COMPARATIVE CHARACTERISTICS OF ENDOGENIC KUTNAHORITE FROM RIBNITSA DEPOSIT AND EXOGENIC KUTNAHORITE FROM KREMIKOVTSI DEPOSIT

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ABSTRACT

The kutnahorite is considered to be a rare mineral with dominant hydrothermal or metamorphic origin. Two genetic types of kutnahorite (endogenic – from the Pb-Zn mineralization in Ribnitsa deposit, Madan ore field, and supergene – from the limonite ore in Kremikovtsi deposit) are objects of examination and comparison in the present paper. The mineral was found in the central parts of the quartz-galena-sphalerite veins, or as creamy to pale rose coloured monomineral veinlets in the Ribnitsa deposit. Kutnahorite, associated with supergene carbonates (spherosiderite, rhodochrosite, calcite), neotocite, goethite and supergene barite, was established at the lowermost levels of the oxidation zone in the Kremikovtsi deposit as colloform milk-white to pale creamy coloured, or snow-white fine needle-like aggregates. The mineral was studied by XRD, chemical and thermal analyses, SEM and TEM. The data obtained show that the two genetic types of kutnahorite studied by their chemical composition and structural ordering. The endogenic kutnahorite is represented by ordered Fe-Mg varieties and the exogenic kutnahorite – by partially ordered Ca varieties.

INTRODUCTION

The kutnahorite is considered to be a rare mineral with dominant hydrothermal or metamorphic origin. Single finds of exogenic kutnahorite, associated with aragonite in sediments and karst terrains in Italy were reported by Bini and Menchetti (1985), Cancian and Princivalle (1991). In Bulgaria this mineral was found in several deposits: Ruen (Dragov, 1965), Ribnitsa (Kolkovski *et al.*, 1980) and Martinovo (Dragov and Neykov, 1991).

The morphology, structure, chemical composition and thermal behaviour of two genetic types of kutnahorite (endogenic – from the Pb-Zn mineralization in Ribnitsa deposit, Madan ore field, and exogenic – from the limonite ore of Kremikovtsi deposit) are objects of examination and comparison in the present paper.

The Ribnitsa Pb-Zn deposit is located in the western part of Madan ore field, Central Rhodopes. Kolkovski *et al.* (1980) distinguished 6 mineralization stages in the deposit describing the kutnahorite as developed in kutnahorite-rhodochrosite-Mn-calcite stage. The mineral has been found in the central parts of the ore veins in association with Mn-calcite. According to Kolkovski *et al.* (1980) the carbonates from this stage are formed in the 275-220°C temperature interval.

The Kremikovtsi complex-ore deposit is composed of three types of iron ores (siderite, hematite and limonite), large reserves of barite ore and low-grade polymetallic sulphide mineralization (Panayotov, 1974; Atanassov, 1977; Damyanov, 1998). It is situated in the Vraca-Kremikovtsi ore district from

the Stara planina metallogenic zone. It is hosted in the dolomitic limestones of the Iskar Carbonate Group (T_2) . A large part of the deposit is occupied by limonite formed during a prolonged three-stage (Pre-Pliocene, Pliocene and Post-Pliocene) secondary alteration. The Pliocene stage of supergene alteration took place under relatively reducing conditions, when secondary ores were overflowed by lake water. During these stages secondary carbonates, barite and sulphides were formed. The kutnahorite was established at the lowermost levels of the oxidation zone in association with supergene carbonates, neotocite, goethite and barite as colloform and stalactite–shaped milk-white to pale creamy coloured or snow-white fine needle-like aggregates in cavities within the limonite.

MATERIALS AND METHODS

The chemical composition, structural characteristics and thermal behaviour of morphologically different representative samples from the two genetic types of kutnahorite were studied. The quantitative chemical analyses were performed in CNIL "Geochemistry" (UMG "St. I. Rilski") and SU "St. K. Ohridski". The distribution of the major elements (Ca and Mn) in characteristic X-rays and the microprobe data were obtained using a JEOL JSM-35-CF device (Tracor Northem TH 2000) in "EUROTEST" PIc. X-ray diffraction (XRD) patterns were obtained with a DRON-1 diffractometer (CuKα radiation, Ni filter) and a 57.3 mm Debye-Scherrer TUR–M–62 camera in UMG "St. I. Rilski" and SU "St. K. Ohridski". DTA curves were recorded with a Derivatograph apparatus in static air at the following conditions: (a) DTA = 1/10, DTG = 1/15, TG = 500,

sample weight – 1 g, rate of heating – 10° /min, and (b) DTA = 1/10, DTG = 1/10, TG = 1000, sample weight – 1 g, rate of heating – 5° /min. The morphology and the phase inhomogeneity of the mineral were studied by a SEM "JSM-T 20" and TEM "EMV 100L" in MSU "M. Lomonosov", Russia.

RESULTS AND DISSCUSSION

Mode of occurrence

Kutnahorite, associated with Mn-calcite, has been established at the lower levels of the ore veins in the Ribnitsa deposit. It forms pale rose to creamy coloured grain aggregates and partially cements or crosscut sulphide minerals. As a rule, the mineral occupies the central parts of the ore veins. It is formed after the main ore parageneses (quartz-galena and quartz-sphalerite-galena).

The kutnahorite from the Kremikovtsi deposit has been found at the lowermost levels of the oxidation zone near the boundary with the primary siderite. It forms colloform, rarely stalactite-shaped, milk-white to pale creamy coloured aggregates (3-4 mm in diameter and up to 15 mm in length). In cross-sections these aggregates show fine concentric-zonal structure and are needle-like at the periphery (Fig. 1a). The kutnahorite is deposited most often over supergene siderite (spherosiderite) in cavities within the limonite and associates with massive or fibrous goethite, neotocite, supergene barite and calcite. Snow-white fine needle-like or radial-fibrous aggregates with rare vellowish to brown surface pigmentation were also found. Fine fibrous white kutnahorite overgrowths over rhodochrosite have been observed rarely as well. SEM observations show rhombohedral habit of kutnahorite individuals (Fig. 1b).

Chemical composition

Chemical compositions of kutnahorite from the present study as well, as from other deposits – Ruen (Dragov, 1965) and Martinovo (Dragov and Neykov, 1991), Franklin, USA (Frondel and Bauer, 1955), Kutna Hora (Trdlička, 1963) and Chvaletice, Czech Republic (Žak and Povondra, 1981), Ryûjima, Japan (Tsusue, 1967), are presented in Table 1 and Fig. 2. The compositions of some rare finds of Ca-rich kutnahorite (Gabrielson and Sundius, 1966; Tanida and Kitamura, 1982; Bini and Menchetti, 1985) are also shown.

The endogenic kutnahorite from Ribnitsa deposit is characterised by increased Mg contents (14,64–19,34 mol% MgCO₃) and according to the classification, proposed by Mincheva-Stefanova and Gorova (1967), should be described as Fe-Mg variety of this mineral. According to these authors, only carbonates containing CaMn(CO₃)₂ in the range 70-100% have to be denoted by the name "kutnahorite". Carbonates with lower contents of this component and respectively with higher CaMg(CO₃)₂ and CaFe(CO₃)₂ content should be considered as Fe-Mg varieties of kutnahorite that reflects more appropriately their chemical features.

The analysed samples from Ribnitsa deposit show compositions relatively close to the kutnahorite from Chvaletice (Žak and Povondra, 1981) and Ryûjima, Japan (Tsusue,1967). The bulk analyses of the carbonates studied have insignificant deviations from the standard composition of this mineral and a

slight excess of Ca (Table 1). The kutnahorite compositional non-stoichiometry has been debated many times in the literature. It has been noted presence in nature of both phases with Ca deficiency (Ca < Mn+Mg+Fe) and Ca excess (Reeder, 1983; Goldsmith, 1983; Essene, 1983; Yanchuk *et al.*, 1991). A part of Ca cations in the non-stoichiometric carbonates with dolomite-type structure and Ca >1 is considered to be in B-positions. Some authors accepted that instead of the preferable disposition of Mn²⁺ in the relatively smaller B-positions, a part of it at least is possible to substitute Ca²⁺ in the A-position at higher temperatures.

The possibility of Mn^{2+} disposition in both cationic positions (A and B) is determined by the Mn^{2+} ionic radius, the size of which is between those of Ca²⁺ μ Mg²⁺ (Lumsden and Lloyd, 1984; Reeder, 1983; Goldsmith, 1983). This fact explains the presence of natural phases with non-stoichiometric compositions and some Ca deficiency as well, as the conventional and often established partial structural disorder of the mineral.

Table 1. Chemical compositions (mol%) of kutnahorite from different deposits.

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	Carbonate component (mol%)										
Nº	Formula coefficient of the respective cation										
	CaCO₃	MnCO₃	MgCO₃	FeCO ₃							
1	54.46	22.94	19.34	3.26							
	(1.09)	(0.46)	(0.39)	(0.06)							
2	53.03	26.20	14.64	6.13							
	(1.06)	(0.53)	(0.29)	(0.12)							
3	51.13	20.12	19.01	9.74							
	(1.02)	(0.40)	(0.38)	(0.20)							
4*	49.00	23.55	13.60	13.85							
	(0.980)	(0.471)	(0.272)	(0.277)							
5	51.50	42.00	5.77	0.73							
	(1.030)	(0.840)	(0.115)	(0.015)							
6	51.00	35.85	10.12	3.03							
	(1.02)	(0.72)	(0.20)	(0.06)							
7	51.22	23.73	12.42	12.63							
	(1.02)	(0.48)	(0.25)	(0.25)							
8	47.45	34.75	11.30	6.50							
	(0.95)	(0.69)	(0.23)	(0.13)							
9	48.53	24.90	24.81	1.76							
	(0.965)	(0.496)	(0.494)	(0.035)							
10	74.00	19.00	7.00	-							
	(1.48)	(0.38)	(0.14)	-							
11*	66.95	26.35	6.50	0.20							
	(1.339)	(0.527)	(0.130)	(0.004)							
12	64.03	31.06	4.12	0.79							
	(1.29)	(0.63)	(0.08)	(0.02)							
13	68.86	25.37	5.36	0.41							
	(1.38)	(0.51)	(0.11)	(0.01)							

* Microprobe data.

1 - Ribnitsa; 2 - Ribnitsa (Kolkovski *et al.*,1980); 3 - Ruen (Dragov, 1965); 4 - Martinovo (Dragov and Neykov, 1991); 5 – Franklin, USA (Frondel and Bauer, 1955); 6, 7 – Kutna Hora, Czech Republic (Trdlička, 1963); 8 - Chvaletice, Czech Republic (Žak and Povondra, 1981); 9 - Ryûjima, Japan (Tsusue, 1967); 10 - Långban, Sweden (Gabrielson and Sundius, 1966); 11 – Levane, Upper Valdarno, Italy (Bini and Menchetti, 1985); 12 - Fujikura, Japan (Tanida and Kitamura, 1982); 13 - Kremikovtsi.

ANNUAL University of Mining and Geology "St. Ivan Rilski", vol. 46 (2003), part I GEOLOGY AND GEOPHYSICS

Vassileva M. et al. COMPARATIVE CHARACTERISTICS OF ENDOGENIC ...



Figure 1. Morphological features of kutnahorite from Kremikovtsi deposit. a) needle-like aggregates of kutnahorite, SEM; b) aggregates of rhombohedral kutnahorite microcrystals, SEM; c) backscattered electron image of kutnahorite grain, SEM; d) MnKα image of kutnahorite, SEM; e) CaKα image of kutnahorite, SEM; f, g) heterogeneous fabric of kutnahorite surface, TEM; h, i) microrelief of fresh-broken kutnahorite surface, TEM.



Figure 2. Compositional variations of kutnahorite in the CaMn(CO₃)₂-CaMg(CO₃)₂-CaFe(CO₃)₂ system. The numbers of analyses are as in Table 1.

The kutnahorite from the Kremikovtsi deposit is represented by Ca-rich varieties (Table 1). The Ca content is lower than that in the Ca-rich kutnahorite from Långban, Sweden. Compositionally, the mineral studied is very similar to the supergene kutnahorite, associated with aragonite in sediments from Levane, Upper Valdarno, Italy (Bini and Menchetti, 1985). The observed area distribution of the major elements (Ca and Mn) in the mineral is characterised by welldeveloped zoning (Fig. 1d, e). In some areas the Ca and Mn distribution is almost equal, whereas in other areas high Ca concentration and absence of Mn are apparent (see lower right corners in Fig. 1d, e).

The Ca and Mn distribution is an indication of phase inhomogeneity in the exogenic kutnahorite studied that was supported by the TEM examinations. In some of the samples micro-fissures and well-expressed cleavage planes were observed, along which irregular micro-inclusions about 1 μ m in length (Fig. 1f, g) were observed. Well-expressed microrelief is visible also in Fig. 1h, i (fresh broken kutnahorite surface). The phase micro-inhomogeneity is typical for the kutnahorite and has been noted by many authors (Žak and Povondra, 1981; Goldsmith, 1983; Peacor *et al.*, 1987).

XRD and thermal data

XRD data of kutnahorite from Ribnitsa and Kremikovtsi deposits are presented in Table 2. They are compared with standards for ordered kutnahorite and Ca-rich kutnahorite. The data obtained show that the mineral from Ribnitsa deposit is distinguished by slightly lower d-values in comparison with the standard from Franklin, USA, because of the differences in chemical composition and higher Mg²⁺ content.

The XRD data of kutnahorite from Kremikovtsi deposit are similar to those of Ca-rich varieties, described in the literature (Gabrielson and Sundius, 1966; Tanida and Kitamura, 1982; Bini and Menchetti, 1985). The XRD patterns are an indication of partially ordered structure. Many authors noted that very often there are no reflexes of distant order on the XRD patterns of ordered natural kutnahorite and synthetic phases with CaMn(CO₃)₂ composition (Winter et al., 1981; Essene, 1983; Reeder, 1983; Goldsmith, 1983; Peacor et al., 1987; Yanchuk et al., 1991). This resulted in terminological difficulties, because the term "kutnahorite" was used the first time for an ordered phase with dolomite-type structure and Mn > Mg. Recently it has been adopted, this term to be applied for all the compositions close to the end member CaMn(CO₃)₂. Distinguishing of disordered natural phases with the same composition is complete by appending an adjective "calcian" or "disordered" (Essene, 1983; Peacor et al., 1987).

As the XRD data and chemical composition are not good enough to distinguish adequate kutnahorite from other carbonates mineral diagnostics can be substantially improved by means of the DTA analysis (Pavlishin and Slivko, 1962; Yanchuk *et al.*, 1991). The kutnahorite has a dolomite-type structure and its DTA curve is characterised by two endothermic peaks related to the two stages of double carbonate decomposition (Pavlishin and Slivko, 1962). According to Yanchuk *et al.* (1991) at thermal examinations of Ca-Mn carbonates in air complication of shape of the thermal curves, because of the practically simultaneous development of two processes – carbonate dissociation and oxidation of the products obtained is possible. Therefore these authors recommend registration of DTA curves in helium.

Published DTA curves of chemically different natural kutnahorites show some differences: in some cases they are of dolomite-type, in other – of ankerite-type (Frondel and Bauer, 1955; Trdlička, 1963; Tsusue, 1967; Tanida and Kitamura, 1982; Bini and Menchetti, 1985; Dragov, 1965; Kostov, 1993). The chemical composition of kutnahorite reflects on the character of the DTA curves. According to Trdlička (1963) the higher Mn²⁺ contents leads to appearance of the first endothermic effect at lower temperatures, whereas the lower Fe²⁺ contents – decreases intensity of the typical for the mineral two endothermic effects. In contrast of the natural phases, the thermal curves of hydrothermally synthesised kutnahorite show an endothermic peak at 862°C

only, corresponding to one-stage decomposition at heating following the reaction:

 $CaMn(CO_3)_2 + O_2 \rightarrow CaMnO_3 + 2CO_2$ (Fazeli and Tarean, 1982). It is possible, that the synthetic phase studied by these authors was with disordered structure of calcite-type.



Figure 3. DTA curves of kutnahorite from Ribnitsa (a) and Kremikovtsi (b) deposits.

The DTA curve of kutnahorite from Ribnitsa deposit (Fig. 3a) shows two intensive endothermic peaks (at 760° and 900°C) and very slightly expressed another one (at 820°C) greatly resembling both the standard curve from Franklin, USA (Frondel and Bauer, 1955), and the curve published by Kostov (1993).

The DTA curve of exogenic kutnahorite from Kremikovtsi deposit (Fig. 3b) is of dolomite-type. It is characterised by the presence of two endothermic peaks at 760° and 850°C, the first one being slightly expressed. It is also scarcely visible endothermic peak 800°C. This DTA curve is very similar to the curve from the classic deposit Kutna Hora, Czech Republic (Trdlička, 1963).

CONCLUSIONS

The results from the present study show that the two genetic types of kutnahorite examined differ in their chemical composition and structural ordering. The endogenic kutnahorite from Ribnitsa deposit is represented by Fe-Mg varieties with high structural ordering. The supergene kutnahorite from Kremikovtsi deposit is formed under subaqueous supergene conditions in association with secondary carbonates. The mineral has partially ordered structure and is represented by calcian varieties.

Table 2. XF	RD data of	f kutnah	orite from R	ibnitsa an	d Kremikovt	si deposits.									
Kutnahorite,		Fe-Mg		Fe-Mg		Ca-rich kutnahorite,		Ca-rich		Ca-rich		Ca-rich			
Franklin, USA		kutnahorite,		kutnahorite,		Långban, Sweden		kutnahorite,		kutnahorite,		kutnahorite,			
(ASTM 11-345)		Ribn	Ribnitsa		Ribnitsa		(ASTM 19-234)		Kremikovtsi		Kremikovtsi		Kremikovtsi		
hkl	d (Å)	1/10	d (Å)	1/1o	d (Å)	1/lo	hki	d (A)	1/10	d (A)	1/10	d (A)	1/1 ₀	d (A)	1/1o
101	4.27	6					101	4.13	10					0.75	
012	3.75	20	3.73	1	3.74	2	012	3.78	40	3.80	8	3.8	4	3.75	2
104	2.94	100	2.902	10	2.916	10	104	2.981	100	2.986	100	2.96	10	2.96	10
006	2.73	6					006, 015	2.771	10	2.786	2				
015	2.59	4													
110	2.44	14	2.429	2	2.475	3	110	2.462	40	2.464	9	2.44	5	2.46	3
113	2.23	20	2.210	2	2.210	5	113, 021	2.248	50	2.253	10	2.25	6	2.24	. 4 .
021	2.10	4													
107	2.04	20	1.982	3	2.030	4	202	2.062	50	2.067	10	2.06	6	2.05	5
024	1.876	10			1.870	1	024	1.896	20	1.899	4				
018	1.837	25	1.828	5			018	1.869	50	1.875	12	1.878	6	1.867	2
009	1.814	30	1.803	5	1.813	7d				-					
							116	1.840	60	1.844	12	1.839	7d	1.831	3
211	1.588	6					211	1.601	20	1.606	2				
122	1.566	4	1.556	2	1.556	3	122, 10 <u>10</u>	1.578	30	1.584	4	1.586	4	1.575	1
212	1.540	4								_					
214	1.486	8	1.477	2	1.482	1	214	1.501	20	1.503	3	1.500	3	1.499	1
028	1.469	4					208	1.487	10	1.492	3				
119	1.465	4					119	1.478	10						
125	1.409	6	1.394	3	1.397	2	125, 10 <u>11</u>	1.448	10						
							300	1.418	30	1.422	3	1.424	2	1.414	1
0.0.12	1.363	6			1.358	1	0012, 217	1.386	20	1.391	2				
2.0.10	1.294	4					02 <u>10</u>	1.311	10						
128	1.258	4	1.246	1	1.246	1	128	1.273	20						
2.0.11	1.189	4					2011	1.229	10						
2.1.10	1.145	4													
	1.141	4			1.137	1						1.138	1		
134	1.126	6	1.119	2	1.119	2									L
0.0.15	1.089	4			1.108	1									
2.0.14	1.022	6	1.016	5	1.013	2						1.033	1	1.029	1
F	eK., (Ni)		FeK,	(Mn)	FeK	" (Mn)		CoK.,		CuK,	, (Ni)	CuK,	, (Ni)	CuK,	u (Ni)

Vassileva M. et al. COMPARATIVE CHARACTERISTICS OF ENDOGENIC

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