MINERALS AND PARAGENESES = OF MINERALS

Cymrite As an Indicator of High Barium Activity in the Formation of Hydrothermal Rocks Related to Carbonatites of the Kola Peninsula

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Abstract—Cymrite, $BaAl_2Si_2O_8 \cdot nH_2O$, is a rare mineral formed during low-grade dynamothermal metamorphism ($T = 250-300^{\circ}$ C, P = 1-3 kbar). Cymrite has been described from many metasedimentary ores and hydrothermal rocks. In carbonatites, it has been found for the first time. Cymrite has been identified in the Kovdor and Seblyavr massifs, Kola Peninsula. In Kovdor, this mineral has been described from one of the hydrothermal veins cutting the pyroxenite-melilitite-ijolite complex at the Phlogopite deposit; cymrite is associated with thomsonite, calcite, and stivensite. In the Seblyavr pluton, cymrite occurs in thin veins of calcite carbonatite that cut pyroxenite contacting with ijolite. Cymrite from the Seblyavr pluton is associated with calcite, natrolite, pyrite, and chalcopyrite. The mineral is optically negative and uniaxial, with extinction parallel to elongation; $\omega \sim 1.607(1)$. According to X-ray diffraction data, cymrite from Seblyavr is monoclinic, space group P1m1; unit-cell dimensions are: a = 5.33, b = 36.96, c = 7.66 Å, $\beta = 90^{\circ}$, V = 1510.55 Å³. According to the results of IR spectroscopy, in the series of samples from different massifs (in the running order Kovdor-Voishor-Seblyavr), the double-layer deformation is enhanced and accompanied by a decrease in the Si-O-Si angle and weakening of hydrogen bonds of interlayer water. The empirical formulas of cymrite calculated from electron microprobe analyses are $Ba_{0.93-0.95}Ca_{0.01-0.02}K_{0.00-0.05}Na_{0.02-0.04}Al_{1.97-2.01}Si_{1.99-2.03}O_8(H_2O)$ and $Ba_{1.00-1.02}Ca_{0.00-0.01}Sr_{0.00-0.01}Fe_{0.00-0.01}Al_{1.94-2.00}Si_{1.98-2.03}O_8(H_2O)$ at Seblyavr and Kovdor, respectively. Cymrite from the carbonatite massifs of the Kola Peninsula was formed under hydrothermal conditions at low temperature (200–300°C), high activity of Ba and Si, and high water pressure. At Kovdor, the mineral crystallized directly from the residual solution enriched in Ba. The sequence of mineral deposition is as follows: thomsonite-cymrite-calcite-stevensite. Cymrite from the Seblyavr pluton is a product of hydrothermal alteration of primary Na-K-Ba silicates of ijolite: nepheline, feldspar, and probably celsian. Natrolite replaces cymrite indicating high alkalinity of late hydrothermal fluids.

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INTRODUCTION

Cymrite, $BaAl_2Si_2O_8 \cdot nH_2O$, where n = 0.5-1.0 (Mandarino and Back, 2004), is a rare mineral; its findings have been sparse worldwide. The formation of cymrite in carbonatites associated with alkaline ultramatic plutons is unique and atypical. Usually, it is formed at metasedimentary or hydrothermal ore deposits, as well as during the late stages of low-grade metamorphism, at a temperature of 250–300°C and a pressure 1–3 kbar (Hsu, 1994; Matsuraba et al., 2000; Moro et al., 2001).

Cymrite was discovered in hydrothermal manganese–silicate ore at the Benallt deposit, Carnarvonshire, Great Britain (Smith et al., 1949); later it was described from the copper ore hosted in metasedimentary carbonate rocks at the Ruby Creek deposit, Alaska (Brosge, 1960; Carron et al., 1964; Runnels, 1964). The mineral is characteristic of contact zones of serpentinized graywacke and ultramafics, California, United States (Essene, 1967) and hydrothermally altered volcaniclastic rocks with pyrite ore at the La Zarza deposit, Spain (Aye and Strauss, 1975). It was found in gold-bearing veins hosted in black shale at the Nelson deposit, New Zealand (Soong and Olovecrona, 1975); in sphalerite ore localized in micaceous and siliceous limestone, eastern Carpathians, Romania (Udubasa, 1986); and in manganese ore at the Shiromaru deposit, Tokyo, Japan (Matsubara and Kato, 1991; Matsubara et al., 2000). Cymrite is frequently deposited in rocks enriched in barium: barite-bearing siliceous metamorphic rocks in Nevada, United Sates (Hsu, 1996), and the Zamora sedex barite deposit in Spain (Moro et al., 2001).

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In Russia, cymrite was described for the first time from the Baikal region (Kashaev, 1966). Later, it was found at deposits in the polar Urals: in base-metal ore at the Saurei deposit hosted in sedimentary carbonate rocks (Shirobokova et al., 1979, 1981), in copper sandstone at the Pad'yaga deposit (Tikhomirova, 1998; Tikhomirova et al., 1999), and at the Voishor basemetal deposit (a sample from the collection of All-Russia Institute of Mineral Resources was kindly placed at our disposal by N.V. Skorobogatova). Cymrite was also found in base-metal ore at the Pavlovsky deposit, Novaya Zemlya, hosted in limestone and orthoquartzite (Gavrilenko et al., 1999).

Mineral assemblages of cymrite from all of the above-mentioned deposits are similar and contain quartz, barite, albite, feldspathoids (including banalsite), sulfides, apatite, and carbonate, as well as micagroup minerals; celsian, hyalophane, and edingtonite are locally observed. The sulfide mineralogy depends on type of base-metal ores; usually, these are pyrite, sphalerite, and galena. As a rule, cymrite is formed at the contact of orebodies and host rocks. It crystallizes under hydrothermal conditions corresponding to the low-grade dynamothermal metamorphism (Hsu, 1994; Matsubara et al., 2000; Moro et al., 2001). Hydrothermal cymrite develops as crystals or their intergrowths and commonly occurs in rock cavities. In metamorphic rocks, the mineral occurs as anhedral grains or flattened crystals in interstices of carbonate, albite, or quartz grains (Smith et al., 1949; Runnells, 1964; Shirobokova et al., 1979; Tikhomirova et al., 1999; Moro et al., 2001). Cymrite intergrown with other associated minerals (including barium ones) fills thin veinlets along contact between ore zones and host rocks (Essene, 1967; Soong and Olivercrona, 1975; Shirobokova et al., 1979).

Morphology of the mineral is uniform; it occurs as elongated lamellar or tabular crystals (Smith et al., 1949; Runnells, 1964; Essene, 1967; Soong and Olovecrona, 1975; Shirobokova et al., 1979; Moro et al., 2001); short-prismatic hexagonal crystals in form of twinned intergrowths are scarce (Bolotina et al., 1991). Opaque cymrite crystals are white, while transparent grains are colorless, with vitreous luster and proper cleavage in line with elongation.

During the ore formation at the base-metal deposits, cymrite is one the earliest minerals. Under the effect of late hydrothermal fluids, the mineral becomes unstable and is replaced by secondary phases (Moro et al., 2001). For example, at the Ruby Creek copper deposit in Alaska (Runnells, 1964), it is replaced by aggregate of quartz and chlorite with contemporaneously formed pyrite, chalcopyrite, bornite, and chalcocite; a fine-grained mixture of kaolinite and barite is observed as secondary minerals after cymrite. In serpentinite at one of the deposits in California (Essene, 1967), cymrite is partially replaced by dark brown segregations of unidentified phases containing inclusions of lawsonite. At the Saurei base-metal deposit, cymrite inclusions were

observed in galena closely intergrown with barite. It has been suggested that cymrite is the a result of replacement of barite due to hydrothermal metasomatic processes (Shirobokova et al., 1979; Moro et al., 2001). Relics of barite are frequently found in hyalophane, celsian, cymrite, and other Ba-bearing minerals (Moro et al., 2001).

CYMRITE IN CARBONATITE

Cymrite was found in the Kovdor and Seblyavr carbonatites. These represent two of the largest carbonatite massifs among 20 Paleozoic alkaline ultramafic plutons in the Kola alkaline province. Like most similar massifs, Seblyavr and Kovdor are differentiated concentrically zoned intrusive complexes. The diverse intrusive rocks are accompanied by unique and variable mineralogy. The greatest quantity of mineral species occurs in the rocks of hybrid zones, contact-metasomatic rocks, and related late vein bodies, pegmatites, and hydrothermal rocks, where primary magmatic minerals are combined with products of secondary hydrothermal metasomatic alteration. The accessory minerals in late carbonatite and hydrothermal rocks are diverse and individualized, with a significant role being played by barium minerals in hydrothermal assemblages of the Seblyavr and Kovdor massifs (Sorokhtina and Pakhomovsky, 2001; Moiseev and Chukanov, 2006). This is direct evidence of an increase in the barium activity of the residual postmagmatic fluids responsible for the origin of these rocks. In addition, potassium feldspar, which would facilitate the scattering of barium, is practically absent in hydrothermal rocks related to carbonatite, in contrast to the hydrothermal rocks from such peralkaline complexes as Khibiny and Lovozero.

In pegmatites of the Kovdor massif, a special stage is characterized by the formation of barium titanosilicates (phosphoinnelite, batisite, Ba-rich shcherbakovite, baritolamprophyllite, nabalamprophyllite) and Ba-bearing minerals of the eudialyte group (Moiseev and Chukanov, 2006). At the hydrothermal stage, barium mainly concentrates in harmotome and in such minerals of the labuntsovite group as lemmleinite-Ba, labuntsovite-Mg, and labuntsovite-Fe.

In the late carbonatite of the Seblyavr massif at the contact zone between ultramafic and alkaline rocks, barium mineralization is also abundant (Sorokhtina et al., 2001; Sorokhtina and Pakhomovsky, 2001). Primary titanium, zirconium, and niobium oxides and hydroxides give way to secondary Ba-bearing oxides (Ba-bearing zirconolite, bariumpyrochlore, Ba–Nb oxides from the hydrous double niobates) and silicates (belkovite, Ba–Zr–Ti silicate). These minerals are associated with the late carbonates including Ba-bearing ones such as ancylite-(Ce), mackelveyite-(Y), strontianite, baritocalcite, alstonite, paralstonite, and olekminskite; phosphates; and sulfates (barite, gypsum). In addition, edingtonite, a barium zeolite, was found in the late carbonatite at the contact with ijolite.



Fig. 1. Spherulites (3 mm in diameter) of cymrite (Cm) overgrowing thomsonite (Tm), Kovdor massif. (Calc) is calcite.

In the Kovdor and Seblyavr massifs, cymrite was identified in two different mineral assemblages.

Calcium peralkaline pegmatites, which are affected by hydrothermal alteration to a variable degree, are abundant at the Phlogopite deposit of Kovdor. Most veins are composed of crystalline aggregate of thomsonite and less frequent scolecite. Locally, thomsonite replaces early feldspathoids (cancrinite, nepheline). Thomsonite is also deposited in the central cavernous parts of pegmatite veins (Moiseev and Chukanov, 2006). Most veins are located in the area uncovered at the northern wall of the Phlogopite open pit composed of mellilite rocks, pyroxenite, blocks of olivine-phlogopite clinopyroxenite and phlogopite clinopyroxenite, ijolite dykes, early calcite carbonatite, metasomatic rocks, and hydrothermal veins. Cymrite was found in one of the hydrothermal veins. The mineral is located in cavities filled by tabular thomsonite crystals and their druses (Fig. 1). Cymrite directly overgrows the thomsonite crystals as light yellow, transparent, radiant or flaky spherulites up to 3 mm in diameter. In turn, cymrite is overgrown by calcite scalenohedrons. Brown aggregates of stevensite probably replacing pyroxene or pectolite are observable in Sr-rich variety of thomsonite-Ca. In some hydrothermal rocks of this area, harmotome, which has the empirical formula $Ba_{2.00}K_{0.71}Ca_{0.42}[(Si_{10.74}Al_{5.26})_{\Sigma 16.00}O_{32}] \cdot nH_2O (n \sim 12),$ is the major carrier of barium (Moiseev and Chukanov, 2006).

In the Seblyavr massif, cymrite was found in 1- to 5-cm-thick veinlets of late calcite carbonatite, which cut pyroxenite at the contact with ijolite (Fig. 2). The host-rock minerals associated with cymrite are diopside, hastingsite, perovskite, phlogopite, apatite, titanite, and pyrrhotite; the minerals from the immediate



Fig. 2. Cymrite (Cm) and natrolite (Nt) in a veinlet of late calcite carbonatite (Calc) crosscutting pyroxenite (Px), Seblyavr massif, Kola Peninsula. (Ij) ijolite, (Sl) sulfides, (Phlg) phlogopite, (Prv) perovskite. Sketch of a polished section.

assemblage are calcite, natrolite, pyrite, and chalcopyrite. Together with pink-white finely acicular natrolite, cymrite occurs as pockets and veinletlike segregations up to 2 cm in size. Apatite and calcite surround the cymrite–natrolite pockets; thin veinlets of calcite intersect host rocks.

Cymrite constitutes bluish white lamellar segregations up to 0.5 cm long. The mineral is opaque, with a silky luster; proper cleavage parallel to elongation and hackly fracture is typical. Internal heterogeneity of the cymrite lamellae is observed in immersion liquids: the needle-shaped domains are enveloped by friable zones of alteration (decomposition), which prevent the observation of anisotropy (Figs. 3a, 3b). The mineral is uniaxial (approximately isotropic), negative, with extinction parallel to elongation; $\omega \approx 1.607(1)$.

CRYSTAL STRUCTURE OF CYMRITE

X-ray powder diffraction data (Table 1) and infrared spectra of cymrite from carbonatite massifs and basemetal deposits of the Polar Urals were obtained (Fig. 4). According to X-ray powder pattern (Table 1), the mineral from the Seblyavr massif corresponds to monoclinic cymrite. Operating conditions (RDK-114.6; Fe K_{α} -radiation) correspond to those of standard samples (Table 1). The comparative X-ray diffraction patterns of standard cymrite (Bolotina et al., 1991) are also given in this table.

The IR spectra were recorded with a Specord 75 IR two-beam spectrophotometer (Carl Zeiss, Jena) within the wavenumber range from 400 to 3800 cm⁻¹ at the bandwidth slit of $<2 \text{ cm}^{-1}$ in a range of 400–1400 cm⁻¹ and of $<8 \text{ cm}^{-1}$ in a range of 1400–3800 cm⁻¹ at the Institute of Problems of Chemical Physics, Russian Academy of Sciences. Standards were polysterene and



Fig. 3. Lamellar crystals of cymrite (Cm) replaced by natrolite (Nt) and calcite (Calc), Seblyavr massif, Kola Peninsula: (a) a closeup of the sample image; (b) individual crystals. BSE images and images in characteristic radiation of Ba, Ca, and Na.

gaseous ammonia. The samples were prepared as pellets with excess KBr. A mineral-free KBr pellet was placed in the beam during recording of spectrum. According to the results, the IR-spectra of cymrite samples from Kovdor and Seblyavr are similar and close to the IR-spectrum of the sample from the Voishor deposit in the polar Urals (collection of N.V. Skorobogatova).

There are additional bands in the IR-spectra of samples from the Seblyavr pluton and Voishor deposit (at 1332 and 1270 cm⁻¹, and within range of 3200– 3400 cm⁻¹, respectively); these bands probably correspond to the alteration products of the mineral. The



Fig. 4. IR spectra of cymrite from (a) Kovdor and (b) Seblyavr massifs, Kola Peninsula and (c) Voishor deposit, the Polar Urals.

weak absorption bands at 1332 and 1270 cm⁻¹ can be assigned to orthoborate $(BO_3^{3-} \text{ ions})$ or H⁺ ion vibrations; however, inference of the latter is unlikely, because of the absence of acid OH group bands in the spectrum. The bands at 1630 and 1623 cm⁻¹ and 3537 and 3550 cm⁻¹ correspond to water molecules in samples from the Seblyavr pluton and Voishor deposit. The bands within range the 3200-3400 cm⁻¹ are related to zeolite-type water, which yield hydrogen bonds of medium strength. The IR-spectrum of cymrite from Kovdor does not show additional bands. A single band of O–H stretching vibrations (3552 cm^{-1}) is assigned to water molecules forming weak hydrogen bonds. The hydrogen bond strength in the samples increases from Kovdor through Voishor to Seblyavr. The frequency of band within the range of 1178–1186 cm⁻¹ (stretching

Table 1. X-ray diffraction data and unit-cell dimensions of cymrite

hhl	Ι	D _{obs}	$D_{\rm calc}$	Ι	$D_{\rm obs}$	$D_{\rm calc}$	
πκι	1			2			
001	4	7.654	7.663	50	7.71	7.698	
140,080	2	4.012	4.019	90	4.02	4.030	
141,081	1	3.830	3.832	10	3.85	3 849	
142, 082	10	2.946	2.948	100	2.96	2.960	
1.12.0, 200	9	2.667	2.667	70	2.67	2.674	
003 _	2	2.558	2.554	10	2.57	2.566	
1.12.1, 201	1	2.515	2.519	10	2.53	2.526	
280, 0.16.0 083 143	3 4	2.309	2.310	20 40	2.31	2.315	
281, 0.16.1	6	2.210	2.211	40	2.21	2.217	
1.12.2	1	2.186	2.190	10	2.195	2.196	
282, 0.16.2	4	1.979	1.977	10	1.962	1.984	
004	4	1.917	1.916	30	1.925	1.925	
1.12.3, 203	5	1.841	1.844	40	1.850	1.851	
084, 144 340, 1,20,0	3	1.769 1.748	1.770 1.746	5	1.770	1.777	
2.16.1, 341, 1.20.1	6	1.701	1.702	20	1.703	1.706	
1.20.2, 2.16.2, 342	6	1.589	1.589	30	1.591	1.593	
$1.12.4, 20\overline{4}$	3	1.556	1.556	20	1.560	1.562	
3.12.0, 0.24.0	3	1.539	1.540	20	1.541	1.543	
$27\bar{4}$	2	1.507	1.492	5	1.496	1.498	
145,085	3	1.455	1.455	20	1.462	1.461	
$2.16.\overline{3}, 343, 1.20.\overline{3}$	1	1.440	1.442	104	1.445	1.446	
2.24.0, 400	4	1.334	1.334	15	1.334	1.337	
0.24.3, 3.12.3	2	1.319	1.319	5	1.321	1.323	
344, 1.20.4, 2.16.4	1	1.298	1.290	5	1.294	1.295	
0.16.5, 285	3	1.284	1.277	20	1.282	1.282	
1.28.1, 481, 3.20.1	3	1.270	1.264	5	1.264	1.267	
146,086	1	1.233	1.231	5	1.236	1.236	
482, 3.20.3, 1.28.2	1	1.215	1.215	5	1.216	2.218	
3.12.4, 0.24.4	1	1.200	1.201	5	1.203	1.204	
$2.24.\bar{3},403$	1	1.183	1.182	5	1.185	1.186	
$34\bar{5}, 1.20.5, 2.16.\bar{5}$	2	1.152	1.152	20	1.155	1.156	
3.20.3, 483	1	1.144	1.145	5	1.146	1.149	
286, 0.16.6	1	1.127	1.118	10	1.123	1.122	
$2.24.\bar{4}, 40\bar{4}, 414$	2	1.095	1.095	10	1.098	1.098	
147, 087 2.31.2. 3.21.4	2	1.068 1.051	1.065 1.047	10 5	1.071 1.050	1.070 1.050	
1.20.6. 2.16.6. 346	_		1.031	5	1.035	1.035	
	Unit-cell dimensions						
a, Å	5.333(8)			5.346(2)			
b, A	36.96(6)			37.05(2)			
c, A B. deg	7.00(1) 90(0(2)			/.098(1) 90.0			
V, Å ³	1510.55			1524.74			

Note: (1) Cymrite from the Seblyavr massif, Kola Peninsula; (2) literature data by Bolotina et al. (1991). D_{obs} is based on JCPDS 17-507; RKD-114.56 mm, Fe K_{α} -radiation; D_{calc} is calculated from the unit-cell dimensions.

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Commonant	Seblyavr			Kovdor			Voishor		
Component	1	2	3	4	5	6	7	8	9
BaO	38.81	39.03	31.89	41.46	40.00	41.10	39.37	38.93	39.40
CaO	0.08	0.23	0.07		0.05	0.10			
SrO					0.39	0.39			
K ₂ O	0.60	0.62	0.22				0.04	0.02	0.05
Na ₂ O	0.34	0.19							
FeO				0.13		0.06			
$A1_2O_3$	27.31	27.36	20.44	26.90	25.95	26.55	26.55	26.21	26.85
SiO ₂	33.17	32.07	25.89	31.44	32.00	32.35	29.99	30.52	30.05
Total	100.31	99.50	78.51	99.93	98.39	100.55	95.95	95.68	96.35
Coefficient in formula (O = 8)									
Ba	0.93	0.95	0.99	1.02	1.00	1.01	1.01	0.99	1.00
Ca	0.01	0.02	0.01			0.01			
Sr					0.01	0.01			
Κ	0.05	0.05	0.02						
Na	0.04	0.02							
Fe				0.01					
Al	1.97	2.01	1.91	2.00	1.94	1.95	2.05	2.01	2.06
Si	2.03	1.99	2.06	1.98	2.03	2.02	1.96	1.99	1.95

 Table 2. Chemical composition of cymrite, wt %

Note: (1, 2) Unaltered and (3) altered domains of a single crystal; (4–9) various crystals.

vibrations of the Si–O–Si bridges bonding two-dimensional tetrahedral sheets into two-story layers) increases in the same order. Thus, the deformation of double layers accompanied by the decrease in the Si–O–Si angle results in a decrease in the hydrogen bond strength formed by water molecules located within these layers.

CHEMICAL COMPOSITION AND PHASE HETEROGENEITY

The chemical composition and formulas of cymrite from the carbonatite massifs are given in Table 2; the sample from the Voishor deposit, polar Urals, used in IR spectroscopy was added for comparison. The composition of cymrite from the carbonatite massifs corresponds to the theoretical one in respect to Al and Si contents. The decrease in barium concentration is balanced out by small amounts of Ca, Sr, K, and Fe in the sample from Kovdor, and Ca, K, and Na, in the sample from Seblyavr.

Cymrite from the Kovdor massif, like the reference sample from the Voishor deposit, is distinguished by homogeneous, stable chemical composition, and absence of zoning. The mineral from Seblyavr is characterized by intraphase and phase heterogeneity (Fig. 3b). The central parts of the mineral grains fit ordinary cymrite in composition. At margins of lamellae, areas are observed that are more friable and that quickly damage under beam of an electron microprobe; in these areas, the mineral structure probably becomes looser and the water content increases. The close intergrowths of cymrite with calcite and natrolite are also observable in marginal zones.

The chemical composition of zeolites associated with cymrite from Kovdor and Seblyavr is given in Table 3.

THERMODYNAMIC CONDITIONS OF CYMRITE FORMATION

The formation conditions of cymrite are treated in publications ambiguously (Seki and Kennedy, 1964; Essene, 1967; Matsuraba and Kato, 1991; Hsu, 1994; Moro et al., 2001). According to the thermodynamic parameters of synthesis of barium silicates—celsian, sanbornite, and cymrite—the latter can form in a hydrous environment under high pressure and variable temperature (Seki and Kennedy, 1964). As shown in the paper cited above, pure cymrite crystallizes under a water pressure of 18 kbar or higher within a wide temperature range of 200–600°C. The decreasing pressure leads to the formation of hexagonal celsian associated with monoclinic cymrite. The field of stability of cym-

Component	Thomsonite-Ca, Kovdor	Natrolite, Seblyavr				
Na ₂ O	3.31	16.46				
K ₂ O	—	—				
CaO	6.65	0.65				
SrO	10.06	—				
BaO	1.62	0.11				
MgO	—	—				
FeO	—	-				
A1 ₂ O ₃	27.87	27.83				
SiO ₂	34.47	46.66				
H ₂ O		8.29				
Total	83.98	100.00				
Coefficient in formula						
Na	0.95	2.00				
Κ	_					
Ca	1.05	0.04				
Sr	0.86					
Ba	0.09					
Mg	-					
Fe	-					
Al	4.88	2.06				
Si	5.12	2.93				
H ₂ O		1.74				
Mode of calculation	Si + Al = 10	O = 10				

Table 3. Chemical composition of zeolites associated with
cymrite in carbonatite, Kola Peninsula, wt %

rite expands toward low pressure, where the mineral can be associated with celsian.

Celsian and cymrite can be final products of interaction of barium and potassium feldspars with water. Seki and Kennedy (1964) suggested two mechanisms of the cymrite formation:

(1) sanidine + $H_2O \longrightarrow$ (KSi-BaAl) solid solution \longrightarrow celsian \longrightarrow cymrite and

(2) sanidine + $H_2O \longrightarrow$ "K-cymrite" KHAlSi₂O₈ · OH \longrightarrow (KH–Ba) solid solution \longrightarrow cymrite \longrightarrow (Al–SiOH) solid solution \longrightarrow celsian.

The equilibrium between barium phases and solid solution is described by the reaction (Seki and Kennedy, 1964): $2 \times \text{cymrite [BaAlSi_3O_8(OH)]} \longrightarrow \text{celsian BaAl_2Si_2O_8)} + \text{sanbornite (BaSi_2O_5)} + 2 \times \text{quartz (SiO_2)} + \text{water (H_2O)}.$

This reaction can shift both to the right and to the left depending on the partial pressure of water. A high partial water pressure, as well as a high hydrostatic pressure, leads to cymrite formation (Seki and Kennedy, 1964).

The above-mentioned experimental data are confirmed by natural relationships, for example, by cymrite formation in metamorphic rocks. In the Franciscan Formation, California, United States, the mineral is associated with lawsonite, albite, and calcite in serpentinite and metagreywacke at the contact with ultramafic rocks, i.e.; it is formed in presence of water (Essene, 1967).

Cymrite can form under low-temperature hydrothermal conditions in association with celsian and zeolites. The joint deposition of cymrite and edingtonite was documented at the Shiromaru hydrothermal manganese deposit, Tokyo, Japan (Matsubara and Kato, 1991; Matsubara et al., 2000), where other barium and strontium phases (celsian, banalsute, strontianite, strontianite, strontiumpiemontite, and barite) were identified as well. Edingtonite combined with celsian fills the crosscutting ore layers of late veinlets and is regarded as the latest mineral replacing celsian under hydrothermal conditions. Cymrite is formed before edingtonite but later than celsian. Its crystallization conditions are close to the conditions of low-grade metamorphism (Matsubara et al., 1991).

The formation of cymrite and other barium phases at the Zamora barite deposit is explained by successive deposition of all these barium phases from the Ba–Al– Si gel (Matsubara et al., 2001). Harmotome or unknown barium hydrosilicate (BaAl₂Si₆O₈·4H₂O) might be primary phases for the formation of (Ba,K)feldspathoids and other barium minerals, including cymrite. Because of dehydration under near-surface conditions, celsian is deposited after cymrite: BaAl₂Si₆O₈·nH₂O \longrightarrow BaAl₂Si₆O₈ (Moro et al., 2001).

Experiments on synthesis of cymrite (Hsu, 1994) showed that the cymrite-like phases $BaAl_2Si_6O_8 \cdot H_2O$ can be stable under hydrothermal near-surface conditions at a pressure higher than 0.5 kbar and a temperature higher than 250°C or under conditions of low-grade metamorphism corresponding to greenschist facies. In the paper cited above, the reaction of cymrite formation by decomposition of barite in alkaline medium has been reported: $BaSO_4 + 2OH^- + Al_2O_3 + C_2OH^-$

 $2\mathrm{SiO}_2 = \mathrm{BaAl}_2\mathrm{Si}_6\mathrm{O}_8\cdot\mathrm{H}_2\mathrm{O} + \mathrm{SO}_4^{2-}.$

ORIGIN OF CYMRITE IN KOVDOR AND SEBLYAVR

In the carbonatite massifs of the Kola Peninsula, cymrite was most probably formed under hydrothermal conditions at low temperature (200–300°C) and high barium activity. In Kovdor, the mineral crystallized directly from residual hydrothermal solution as indicated by free growth in druse cavities of carbonatite and the succession of mineral deposition: thomsonite–cymrite–calcite–stevensite. In addition, early minerals (pyroxene and/or pectolite) associated with cymrite are replaced by smectite (stevensite) rather than amphibole as an indirect indication of high water activity.

The alkali-earth elements in the Kovdor assemblage are clearly partitioned between mineral phases: barium is incorporated into cymrite; strontium, into thomsonite; calcium, into thomsonite and calcite; and magnesium, into stevensite. The cymrite deposition is probably facilitated by the low concentration of SO_4^{2-} and CO_3^{2-} ions, which prevents formation of nonsilicate barium phases, carbonates, and barite. As a result of thomsonite deposition, the concentration of strontium in fluid decreases. The precipitation of phosphoinnelite instead of common sulfate-dominant innelite also testifies to the low activity of SO_4^{2-} ions in hydrothermal vein bodies of Kovdor.

According to the deposition conditions of zeolites in hydrothermal rocks of alkaline plutons, thomsonite crystallizes later than natrolite with the upper limit of stability at about 300°C (Pekov et al., 2004). On the basis of data on synthesis of barium zeolites, Barrer (1982) showed that they formed at a temperature as high as 300°C, whereas celsian crystallizes at 380°C or higher. Because cymrite in Kovdor formed later than thomsonite, the temperature of its formation can be estimated at 250–300°C in consistence with experimental data (Hsu, 1994).

In the Seblyavr massif, cymrite is closely associated with natrolite, calcite, and pyrite and predates the replacement of natrolite. It can be suggested that these minerals were formed as products of alteration of primary Na–K–Ba silicates of ijolite, nepheline or feldspathoids, for instance, celsian. The formation of cymrite after celsian under hydrothermal conditions was described from the Shiromaru manganese deposits, Tokyo, Japan, by Matsubara and Kato (1991). Development of natrolite after cymrite in Seblyavr indicates a high-alkalinity medium favorable for dissolution of the mineral, substitution of Na for Ba, and deposition of zeolites.

According to the conditions of cymrite crystallization described above, an aqueous environment, variable temperature, and enrichment in barium are necessary to form this mineral (Seki and Kennedy, 1964). Two ways of enrichment of the hydrothermal solution in barium are possible. The first variant is applicable to Seblyavr, where hydrothermal fluids interacting with rocks from contact zones are enriched in alkali-earth elements (for example, derived from feldspathoids and micas) and take part in exchange with primary minerals of ijolites (nepheline, feldspar, etc.). The decomposition of primary minerals leads to cymrite formation and afterward to the deposition of zeolites. The second way looks plausible for the case of Kovdor, where the solution is initially enriched in barium, because early rocks are depleted in barium-bearing orthoclase. There is hardly any orthoclase in pegmatites either. While the hydrothermal solution cools, barium is captured by the progressively formed minerals, titanosilicates, cymrite, and harmotome.

CONCLUSIONS

(1) Cymrite was found in the Kovdor and Seblyavr carbonatite massifs for the first time.

(2) In Kovdor, cymrite is the primary barium mineral of the hydrothermal assemblage, whereas in Seblyavr, this mineral is secondary.

(3) In both massifs, cymrite was formed under hydrothermal conditions at elevated chemical activities of barium and silicon, as well as relatively high partial pressure of water and low temperature (up to 300°C). In Kovdor, deposition of cymrite was accompanied by a decrease in Sr^{2+} , SO_4^{2-} , and CO_3^{2-} activity.

(4) In Kovdor, cymrite crystallized directly from the late hydrothermal solution that had inherited barium from the primary fluid; in Seblyavr, cymrite is a result of replacement of potassium–barium feldspathoids.

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