

Peretaite, $\text{CaSb}_4\text{O}_4(\text{OH})_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, a new mineral from Pereta, Tuscany, Italy

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Abstract

Peretaite, a new calcium and antimony sulfate mineral, occurs as aggregates of colorless tabular crystals in the antimony-bearing vein at Pereta, Tuscany, Italy. It is monoclinic, space group $C2/c$, with $a = 24.641$, $b = 5.598$, $c = 10.180\text{\AA}$, $\beta = 95.95^\circ$. The calculated density is 4.06 g cm^{-3} . The cleavage $\{100\}$ is perfect. Crystals are always twinned (100). Peretaite is biaxial (+) with mean refractive index 1.841. The five strongest lines in the X-ray diffraction pattern are (d in \AA , l , hkl): 12.19 100 200; 6.12 21 400; 3.10 24 512; 3.06 67 800; 2.451 31 10.00. On the basis of the wet-chemical analysis, the IR spectroscopy, the TGA spectrum, and especially the structure determination, the chemical formula is $\text{CaSb}_4\text{O}_4(\text{OH})_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$.

Introduction

In a paper dealing with a new find of klebelsbergite (Cipriani *et al.*, 1980), some of us pointed out that a new mineral is present among the accessory minerals of the antimony-bearing vein at Pereta, Tuscany, Italy. Further study fully confirmed the thesis.

The new species, $\text{CaSb}_4\text{O}_4(\text{OH})_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, is named peretaite for the locality. Both the mineral and the name have been approved by the Commission on New Minerals and Mineral Names, IMA. Type specimens are deposited in the mineralogical museums of Florence University (regional collection, #164/I) and Pisa University.

Occurrence and paragenesis

The environment where peretaite was found has been described by Cipriani *et al.* (1980). Peretaite occurs, in small quantities, as aggregates of tabular crystals in the geodes of a deeply silicified limestone from "Calcare Cavernoso," and also in the cavities of

columnar stibnite. Crystals of peretaite associated with acicular crystals of klebelsbergite are shown in Figure 1. Other associated minerals are stibnite, quartz, calcite, pyrite, valentinite, kermesite, sulfur, and gypsum. Aggregates of klebelsbergite crystals and rarely of peretaite are often red from incrustations of valentinite. Unlike klebelsbergite, which was found rather abundantly in the fissures of the stibnite veinlets, peretaite occurs closer to the boundary with limestones. The mineral, as well as klebelsbergite, has apparently been formed by the action of sulfuric acid on stibnite; the source of the calcium in peretaite is likely the limestone of the country rock.

Chemistry

Preliminary qualitative analyses of peretaite were made with an ORTEC X-ray microanalyzer and an ARL SEMQ electron microprobe. However, since the crystals decompose under the electron beam, microprobe results were considered not reliable for a quan-



Fig. 1. Crystals of peretaite associated with acicular crystals of klebelsbergite; the largest crystal is 1.5 mm long (photo P. B. Scortecci).

titative determination, especially for sulfur. Therefore a wet-chemical analysis was performed. About 20 mg of purified material was dissolved in 1:5 HCl and diluted to 25 ml with distilled water. Calcium was determined by atomic absorption spectrometry, using a Perkin Elmer 303 instrument. Antimony was determined by alternating current anodic stripping voltammetry, on hanging-drop mercury electrode in 1M HCl. Total sulfur was potentiometrically titrated with $Pb(ClO_4)_2$ and an ORION 94-82 lead ion electrode. The water content was inferred from a TGA spectrum. The result, given in Table 1, corresponds

Table 1. Chemical analysis of peretaite. All values are weight percent

Oxide	(1)	(2)
Sb_2O_3	68.31	69.09
CaO	6.58	6.44
SO_3	18.78	17.62
H_2O	6.33	6.0
	100.00	99.15

(1) Ideal peretaite

(2) From analytical results

Table 2. X-ray powder diffraction data for peretaite; d values are in Å

I/I_0	d_{obs}	d_{calc}	h k l	I/I_0	d_{obs}	d_{calc}	h k l
100	12.19	12.254	2 0 0	31	2.451	2.451	10 0 0
21	6.12	6.127	4 0 0		2.449		9 1 0
16	5.45	5.457	1 1 0	17	2.068	2.066	8 2 0
5	4.85	4.851	-1 1 1		2.070		11 1 0
4	4.76	4.758	1 1 1	3	2.059	2.059	-8 0 4
5	4.08	4.085	6 0 0		2.058		6 0 4
5	3.68	3.688	5 1 0	16	1.878	1.878	-2 2 4
2	3.55	3.556	-5 1 1		1.877		0 2 4
11	3.51	3.516	-3 1 2	3	1.858	1.859	8 0 4
3	3.38	3.381	5 1 1		1.860		-10 0 4
5	3.35	3.354	-6 0 2	5	1.844	1.844	10 2 0
12	3.31	3.316	3 1 2	4	1.710	1.710	-14 0 2
24	3.10	3.098	-5 1 2	3	1.699	1.700	3 3 2
67	3.06	3.064	8 0 0	4	1.684	1.684	-11 1 4
4	3.03	3.029	6 0 2	2	1.668	1.668	-5 3 2
4	2.967	2.968	7 1 0	1	1.609	1.609	-12 2 2
14	2.874	2.876	5 1 2	2	1.604	1.604	14 0 2
12	2.799	2.799	0 2 0	2	1.582	1.582	-5 1 6
13	2.727	2.729	2 2 0	2	1.556	1.556	3 1 6
5	2.696	2.698	0 2 1	2	1.549	1.549	8 2 4
20	2.532	2.532	-2 0 4	6	1.532	1.532	16 0 0
		2.531	0 0 4	1	1.511	1.510	-16 0 2
				4	1.397	1.396	17 1 0

to $Ca_{1.01}Sb_{4.17}S_{1.94}O_{16}H_{5.86}$ on the basis of 16 oxygens, or ideally $CaSb_4^{3+}O_4(OH)_2(SO_4)_2 \cdot 2H_2O$ from the structural results and the infrared spectrum. Indeed, both the structural determination and the IR spectroscopy gave clear indications, the first without any doubt, on the presence of sulfate groups as well as of H-bonded water molecules and hydroxyl groups.

Crystallography

X-ray single-crystal study (Weissenberg camera and single-crystal diffractometer) indicated Laue symmetry $2/m$. Systematic extinctions are consistent with the space groups $C2/c$ or Cc . The former, however, is the correct one from the structural study (Menchetti and Sabelli, 1980b). All the examined crystals appeared to be twinned with (100) as twin plane.

The X-ray powder diffraction pattern (Table 2) was obtained by means of a Philips diffractometer, with $CoK\alpha$ radiation, NaF as internal standard, and 0.25° per min scanning speed. Indexing was per-

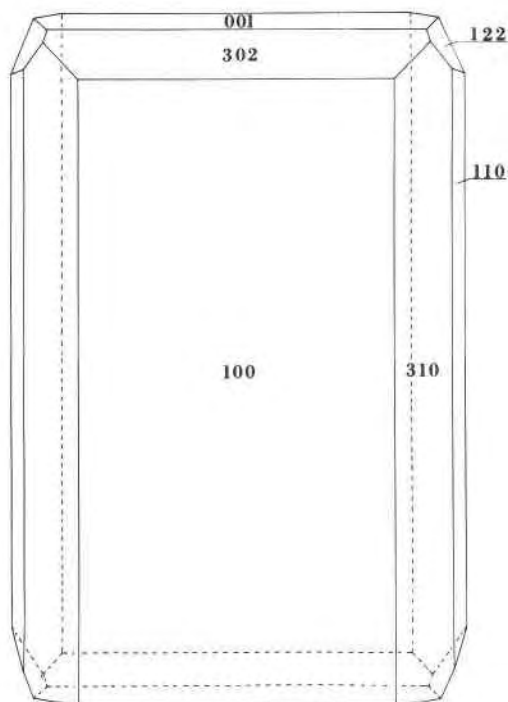


Fig. 2. Typical habit of a peretaite crystal.

formed on the basis of single-crystal data and taking into account the intensities of the reflections collected for the structural study. In the powder pattern there is a systematic enhancement of the intensities of $h00$ reflections because of a preferential orientation due to the $\{100\}$ cleavage. The unit-cell parameters, determined from powder data by means of least-squares calculations, are: $a = 24.641(2)$, $b = 5.598(2)$, $c = 10.180(1)\text{\AA}$, $\beta = 95.95(1)^\circ$.¹

Peretaite crystals appear flattened $\{100\}$ and sometimes elongated $[001]$. Two typical habits of peretaite are shown in Figures 2 and 3. The observed forms are $\{100\}$, $\{310\}$, $\{110\}$, $\{122\}$, $\{001\}$, $\{010\}$, $\{210\}$, $\{201\}$, $\{302\}$, and $\{601\}$. The largest crystals have dimensions up to $5 \times 2 \times 0.5$ mm.

Physical properties

Crystals of peretaite are transparent and colorless, with vitreous luster and $\{100\}$ cleavage. A density >3.8 g cm⁻³ was determined by the heavy-liquid method; crystals seem to float in Clerici solution with a density of about 4.0 g cm⁻³. The calculated density (for the ideal formula) is 4.06 g cm⁻³. The micro-

indentation hardness (VHN) with a 15-g load is between 170 and 190 kg mm⁻².

Crystals are optically biaxial positive (+) with a very large axial angle. The value of $2E\alpha$ measured with a universal stage, using hemispheres with refraction index of 1.649, is nearly 102° . The optical plane is parallel to (010) . By the prism method $[(100) \wedge (3\bar{1}0)]$ a first index of refraction of 1.841(1) was measured. The corresponding vibration direction makes an angle of about 28° with the b axis. A second index of 1.935(1) was measured for a vibration direction almost parallel to c . The mean index of refraction calculated from the Gladstone–Dale relationship, using the ideal chemical formula, the calculated density, and the constants given by Mandarinò (1976), is 1.841.

The TGA spectrum (taken under nitrogen atmosphere) shows a weight loss of about 6%, which is attributed to a dehydration reaction including both H₂O and OH. The tracing is not very sharp; however, it seems possible to identify two successive steps in the temperature range 200–240°C. This temperature is about 60–70°C lower than that found for the corresponding effect in klebelsbergite. In the latter, however, only OH groups are present.

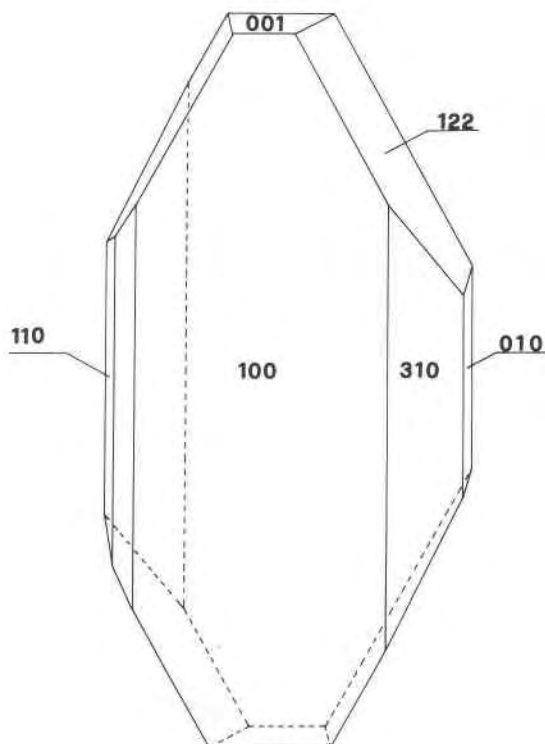


Fig. 3. Another frequently encountered crystal habit. Sometimes the form $\{001\}$ is lacking.

¹ Lattice parameters used in the crystal structure determination are those measured with a single-crystal diffractometer. They are $a = 24.665(4)$, $b = 5.6006(9)$, $c = 10.185(1)\text{\AA}$, $\beta = 95.98(1)^\circ$.

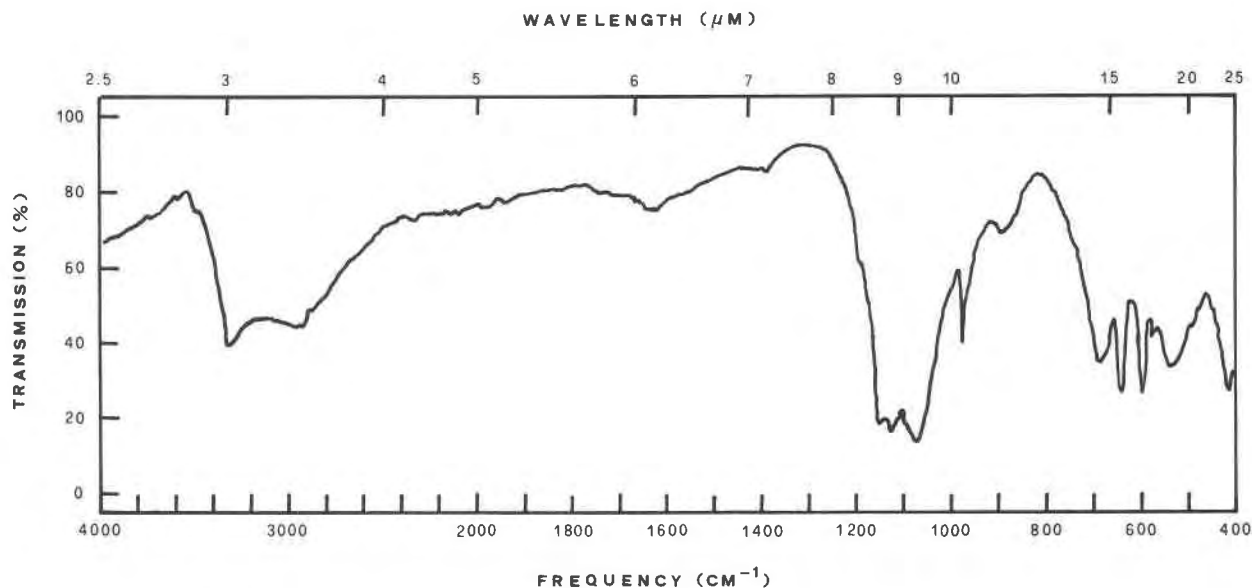


Fig. 4. Infrared absorption spectrum of peretaite.

The infrared spectrum was obtained from a potassium bromide disc containing peretaite. The pellet was heated at 120°C for two hours. The spectrum, taken from 4000 to 400 cm^{-1} , is shown in Figure 4. The sharp absorption at 3310 cm^{-1} due to the O-H stretching mode supports the presence of hydroxyl groups, with H-bonds stronger than that of klebelsbergite, which has the same peak at 3435 cm^{-1} . The occurrence of a very broad band, ranging from 3500 to 2500 cm^{-1} with a maximum at about 3000 cm^{-1} , and of a weak band at 1640 cm^{-1} , indicates the presence of water of hydration with strong H-bonds. In klebelsbergite the corresponding peaks are absent: in the structure of this mineral there are no water molecules (Menchetti and Sabelli, 1980a). Of the SO_4^{2-} stretching vibrations, ν_3 , ν_1 , and ν_4 were observed, at frequencies slightly different from klebelsbergite. The presence of ν_1 (at 975 cm^{-1}) shows that the sulfate tetrahedron is distorted. In addition ν_1 appears as a single peak and ν_3 shows fewer structures than in klebelsbergite: this may be due to the presence of the

inversion center in the structure of peretaite and to more strict selection rules.

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