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Cattiite, $Mg_3(PO_4)_2 \cdot 22H_2O$, a new mineral from Zhelezny Mine (Kovdor Massif, Kola Peninsula, Russia)

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With 1 figure and 1 table

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Abstract: Cattiite, $Mg_3(PO_4)_2 \cdot 22H_2O$, is a new mineral from Zhelezny (Iron) Mine (Kovdor carbonatite massif, Kola Peninsula, Russia). It appears as crystalline masses up to 1.5 cm in size filling up cavities of dolomite carbonatite. Associated minerals are dolomite, bakhchisaraitsevite, nastrophite, magnetite, sjogrenite and carbonate–fluorapatite. Rare {001} tabular crystals are observed within the masses. Colourless, transparent. Lustre vitreous with pearly sheen on cleavage fractures. Perfect {001} cleavage. Brittle; Moh's hardness 2. *D*(meas) 1.65(2) g/cm^3, *D*(calc) 1.640(1) g/cm^3. In immersion liquids cattiite is colourless and non-pleochroic. Biaxial (–), α 1.459(1), β 1.470(1), γ 1.470(1), 2V(meas) 25(5)° for λ 589 nm; weak dispersion r < v. Optical orientation: X^[001] = 80°, Y^[100] = 10°, Z ⊥ [001]; optical axis plane close to the cleavage plane. IR spectrum (the strongest bands are underlined): 3490, <u>3390</u>, 3050, 2410, 2102, 1665, 1602, 1055, <u>1006</u>, 900, 805, 727, 557 cm^{-1}. Chemical analysis (wet): MgO 18.0, FeO 0.1, P_2O_5 21.8, H_2O 60.8, total 100.7 wt.%. Empirical formula (O = 30): $(Mg_{2.92}Fe_{0.01})_{\Sigma 2.93}P_{2.01}O_{7.955} \cdot 22.055H_2O$. Simplified formula $Mg_3(PO_4)_2 \cdot 22H_2O$. Easily soluble in cool 10 % HCl. Dehydration begins over 40 °C. Triclinic $P\bar{1}$, *a* 6.932(2), *b* 6.925(3), *c* 16.154(5) Å, α 82.21(4), β 89.70(4), γ 119.51(3)°, V 666.3(3) Å^3 from X-ray powder and single-crystal diffractometry, Z = 1. Interplanar spacings (Å), intensity and *hkl* for the strongest lines in the X-ray powder diffraction pattern: 7.98(100)(002), 5.32(63)(003), 3.190(45)(005), 2.896(33)(202), 2.867(30)(–222), 2.728(32)(1–15), 2.658(37)(006). Cattiite corresponds to the synthetic polytype 1*A*2 of $Mg_3(PO_4)_2 \cdot 22H_2O$; the polytype 1*A*1 is known for synthetic material only. It is

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named in honour to Michele Catti (b. 1945), Professor of Physical Chemistry, University of Milano Bicocca (Italy).

Key words: cattiite, new mineral, phosphate, Kola Peninsula, Kovdor massif.

Introduction

The veins of dolomite carbonatites exposed in the Zhelezny (Iron) Mine (Kovdor massif, Kola Peninsula, Russia) are enriched in late hydrothermal Mg-rich phosphates as kovdorskite, girvasite, rimkorolgite, strontiowhitlockite, krasnovite, juonniite, bakhchisaraitsevite, bobierrite and collinsite (Kapustin et al. 1980, Britvin et al. 1990, Britvin et al. 1991, Britvin et al. 1995, Liferovich et al. 2000). During field work in Summer 1999, an unknown mineral has been found in the same association and tentatively identified as $Mg_3(PO_4)_2 \cdot 22H_2O$, a high hydrate magnesium orthophosphate known as synthetic phase since 19th century (Haushofer 1882, Pietsch 1938). Structural studies by Schroeder et al. (1978) and Catti et al. (1981) revealed the existence of two polytypes named $Mg_3(PO_4)_2 \cdot 22H_2O{-}I$ and $Mg_3(PO_4)_2 \cdot 22H_2O{-}II$, respectively. Both polytypes are triclinic (see Crystallography) and according to the nomenclature of polytypes (Guinier et al. 1984) shall here be indicated, in the same order, as $Mg_3(PO_4)_2 \cdot 22H_2O{-}1A1$ and $Mg_3(PO_4)_2 \cdot 22H_2O{-}1A2$, where the index 1 and 2 applied to A (for anorthic) indicates the order of discovery.

The characterisation of the new phosphate from Kovdor showed that it corresponds to $Mg_3(PO_4)_2 \cdot 22H_2O{-}1A2$ polytype. Both the mineral and the name have been approved (2000–032) by the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (IMA). The mineral is named cattiite, in honour to Michele Catti (b. 1945), Professor of Physical Chemistry, University of Milano Bicocca (Italy), for his contributions to the crystal chemistry of hydrated oxysalts. The holotype specimen of cattiite is deposited at the Mineralogical Museum, Department of Mineralogy, Saint-Petersburg State University, catalogue number 1/18618.

Occurrence and physical properties

Cattiite has been found in several cm-sized cavities within a 20–40 cm thick vein of dolomite carbonatites; the vein cross-cuts forsterite–magnetite ore at the bottom of the Zhelezny Mine quarry. Associated minerals are nastrophite, bakhchisaraitsevite, sjogrenite, magnetite, and carbonate–fluorapatite. The mineral occurs as masses up to 1.5 cm in size filling up free space of cavities and interstices of associated minerals. The masses of cattiite usually contain single-crystals which sometime show {001} as dominant form. Cattiite is colourless and transparent, with {001} perfect cleavage and uneven fracture in other directions. Lustre is vitreous, with gypsum-like pearly sheen on cleavage planes; brittle; Mohs' hardness 2. D(obs) = 1.65(2) g/cm^3 (floating in $CHBr_3$ – $C_5H_{11}OH$ solution), D(calc) = 1.64 g/cm^3 for the ideal formula and unit cell given below.

In immersion liquids, the mineral is colourless and non-pleochroic. Biaxial (–), $\alpha = 1.459(1)$, $\beta = 1.470(1)$, $\gamma = 1.470(1)$, 2V(meas) = 25(5)° for λ 589 nm; 2V(calc) = 0°, a value strongly influenced by even a slight difference between β and γ. Optical orientation: $X \wedge [001] = 80°$, $Y \wedge [100] = 10°$, $Z \perp [001]$ (optical axes plane close to the cleavage plane). Dispersion weak, r<v.

IR-spectroscopy and chemical composition

The infrared (IR) absorption spectrum of cattiite (Fig. 1) was obtained using a Perkin-Elmer FTIR spectrophotometer with the sample dispersed in mineral oil (nuyol) at 12 °C and 90 % relative air humidity. The absorption bands of the oil were subtracted from the spectrum. The strongest and broad

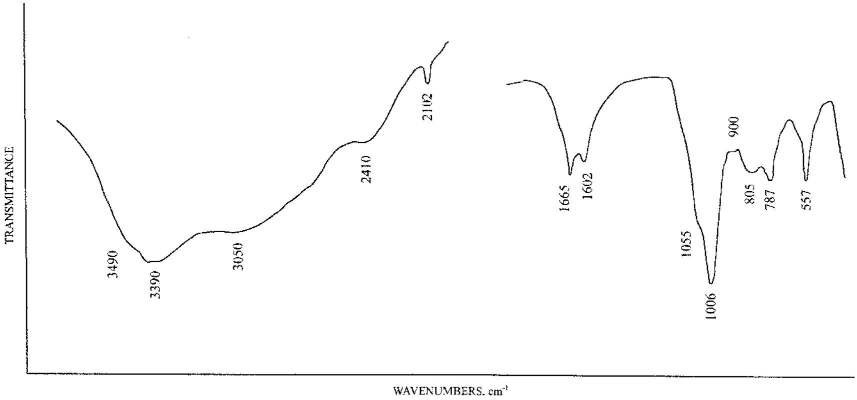

Fig. 1. IR spectrum of cattiite.

bands in the cattiite IR spectrum are observed in the region of OH stretching vibrations of H_2O molecules, at 3490, 3390 (strongest band) and 3050 cm^{-1}. A weak broad band at 2410 cm^{-1} and a weak narrow band at 2102 cm^{-1} correspond to the stretching vibrations of the $PO{-}H^{+\delta}$ bond and free H^+ ions respectively. Taking into account this fact and lack of octahedral cations in the empirical formula (0.07 atoms per formula unit, see below), we can suggest that a minor part of the phosphate ions is involved into the equilibrium $H^+ + (PO_4)^{3-} \leftrightarrow (HPO_4)^{2-}$. The bands at 1665 and 1602 cm^{-1} correspond to in-plane $H{-}O{-}H$ bending vibrations of at least two different types of water molecules. The other bands are assigned to asymmetrical (at 1055 and 1006 cm^{-1}) and symmetrical (900 cm^{-1}) stretching vibrations of $(PO_4)^{3-}$, out-of-plane vibrations of H_2O (805, 727 cm^{-1}), and bending vibrations $(PO_4)^{3-}$ (557 cm^{-1}). According to the IR data, cattiite does not contain borate, carbonate or nitrate anions as well as $(NH_4)^+$ cations and $C{-}H$ bonds.

Due to its high hydration, cattiite is unstable under heating. Thermal studies by Bakaev et al. (1974) showed that synthetic $Mg_3(PO_4)_2 \cdot 22H_2O$ is partially dehydrated above 70 °C. According to our observations, partial dehydration of cattiite begins at 40–60 °C, depending probably on the relative air humidity. The product of partial dehydration is a white powder whose X-ray powder diffraction pattern is similar to that of bobierrite, $Mg_3(PO_4)_2 \cdot 8H_2O$. Cattiite is easily soluble in diluted cold 10 % HCl and looses water under vacuum when studied by electron microprobe. The following chemical composition (wt.%) was determined by wet analysis from 243.5 mg of sample: MgO 18.0, FeO 0.1, P_2O_5 21.8, H_2O 60.8 (weight loss at 1000 °C), total 100.7. No measurable amounts of other elements were detected by ICP. The empirical formula calculated on the basis of 30 oxygen atoms is $(Mg_{2.92}Fe_{0.01})_{\Sigma 2.93}P_{2.01}O_{7.955} \cdot 22.055H_2O$; it well corresponds to the ideal formula $Mg_3(PO_4)_2 \cdot 22H_2O$.

Crystallography

As mentioned above, two polytypes of $Mg_3(PO_4)_2 \cdot 22H_2O$ are known. Both phases are triclinic with very close cell parameters and their crystal structures, as discussed by Catti et al. (1981), are very close too. In fact, the structures of both polytypes are based on isolated PO_4 tetrahedra and $Mg(H_2O)_6$ octahedra which are connected by hydrogen bonds. A part minor features, in both structures a (001) sheet of octahedra plus a sheet consisting of octahedra and tetrahedra form a polar (001) slab which is duplicated by a centre of symmetry to form a layer with thickness corresponding to the c parameter. Two different centres of symmetry locally connect two polar (slightly modified) (001) slabs; consequently, two different one-layer polytypes can be formed. The cell parameters of the two polytypes are:

- $a = 6.902$, $b = 6.961$, $c = 15.982$ Å, $\alpha = 87.66$, $\beta = 94.78$, 147 = 119.19° (space group $P\bar{1}$; $Z = 1$) for the polytype 1A1 described by Schroeder et al. (1978) (original cell transformed by 100/0$\bar{1}$0/00$\bar{1}$);
- $a = 6.937$, $b = 6.932$, $c = 16.132$ Å, $\alpha = 82.15$, $\beta = 89.72$, $\gamma = 119.49°$ (space group $P\bar{1}$; $Z = 1$) for the polytype 1A2 described by Catti et al. (1981).

A study by X-ray single-crystal diffractometry of cattiite showed that its cell [$a = 6.932(2)$, $b = 6.925(3)$, $c = 16.154(5)$ Å, $\alpha = 82.21(4)$, $\beta = 89.70(4)$, $\gamma = 119.51(3)°$, V = 666.3 (3) Å^3, Z = 1, space group $P\bar{1}$] corresponds to that published by Catti et al. (1981) for the polytype 1A2. Identity of composition between natural and synthetic phases and the low quality of the diffraction shown by our crystals of cattiite (which easily loose water) suggested the uselessness of repeating a structural refinement.

Table 1 shows (*i*) the observed and calculated X-ray powder diffraction patterns of cattiite and of the corresponding synthetic polytype 1A2 taken from Catti et al. (1981); (*ii*) calculated data for the synthetic polytypes 1A1. The data of synthetic polytypes are limited to $d = 2.4$ Å. The structural information for calculation is taken from Catti et al. (1981) for 1A2 and from Schroeder et al. (1978) for 1A1. The X-ray powder diffraction pattern of cattiite was acquired using a DRON 2 diffractometer (Co$K\alpha$, quartz monochromator, 20kV, 30mA, scan speed 0.5°/min). The indexing of the experimental patterns was done by comparing observed (I_{obs}) with calculated diffraction intensities (I_{calc}) and observed (d_{obs}) with calculated (d_{calc}) interplanar distances. Refined cell parameters from the powder diffraction data of cattiite are reported above. Note that without single-crystal data, the powder diffraction pattern of cattiite could not be easily identified with that of one of the two described polytpes; in fact, as expected in general for polytypes, very similar patterns are shown by the two polytypes. The weak reflection with $d_{\mathrm{obs}} = 4.83$ Å cannot be indexed by the cell of cattiite but corresponds to one of the strongest lines of $Mg_3(PO_4)_2 \cdot 22H_2O$–1$A$1. The intensity of this reflection depends on the sample preparation (i.e. by grinding with water or with ethanol) and one can suppose that some formation of polytype 1A1 depends on the grinding procedure.

Table 1. X-ray powder diffraction data for cattiite (Co*K*α radiation, λ = 1.78901 Å, quartz monochromator). Observed data for synthetic 1*A*2 and all data for 1*A*2 are limited to d_{calc} = 2.371 Å. See text for further explanation.

Cattiite		Synthetic 1*A*2					Synthetic 1*A*1			Cattiite		Synthetic 1*A*2		
I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{calc}	d_{calc}	*hkl*	I_{calc}	d_{calc}	*hkl*	I_{obs}	d_{obs}	I_{calc}	d_{calc}	*hkl*
100	7.98	50	7.97	100	7.97	002	95	7.96	002	4	2.363	25	2.362	1-16
22	6.01	35	6.03	49	6.01	100	92	6.01	100	13	2.310	31	2.309	–204
7	5.88			30	5.89	011				6	2.286	13	2.285	205
17	5.80	10	5.75	64	5.79	101	11	5.72	111			5	2.267	2-2-5
							25	5.68	011	5	2.265	5	2.265	3-20
6	5.45	10	5.47	10	5.45	1-11	18	5.46	11-1	2	2.233	3	2.234	3-21
63	5.32	35	5.32	53	5.32	003	50	5.31	003	16	2.184	18	2.185	–117
2	5.18			10	5.18	012				3	2.167	7	2.165	–312
16	5.00			30	5.01	102				1	2.112	1	2.113	21-2
27	4.96	40	4.96	58	4.96	–112	57	4.95	112	4	2.101	10	2.101	2-25
5	4.83						62	4.83	01-2	2	2.077	1	2.079	206
8	4.62	5	4.63	2	4.62	10-2	45	4.64	10-2			1	2.076	1-17
26	4.44			97	4.44	01-2				2	2.063	2	2.065	–234
4	4.32			11	4.32	013						2	2.064	–313
26	4.13	40	4.12	42	4.13	–113	46	4.12	113	2	2.036	3	2.038	117
23	3.99	15	3.985	13	3.99	004	21	4.00	01-3	3	2.024	5	2.023	01-7
4	3.83			3	3.83	1-13	18	3.84	10-3			5	2.001	032
2	3.59			4	3.59	014				4	1.994	7	1.992	–324
11	3.46	10	3.467	5	3.47	2-10	25	3.48	120	6	1.967	14	1.966	027
				11	3.46	104	3	3.45	1-11	2	1.946	5	1.946	3-1-4
9	3.44			18	3.43	1-20	4	3.44	104	4	1.938	2	1.936	1-1-8
10	3.39			24	3.39	2-11	20	3.39	1-1-1			13	1.914	2-26
10	3.35			30	3.35	112	34	3.31	21-1	7	1.913	10	1.914	20-6
5	3.26	5	3.266	5	3.26	1-21	18	3.26	1-12	4	1.882	6	1.881	2-2-7
45	3.19	40	3.186	9	3.20	1-14	9	3.21	11-4			5	1.881	3-15
				23	3.19	005	26	3.19	005	4	1.842	6	1.841	216
				16	3.18	2-12				4	1.821	10	1.826	2-3-6
2	3.079			6	3.079	–123	6	3.065	21-2	2	1.791	6	1.790	11-7
5	3.005	10	3.005	4	3.006	200	6	3.005	200	1	1.773	1	1.777	019
				6	3.000	201	15	2.985	021	4	1.746	12	1.744	221
5	2.977			5	2.975	020				11	1.731	17	1.731	2-4-1
				7	2.974	2-2-1	16	2.967	123			5	1.723	4-21
				11	2.910	20-1	74	2.914	20-1	4	1.721	7	1.719	2-2-8
15	2.902	15	2.905	11	2.898	2-1-3	7	2.898	115	1	1.700	1	1.702	3-26
33	2.896	20	2.901	78	2.894	202	7	2.893	22-1	3	1.675	3	1.673	224
30	2.867	100	2.865	77	2.867	–222	86	2.861	222	2	1.662	1	1.660	4-30

Table 1. Continued.

Cattiite		Synthetic 1A2					Synthetic 1A1			Cattiite		Synthetic 1A2		
I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{calc}	d_{calc}	*hkl*	I_{calc}	d_{calc}	*hkl*	I_{obs}	d_{obs}	I_{calc}	d_{calc}	*hkl*
22	2.845	90	2.846	69	2.844	0-21	100	2.839	02-2	2	1.652	3	1.651	3-40
4	2.795	10	2.795	6	2.796	023	6	2.821	015			6	1.649	4-23
32	2.728			29	2.728	1-15	32	2.729	11-5	3	1.630	2	1.631µ	11-8
37	2.658	45	2.658	29	2.658	006	29	2.654	006			3	1.630	1-28
				19	2.653	02-2	18	2.637	023	1	1.614	8	1.612	4-32
9	2.590			38	2.590	024	4	2.637	02-3	1	1.605	1	1.606	0110
7	2.526	15	2.523	11	2.521	2-23	20	2.537	20-3	1	1.578	1	1.577	2-2-9
6	2.506			8	2.503	204	10	2.523	22-3	3	1.450	1	1.444	4-16
				7	2.442	1-24	10	2.487	204	3	1.435	2	1.434	4-4-4
4	2.438			10	2.437	02-3	27	2.416	024	2	1.412	1	1.414	3-2-9
4	2.371			12	2.371	025	3	2.362	11-6	3	1.377	5	1.377	04-3

depends on the sample preparation (i.e. by grinding with water or with ethanol) and one can suppose that some formation of polytype 1*A*1 depends on the grinding procedure.

Conclusions

Preparations of synthetic $Mg_3(PO_4)_2 \cdot 22H_2O$ (Pietsch 1938, Bakaev et al. 1974, Schroeder et al. 1978, Catti et al. 1981) do not differ for the two polytypes and were carried out in cold water solutions at 5–25 °C; presumably the appearance of one more than another polytype depends on subtle conditions. We suggest that in the Zhelezny mine of Kovdor massif, cattiite formed from cold Mg-rich phosphate solutions during post-hydrotermal stage of carbonatite formation. Under heating, as mentioned above, dehydration of cattiite does not appear below about 40 °C; therefore the species can be considered a stable phase under the mine conditions.

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