

## Genesis and Compositional Characteristics of Natural $\gamma$ -CrOOH

A. K. Shpachenko<sup>a</sup>, N. V. Sorokhtina<sup>b</sup>, N. V. Chukanov<sup>c</sup>,  
A. N. Gorshkov<sup>d</sup>, and A. V. Sivtsov<sup>d</sup>

<sup>a</sup>*Geological Institute, Kola Research Center, Russian Academy of Sciences, ul. Fersmana 14,  
Apatity, Murmansk oblast, 184200 Russia*

<sup>b</sup>*Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences,  
ul. Kosygina 19, Moscow, 119991 Russia*

<sup>c</sup>*Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*

<sup>d</sup>*Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences,  
Staromonetnyi per. 35, Moscow, 109017 Russia*

Received October 13, 2004

**Abstract**—Natural  $\gamma$ -CrOOH was first found and studied in rischorrite of the Khibina Massif, in which this mineral is associated with gonardite, natrolite, phillipsite, and saponite and usually forms microcrystallites in a matrix of amorphous CrOOH hydrogel or, more rarely, occurs as fine-crystalline, thin acicular, and lumpy aggregates of a green and emerald-green color. X-ray powder diffraction data indicate that crystalline blocks consist of a mineral with a rhombohedral unit cell, *Cmcm*,  $a = 3.86 \text{ \AA}$ ,  $b = 12.78 \text{ \AA}$ , and  $c = 3.04 \text{ \AA}$ . Chromium oxyhydroxide from the Khibina Massif is isostructural with  $\gamma$ -CrOOH from the Iksinskoe deposit, but significantly differs from it in bearing low Al concentrations. The empirical formula of the Khibina  $\gamma$ -CrOOH is  $(\text{Cr}_{0.94}\text{Mg}_{0.03}\text{Al}_{0.02}\text{Ti}_{0.01}\text{Fe}_{0.01})_{1.01}\text{O}(\text{OH}) \cdot n\text{H}_2\text{O}$ . The Cr oxyhydroxide and associated zeolites crystallized from low-temperature hydrothermal solutions rich in Na. The most probable source of Cr for the  $\gamma$ -CrOOH in the Khibina Massif was titanomagnetite in xenoliths of ultrabasic rocks in the rischorrites affected by postmagmatic alterations.

**DOI:** 10.1134/S0016702906070056

### INTRODUCTION

Oxyhydroxides of Cr were studied for more than eight decades. Brief historical reviews on the synthesis and studying of Cr compounds were published by Rode [1], Chalyi [2], and Milton et al. [3]. The first synthesized Cr oxyhydroxide was the trigonal modification of CrOOH, which was erroneously identified as  $\alpha$ -CrOOH [1]. There are three currently known synthetic polymorphs of CrOOH: trigonal CrOOH, orthorhombic  $\beta$ -CrOOH, and  $\gamma$ -CrOOH (which was synthesized in the late 1950s [4]). Neither orthorhombic  $\alpha$ -CrOOH nor a bracewellite analogue have been synthesized (Tables 1, 2).

The naturally occurring chromium oxyhydrates approved in 1977 by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (IMA-CNMMN) include three species: bracewellite (orthorhombic CrOOH), gyanite (orthorhombic  $\beta$ -CrOOH), and grimaldiite (trigonal CrOOH). In this paper, we adhere to the name *gyanite* (after the locality where the mineral was first found in nature in Guyana), which was approved by IMA-CNMMN [5, 17]. In the national literature, this mineral was also often referred to as *guianite* [18], named after British Guiana (the country's name until 1966).

Bracewellite, gyanite, and grimaldiite were first identified in eskolaite from alluvial shingle deposits of the Merume River in Guyana. The minerals occur in intricate fine-grained aggregates with one another and with mcconnellite. These mineral aggregates were first named *merumite* [19] and had been thought to be an individual mineral species until 1958. Later, “merumite” was proved to contain eskolaite and, perhaps, two new minerals of Cr oxides [17] as well. When X-ray diffraction data on synthetic and natural Cr oxyhydroxides were compared [5, 17], merumite was proved to contain, in addition to eskolaite, gyanite, bracewellite, grimaldiite, and mcconnellite as well. These minerals were described in small (no larger than a few centimeters) rounded shingles, in close association with quartz, Cr-bearing pyrophyllite, gold, silver, and tourmaline. Some samples contain polycrystalline grimaldiite–mcconnellite aggregates in association with Cr-bearing gahnite. Other minerals identified in the alluvial material include diamond, topaz, goeite, and others. No primary rocks that could provide Cr-bearing minerals for the alluvial deposits were found, so that the source of Cr remains uncertain.

An unknown Cr oxyhydroxide was found and documented in 1968 in sulfide-rich veins cutting skarnified quartzites at the Outokumpu deposit, Finland [7]. The

**Table 1.** Structural characteristics of naturally occurring Cr oxyhydroxides

Mineral, formula	Crystal system	Unit cell parameters, Å			Space group	Deposit	Reference
		<i>a</i>	<i>b</i>	<i>c</i>			
Bracewellite CrOOH	Orthorhombic	4.492(3)	9.860(5)	2.974(2)	<i>Pbnm</i>	Merume, Guyana	[5]
Guyanite CrOOH	Orthorhombic	4.857	4.295	2.958	<i>Pnmm</i>		
Grimaldiite CrOOH	Trigonal	2.983		13.392	<i>R3m</i>		
Grimaldiite CrOOH	Trigonal					Hiaca, Bolivia	[6]
Guyanite 2(Cr <sub>2</sub> O <sub>3</sub> ) · 3H <sub>2</sub> O	Orthorhombic	2.959	4.305	4.864		Outokumpu, Finland	[7], [5]
γ-CrOOH	Orthorhombic	3.02	12.44	3.86	<i>Cmcm</i>	Iksinskoe, Russia	[8]
γ-CrOOH	Orthorhombic	3.86	12.78	3.04	<i>Cmcm</i>	Khibina, Russia	Our data

**Table 2.** Synthetic chromium oxyhydroxides

Polymorphic modification	Crystal system	Unit cell parameters, Å			Space group	Isostructural compounds	Reference
		<i>a</i>	<i>b</i>	<i>c</i>			
α-CrOOH	Trigonal	2.984(3)		13.40(1)	<i>R3m</i>	Compounds isostructural with NaHF <sub>2</sub> <sup>*</sup> , like CoOOH and NiOOH	[9], [10]
		2.976(1)		13.36(1)			[11]
		2.979(5)		13.37(2)			[12]
β-CrOOH	Orthorhombic	4.861	4.292	2.960	<i>Pnmm</i>	Compounds isostructural with InOOH, like γ-FeOOH (akaganeite)	[13]
		4.861	4.292	2.960			[14]
		4.862	4.298	2.995			[12]
		4.858	4.292	2.955			[15]
γ-CrOOH	Orthorhombic	3.89(2)	12.70(13)	2.92(2)		γ-FeOOH (lepidocrocite), γ-AlOOH (boehmite), and others	[5]
		12.35	3.83	3.01			[15]
γ-CrOOH**					Amorphous		[15]

\*Determined as isostructural with NaHF<sub>2</sub> [15].

\*\*Relations with γ-CrOOH were inferred from physicochemical characteristics [16].

mineral developed in the form of fibrous pseudomorphs after eskolaite crystals. The mineral associations of the veins also included carbonate, Zn-bearing chromite, rutile, uraninite, nolanite, graphite, zircon, titanite, and corundum. It is worth mentioning the inner structures of the pseudomorphs: Cr oxyhydroxide replaces only small crystals of eskolaite (<1 mm in size), whereas its large crystals (up to 1 cm long) remain unaltered. The pseudomorphs contain relics of eskolaite, which are sometimes armored with fine-grained graphite and, in places, secondary fuchsite. The pseudomorphs were likely produced in a supergene environment, during the weathering of eskolaite, because the alterations developed mostly along tiny cracks cutting single crystals. Based on X-ray diffraction data, Milton et al. [5] arrived at the conclusion that the unknown Cr oxyhydroxide in these pseudomorphs after eskolaite from the Outokumpu deposit is guyanite. In compliance with the description published by Vuorelainen et al. [7], it was

suggested that the guyanite pseudomorphs are of a hydrothermal, but not of a supergene, genesis [5].

Grimaldiite was later found at the Hiaca Mine, Bolivia [6], where it occurs as radiating acicular aggregates up to 0.25 mm across in thin cracks and caverns in penroseite and, in places, also as spherical and scalloped flattened aggregates up to 5 mm across. Minute grimaldiite inclusions were occasionally identified in unknown Pb and Hg selenides, in association with cobaltomenite and barite. Minerals from the Hiaca Mine were studied in a limited amount of the material, because of which the authors did not draw any genetic conclusions, but only mentioned that the paragenetic relations of the Bolivian grimaldiite differ from those known in Guyana. As can be inferred from the scarce information on the mineral association of grimaldiite with barite and selenides, the grimaldiite crystallized after penroseite and before or simultaneously with the unidentified Pb and Hg selenides and is most probably hydrothermal.

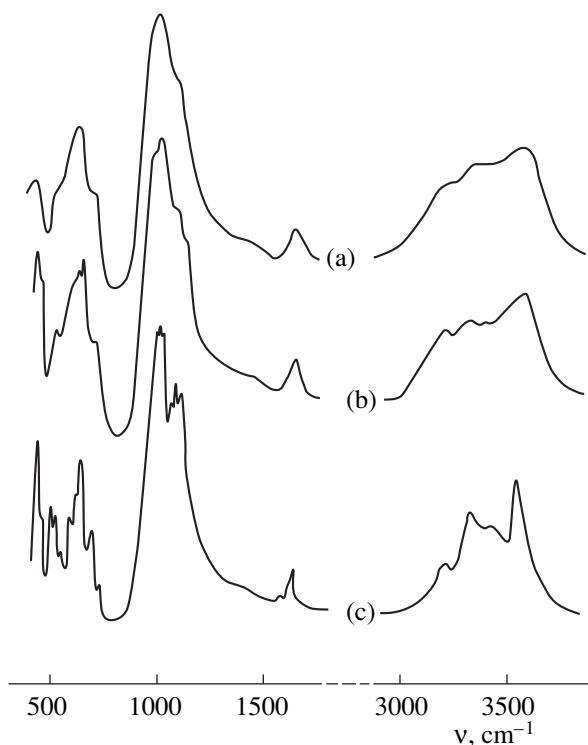
DISTRIBUTION AND MORPHOLOGY  
OF NATURAL  $\gamma$ -CrOOH

The natural analogue of synthetic  $\gamma$ -CrOOH is very rare and was found only twice. First,  $\gamma$ -CrOOH was found in Cr-bearing bauxites at the Iksinskoe deposit of the Severoonezhskii bauxite mine. These rocks were studied by Bardossy et al. [20]. According to these researchers, the fine-grained mixture of boehmite, gibbsite, kaolinite, goethite, hematite, and other minerals may have contained Cr-bearing boehmite and Al-bearing Cr hydroxide. Gorshkov et al. [8] managed to extract the Cr-bearing mineral phase from the mixture of bauxite minerals and examine it. The  $\gamma$ -CrOOH from the Iksinskoe deposit is disseminated in the bauxite and accounts for a few tenths of a percent of the rock mass. The mineral occurs as tiny fibrous polycrystalline aggregates (with individual fibers no more than 0.1  $\mu\text{m}$  long and no thicker than 0.015  $\mu\text{m}$ ).

In the Khibina massif,  $\gamma$ -CrOOH was found in a principally different geological setting, which allows us to suggest that this mineral is spread more widely than was thought previously. It should be mentioned that Cr-bearing minerals are very rare in this massif. Shlyukova [21] described submicrometer-sized inclusions of eskolaite in nepheline from nepheline syenite pegmatite from Mount Kukisvumchorr. The mineral occurs in association with nepheline, corundum, and hercynite.

In the Khibina alkaline massif,  $\gamma$ -CrOOH was found in some rischorrite blocks in contact with the orebody on the western slope of Mount Yuksporr. The mineralized zone rests on lenticular-banded and massive urtite and is dominated by banded apatite-nepheline ore and ore breccia. The roof of the mineralized zone consists of apatite-titanite ijolite (the so-called sphene zone), which gives way to rischorrite. The rischorrite is a rock consisting of poikilitic potassic feldspar crystals abounding in small inclusions of euhedral crystals of nepheline, aegirine, titanite, magnesioastrophyllite, and lamprophyllite. Some samples of the rock are cut by thin (approximately 2–3 mm thick) zonal zeolite veinlets. Their central parts commonly consist of gonnardite (Fig. 1a), which grades into partly ordered natrolite toward the selvages (Fig. 1b) and, further, into fully ordered natrolite (Fig. 1c). The central parts of the veinlets are sometimes made up of phillipsite with minor amounts of saponite and a Mg-bearing zeolite phase that was not conclusively identified and whose composition corresponds to the theoretical formula  $\text{Na}_{0.2-0.6}\text{K}_{0.3-0.5}\text{Ca}_{0.3-0.4}\text{Mg}_{0.9-1.15}(\text{Al}_{3.5-3.6}\text{Si}_{4.4-4.5}) \cdot n\text{H}_2\text{O}$ . The ore minerals in the zeolites are rare tiny (no larger than 2–3  $\mu\text{m}$ ) inclusions of pyrite.

The Khibina  $\gamma$ -CrOOH was found in the form of thin (no thicker than 0.02 mm) stringers in the central parts of the zeolite veinlets. In some instances, Cr oxyhydroxide fills interstices between zeolite grains in the form of cellular and reticulate films. The mineral is finely crystalline or lumpy (Figs. 2, 3). The lumpy aggregates sometimes contain minute crystals of flat-



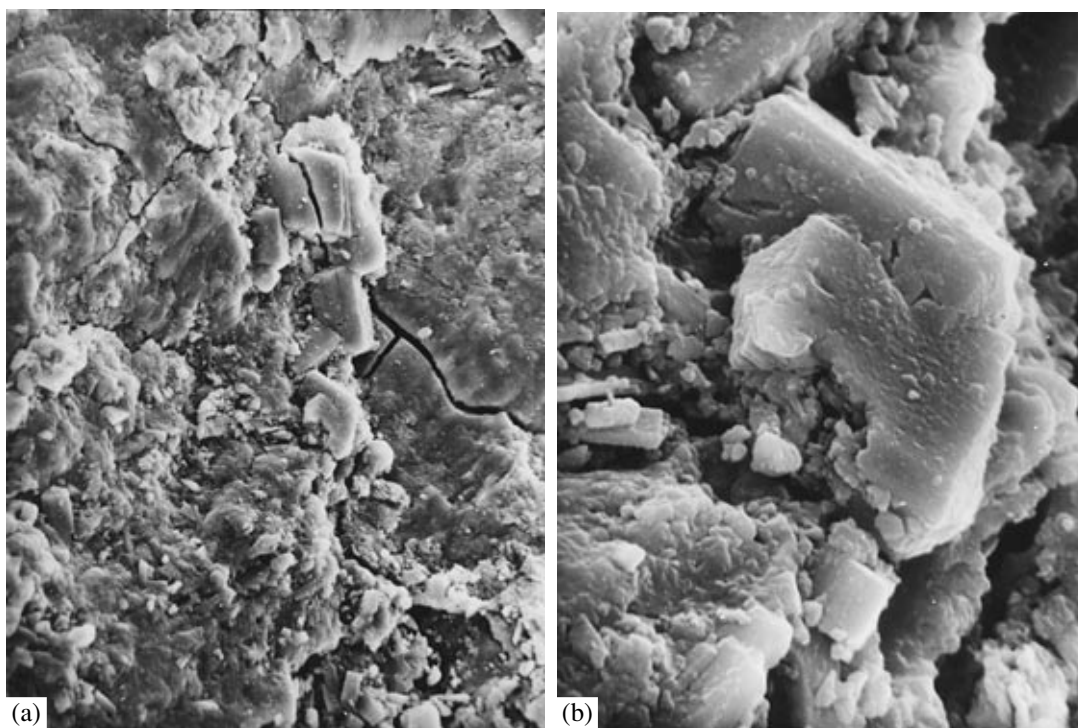
**Fig. 1.** IR spectra of (a) gonnardite from the central part of a zeolite veinlet, (b) partly ordered natrolite from the intermediate zone, and (c) completely ordered natrolite from the selvages of the veinlet.

tened prismatic habit (Fig. 2b), but most often this material is colloform and cryptocrystalline. Individual crystals of  $\gamma$ -CrOOH are green (emerald green) to dark green and are variably unstable under an electron beam (the phase burns and becomes cut by surface cracks, which acquire the form of shaly parting in the lumpy aggregates; Figs. 3a, 3b).

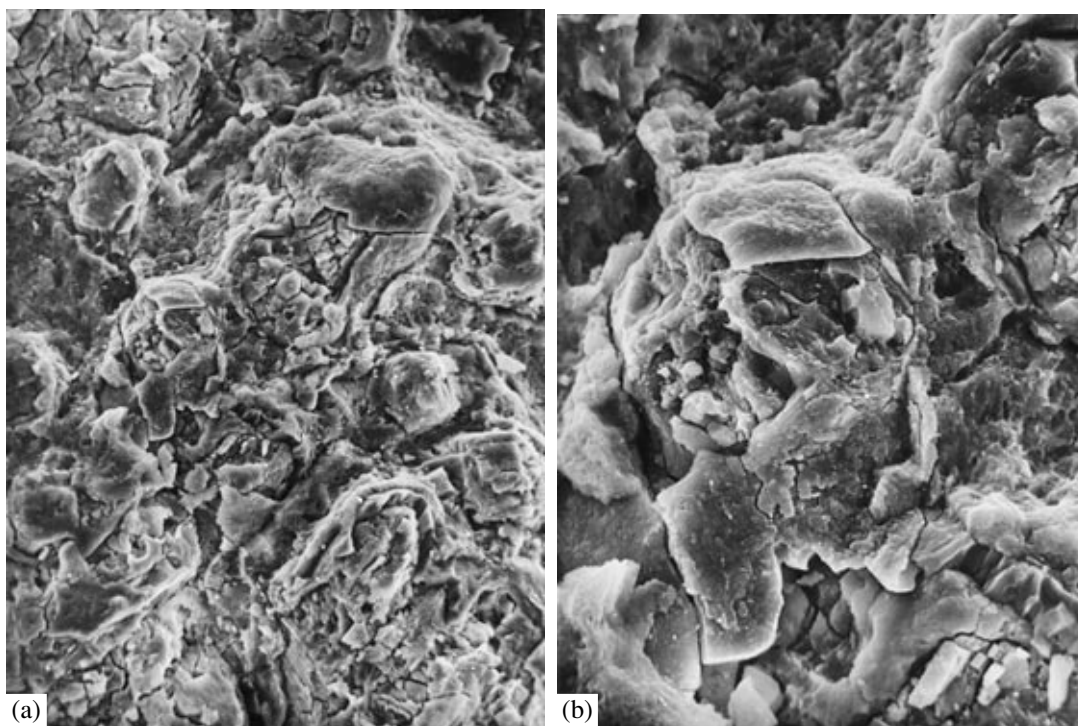
## METHODS

It is pertinent to mention that the examination and identification of the composition of our  $\gamma$ -CrOOH samples was extremely difficult because of the state of the material and, sometimes, the impossibility of obtaining monomineralic fractions. Because of this, we applied a complex of methods in order to examine both the Cr oxyhydroxide itself and the accompanying minerals. Wherever possible, we conducted a comparative analysis of the characteristics of Cr oxyhydroxide from the two associations: from the Iksinskoe deposit and Khibina Massif.

The micromorphology and qualitative composition of minerals from the Khibina Massif were examined on a Hitachi S-430 scanning electron microscope equipped with a Link EDS analytical setup for X-ray spectral analysis. The latter was utilized to determine the qualitative composition of the mineral (the analyses were conducted by N.V. Sorokhtina at the Geological



**Fig. 2.** Morphology of  $\gamma$ -CrOOH from the Khibina Massif. REM images, magnification (a) 675 and (b) 4500.



**Fig. 3.** Surface of nonrecrystallized  $\gamma$ -CrOOH. REM images, magnification (a) 315 and (b) 990.

Institute, Kola Research Center, Russian Academy of Sciences).

The X-ray diffraction characteristics of the mineral were obtained on a JEM-100C transmitting electron microscope equipped with a goniometer (with a tilt angle  $\pm 60^\circ$ ) and a Kevex-5100 EDS analytical setup (analyses were carried out by A.I. Gorshkov at the Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences).

The X-ray diffraction measurements of the Cr oxyhydroxide were conducted on DRON-3 with  $\text{CuK}\alpha$  radiation, 1000 imp/s, and 0.5 grad/min (conducted by O.V. Kuz'mina, same institute). The X-ray powder diffraction patterns of the zeolites were obtained on an RKD-57 camera and  $\text{FeK}\alpha$  radiation (conducted by Yu.P. Men'shikov, Geological Institute, Kola Research Center, Russian Academy of Sciences).

The IR spectra of the samples (which were prepared in the form of pellets with KBr) were registered on a Specord 75 IR spectrophotometer (conducted by N.V. Chukanov, Institute of Problems of Chemical Physics, Russian Academy of Sciences).

The quantitative chemical analysis of the zeolites and Cr oxyhydroxide from the Khibina Massif were conducted on a CAMEBAX electron microprobe equipped with a LINK AN 10 000, at an angle of  $40^\circ$ , an accelerating voltage  $V = 40$  kV, and a current  $I = 1$ – $1.5$  nA (analyst A.N. Nekrasov, Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences).

#### STRUCTURAL CHARACTERISTICS OF NATURAL $\gamma$ -CrOOH

According to the electron diffraction data, the fibrous aggregates of  $\gamma$ -CrOOH from the Iksinskoe deposit of the Severoonezhskoe bauxite mine are close to the analogous parameters of lepidocrocite. The space group inferred from these results is  $Cmcm$ , i.e., the same as the space group of lepidocrocite and boehmite. The parameters of the orthorhombic unit cell of  $\gamma$ -CrOOH are as follows:  $a = 3.02$  Å,  $b = 12.44$  Å, and  $c = 3.86$  Å [8].

The electron diffraction patterns of colloform  $\gamma$ -CrOOH aggregates from the Khibina Massif include three to five reflections. The cryptocrystalline masses were determined to include aggregates of acicular crystals analogous to those described earlier for  $\gamma$ -CrOOH from the bauxite ores of the Iksinskoe deposit [8]. The electron diffraction pattern of the cryptocrystalline mineral from the Khibina Massif (Fig. 4) contains more ring reflections than the patterns of the colloform masses. The indices of the ring reflections of the acicular crystals are displayed in Fig. 4. The spacings calculated from the SAED data are presented in Table 3, and correspond to an orthorhombic cell with  $a = 3.86$  Å,  $b = 12.78$  Å, and  $c = 3.04$  Å, space group  $Cmcm$ .

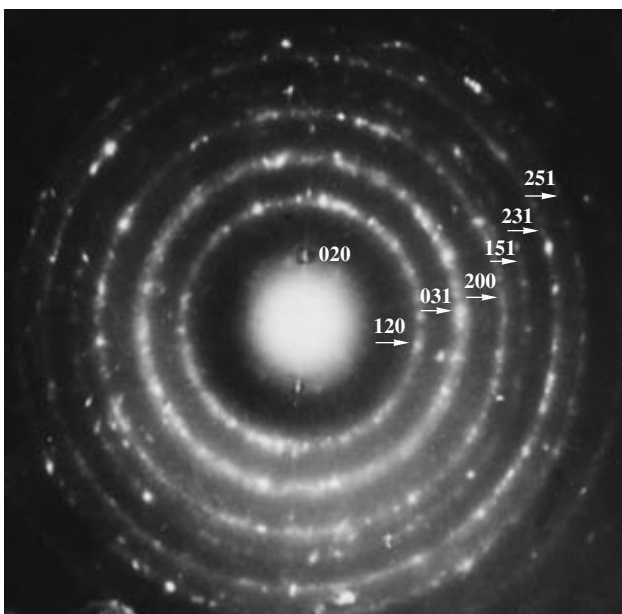


Fig. 4. SAED patterns of an aggregate of  $\gamma$ -CrOOH crystal-lites from the Khibina Massif.

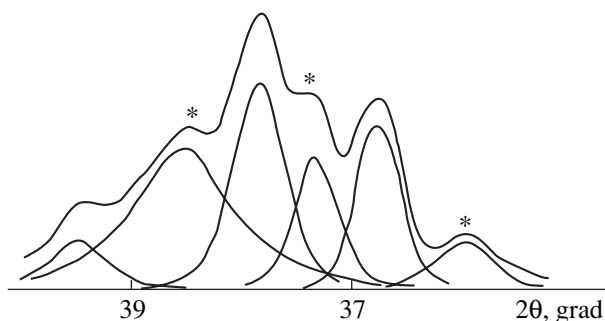


Fig. 5. Example of the resolution of the X-ray diffraction curve of a mixture of  $\gamma$ -CrOOH and gibbsite from the Iksinskoe deposit into individual Voigt components (asterisks mark reflections belonging to  $\gamma$ -CrOOH).

In order to test the absence of phase transitions under the electron beam, we conducted an X-ray diffraction investigation of the Cr oxyhydroxide from the sample from the Iksinskoe deposit (provided for us by courtesy of V.V. Zhukov), because no material suitable for the X-ray study could be obtained from the Khibina Massif samples. The X-ray diffraction study allowed us to obtain extended reflection profiles. The X-ray diffraction pattern shows the reflections of both the mineral in question and the partly overlapping reflections of gibbsite, which occurred in a fine mixture with  $\gamma$ -CrOOH. Because of this, we deconvoluted the envelope into Voigt peaks using the Shape computer program (Fig. 5). The spacings thus identified for the  $\gamma$ -CrOOH are listed in Table 3. As can be seen from these data, the spacings calculated from the X-ray and electron diffraction patterns are similar.

**Table 3.** X-ray diffraction characteristics of  $\gamma$ -CrOOH

$d_{\text{obs}}, \text{\AA}$	$d_{\text{calcd}}, \text{\AA}$	$hkl$	$I$	$d_{\text{obs}}, \text{\AA}$	$hkl$	$I$	$d_{\text{obs}}, \text{\AA}$	$d_{\text{calcd}}, \text{\AA}$	$hkl$	$I$	
Khibina deposit***				Iksinskoe deposit*			Synthetic analogue**				
6.25	6.39	020	av.	6.13	020	av.	6.38	6.35	020	40	
3.28	3.195	040	s				3.30	3.31	120	40	
				3.20	120	av.		2.84	011		
	(2.47)	(031)		2.50							
2.46	2.35	111	s	2.44	031	s	2.40	2.40	031	90	
				140							
				2.41							
				234	111	s		2.29	111		
								2.11	060		
1.93	1.93	200	s	1.96	200	av.	1.962	1.943	200	100	
							1.885	1.916	051	10	
				1.84	220	av.		1.858	160		
1.72	1.745	151	s	1.73	151	tr		1.718	151		
	1.744	061	s								
								1.588	080		
1.51	1.520	002	s	1.517	231	tr	1.512	1.511	231	10	
								1.470	180		
								1.432	171		
							1.406	1.422	022	60	
1.36	1.373	042	o tr	1.36	152	av. tr		1.364	251		
								1.270	091		
								1.229	280		
								1.208	191		
								1.207	1.10.0		
1.19	1.194	202		1.186	0.10.1	tr	1.183	1.199	340	30	
								1.179	311		
								1.105	360		
								1.095	242		
								1.074	082		

\*SAED data.

\*\*X-ray diffraction data [5, 16].

\*\*\*X-ray diffraction data, our results.

#### OPTICAL CHARACTERISTICS AND IR SPECTROSCOPY OF NATURAL $\gamma$ -CrOOH

The colloform character of the predominant type of  $\gamma$ -CrOOH aggregates in samples from the Iksinskoe deposits and Khibina Massif, their instability under an electron beam, and the diffuse character of the diffraction patterns indicate that the  $\gamma$ -CrOOH phase is contained in the material mostly in the form of minute crystals submerged in a matrix of amorphous hydrogel of Cr oxyhydroxide.

This conclusion is also confirmed by the optical isotropy of the colloform aggregates, which testifies

that the crystalline blocks are much smaller than the wavelength of visible light. A high water concentration in the mineral indirectly follows from its low index of refraction:  $n = 1.609(2)$ . An evaluation of the average index of refraction for  $\gamma$ -CrOOH from Gladstone–Dale relation [22] for an ideal composition (89.4%  $\text{Cr}_2\text{O}_3$  and 10.6%  $\text{H}_2\text{O}$ ) and  $D_{\text{theor}} = 3.87 \text{ g/cm}^3$  (which of was calculated for the ideal unit cell parameters at  $Z = 4$ ) yields a value of  $n = 2.14$ . Conceivably, the value  $n = 1.609$  should be attributed to the amorphous constituent of the aggregates.

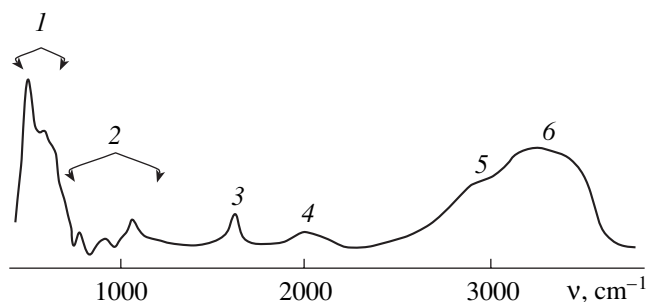
We failed to obtain the IR spectra of Cr oxyhydroxide from the Khibina Massif because of the paucity of the pure material. Figure 6 demonstrates the IR spectra of  $\gamma$ -CrOOH from the Iksinskoe deposit. These spectra were calculated by an automated subtraction of the spectrum of accompanying gibbsite. The resultant spectrum shows characteristic bands of stretching vibrations of the Cr–O and CrO–H bonds and the intense absorption bands of water molecules (Table 4).

#### CHEMICAL COMPOSITION OF NATURAL $\gamma$ -CrOOH

The qualitative evaluation of the chemical composition of Khibina  $\gamma$ -CrOOH indicates that the sample with denser aggregates contains Cr as the predominant element, but the instability of the aggregates under the electron beam and the effect of the zeolite matrix caused the “appearance” of Al and Si in the mineral. Its analyses practically always contain K and Na, whose proportions significantly vary. The rare crystals contain virtually no admixtures. The quantitative analysis of the Khibina Cr oxyhydroxide allowed us to calculate its theoretical formula as the difference spectrum obtained by subtracting the composition of the matrix zeolite. At [Si] = 0, the empirical formula of the mineral has the form  $(\text{Cr}_{0.94}\text{Mg}_{0.03}\text{Al}_{0.02}\text{Ti}_{0.01}\text{Fe}_{0.01})_{1.01}\text{O}(\text{OH}) \cdot n\text{H}_2\text{O}$ , i.e., is notably different from the composition of the mineral from the Iksinskoe deposit, whose formula is  $(\text{Cr}_{0.71}\text{Al}_{0.29})\text{OOH} \cdot n\text{H}_2\text{O}$  (Table 4).

#### GENESIS OF $\gamma$ -CrOOH

The genesis of Cr oxyhydroxide cannot be understood without information on the synthesis of this mineral. Data on its finds in nature are scarce: it was identified only twice, each time in rocks with a different origin. Of course, the starting materials from which Cr oxyhydroxide was formed in nature (Cr-bearing minerals) and synthesized in experiments (hydrogel of Cr salts) were different, and thus, these data provide merely indirect information on the conditions under which the mineral could crystallize in nature. Cr oxyhydroxide is precipitated in an aqueous environment by various Cr salts:  $\text{Cr}_2(\text{SO}_4)_3$ ,  $\text{CrCl}_3$ ,  $\text{Cr}(\text{NO}_3)_3$  [2], or  $\text{Na}_2\text{CrO}_4$  in alkaline environments with NaOH [12, 16]. A distinctive feature of the precipitates is their amorphous character with respect to X-ray radiation. However, upon aging in hydrothermal environments, these precipitates tend to form crystalline compounds. With the change from neutral to alkaline environments and a temperature and pressure increase, the process of aging is accelerated, so that the final aging product in hydrothermal environments is oxyhydroxide [1]. Synthesized crystalline compounds of Cr oxyhydroxide were held under low-temperature hydrothermal conditions [1, 2, 12, 14, 16]. The amorphous phase starts to form already at 230–250°C and a pressure of about 50 atm, and the temperature and pressure increase results in the follow-



**Fig. 6.** IR spectrum of  $\gamma$ -CrOOH from the Iksinskoe deposit (the gibbsite spectrum is subtracted). (1)  $\nu(\text{Cr}-\text{O})$ ; (2)  $\delta(\text{OH})$ ; (3)  $\delta(\text{H}_2\text{O})$ ; (4)  $\nu(\text{O}\cdots\text{H}\cdots\text{O})$ ; (5)  $\nu(\text{CrO}-\text{H})$ ; (6)  $\nu(\text{H}_2\text{O})$

ing succession of phase transitions: amorphous Cr hydroxide  $\rightarrow$  hydrated oxide  $\rightarrow$   $\gamma$ -CrOOH (no higher than 310–320°C)  $\rightarrow$   $\alpha$ -CrOOH (340–360°C)  $\rightarrow$  cubic  $\gamma$ - $\text{Cr}_2\text{O}_3$  (420–450°C)  $\rightarrow$  rhombohedral Cr oxide (calcinations at 850°C). It is important to mention the fact that the synthesis of  $\gamma$ -CrOOH is accelerated under alkaline conditions (in a NaOH solution), and its transition into  $\alpha$ -CrOOH is, conversely, decelerated, i.e.,  $\gamma$ -CrOOH becomes a more stable phase [12, 14, 16]. Hence, one of the factors facilitating the origin of  $\gamma$ -CrOOH is an alkaline environment in a hydrothermal system.

According to data on the hydrothermal synthesis of  $\gamma$ -CrOOH, the genesis of this phase in the rischorrites of the Khibina Massif could be considered quite usual if the Cr source was the hydrothermally altered

**Table 4.** Wavenumbers of bands in the IR spectra of Cr-oxyhydroxide from the Iksinskoe deposit and lepidocrocite

Cr oxyhydroxide	Lepidocrocite	Affiliation of bands
3450 sh		$\nu(\text{H}_2\text{O})$
3240 s		
2900 sh	3090 s	$\nu(\text{MO}-\text{H})$
	2860 sh	
2030	2100 sh	$\nu(\text{O}\cdots\text{H}\cdots\text{O})$
1625		$\delta(\text{H}_2\text{O})$
1050	1157	$\delta(\text{M}-\text{O}-\text{H})$
920	1023 s	
763	745	
700 sh	660 sh	
615 sh		$\nu(\text{M}-\text{O})$
565 s	520 sh	
484 s	472 s	
420 sh	398 s	

\* Cr oxyhydroxide in the form of hydrogel containing dispersed colloid particles of  $\gamma$ -CrOOH. M—Cr or Fe, s—strong band, sh—shoulder,  $\nu$ —stretching vibrations,  $\delta$ —deformation vibrations.

Cr-enriched host rocks or some primary Cr-bearing mineral. However, according to the literature and our data, the Khibina rischorrites do not contain enough Cr to produce its oxyhydroxide. The average Cr concentration in these rocks is low: 0.0007% [23]. Higher concentrations of this element (up to 0.06%) in the Khibina Massif occur in the rocks of the ijolite–urtite complex [24], in which Cr is contained as an admixture in pyroxene, titanite, amphibole, micas, and titanomagnetite. The relatively high Cr concentrations in the rocks of the ijolite–urtite complex is thought to be related, first of all, to the isomorphous accommodation of this element in Fe-bearing minerals, including titanomagnetite.

The rocks of the ijolite–urtite complex and apatite (apatite–titanite) ore of the Khibina Massif quite commonly contain titanomagnetite with elevated  $\text{Cr}_2\text{O}_3$  concentrations. For example, this mineral found in the ijolites and melteigites contained up to 0.5–1.43 wt %  $\text{Cr}_2\text{O}_3$  [25]. High-Cr titanomagnetite was also found in the taxitic ijolites overlying the apatite–nepheline orebody and, occasionally, in the apatite–nepheline rocks themselves [25]. Ultramafic xenoliths in the ijolite–urtite complex contain titanomagnetite with 0.57–4.33 wt %  $\text{Cr}_2\text{O}_3$ , in association with forsterite, Ca–Mg pyroxene, and perovskite [26]. A zonal titanomagnetite crystal was found in the lenticular–banded apatite ores of the Yukspor deposit, in which it occurs in association with perovskite. The core of this crystal had the following composition: 3.28 wt %  $\text{Cr}_2\text{O}_3$ , 1.8 wt %  $\text{Al}_2\text{O}_3$ , and 2.19 wt %  $\text{SiO}_2$ . The peripheral zones of the crystal consisted of ordinary titanomagnetite [27].

Obviously, the titanomagnetite is enriched in Cr in the early high-temperature phases and devoid of this element or contains it in much lower amounts in younger phases. This suggests that the evolution of titanomagnetite from the higher to lower temperature phases (of hydrothermal genesis) was associated with the loss of its Cr, which could enrich the hydrothermal solution and be eventually incorporated into secondary minerals in the form of an admixture or produce individual chemical compounds analogous to those described in this publication. The fact that titanomagnetite is extremely unstable in hydrothermal solutions is corroborated by experimental data on Cr-spinels [28], which are easily decomposed in alkaline solutions. Cr passes into solutions in both alkaline and acid environments, and, thus, it is logical to suggest that one of the most probable sources of this element for the origin of  $\gamma\text{-CrOOH}$  in the Khibina Massif could be titanomagnetite. At the same time, according to Kogarko et al. [24], Cr can enrich the residual alkaline melt during the crystallization of the magma.

Data on the synthesis of  $\gamma\text{-CrOOH}$  and the occurrence mode of its natural analogue in the Khibina Massif in association with zeolites and smectite suggest low-temperature hydrothermal conditions of its crystallization. According to the results of hydrothermal synthesis of zeolites [30], natrolite, gonnardite, phillipsite,

and saponite in our samples, they could crystallize at temperatures of approximately 200°C, with zeolites usually formed at  $\text{pH} > 10$  and smectites (including saponite) at  $\text{pH} < 9$ . According to these conditions, Cr oxyhydroxide could overgrow zeolites (together with saponite) at  $\text{pH}$  close to 9.

## CONCLUSIONS

Summarizing data on the genesis of natural Cr oxyhydroxides, we consider two hypotheses of the genesis of these compounds.

(1) Supergene genesis [7, 8, 29].

Ramdohr [29] believed that merumite from Guyana was formed during the weathering of chromite. According to Gorshkov et al. [8], Cr oxyhydroxide from the Iksinskoe deposit is also of supergene genesis related to laterite. The source of the ore material of bauxites could be basic and ultrabasic rocks, whose weathering products were redeposited in the sedimentation basin.

(2) Hydrothermal genesis [5 and this publication].

According to Milton et al. [5], Cr oxyhydroxides from Guyana are of hydrothermal genesis and crystallized at low or intermediate temperatures. Based on the results of our research, we believe that our  $\gamma\text{-CrOOH}$  was formed hydrothermally, in late zeolite veins, by means of Cr precipitation under the effect of Na, at  $\text{pH}$  close to 9, and temperatures of about 230–300°C. The source of Cr was Cr-enriched rocks, first of all, those containing Cr-bearing titanomagnetite of early magmatic stages. These rocks were affected by hydrothermal decomposition. The occurrence of zeolites provide further support for the hydrothermal hypothesis of the genesis of the Cr oxyhydroxide in the rischorrites of the Khibina Massif.

Our samples of  $\gamma\text{-CrOOH}$  from the Khibina Massif were handed over to the Mining Museum at the St. Petersburg Mining Institute–Technical University and to the Geological Museum at the Geological Institute, Kola Research Center, Russian Academy of Sciences.

## ACKNOWLEDGMENTS

The authors thank Yu.P. Men'shikov, A.E. Zadov, and A.N. Nekrasov for their help in this research. The authors also thank Acad. L.N. Kogarko for attention to this research and discussion of its results.

## REFERENCES

1. T. V. Rode, *Oxygen-Bearing Compounds and Chromium and Chromium Catalysts* (Nauka, Moscow, 1962) [in Russian].
2. V. P. Chalyi, *Metal Hydroxides (Regularities of the Formation, Composition, Structure, and Properties)* (Naukova Dumka, Kiev, 1972) [in Russian].



3. Ch. Milton and E. C. T. Chao, "Eskolaite,  $\text{Cr}_2\text{O}_3$ , in 'Merumite' from British Guiana," *Am. Mineral.* **43** (11–12), 1203 (1958).
4. F. Hund, "Struktur von  $\gamma$ -CrOOH," *Die Naturwissenschaften* **46**, 320–321 (1959).
5. Ch. Milton, D. E. Appleman, M. H. Appleman, et al., "Merumite, a Complex Assemblage of Chromium Minerals from Guyana," *U.S. Geol. Surv. Prof. Pap.*, No. 887, 1–29 (1976).
6. A. Livingstone, B. Jackson, and P. J. Davidson, "Grimaldiite CrOOH, a Second Occurrence from the Hiaca Mine, Colquechaka, Bolivia," *Miner. Mag.* **48** (349), 560–562 (1984).
7. Y. Vuorelainen, T. A. Hakli, and M. Kataja, "A Hydrated Oxide of Chromium as a Pseudomorph after Eskolaite, Outokumpu, Finland," *Bull. Geol. Soc. Finl.* **40**, 125–129 (1968).
8. A. I. Gorshkov, V. N. Demina, A. V. Mokhov, et al., "New Chromium  $\gamma$ -Hydroxide in Bauxite Ores of the Northern Onega Deposits," *Dokl. Akad. Nauk SSSR* **320** (6), 1455–1458 (1991).
9. R. M. Douglas, "The Crystal Structure of  $\text{HCrO}_2$ ," *Acta Crystallogr.* **10** (6), 423–427 (1957).
10. B. J. Thamer, R. M. Douglas, and E. Staritzky, "The Thermal Decomposition of Aqueous Chromic Acid and Some Properties of the Resulting Solid Phases," *J. Am. Chem. Soc.* **79** (3), 547–550 (1957).
11. W. C. Hamilton and J. A. Ibers, "Structure of  $\text{HCrO}_2$  and  $\text{DCrO}_2$ ," *Acta Crystallogr.* **16** (12), 1209–1212 (1963).
12. A. N. Christensen, "Hydrothermal Preparation and Magnetic Properties of  $\alpha$ -CrOOH,  $\beta$ -CrOOH, and  $\gamma$ -CrOOH," *Acta Chem. Scandinavica* **A30** (2), 133–136 (1976).
13. N. C. Tombs, W. J. Croft, J. R. Carter, and J. F. Fitzgerald, "A New Polymorph of CrOOH," *Inorganic Chemistry* **3** (12), 1791–1792 (1964).
14. A. N. Christensen, "The Crystal Structure of a New Polymorph of CrOOH," *Inorg. Chem.* **5** (8), 1452–1453 (1966).
15. J. Chenavas, J. C. Joubert, J. J. Capponi, and M. Marezio, "Synthese de Nouvelles Phases Denses D'Oxyhydroxydes  $\text{M}^{3+}\text{OOH}$  des Metaux de la Premiere Serie de Transition, en Milieu Hydrothermal a Tres Haute Pression," *J. Solid State Chem.* **6** (1), 1–15 (1973).
16. A. N. Torokin, T. D. Averbukh, N. V. Belova, and P. S. Rempel, "Study of Polymorphism in Hydrates of Chromium Oxides Obtained by the Hydrogen Reduction of Sodium Chromate," *Zh. Neorg. Khim.* **13** (1), 27–31 (1968).
17. Ch. Milton, D. E. Appleman, E. C. T. Chao, et al., "Mineralogy of Merumite, a Unique Assemblage of Chromium Minerals from Guyana (Abstract)," *Spec. Pap.* **115**, 151–152 (1968).
18. M. Fleisher, *Glossary of Mineral Species. Mineralogical Record* (Tucson, Arizona, 1980; Mir, Moscow, 1990) [in Russian].
19. S. Bracewell, "Geology and Mineral Resources of British Guiana," *Handbook of Natural Resources of British Guiana, Interior Development Committee of British Guiana* (Georgetown, 1946), pp. 20–40.
20. G. Bardossy, K. Jonas, A. Imre, and K. Solimar, "Interrelations of Bauxite Texture, Micromorphology, Mineral Individualism, and Heteromorphism," *Econ. Geol.* **72**, 573–581 (1977).
21. Z. V. Shlyukova, *Mineralogy of the Contact Rocks of the Khibina Massif* (Nauka, Moscow, 1986) [in Russian].
22. J. A. Mandarino, "The Gladstone–Dale Relationship: Pt. IV. The Compatibility Concept and Its Application," *Can. Mineral.* **19**, 441–450 (1981).
23. A. V. Galakhov, *Petrology of the Khibina Alkaline Massif* (Nauka, Leningrad, 1975) [in Russian].
24. L. N. Kogarko, N. V. Laktionova, and N. S. Klassova, "Geochemistry of the Iron-Group Elements in the Ijolite–Urtite Complex of the Khibina Massif," *Geokhimiya*, No. 7, 985–997 (1973).
25. A. N. Kulakov and K. I. Polyakov, "Chromium-bearing Titanomagnetite of the Khibina Massif and Problems of the Chromium Geochemistry in Alkaline Plutons," in *New Data on Minerals of the Kola Peninsula* (KolFAN SSSR, Apatity, 1979), pp. 3–11 [in Russian].
26. A. K. Shpachenko, Extended Abstract of Candidate's Dissertation in Geology and Mineralogy (SPGGI, St. Petersburg, 1997).
27. E. G. Balaganskaya and E. E. Savchenko, "Perovskite in the Rocks of the Ijolite–Urtites Arc of the Khibina Massif," *Zap. Vseross. Mineral. O-va*, No. 1, 69–80 (1998).
28. V. N. Sazonov, *Chromium in Hydrothermal Processes* (Nauka, Moscow, 1978) [in Russian].
29. P. Ramdohr, *Die Erzminerale und Ihre Verwachsungen* (Berlin, Akademie-Verlag, 1960; Inostrannaya Literatura, Moscow, 1962) [in Russian].
30. R. M. Barrer, *Hydrothermal Chemistry of Zeolites* (Academic Press, New York, 1982; Mir, Moscow, 1985).