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Chukanovite, $Fe_2(CO_3)(OH)_2$, a new mineral from the weathered iron meteorite Dronino

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Abstract: The new mineral chukanovite, $Fe_2(CO_3)(OH)_2$, occurs in cavities of weathered fragments of the Dronino ataxite iron meteorite found near the Dronino village, Kasimov district, Ryazan' Oblast, Russia. It is a product of terrestrial alteration of meteorite iron. Associated minerals are goethite, akaganéite, hematite, hibbingite, reevesite, honessite, *etc*. Chukanovite forms acicular to fibrous individuals (up to 0.5 mm long and up to 2–3 μm thick) combined in spherulites up to 1 mm in diameter, botryoidal spherulitic clusters and parallel- or radial-columnar aggregates which form crusts up to 1 mm thick. Unaltered chukanovite is transparent, pale-green or colourless. The surface of aggregates is brownish-green. Streak is white. Lustre is vitreous. Cleavage is perfect, probably on {0–21}, fracture is uneven. The mineral is brittle, the Mohs' hardness is 3.5–4, the calculated density is 3.60 g/cm^3. It is optically biaxial (–) with α 1.673(3), β 1.770(5), γ 1.780(5), $2V_{\text{meas.}}$ 10(5)°. Average chemical composition (wt. %; electron probe, H_2O by modified Penfield method, CO_2 by selective sorption) is: MgO 0.1, FeO 68.8, NiO 0.6, CO_2 19.8, H_2O 10.9, total 100.2. The empirical formula calculated on the basis of two metal atoms is $(Fe^{2+}_{1.97}Ni_{0.02}Mg_{0.01})_{\Sigma 2.00}(CO_3)_{0.93}(OH)_{2.14}\cdot 0.18H_2O$, ideally $Fe_2(CO_3)(OH)_2$. Chukanovite is monoclinic $P2_1/a$, with a = 12.396(1) Å, b = 9.407(1) Å, c = 3.2152(3) Å, β = 97.78°. The strongest lines of the X-ray powder pattern [d(Å), I, (hkl)] are: 6.14, 40, (200); 5.15, 60, (231); 3.73, 80, (310); 2.645, 100, (230); 2.361, 40, (510); 2.171, 40, (520). The structure of chukanovite was refined on synchrotron data by the Rietveld method up to Rp = 3.43 %, wRp = 4.51 %, R_{Bragg} = 2.48 %. Chukanovite is closely related to the minerals of the malachite-rosasite group. It was named in honour of Nikita V. Chukanov (b. 1953), Russian physicist and mineralogist. The holotype specimen is deposited in the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow.

Key-words: chukanovite, new mineral, iron hydroxide-carbonate, malachite-rosasite group, Rietveld refinement, Dronino meteorite.

Introduction

In the present paper, we describe a new mineral species, an iron hydroxide-carbonate closely related to pokrovskite, malachite and rosasite-group members. It was named **chukanovite** (Cyrillic: чуканOВИТ) in honour of Nikita Vladimirovich Chukanov (b. 1953), Russian physicist and mineralogist, well-known specialist in the IR spectroscopy of minerals and synthetic compounds, a discoverer of many new mineral species, working at the Institute of Problems of Chemical Physics of the Russian Academy of Sciences, Chernogolovka, Russia. Both the new mineral and its name have been approved by the IMA Commission on New Minerals and Mineral Names (IMA no. 2005-039). The holotype specimen of chukanovite has been deposited in the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow (catalogue no. 92013).

Occurrence and general appearance

Chukanovite occurs in cavities of weathered fragments of the Dronino meteorite which fell in prehistoric time and was found in 2000 near the Dronino village in Kasimov district, Ryazan' Oblast, 350 km east-south of Moscow, Russia (54°44.8′ N; 41°25.3′ E).

The Dronino meteorite is an ataxite iron meteorite mainly consisting of kamacite and containing minor amounts of taenite and chromite. Sporadically it is extremely enriched in troilite and poorly-studied Fe-Ni sulfides (Russell *et al.*, 2004; Grokhovsky *et al.*, 2005).

The Dronino meteorite shower fell approximatively 5000–8000 years ago, after the last glaciation on the territory of the present European Russia. Its numerous fragments have been found in glacial and post-glacial deposits, mainly at a depth of 0.5–1 m under the surface. The

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fragments situated in the waterproof clay layers are unaltered, except for a thin rusted film. In contrast, the meteorite fragments situated in the sand layers and lenses are intensively weathered ("corroded"). Some of them are completely replaced by Fe^{3+} hydroxides and oxides.

Chukanovite was found in cavities and fractures in several partially altered meteorite fragments, 10 to 20 cm in size and mainly consisting of goethite, hematite, akaganéite and X-ray amorphous iron hydroxides. Abundant relics of kamacite and minor relics of taenite and Fe-Ni sulfides occur in massive aggregates of secondary minerals. Chukanovite, hibbingite, reevesite, honessite and an unidentified iron sulfate-hydroxide have been found in cavities.

Chukanovite occurs as acicular to fibrous individuals, elongated along [001], up to 0.5 mm long and up to 2–3 μm thick usually combined in spherulites up to 0.3 mm (rarely up to 1 mm) in diameter. Botryoidal spherulitic clusters and parallel- or radial-columnar aggregates forming crusts up to 1 mm thick (Fig. 1) are typical. Aggregates are usually porous, the core of some spherulites contains grains of kamacite, taenite, sulfides or iron hydroxides. Tiny siderite ingrowths occur between chukanovite individuals. Aggregates of chukanovite are very similar in their morphology to well-known spherulitic aggregates of malachite, a structurally related mineral.

In weathered fragments of the Dronino meteorite, chukanovite was probably formed as a product of the reaction of iron (kamacite) with cold CO_2-bearing sub-surface water. This reaction took place under local reducing conditions caused by the presence of iron in the mineral-forming medium inside a cavity. This mineral-forming system is isolated from common system of sub-surface water, which is oxidizing because of the saturation by atmospheric oxygen and leads to the alteration of iron meteorite fragments to Fe^{3+} hydroxides and oxides from the outside. The reducing medium seems necessary for the formation and preservation of this Fe^{2+} hydroxide-carbonate unstable under atmospheric conditions. Such instability seems the main cause for the rarity of chukanovite in nature (and probably the main cause of absence of other Fe^{2+} hydrous carbonate and carbonate-hydroxide minerals), in spite of its simple composition, with widespread chemical constituents, and a common structure type. The compound $Fe^{2+}(CO_3)(OH)_2$ can be completely decomposed very fast, in several years or even several months, as a result of easy Fe^{2+} oxidation. We have observed the first stage of this process in room air. Formation and preservation of chukanovite in cavities of partially altered fragments of the Dronino meteorite was possible because of the conditions unusual for nature: an isolated system with abundant native iron that acts not only as reagent but also as reducing agent. Thus, chukanovite could be found also in the inner parts of the weathered zone of terrestrial native iron occurrences.

Physical and optical properties

Unaltered chukanovite (on fresh fracture) is transparent, pale-green or colourless with white streak and vitreous lustre. The surface of aggregates is brownish-green. Under room conditions, chukanovite alters from the surface in several months: it becomes translucent brownish-green and further dull and opaque, brown with yellowish streak. Chukanovite is brittle. Under the microscope, one perfect cleavage plane was observed; on the basis of the relationships between the unit-cell parameters of chukanovite and malachite discussed in the following, the cleavage is on {0–21}. Fracture is uneven in individuals and splintery in aggregates. The Mohs' hardness is 3.5–4. Attempts to obtain a reasonable value of the measured density of chukanovite were unsuccessful because of the porosity of its aggregates; D(calc.) is 3.60 g/cm^3.

Optical data were obtained for a sample selected from the parallel-columnar aggregate. Chukanovite is optically biaxial (–) with α 1.673(3), β 1.770(5), γ 1.780(5), $2V$(meas.) 10(5)°, $2V$(calc.) 34°. Orientation: $X \approx c$. Under the microscope, the mineral is colourless and nonpleochroic.

Infrared spectroscopy

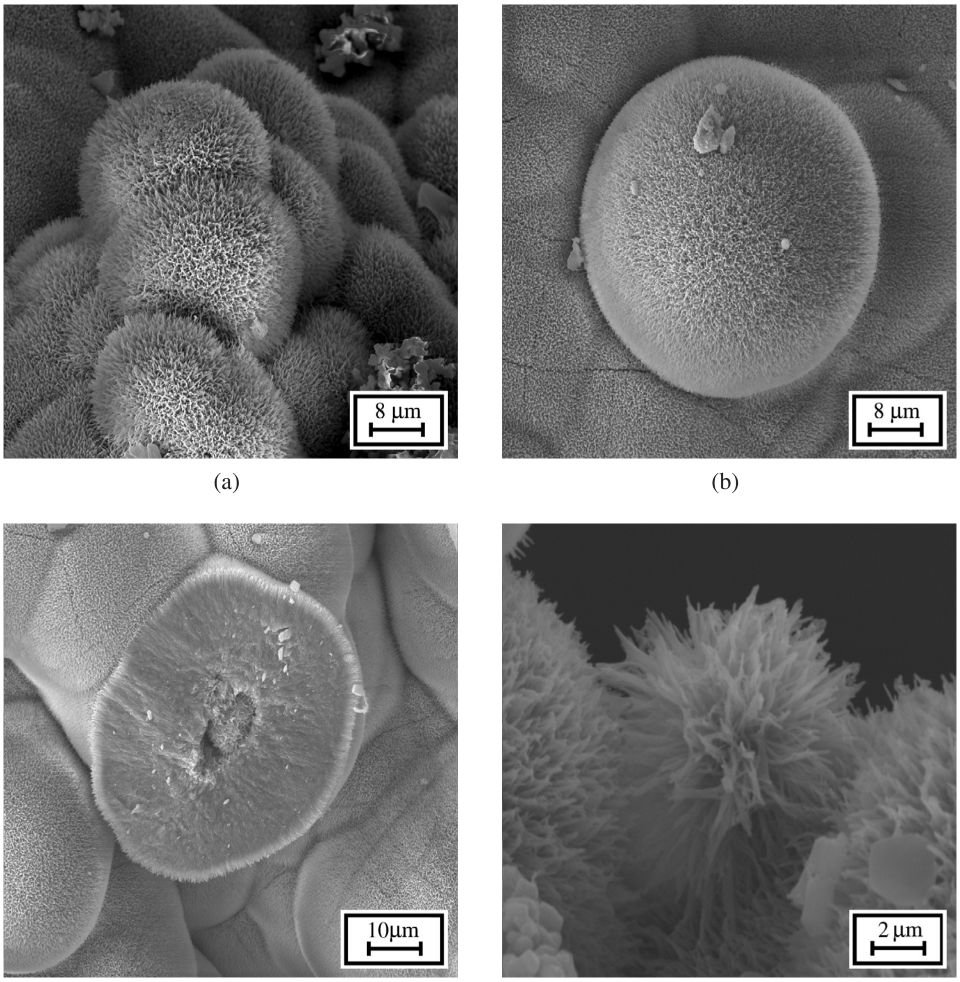
The infrared-absorption spectrum of chukanovite was obtained using a Specord 75 IR spectrophotometer (powder sample was prepared in KBr tablet, polystyrene and gaseous NH_3 were used as frequency standards). The IR spectrum of the new mineral is close to the spectra of pokrovskite (the most similar), malachite and members of the rosasite group (Fig. 2). Absorption bands in the IR spectrum of chukanovite (in cm^{-1}; frequencies of the most intensive bands are underlined, sh – shoulder) are: $\underline{3475}$, $\underline{3325}$, 1755, $\underline{1521}$, 1400sh, $\underline{1364}$, 1069, 1055sh, 955, 861, $\underline{837}$, 781, 710sh, 695, 655, 504, 452.

The IR spectrum of technogene "malachite-like basic iron carbonate" (Erdös & Altorfer, 1976) is practically identical to the spectrum of chukanovite as regards the wavenumbers of absorption maxima.

Chemical data

Contents of cations in chukanovite were determined from electron-microprobe data obtained with a Camebax microbeam instrument in wavelength-dispersion (WDS) mode using an operating voltage of 20 kV and an estimated beam-current of 20 nA. The electron beam was rastered over an area of 10 × 10 μm^2 to minimize damage to the sample. We used the following standards: diopside (Mg), FeO (Fe), Ni (Ni). Contents of Na, K, Ca, Mn, Cr, V, Ti, Co, Cu, Zn, Si, P, F, Cl are below detection limits. Some point analyses show the presence of S (up to 0.25 wt.%) probably caused by micro-inclusions of iron sulfate-hydroxide. Several point analyses show 0.02–0.04 wt.% Al.

The H_2O content was determined by Alimarin method adopted for micro-samples: heating to 1000 °C under oxygen stream with H_2O absorption in pipes filled with $Mg(ClO_4)_2$. The CO_2 content was determined using a selective sorption method: heating to 1000 °C under oxygen stream with CO_2 absorption in pipes filled with "ascarite", an asbestiform material saturated with NaOH.



(a) (b)

(c) (d)

Fig. 1. Aggregates of chukanovite: *a* – spherulitic crust; *b* – separate spherulite as part of a crust; *c* – section of a spherulite; *d* – cluster of curved fibrous individuals. SEM images.

The average results (wt.%, ranges for sixteen analyses are given in parentheses) are: MgO 0.1 (0.05–0.2), FeO 68.8 (67.5–69.9), NiO 0.6 (0.5–0.8), CO_2 19.8, H_2O 10.9, total 100.2. The empirical formula calculated on the basis of two metal atoms, with (OH)/H_2O ratio from charge balance, is: $(Fe^{2+}_{1.97}Ni_{0.02}Mg_{0.01})_{\Sigma 2.00}(CO_3)_{0.93}(OH)_{2.14}\cdot 0.18H_2O$, whereas the formula calculated on the basis of five oxygen atoms is $(Fe^{2+}_{1.93}Ni_{0.02}Mg_{0.01})_{\Sigma 1.96}(CO_3)_{0.91}(OH)_{2.09}\cdot 0.18H_2O$. The simplified formula is: $Fe^{2+}_2(CO_3)(OH)_2$ which requires: FeO 69.85, CO_2 21.39, H_2O 8.76, total 100.00 wt.%. Samples used for H_2O and CO_2 determination were probably slightly contaminated with Fe hydroxides that could be the cause of higher H_2O content and lower CO_2 content in comparison with values calculated for the ideal formula.

The determination of the valence state of Fe was one of the problems when chukanovite was in study. The Mössbauer study or wet-chemical analysis were not carried out because of scarcity of pure material. The presence of Fe^{2+} and absence of Fe^{3+} in unaltered chukanovite were confirmed using well-known colour reactions with potassium hexaferricyanide, $K_3Fe^{3+}(CN)_6$, and potassium hexaferrocyanide, $K_4Fe^{2+}(CN)_6$. For these tests, chukanovite was dissolved in dilute (3 vol.%) HCl bubbled with CO_2 (10 min) for the protection of Fe^{2+} (when the mineral dissolves) from oxidation by atmospheric oxygen "dissolved" in the solution. Solutions of $K_3Fe^{3+}(CN)_6$ and $K_4Fe^{2+}(CN)_6$ were prepared using the same dilute HCl bubbled with CO_2. After the mixing of $K_3Fe^{3+}(CN)_6$ solution with the "solution of chukanovite", strong blue colouring appears at once, which is a clear indicator of the presence of Fe^{2+}: $K_3Fe^{3+}(CN)_6 + Fe^{2+} \rightarrow$ blue $KFe^{2+}Fe^{3+}(CN)_6$. Conversely, after the mixing of $K_4Fe^{2+}(CN)_6$ solution with the "solution of chukanovite", no blue colouring appeared, which shows an absence of Fe^{3+}. For the checking, the same tests were carried out with siderite, $Fe^{2+}CO_3$, and goethite, $Fe^{3+}O(OH)$. Tests with siderite, a mineral with only Fe^{2+}, show the same results as those with chukanovite. Tests with goethite, a mineral with only Fe^{3+}, show a different result: no colouring with $K_3Fe^{3+}(CN)_6$ but strong blue colouring with $K_4Fe^{2+}(CN)_6$ which is evidence for the presence of Fe^{3+}: $K_4Fe^{2+}(CN)_6 +$

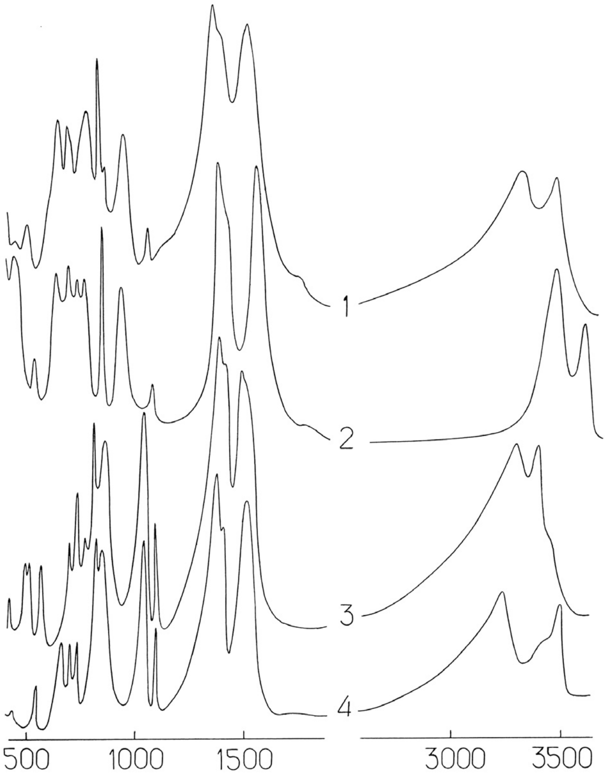


Fig. 2. IR spectra of chukanovite (1), pokrovskite (the type specimen from the Zlatogorskaya intrusion, Kazakhstan) (2), malachite (Nizhniy Tagil, Central Urals, Russia) (3), and rosasite (Ojuela mine, Mapimi, Durango, Mexico) (4).

Fe^{3+} → blue $KFe^{2+}Fe^{3+}(CN)_6$. Thus, these direct methods confirm that chukanovite contains only Fe^{2+}, like structurally related minerals containing only bivalent cations: Cu^{2+}, Mg, Co^{2+}, Ni^{2+} and Zn.

Chukanovite easily dissolves in cold dilute HCl with strong effervescence.

The Gladstone-Dale compatibility index (Mandarino, 1981) for chukanovite is 0.016 (superior).

X-ray crystallography and crystal structure refinement

Experimental

A preliminary X-ray powder diffraction pattern of chukanovite, reported in Table 1, was collected using a RKU Debye-Scherrer camera (114.6 mm in diameter) with Fe$K\alpha$ radiation. Some diffraction lines corresponding to minor additional phases, such as hibbingite (5.70 Å), goethite (4.18 Å), siderite (3.61, 2.80, 1.733 Å), taenite (3.38 Å), are present in the chukanovite powder pattern and are highlighted in italic.

Some fragments of fibrous pale-green microcrystalline chukanovite aggregates were carefully selected with the aid of both a polarizing and a binocular microscope, so as to minimize the presence of impurities, gently hand ground

Table 1. X-ray powder data of chukanovite. The patterns obtained with conventional and synchrotron radiation are reported. Diffraction effects due to impurities present in the conventional source pattern are highlighted in italic.

Conventional radiation		*Synchrotron radiation*		
I_{obs}	d_{obs}, Å	d_{obs}, Å	I_{calc}	*hkl*
5	*9.58*			
15	7.53	7.47	4	110
5	*6.52*			
40	6.13	6.14	23	200
5	*5.70*			
60	5.15	5.14	40	210
15	4.73	4.704	8	020
10	*4.18*			
80	3.73	3.754	17	310
		3.734	49	220
35	*3.61*			
< 5	*3.38*			
5	3.21	3.186	3	001
30	3.05	3.088	2	320
		3.070	7	400
		3.038	8	130
		3.021	3	–111
		2.998	6	–201
25	2.916	2.919	13	410
		2.847	2	111
95	*2.798*	2.793	3	230
		2.683	8	201
100	2.645	2.637	100	021
35	2.56	2.571	27	420
		2.528	17	–221
		2.521	3	121
		2.459	5	330
40	2.361	2.377	12	510
		2.377	7	–401
10	2.236	2.236	2	–131
		2.235	5	031
		2.196	5	240
40	2.171	2.177	9	520
		2.167	15	–231
30	2.137	2.121	1	–421
		2.075	5	
		2.047	6	600
20	2.04	2.039	7	231
		2.037	4	
		2.000	4	
15	1.966	1.934	4	530
<*5*	1.901	1.907	1	–521
		1.887	6	331
10	1.875	1.877	2	620
5	1.85	1.850	5	–241
		1.805	4	–611
20	1.797	1.798	4	250
		1.796	7	511
10	1.766	1.768	12	241
50	*1.733*	1.737	5	–531
		1.730	5	431
		1.725	4	710

Table 1. continued.

Conventional radiation		*Synchrotron radiation*		
I_{obs}	d_{obs}, Å	d_{obs}, Å	I_{calc}	*hkl*
10	1.667	1.672	17	341
		1.609	7	–711
25	1.592	1.595	6	–202
		1.594	4	–251
		1.593	9	002
		1.592	4	151
10	1.576	1.586	3	–631
		1.580	4	531
10	1.528	1.531	5	730
		1.519	4	260
		1.515	4	810
15	1.509	1.493	4	550
< 5	1.489			
		1.438	4	711
25	1.428	1.428	5	–422
		1.423	4	222
15	1.397	1.396	5	460
< 5	1.382	1.389	2	–261
30	1.356			–361
10	1.335	1.335	3	–612
15	1.282	1.277	2	370

and placed into a borosilicate Lindemann capillary 0.5 mm in diameter.

The synchrotron X-ray powder diffraction data were collected at the BM8-GILDA beamline (ESRF, Grenoble, France). A monochromatic beam (λ = 0.79593 Å, calibrated against X-ray absorption of pure metal foils) was used and the diffractions were collected with a Fuji Imaging-Plate (IP) detector. The beam dimension on the sample was 0.2×0.2 mm. The sample to detector distance and the image plate tilt were calibrated with X-ray powder diffraction of standard LaB_6 (NIST-SRM 660a). Data were collected up to 48° 2θ, corresponding to a *d*-space resolution of 0.978 Å. Data were reduced with the Fit2D software (Hammersley, 1997).

Rietveld refinement of chukanovite

The close similarities, both in chemical formula and in X-ray powder pattern between pokrovskite, ideally $Mg_2(CO_3)(OH)_2$, and chukanovite suggested a reliable starting model for this last phase, based on the cell parameters and atomic coordinates obtained for pokrovskite (Perchiazzi & Merlino, 2006). The subsequent Rietveld refinement was performed with the TOPAS-Academic program (Coelho, 2004). A preliminary Pawley refinement (Pawley, 1981) was performed to get starting values for background, modelled with a 6-term Chebyschev function, cell parameters and peak shapes. The refined region was from 5.5 to 48° 2θ, excluding from the refinement the region between 10 and 11.6° in 2θ, which presents a large bump due to a poorly crystalline phase and only one small peak from chukanovite. It is worth noticing that this bump is just centered on the 2θ position of the strongest peak of goethite.

In the early stages of the refinement, constraints on the Fe-O bonds were introduced and subsequently removed at the end of refinement; the carbonate group was refined as a rigid body, fixing the C-O distance to 1.284 Å (Zemann, 1981). Assuming as starting values for the atomic displacement parameters those coming from the single-crystal structure refinement of siderite, $FeCO_3$, namely B_{eq} = 0.44, 0.63, 0.44 Å^2 for Fe, O and C respectively (Effenberger *et al.*, 1981), isotropic displacement parameters were refined for all the atoms, constraining atoms of the same species to keep the same value. The isotropic displacement parameter of iron atoms obtained in this way was anomalously larger than the displacement parameter of oxygen atoms, therefore suggesting a possible small vacancy in the iron sites. According to the indications of chemical data, a full occupancy was anyway assumed for the Fe1 and Fe2 sites, imposing for both Fe sites a common displacement parameter fixed to 70 % of the oxygens displacement parameter, namely to the ratio suggested by the siderite refinement.

The structure of chukanovite was refined up to Rp = 3.43 %, wRp = 4.51 %, R_{Bragg} = 2.48 %; a final Rietveld plot of the refinement is reported in Fig. 3.

Structure description and discussion

Refined cell parameters for chukanovite are compared in Table 2 with the crystallographic data coming from structural refinements of the other phases of the rosasite-malachite group. For nullaginite, ideally $Ni_2(CO_3)(OH)_2$, Nickel & Berry (1981) report the space group $P2_1/m$ and cell parameters a = 9.236 Å, b = 12.001 Å, c = 3.091 Å, β = 90.48°. Apparently, nullaginite is neither straightforwardly related with a malachite-like cell nor with a rosasite-like cell; further investigations are needed to clearly define the true nature of this rare phase.

Final atomic coordinates and isotropic displacement parameters are reported in Table 3, and the geometry of the two independent iron coordination polyhedra is given in Table 4.

The crystal structure of chukanovite, projected along the ***c*** axis, is illustrated in Fig. 4. The Fe1 and Fe2 octahedra share edges to build octahedral "ribbons", two-column wide and running along [001]. "Corrugated" layers parallel to (100) are formed through interconnection of those ribbons by corner-sharing, with the carbonate groups inserted in the octahedral frame to strengthen the intralayer connections, and also assuring an interlayer linking.

The octahedral environment of Fe1 is made up of four oxygen atoms, belonging to carbonate groups, and of two hydroxyls, whereas Fe2 is surrounded by four hydroxyls and two oxygen atoms. Bond lengths range from 2.04 to 2.47 Å for Fe1, and from 2.01 to 2.31 Å for Fe2 octahedra. The mean octahedral quadratic elongation parameter λ_{oct} (Robinson *et al.*, 1971), was calculated in order to estimate the degree of distortion of the Fe octahedra.

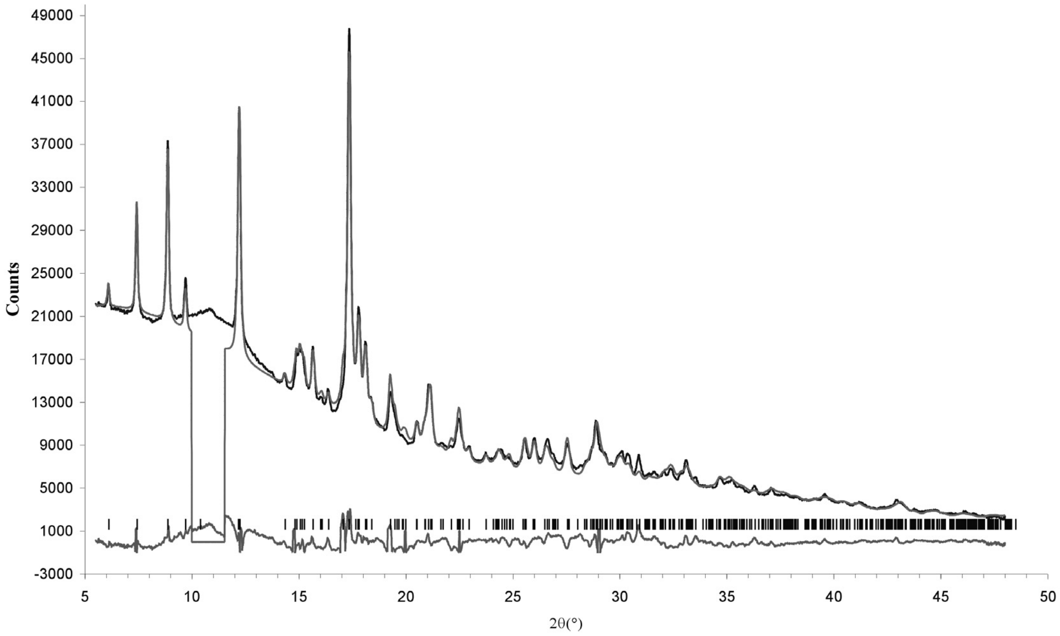


Fig. 3. Final Rietveld plots for the synchrotron diffraction pattern of chukanovite.

Table 2. Crystallography of the phases of the malachite-rosasite group (Å, °) as resulting from the available crystal-structure refinements.

Phase	Me^{2+}	sp. gr.	*a*	*b*	*c*	*β*	Ref.
Chukanovite	Fe	$P\,1\,2_1/a\,1$	12.396(1)	9.407(1)	3.2152(3)	97.78(2)	(1)
Glaukosphaerite	(Cu,Ni)	$P\,1\,2_1/a\,1$	12.0613(4)	9.3653(4)	3.1361(1)	98.085(5)	(2)
Kolwezite	(Cu,Co)	$P\,1\,2_1/a\,1$	12.359(1)	9.451(1)	3.1814(3)	99.01(1)	(3)
Mcguinnessite	(Mg,Cu)	$P\,1\,2_1/a\,1$	12.1531(3)	9.3923(3)	3.1622(1)	97.784(4)	(4)
Pokrovskite	Mg	$P\,1\,2_1/a\,1$	12.2397(3)	9.3489(4)	3.1595(1)	96.422(6)	(2)
Rosasite	(Cu,Zn)	$P\,1\,2_1/a\,1$	12.2413(2)	9.3705(2)	3.1612(2)	98.730(3)	(4)
Malachite	Cu	$P\,1\,2_1/a\,1$	9.502	11.974	3.240	98.75	(5)

(1) This study; (2) Perchiazzi & Merlino (2006); (3) Perchiazzi & Merlini, in prep.; (4) Perchiazzi, (2006); (5) Zigan *et al*. (1977).

Table 3. Final fractional atomic coordinates and isotropic displacement parameters for chukanovite.

	Fe1	Fe2	C	O1	O2	O3	OH4	OH5
x	0.2114(5)	0.3983(5)	0.143	0.139	0.233	0.055	0.379(1)	0.427(1)
y	0.0005(9)	0.7675(7)	–0.265	–0.135	–0.332	–0.328	0.900(1)	0. 619(2)
z	0.979(2)	0.554(2)	0.493	0.368	0.546	0.556	0.058(7)	0.132(9)
B_{eq}	1.12	1.12	3(1)	1.6(1)	1.6(1)	1.6(1)	1.6(1)	1.6(1)

As it may be seen from Table 4, the Fe1 octahedron is distinctly larger and more distorted than the Fe2 octahedron. Also in pokrovskite (Perchiazzi & Merlino, 2006) the corresponding Mg1 octahedron is larger than Mg2 octahedron, their polyhedral volumes being 13.1 and 12.2 Å^3 respectively, but in pokrovskite the two polyhedra display the same mean octahedral quadratic elongation $\lambda_{\text{oct}} = 1.01$.

Bond-valence balance, calculated according to Breese & O'Keeffe (1991), is reported in Table 5. In the calculations, full occupancy was assumed for both Fe1 and Fe2 sites. Hydrogen bonds were detected examining all $O\cdots O$ distances shorter than 3.1 Å and not belonging to the same coordination polyhedron. As it may be seen from Table 5, their contributions to the valence balance, evaluated according to Ferraris & Ivaldi (1988), are critical for the structural stability of chukanovite. The balance can be considered as satisfactory, with only small deviations from the expected values for the anions.

As firstly reported by Perchiazzi (2006), two structure types are realized in the rosasite-malachite group, namely a malachite-like and a rosasite-like structure. An exhaustive description of the relationships between the two types is reported in Perchiazzi & Merlino (2006). The "rosasite" model is the most widely represented, being adopted by rosasite and mcguinnessite (Perchiazzi, 2006), glaukosphaerite and pokrovskite (Perchiazzi & Merlino,

Table 4. Bond distances (Å) in Fe coordination polyhedra of chukanovite. Mean octahedral quadratic elongation λ_{oct} (Robinson *et al.*, 1971) and polyhedral volume (Å^3) are also reported.

Fe1-OH5	2.04(2)	Fe2-OH5	2.01(2)
O1	2.07(3)	OH4	2.01(2)
O2	2.23(2)	O3	2.02(3)
OH4	2.26(2)	OH4	2.09(2)
O1	2.41(2)	O2	2.24(2)
O2	2.47(3)	OH5	2.31(3)
mean	2.24	mean	2.11
polyhedral volume	14.9		12.1
λ_{oct}	1.01		1.03

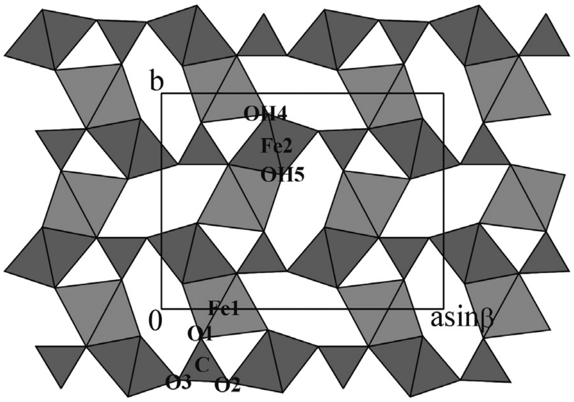


Fig. 4. The chukanovite structure projected along [001]. Edge-sharing between octahedra form "ribbons", two-column wide and running along c, interlinked through corner sharing to form corrugated octahedral layers, parallel (100). Carbonate triangles are inserted in the octahedral frame, assuring further intra- and inter-layer linking.

2006) and by chukanovite, as shown by the present work. A crystal structure refinement of kolwezite (Cu, Co)$_2$(CO)$_3$(OH)$_2$, presently in progress, strongly supports a rosasite-like model (Perchiazzi & Merlini, in prep.).

The technogene $Fe_2(CO_3)(OH)_2$ compound

Erdös & Altorfer (1976) reported the occurrence of a "malachite-like basic iron carbonate", henceforth denoted with the acronym IHC (iron hydroxide-carbonate), from the corrosion product in the hot-water exchanger of an industrial plant in Beringen, Switzerland. Actually, IHC was found in the steel valve of the exchanger, as the main constituent of a crust, associated with siderite and magnetite. Chemical data obtained by wet chemical analysis on a purified fraction were FeO 61.2 %, Fe$_2$O$_3$ 7.5 %, CO$_2$ 20.8 %, H$_2$O % 9.3, MnO % 0.4, total 99.2 %, resulting in the chemical formula $Fe^{2+}_{1.8}Fe^{3+}_{0.2}(OH)_{2.2}(CO_3)$. About the occurrence of Fe^{3+}, the authors remark anyway that an admixture with goethite cannot be excluded, and IHC was ideally considered as $Fe^{2+}_2(OH)_2(CO_3)$.

Table 5. Bond valence balance (*v.u.*) for chukanovite. O··O distances (Å) and hydrogen bond strengths (*v.u.*) are also reported.

Anion O1	O2	O3	OH4	OH5
Sum 2.14	1.98	1.94	0.94	0.87
Hydrogen bonds	OH4···O3		2.90(3) Å	*v.u.* 0.15
	OH5···O1		2.65(2) Å	*v.u.* 0.25

The authors also stressed the close relationships between IHC, malachite and rosasite, on the basis of X-ray powder-diffraction and infrared data; IHC powder-diffraction pattern was indexed on the basis of an orthorhombic cell (no space group assigned) with a = 9.39, b = 24.53, c = 3.21 Å, V = 739.9 Å^3, Z = 8; D(calc.) = 3.693, D(meas.) = 3.59 g/cm^3 (Erdös & Altorfer, 1976). We may now confidently maintain that IHC is the technogene analogue of chukanovite. The diffraction pattern presented by Erdös & Altorfer (1976) closely corresponds to that of chukanovite presented in Table 1; it is proper to remark the absence of the additional extraneous reflections reported in Col. 1 of Table 1. All the diffraction lines reported by these authors are easily indexed on the basis of a unit cell of chukanovite-type, and a least squares refinement converges to the following unit-cell parameters: a = 12.373(3) Å, b = 9.390(2) Å, c = 3.220(1) Å, β = 97.65(3), fairly matching the corresponding parameters of chukanovite.

The study of the thermal behaviour in oxygen atmosphere (Erdös & Altorfer, 1976) shows that over 197 °C IHC transforms (topotactical replacement) to $Fe^{3+}_2O_2(CO_3)$, which decomposes (at ~ 600 °C) to α-Fe$_2$O$_3$ (hematite) and CO$_2$. Slight dehydration and oxidation of the IHC was observed under room conditions in one year.

More recently, IHC was also observed as the transformation product of biogenic magnetite (Kukkadapu *et al.*, 2005).

Relation of chukanovite with pokrovskite

Chukanovite is a Fe^{2+}-dominant member of the rosasite-malachite group of carbonate minerals, a group including several phases whose symmetry and cell constants are reported in Table 2. Very close relationships exist especially with the Mg-dominant phase, pokrovskite, ideally Mg$_2$(CO$_3$) (OH)$_2$ (Ivanov *et al.*, 1984). Technogene analogue of pokrovskite was found as a corrosion product, in this case of an In-Mg alloy (Uszynski & Kubiak, 1995).

The chemical data of chukanovite suggest a possible excess of water and a very slight deficiency of iron with respect to their ideal values in Fe$_2$(CO$_3$)(OH)$_2$. A similar case is presented by pokrovskite. Both the chemical data (Fitzpatrick, 1986), and the structural result (Perchiazzi & Merlino, 2006), gathered on pokrovskite from Sonoma County, California, USA, pointed to a partial occupancy in the Mg sites and a corresponding substitution of hydroxyl anions by water molecules, resulting in the crystal chemical formula $(Mg_{1.77}\square_{0.23})(CO_3)[(OH)_{1.54}/(H_2O)_{0.46}]$.

As it happens in pokrovskite, also in chukanovite the only possible way to locate more water is by partial substitution of hydroxyl anions by water molecules, thus balancing the charge deficiency due to the possible vacancies in the Fe sites. As already stated, the present structural refinement has been carried out assuming full occupancy of iron in the two independent Fe sites, and all the preceding discussion and consideration are related to the results of that refinement. However, a parallel refinement has been carried out, including the occupancy of Fe1 and Fe2 sites among the refined parameters, and an occupancy of 0.9 has been obtained. The comparison of the results of the two refinements, including all the structural details, in particular the O-O distances in the iron coordination polyhedra, leads us anyway to prefer the crystal chemical model resulting from the refinement with full occupancy of iron sites.

Further structural investigations with better material could probably definitely assess the crystal chemistry of chukanovite; to this aim we are presently trying to synthesize the artificial analogue of chukanovite.

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