C the mineral becomes X-ray amorphous. The product of heating to 300° C is light gray, transparent, and optically isotropic. The first exothermic effect at 480° C records formation of a new crystalline phase showing MoO_3 and CaMoO_4 lines on the diffractogram. Heating to the second exothermic maximum at 550° C intensifies the CaMoO_4 lines. Formation of iron molybdate may be expected because of the high iron content in melkovite ($\sim 11\% \text{Fe}_2\text{O}_3$), and this is confirmed by the fact that the mineral fuses at 870° C, while calcium molybdate does not fuse even at higher temperatures.

Melkovite formed in the oxidized zone as a by-product of decomposition of molybdenite. It is intimately associated with jarosite and ferrimolybdate, whose suspensions have pH varying from 5.1 to 5.6, and indicate the weakly acid nature of the supergene solutions. Another recently described mineral, betpakdalite (Yermilova and Senderova, 1961), occurs in a similar environment. The similar conditions of

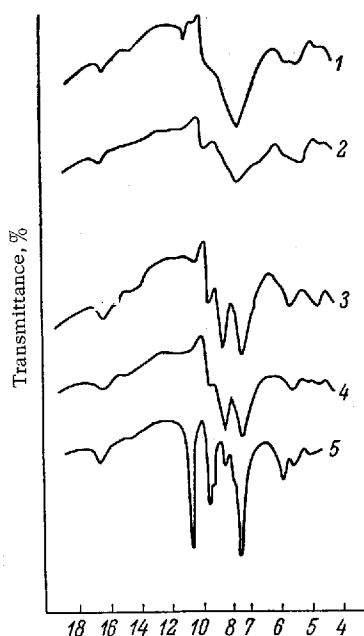


FIGURE 4. IR absorption spectra of - Ferrimolybdate (1 - Karaoba, 2 - Dzhiba) betpakdalite (3 - Betpakdala, 4 - Karaoba), 5 - melkovite.

formation of melkovite, ferrimolybdate, and betpakdalite, the fact that they are associated with the same minerals, and close chemical and structural similarity (as shown by the X-ray diffraction patterns), suggest that betpakdalite and melkovite are derived from ferrimolybdate by partial substitution of $[\text{AsO}_4]^{3-}$ (betpakdalite) or $[\text{PO}_4]^{3-}$ (melkovite) and $[\text{MoO}_4]^{2-}$. At the same time Fe^{3+} of ferrimolybdate is partially replaced by calcium and subordinate sodium, and it is probable that these substitutions are accompanied by formation of complexes.

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TABLE 2. Interplanar distances in melkovite (Å)

Temperature of heating, °C							
20		100		500		800	
<i>I</i>	$\frac{d_x}{n}$	<i>I</i>	$\frac{d_x}{n}$	<i>I</i>	$\frac{d_x}{n}$	<i>I</i>	$\frac{d_x}{n}$
7	8.42	10	8.31	—	—	—	—
1	6.91	—	—	1	6.91	—	—
1	5.58	—	—	—	—	—	—
1	4.659	1	4.66	3	4.66	—	4.78
1	4.278	2	4.31	2	4.18	1	4.34
1	3.895	1	3.95	10	3.77	1	3.98
8	3.537	9	3.54	5	3.38	1	3.56
1	3.477	—	—	5	3.19	3	3.36
1	3.186	2	3.17	10	3.06	10	3.09
7	3.036	8	3.09	4 b.	2.85	4	2.84
9	2.916	8	2.95	4 b.	2.59	3	2.70
1	2.816	—	—	1	2.47	4	2.48
1	2.675	—	2.68	2	2.28	3	2.27
3	2.565	4	2.58	1	2.20	2	2.20
5	2.415	3	2.43	2	2.11	4	2.12
1	2.375	—	—	1	1.999	1	1.986
2	2.255	—	—	1	1.915	8	1.921
2	2.194	2	2.20	4	1.834	7	1.834
1	2.134	—	—	1	1.799	1	1.732
1	2.054	—	—	1	1.738	—	—
6	1.992	5	1.999	1	1.689	8	1.689
1	1.932	1	1.898	1	1.625	1	1.633
1	1.880	1	1.865	8	1.577	8	1.581
7	1.789	7	1.804	1	1.553	5	1.543
3	1.746	2	1.756	1 b.	1.468	4	1.448
2	1.685	1	1.685	3	1.426	1	1.440
4	1.633	6	1.649	2	1.375	2	1.378
5	1.543	6	1.546	2	1.346	2	1.352
5	1.507	6	1.511	—	—	2	1.327
1	1.477	—	—	1	1.304	4	1.304
1	1.432	—	—	1	1.284	—	—
2	1.400	2	1.410	9	1.246	9	1.249
2	1.366	1	1.366	3	1.197	6	1.200
1	1.343	1	1.347	3	1.184	6	1.189
2	1.300	1	1.304	4	1.168	6	1.171
2	1.232	1	1.214	1	1.134	6	1.131
2	1.211	1	1.195	1	1.120	—	—
2	1.185	1	1.172	1	1.109	3	1.112
2	1.151	1	1.156	1 b.	1.088	4	1.093
1	1.141	1	1.143	1 b.	1.079	6	1.080
1	1.089	—	—	2	1.071	2	1.071
1	1.079	1	1.079	2	1.057	2	1.062
1	1.056	1	1.054	3	1.039	4	1.037
2 b.	1.043	1	1.046	5	1.012	10	1.010
1	1.020	—	—	—	—	—	—

NOTE: Fe anticathode, D = 57.3 mm, d = 0.5 mm, 35 kv, 12 ma, exposure 3 hours without filter; rotating crystal method; b - broad.

Investigation of these minerals by infrared absorption spectroscopy confirms presence of absorption bands corresponding to ion $[\text{AsO}_4]^{3-}$ in betpakdalite and of ion $[\text{PO}_4]^{3-}$ in melkovite (fig. 4). The IR spectra of ferrimolybdate, betpakdalite, and melkovite, obtained by E.S. Rudnitskaya (IGEM Akad. Nauk SSSR), show bands in the $800\text{-}830\text{ cm}^{-1}$ region, indicating presence of $[\text{MoO}_4]^{2-}$. The $[\text{AsO}_4]^{3-}$ bands also lie in approximately the same region. On the melkovite spectrum the absorption band of $[\text{PO}_4]^{3-}$ lies in the 1050 cm^{-1} region, and as in the case of betpakdalite the spectrum is complicated by the presence of a complex in the structure of the mineral.

The interplanar distances, calculated by A.D. Dara (Central Laboratory of Central Geological Survey Expedition) from the X-ray diffraction pattern of melkovite, are shown in Table 2. Considerable time will elapse before all of the data on melkovite are obtained and this

paper must be regarded as a preliminary report on the new mineral.

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Type samples of melkovite have been placed in the collection of the Mineralogical Museum, Academy of Sciences USSR.

REFERENCE

Yermilova, L.P., and Senderova, V.M., 1961, BETPAKDALITE, A NEW MINERAL FROM THE OXIDIZED ZONE OF THE KARAOBA WOLFRAMITE DEPOSIT: Zap. Vses. Min. Obshch., v. 90, no. 4.

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