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Original scientific paper

ASSOCIATION OF THE WORLD BIGGEST CRYSTALS OF THE BRUCITE, Mg(OH)₂, FROM 'RŽANOVO, MACEDONIA

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A b s t r a c t: Within highly altered peridotite host rock in 'Ržanovo region, south of Kavadarci, big acicular, colorless crystals were found. X-ray powder diffraction pattern shows that this mineral is brucite.

Crystals up to 80 cm in size were found in serpentinized ultrabasic rocks, within veins. Needles are perpendicular to vein walls.

Its unit cell is: a = 4.648, c = 14.95 Å (rhombohedral a = 5.660 Å, $\alpha = 48.49^{\circ}$) V 279.7 Å³, Z 6 (rhombohedral 2).

Means of 4 sets of microprobe data combined with thermogravimetric measurement of H_2O yield in complete analysis: MgO 61.460, FeO 1.490, MnO 0.316, CaO 0.152, Na₂O 2.310, K₂O 0.102, SiO₂, 1.840, Al₂O₃ 3.230, H₂O 29.705. Total 100.495 wt.%.

The empirical formula is: $(Mg_{0.898}Fe_{0.012}Mn_{0.003}Na_{0.040}K_{0.001}Ca_{0.002}Al_{0.037}Si_{0.018}P_{0.001})(OH)_2$.

Key words: brucite; crystal; carbonate; fibrous mineral; IR spectroscopy; termogravimetric measurments; unit cell

INTRODUCTION

'Ržanovo region, nearby the village of Mrežičko, about 40 km south of Kavadarci (Fig.1) is a well known mine supplying ore for Fe-Ni metallurgy. The ore is placed in the central part of Kožuf Mountain on the right side of Porska River.

Geological position and characteristics of the ore deposit was described in many papers (Ivanov, 1959, 1960; Grafenauer and Strmole, 1966; Maksimović, 1981; Boev, 1982; Boev and Stojanov, 1985; Boev and Serafimovski, 1992; Boev and Lepitkova, 1994a; Boev and Lepitkova, 1994b; Boev and Serafimovski, 1995).

Open pit is part of the zone with ultrabasic rocks in the region Studena Voda-'Ržanovo-Nikodin-Klepa-Veles-Groot. The result of many faults and deformations in 'Ržanovo is very complex composition with serpentinized harzburgite, rare dunite, gabbropegmatite and rodingite, cretaceous sediments and sometimes with Triassic sediments. Triassic sediments are represented with two types of slightly metamorphosed rocks – quartz-sericite-clay schists sometimes with talc and limestones partly recrystallized. It is possible to distinguish two various types of serpentinized harzburgite. The first one is dark green to black tectonized breccia with fragments from few centimetres up to a meter in size. Breccia is cemented in very hard rock. Another type is grayish yellow altered serpentine. Milonitization and tectonization were significant processes during incorporation of the rock in the early host. It is believed that this process happened during the Jurassic period. Final deposition of this complex happened during Laramic orogen phase.

Ore layer is about 750 m long and 15 to 25 m thick and ended with the faults on NW and SE part of the deposit.

Within serpentinized ultrabasic rocks it is possible to find many veins filled with fibrous white minerals. Sometimes these veins could be up to 80 cm thick.

The present study was performed to describe an occurrence of very big crystals of brucite and its associated minerals. It was also intended to describe the conditions of crystallization of such a big crystal.



Fig.1. Map of Macedonia with the position of 'Ržanovo mine

EXPERIMENTAL

Within the veins two mineral phases could be found. One mineral is fibrous mineral with very long, brittle needles, white in color, sometimes a little greenish. Its hardness is $2\frac{1}{2}$.

The other one is compact white mineral with a little porcelaneous luster. It has also good rhombohedral cleavage and its hardness is $3\frac{1}{2}$. These minerals were investigated by using polarizing microscope, X-ray diffraction – powder method, and microprobe analysis combined with IR spectroscopy and thermogravimetric measurements. Indexed powder patterns (after JCPDS 44-1482) were used for calculation of unit cell dimensions for both minerals investigated.

RESULTS

Few big needles were fixed with Canada balsam to have thin section for investigation with polarizing microscope. It was obvious that the mineral has very good cleavage perpendicular to needles elongation. The mineral has high birefringence and is optically positive. It is optically biaxial with moderate optical axial angle (about $20 - 30^{\circ}$).

X-ray diffraction of fibrous mineral was undoubtfully identified to be a pattern of brucite (Table 1).

Calculated unit cell parameters are:

a = 3.1458(7) Åc = 4.766(2) Å $V = 40.84(2) \text{ Å}^3$

Relative intensity of basal reflection is enhanced in this pattern, most likely because of preferred orientation, due to perfect basal cleavage.

Table 1

Powder diffraction pattern of brucite from 'Ržanovo

20	dhkl	hkl	1	I (44–1482)
18.62	4.772	001	100	53
32.84	2.7317	100	0.3	6
38.01	2.3712	101	12	100
50.85	1.7986	102	8	29
58.65	1.5765	110	1.4	33

The other mineral was also prepared for Xray powder method. But its pattern is attributed to some dolomite-type carbonate mineral. It was not possible to judge which one, because of their similar unit cells (Table 2).

Table 2

Powder diffraction pattern of dolomite-type carbonate from 'Ržanovo.

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20	dhk]	hkl	I	I (36–426)
22.13	4.0235	101	0.2	1
24.15	3.6913	012	0.5	4
31.045	2.8855	104	100	100
33.620	2.6701	006	1	4
35.395	2.5402	015	1	3
37.430	2.4066	110	1	7
41.215	2.1940	113	4	19
43.885	2.0665	021	0.2	3
45.020	2.0170	202	1.5	10
49.360	1.8493	024	0.5	3
50.600	1.8069	018	5	10
51.155	1.7886	116	2	13
51.305	1.7837	009	1.5	2
59.165	1.5642	211	0.1	2

From these data calculated unit cell parameters are:

> a = x.1458(7)Å c = xx.766(2)Å V = 319.1(2)Å³

Such optical and X-ray diffraction data are not consistent, because brucite has to be optically uniaxial. For such peculiar optical properties it is necessary to find the reason. Although it was already reported that brucite could be slightly biaxial, such a big optical axial angle is not common.

This is a good reason to look at the chemical composition, just to make sure if there is any chemical reason for deviation of the optical properties. The other reason is to see which mineral is in association with this unusual brucite.

The results of microprobe analyses of both, brucite and carbonate are listed in Table 3.

IR spectra and thermogravimetric curves were produced to distinguish CO_2 and H_2O contents of observed minerals.

IR spectrum of brucite shows just very sharp absorptions at 3700 cm⁻¹ due to OH vibrations. On the opposite, IR spectrum of carbonate contains absorptions at 2800 to 3000 cm⁻¹ due to CO₃ vibrations. In both spectra there are also vibrations about 2300 cm⁻¹ due to CO₂ vibrations from the air.

Table 3

Microprobe analyses of brucite and associated carbonate from 'Ržanovo.

Element	Brucite	Carbonate	
	%	%	
Na ₂ O	2.130	0.012	
K ₂ O	0.102	0.012	
MgO	61.460	21.63	
CaO	0.152	30.07	
MnO	0.316	0.835	
FeO	1.490	0.468	
Al ₂ O ₃	3.230	0.006	
SiO ₂	1.840	-	
LOI	29.705	47.22	
Total	100.425	100.253	
Na	0.041	0.001	
К	0.001	0.000	
Mg	0.899	0.995	
Ca	0.002	0.994	
Mn	0.003	0.022	
Fe	0.012	0.012	
Al	0.037	0.000	
Si	0.018		
Н	1.943		
С		1.998	



Fig. 2. DTA-TG curves of brucite



Fig. 3. DTA-TG curves of carbonate



Fig. 4. IR spectra of brucite



Fig. 5. IR spectra of carbonate

Thermogravimetric curves gave 29.705 wt% H_2O in the case of brucite and 47.22 wt% of CO_2 in case of carbonate. Carbonate was decomposed in two distinct steps, which is in accordance to dolomite type carbonate.

All the elements are included in formula calculations. In that case calculated density is 2.447 g/cm³ for brucite.

The other mineral, dolomite, is also very pure and close to the end-member. Microprobe analyses gave formula:

 $(Ca_{0.99}Mg_{0.99}Mn_{0.02}Fe_{0.01})_{\Sigma_{2.01}}(CO_{3})_{2}$.

This is nice and rare example of nearly pure end-member of one mineral.

Among the measured trace elements, just Ni is elevated (about 2 ppm) in brucite and Sr (about 1 ppm) in associated dolomite and all other elements are insignificant (As, Ag, Cr, Zn, Cu, Pb, Cd, Co, Tl, Y, Sr, Ba, and Ga).

DISCUSSION

It is not likely that Si, Al, Ca, K, and Na are really incorporated in crystal structure of brucite, but there was no single solid inclusion visible in the optical microscope. Thin sections of this mineral show moderate to high birefringence and significant optical axial angle (estimated, but not measured, about 20 to 30°). It is uncommon that needles of brucite show biaxial optical figure, with high optical axial angle. It is normally, as hexagonal mineral, uniaxial, but this anomaly could be explained due to the pressure acting to the extremely long crystals. Structural anomalies are not expected. It is also possible that needles of brucite are mixed with much less needles of serpentine. This would explain small percentage of Si and Al in the analyses.

There is no high Mn content in the brucite from 'Ržanovo, which explaines the acicular growth of this mineral in many other occurrences.

Brucite from 'Ržanovo is the example of the biggest known crystal of these mineral in the world. Probable reason for the formation of such big crystals in circulation of hydrothermal solutions through the fractures in the rock whose thickness increased due to relaxation of the rock during uplift. It is a product of hydrothermal alteration of peridotitic host rock. In this process dolomite is also produced. Association of the world biggest crystals of the brucite, Mg(OH), from 'Ržanovo, Macedonia

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Резиме

АСОЦИЈАЦИЈА НА СВЕТСКИ НАЈГОЛЕМИТЕ КРИСТАЛИ НА БРУЦИТ (Mg(OH)₂), ОД 'РЖАНОВО, МАКЕДОНИЈА

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Клучни зборови: бруцит; кристал; карбонати; фиброзен минерал; спектроскопски и термогравиметриски испитувања

Во матичните високо алтерисани перидотитски стени во 'ржановскиот регион, јужно од Кавадарци, се најдени големи иглести безбојни кристали. Рендгенско-дифракционите испитувања покажуваат дека се работи за минералот бруцит.

Кристалите долги до 80 cm беа откриени во серпентинизираните ултрабазични карпи, во самите жили. Иглите се перпендикуларни на ѕидовите на жилите.

Димензиите на елементарната ќелија се: a = 4,648, c = 14,95 Å (ромбоедричен), a = 5,660 Å, $\alpha = 48,49$ °, V 279,7 Å, Z 6 (ромбоедричен 2). Податоците добиени од 4 микропробни анализи заедно со термогравиметриски мерења на H₂O даваат комплетна анализа:

MgO 61,460, FeO 1,490, MnO 0,316, CaO 0,152, Na₂O 2,310, K₂O 0,102, SiO₂ 1,840, Al₂O₃ 3,230, H₂O 29,705. Вкупно: 100,495 wt%.

Емпириската формула е :

 $(Mg_{0.898}, Fe_{0.012}, Mn_{0.003}, Na_{0.040}, K_{0.001}, Ca_{0.002}, Al_{0.037}, Si_{0.018}, P_{0.001})$ (OH)_{2.}