MINERALOGY

PYROSMALITE FROM THE DZHUMART AND USHKATYN DEPOSITS, CENTRAL KAZAKHSTAN[1]

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Abstract: Pyrosmalite was found in the USSR for the first time at the Dzhumart and Ushkatyn deposits where the ore forms discordant stringers with virtually the same composition as hematite, magnetite or jacobsite-magnetite. Trace-element studies suggest that the iron and polymetal ores of the Atasu deposits have a common, hydrothermal source, unrelated to lower and middle Paleozoic intrusions of the district.

Pyrosmalite $(Mn, Fe)_8Si_6O_{15}(OH, Cl)_{10}$, a fairly rare silicate of iron and manganese, was first found in the USSR at the Dzhumart and Ushkatyn deposits, central Kazakhstan. It was previously known at deposits in Sweden, USA, Australia, Japan, China and England [4-9]. The information on pyrosmalite from these foreign deposits is partly summarized by Fan Te-Lien [3] from the data of other investigators.

The Dzhumart and Ushkatyn deposits lie in the west of the Atasu district, central Kazakhstan, within the Dzhail'ma synclinal structure of sedimentary, virtually calcareous and, to a lesser extent, volcanic rocks of Devonian and Lower Carboniferous age. Stratiform and lenticular bodies of iron and manganese ore as well as shows of lead-zinc mineralization of the same stratified type are confined to Upper Devonian rocks of the Fammenian stage.

The beds of iron-manganese ore are conformable to their host rocks at both deposits and, like them, are folded and faulted.

At the Dzhumart deposit the iron and manganese ores are isolated into individual bands and beds. The manganese ores here are mainly of the oxide (hausmannite-braunite) and silicate-oxide (tephroite-rhodonite-hausmannite-braunite) varieties. Besides the main rock-forming minerals, the manganese ores of the Dzhumart deposit include such minerals as friedelite, spessartine, Fe- and Al-bearing manganesic richterite, fowlerite, manganesic chlorite, franklinite, sarkinite, silicomanganesic berzeliite, etc., whose genesis, as we believe, was due to later hydrothermal metasomatic activity [1, 2].

The iron ores consist chiefly of hematite and magnetite. In the iron-ore body there are chlorite, tourmaline, albite, orthoclase, apatite, talc, fluorite, siderite, ankerite, etc. As already mentioned [1], the deposit also exhibits pyrosmalite forming a few crystalline to granular aggregates among iron ores with the virtual composition of magnetite, in association with chlorite, calcite and quartz.

At the Ushkatyn I deposit, unlike the Dzhumart deposit, the iron-manganese ores consist of hematite, magnetite, jacobsite and franklinite, with braunite and hausmannite completely absent. Fairly common in the ore horizon of this deposit are pyrosmalite, friedelite, arsenofriedelite, schallerite, tephroite, garnet, manganophyllite (?), severginite, penwithite, sphalerite, galena, etc. The sulfides of Zn, Pb and Cu and barite were formed after the hydrothermal Fe and Mn minerals.

The pyrosmalite described here forms discordant stringers, up to 3 cm thick, in ore with the virtual composition of hematite, magnetite or jacobsite-magnetite. It is associated with chlorite and calcite or calcite, galena, sphalerite, chalcopyrite and barite.

The specific gravity of pyrosmalite from the Ushkatyn I deposit as determined by the method of hydrostatic weighing is 3.07; the hardness is 4.5 to 5. It forms tabular or lamellar aggregates of a dirty green and brown color (Figs. 1 and 2).

The lamellar pyrosmalite crystals have a perfect (0001) cleavage (Fig. 2). The mineral is colorless in thin section with a yellowish green tone. It is slightly pleochroic: greenish yellow along β, colorless along γ. The extinction is straight, and the elongation positive. It is optically negative and uniaxial. The refractive indices are as follows:

$$N_0 = 1.671 \pm 0.001;\ N_e = 1.636 \pm 0.001;$$
$$N_0 - N_e = 0.035.$$

Pyrosmalite from the Ushkatyn deposit (sample No. 167, hole No. 1494, depth 117.00 m) was analyzed by R. I. Zaytseva in the institute's chemical laboratory. The chemical analysis of pyrosmalite from the Broken Hill deposit (Australia) is given for comparison.

Spectral analysis of pyrosmalite from the Ushkatyn I deposit showed that it contained hundredths of a per cent of lead, zinc and arsenic; thousandths of a per cent of beryllium and germanium; and traces of silver, copper and titanium.

Fig. 1. Hexagonal tablets of pyrosmalite. Thin section. 86 X.

Fig. 2. Lamellar pyrosmalite crystals with perfect cleavage. Thin section. 86 x.

Table 1

Chemical Analyses and Unit Cell Composition of Pyrosmalite

Constituent	Content, wt %		Atomic quantities		Unit cell composition, %				
					calculated				theoretical
	1	2	1	2	1		2		
FeO	17.05	21.41	0.2371	0.3000	Fe=5.02	15.84	Fe=6.30	16.03	16
MnO	32.96	32.39	0.4648	0.4562	Mn=9.83		Mn=9.67		
ZnO	1.92	0.07	0.0235	—	Zn=0.50				
CaO	1.29		0.0230	—	Ca=0.49				
MgO	—		—	—					
SiO_2	33.42	32.39	0.5562	0.5400	Si=11.76		Si=11.45		12
As_2O_3	—								
Al_2O_3			—	—	O=29.52		O=29.74		30
Fe_2O_3			—	—					
Cl	3.78	3.62	0.1064	0.1020	Cl=2.26	19.67	Cl=2.16	19.93	20
H_2O^+	9.36	10.22	0.8212	0.8410	OH=17.41		OH=17.83		
H_2O^-	0.07	—	—	—	H_2O=2.28		H_2O=3.10		
Total	99.85	100.10							
— O=Cl	0,85	0.81							
	99,00	99,29							

Footnote: 1) pyrosmalite from the Broken Hill deposit, Australia. Based on analysis, its formula is given as [6]: $2[(Mn, Fe, Zn, Ca)_8Si_6(OH, Cl)_{10}1.1\ H_2O]$. 2) pyrosmalite from the Ushkatyn I deposit. Based on the analysis given in Table 1, its formula may be written as $2[(Mn, Fe)_8Si_6O_{15}\ (OH, Cl)_{10}1.5H_2O]$.

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[1] Translated from: Pirosmalit iz mestorozhdeniy Dzhumart i Ushkatyn v Tsentral'nom Kazakhstane. Doklady Akademii Nauk SSSR, 1964, Vol. 159, No. 3, pp. 560-563.

Table 2

Interplanar Spacings and Relative Diffraction Line Intensities on X-Ray Powder Patterns of Pyrosmalite

Broken Hill, Australia [6]		Sterling Hill, USA [4]		Bafangtze, CPR [3]		Ushkatyn, USSR	
I	$\frac{d_\alpha}{n}$	I	$\frac{d_\alpha}{n}$	I	$\frac{d_\alpha}{n}$	I	$\frac{d_\alpha}{n}$
2	11.5	3	11.60	8*	10.36	—	—
8	7.16	10	7.16	9	7.07	4	7.170
1/2	6.65	1	6.71	—	—	—	—
3	6.06	3	6.09	1*	6.20	1	6.070
1/2	5.74	1	5.77	—	—	—	—
2	4.87	2	4.886	2*	4.70	2**	4.885
1	4.50	1	4.509	—	—	2**	4.427
2	4.35	1	4.376	2	4.32	—	—
2	3.73	2	3.736	—	—	2	3.704
5	3.58	8	3.583	5	3.53	7	3.578
4	3.41	4	3.419	2	3.38	4	3.418
1/2	3.34	3	3.338	—	—	—	—
trace	3.15	—	—	—	—	—	—
2	3.03	2	3.035	—	—	2	3.042
1	2.89	2	2.882	7	2.82	4	2.957
1	2.77	2	2.770	—	—	2	2.774
10	2.69	9	2.683	10	2.70	10	2.686
trace	2.61	—	—	—	—	—	—
1/2	2.52	2	2.549	—	—	1	2.543
—	—	—	—	—	—	1	2.475
1	2.38	2	2.385	2	2.38	1	2.401
—	—	1	2.334	—	—	1	2.357
7	2.25	7	2.251	8	2.23	8	2.251
trace	2.20	—	—	—	—	—	—
trace	2.13	1*	2.102	2	2.16	1	2.096
1/2	2.09	—	—	3	1.998	—	—
trace	2.02	—	—	—	—	1*	2.031
trace	1.930	—	—	—	—	—	—
trace	1.912	—	—	—	—	—	—
trace	1.892	—	—	—	—	1*	1.902
5	1.840	4	1.843	6	1.930	7	1.845
trace	1.797	1**	1.790	—	—	1	1.797
1/2	1.766	1	1.768	4	1.757	—	—
trace	1.734	1*	1.733	—	—	—	—
5	1.672	5	1.672	5	1.665	6	1.679
4	1.629	4	1.627	4	1.620	5	1.630
trace	1.608	—	—	—	—	—	—
trace	1.588	—	—	—	—	1**	1.585
trace	1.566	—	—	—	—	1**	1.575
5	1.521	5	1.523	4	1.514	5	1.524
1/2	1.459	—	—	1	1.447	1**	1.460
trace	1.427	1	1.432	—	—	—	—
4	1.419	2	1.419	3	1.416	4*	1.422
trace	1.397	1**	1.406	—	—	1*	1.395
2	1.370	2	1.371	1	1.370	3*	1.371
2	1.342	2	1.342	2	1.335	3*	1.346
trace	1.287	2	1.285	1	1.303	—	—
3	1.282	—	—	2	1.278	3	1.286
1/2	1.268	1	1.266	—	—	1*	1.271
trace	1.259	—	—	—	—	—	—
trace	1.245	—	—	—	—	—	—
3	1.238	1	1.238	2	1.233	3	1.241
trace	1.226	—	—	—	—	—	—
trace	1.216	—	—	—	—	—	—
trace	1.192	1	1.194	1	1.193	1*	1.187
1/2	1.178	—	—	1	1.174	1*	1.180
trace	1.152	—	—	—	—	—	—
1/2	1.142	—	—	—	—	2*	1.140
4	1.126	2*	1.126	3	1.122	3	1.125
trace	1.118	—	—	—	—	—	—
1	1.102	1**	1.106	3	1.099	1*	1.104
trace	1.094	—	—	—	—	—	—
2	1.0873	2**	1.089	—	—	4*	1.088
4	1.0820	2**	1.082	4*	1.081	4*	1.083
trace	1.060	1**	1.063	—	—	—	—
4	1.0472	1**	1.047	4	1.042	2*	1.048
1/2	1.0298	—	—	1	1.029	2*	1.030
1/2	1.0180	—	—	—	—	—	—
1/2	1.0100	—	—	—	—	—	—
trace	1.0055	—	—	—	—	—	—
5	0.9953	—	—	—	—	—	—

*Diffuse lines.
**Very diffuse lines.

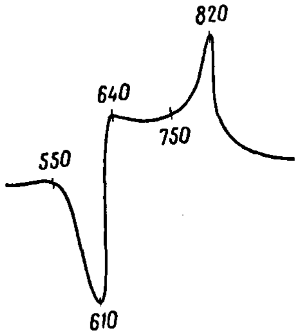

Fig. 3. Heating curve of pyrosmalite from the Ushkatyn deposit.

Figure 3 gives the heating curve of Kazakhstan pyrosmalite obtained on a UTA-1 unit at a heating rate of 67° per minute. The analysis was made by N. R. Pshenichnaya in the institute's thermographic laboratory. The heating curve of pyrsomalite reveals one pronounced endothermal effect between 550° and 620° plus two exothermal effects. The first exothermal effect at 620° to 640° is weaker than the second between 750° and 820°.

Table 2 gives the results of X-ray analysis of the pyrosmalite described. The survey was made with iron radiation; the camera had a diameter of 57.3 mm and a manganese filter. The unit cell constants were analyzed and calculated by T. P. Polyakova in the institute's X-ray laboratory.

Comparison of X-ray data for pyrosmalite from different deposits shows that there is good agreement between both the interplanar spacing values and the diffraction line intensities.

The X-ray data calculations performed for pyrosmalite from the Ushkatyn deposit yielded the following values for its unit cell constants: 13.39 Å along a_0, 7.18 Å along c_0. The figures obtained are very close to those of C. Frondel and L. Bauer [4].

A study of the mineralogy of the iron and manganese ores in various iron-manganese deposits of the Atasu district (Dzhumart, Kamys, Dzhayrem, Ushkatyn) leads to the following conclusions. 1. The primary iron and manganese minerals in these deposits belong to age and genetic groups: an early group, coeval with the host rocks, and a later epigenetic group, related to hydrothermal activity. The mineral-forming constituents of both genetic groups seem to have come from a long existing, deep magma chamber (or chambers) of Devonian – Early Carboniferous extrusive to intrusive volcanism. 2. The presence of arsenic and zinc in some hydrothermal minerals of iron and manganese [2] seems to imply that the iron-manganese and polymetal ores of the Atasu deposits have a common source. 3. Together with other features, the fairly wide development in the Atasu deposits of rare minerals like friedelite, franklinite, pyrosmalite, etc., found for the first time in our country [1, 2], differentiates them sharply from other iron-manganese deposits in the USSR and allows them to be regarded as a special, Atasu type. 4. Neither genetic group of iron and manganese minerals seems to have any direct relation to the intrusive rocks of the district situated in the lower and middle Paleozoic structural stages.

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REFERENCES

1. Kayupova, M. M. Izv. Akad. Nauk KazSSR, ser. geol., fasc. 2 (43), 1961.
2. Kayupova, M. M. Izv. Akad. Nauk KazSSR, ser. geol., fas. 6 (57), 1963.
3. Fan, Te-Lien. Dokl. Akad. Nauk, 126, No. 6, 1338, 1958.
4. Frondel, C. and L. Bauer. Am. Mineral., 38, No. 9/10, 755, 1953.
5. Osborne, H. Am. Mineral., 41, No. 7/8, 581, 1956.
6. Stillwell, F. and J. McAndrew. Mineral Mag., 31, No. 236, 371, 1957.
7. Watanable, T. and A. Kato. Mineral. J., 2, No. 3, 180, 1957.
8. Brown, P. E. Mineral. Mag., 32, No. 246, 242, 1959.
9. Watanabe, T. and A. Kato. Mineral. J., 3, No. 3, 130, 1961.

INVESTIGATION OF LAUMONTITE BY THE METHOD OF NUCLEAR MAGNETIC RESONANCE[1]

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Abstract: Investigation by the method of nuclear magnetic resonance indicates the crystallochemical formula of laumontite from the Nidym River locality is $(Ca_{3.85}Na_{0.23}K_{0.06})[Al_{7.96}Si_{16.03}O_{4.6}(OH)_2](OH)_2\cdot 14.1H_2O$.

Laumontite, a hydrous aluminosilicate of the zeolite group, is monoclinic and has the space group [3, 4] C2 or Cm. Its structure has not been studied. Its idealized crystallochemical formula [3] is $Ca_4Al_8Si_{16}O_{48}\cdot 16H_2O$.

To ascertain the position of protons, the n. m. r. spectra of protons in laumonite from dolerite-basalt mandelstone of the Nidyn River (Siberian platform) were recorded. The laumontite was carefully picked out under the binocular and analysed by the optical crystallographic, X-ray, chemical and thermal methods. To avert the atmospheric dehydration habitual to laumontite, involving the loss of 1/8 of its H_2O and its transition to β-leonhardite (caporcianite), the samples were kept in water while being transported from the deposit as well as during all subsequent stages of preparation. The material prepared (0.05-0.10 mm fraction) was pressed into tablets (d = 12 mm, h = 16 mm), which were packed into hermetically sealed quartz sample bottles (d = 14 mm, h = 20 mm).

The n. m. r. unit on which the investigations were carried out has been described in other work [7] [sic]. The spectra were photographed at temperatures of + 20, - 183 and - 196° and recorded with a time constant of 1 sec. The amplitude of magnetic field modulation was about 0.8 oe. The spectral derivatives obtained are presented in Fig. 1.

The spectra of laumontite at - 183 and - 196° (they are identical) are forbidden triplets. The proton resonance spectra of crystalline hydrates are known [6] to be doublets with intercomponent distances of some 10 oe. The spectra obtained can be regarded as a doublet with an intercomponent distance of some 10 oe plus a

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[1] Translated from: Issledovaniye lomontita metodom yadernogo magnitnogo rezonansa. Doklady Akademii Nauk SSSR, 1964, Vol.159, No.5, pp.1038-1040.