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Petersite, a REE and phosphate analog of mixite

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Abstract

The new mineral petersite (Y,REE,Ca)$Cu_6(PO_4)_3(OH)_6 \cdot 3H_2O$) occurs as a supergene mineral at the traprock quarry at Laurel Hill in Secaucus, New Jersey. It occurs in a brecciated and mineralized hornfels near a diabase contact, in association with opal and malachite. Prismatic crystals less than 0.1 mm in length with forms $\{10\bar{1}0\}$ and {0001} occur as radiating sprays. It is optically uniaxial, positive, with ω = 1.666 (4) and ϵ = 1.747 (4). The measured density is 3.41 g/cm^3. Petersite is hexagonal, probable space group $P6_3/m$ or $P6_3$, with a = 13.288(5) c = 5.877(5)Å, V = 898.6(8)Å^3, and Z = 2. The strongest lines in the powder diffraction pattern are: (d, intensity, index) 11.6, 100, 100; 4.36, 50, 210; 3.49, 40, 211; 2.877, 40, 400; 2.433, 60, 212. The name is in honor of Thomas and Joseph Peters.

Introduction

The new mineral described herein was sent to us for examination by Mr. Thomas Peters of the Paterson Museum, who had obtained it from Mr. Nicholas Facciolla, who found it in early 1981. Mr. Peters' examination by SEM techniques suggested a hexagonal morphology for the mineral and our subsequent X-ray diffraction study showed it to be hexagonal and isostructural with members of the mixite group. Preliminary electron microprobe data showed that phosphorus is present as a major element but that arsenic is not present. A detailed examination has confirmed that it is a new member of the mixite group, and that it is the first phosphate analogue of this group of arsenates.

We take great pleasure in naming this new mineral petersite in honor of Messers. Thomas and Joseph Peters, brothers, in recognition of their contributions to the mineralogy of New Jersey and their devotion to curating at the Paterson Museum in Paterson, New Jersey, and the American Museum of Natural History in New York, respectively. The mineral and the name were approved by the IMA Commission on New Minerals and Mineral Names, prior to publication. Type material is preserved under catalog # NMNH 148973 at the Smithsonian Institution.

Morphology

Petersite occurs as prismatic hexagonal crystals of simple morphology. The only forms present are the prism $\{10\bar{1}0\}$, and the pinacoid {0001}. The crystals are usually euhedral and occur in radiating clusters and sprays which are somewhat isolated on the matrix (Fig. 1). Radial aggregates, which consist of a large number of prismatic crystals (Fig. 2), appear hemispherical and slightly dull due to a dull luster on the exposed pinacoids, as compared with the highly vitreous luster on the less exposed prism faces. The habit of petersite is in marked contrast to that of the arsenate members of the series, goudeyite, mixite, and agardite, which usually occur in wispy aggregates of extremely acicular crystals. The maximum size of crystals examined was less than 0.1 mm in length, and most are considerably smaller. The diameter of radiating clusters approaches 0.1 mm (Fig. 2).

X-ray crystallography

Single crystals were studied using Weissenberg techniques. The resulting photographs confirmed

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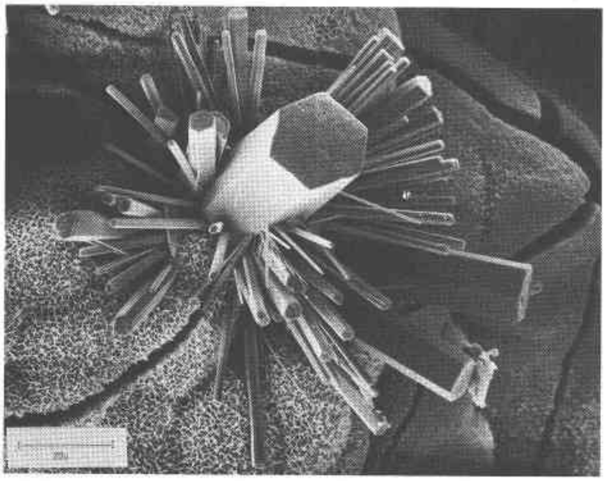

Fig. 1. Scanning electron microscope photomicrograph showing divergent radiating spray of petersite crystals.

Table 1. X-ray powder diffraction data for petersite, obtained using a 114.6 mm diameter Gandolfi camera

d(Obs)	d(Calc.)	hkl[+]	I/I_0*	d(Obs.)	d(Calc.)	hkl	I/I_0
11.6	11.5	100	100	1.767	1.769	332	10
4.36	4.35	210	50	1.742	1.745	303	20
4.12	4.11	201	10	1.687	1.691	512	15
3.84	3.84	300	10		1.687	223	
3.49	3.50	211	40	1.659	1.661	440	2
3.32	3.32	220	10	1.603	1.606	602	5
3.19	3.19	310	5		1.598	441	
2.877	2.877	400	40	1.583	1.583	531	1
2.806	2.805	311	10		1.583	701	
2.687	2.687	112	10	1.559	1.561	522	5
2.634	2.640	320	15	1.523	1.524	710	2
2.509	2.511	410	30	1.505	1.507	612	5
2.433	2.435	212	60	1.466	1.469	004	5
2.411	2.408	321	1		1.467	333	
2.197	2.201	222	5	1.444	1.446	442	5
2.161	2.162	312	2	1.403	1.406	720	5
2.061	2.162	510	2		1.402	622	
	2.056	402		1.394	1.397	801	2
1.961	1.964	322	20		1.392	214	
1.888	1.892	430	1	1.265	1.268	722	15
					1.268	414	
					1.267	443	
					1.264	731	

*Intensities visually estimated.

[+] Indexed on the basis of a hexagonal unit cell with a=13.228(5) and c=5.877(5)Å.

that petersite is hexagonal, with point group symmetry 6/*m*. Extinctions occurred for 00*l* reflections having $l = 2n + 1$. However, as all crystals are exceptionally small and the reflections are very weak even for very long exposures, this extinction rule is not as well defined as we would like. Assuming that it is present, however, the space group must be $P6_3/m$ or $P6_3$.

Powder diffraction data were obtained using a polycrystalline sample in a Gandolfi camera (114.6 mm diameter), Cu$K\alpha$ radiation, and Si as an internal standard. The data are presented in Table 1. Unit cell parameters (a = 13.288(5), c = 5.877(5)Å V = 898.6(8)Å^3) were obtained through least-squares refinement of the powder diffraction data. These crystallographic parameters are in general agreement with other members of the mixite group. For example, Wise (1978) reports the probable space group of goudeyite as $P6_3/m$ or $P6_3$, with a = 13.472(1) and c = 5.902(4)Å.

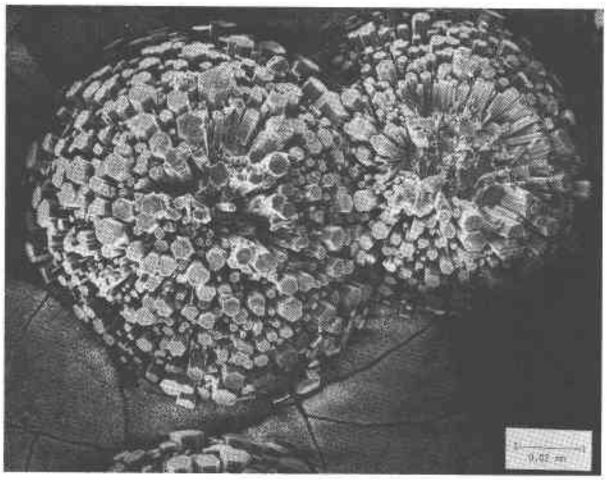

Fig. 2. Scanning electron microscope photomicrograph showing semispherules of tightly packed petersite crystals.

Physical and optical properties

Petersite is bright yellowish green in color, quite similar in hue to cuprosklowdowskite. The hardness could not be determined due to the very small crystal size and a high degree of brittleness. The density, obtained using heavy liquid techniques, is 3.41 g/cm^3, in excellent agreement with the calculated value of 3.40 g/cm^3 based on the measured composition. The luster of fracture surfaces could not be accurately observed, but the luster of the prism faces is vitreous. Petersite is readily soluble in 1:1 hydrochloric acid, coloring the solution light greenish yellow.

Optically, petersite is uniaxial (+) with indices of refraction ϵ = 1.747(4) and ω = 1.666(4). The birefringence is similar to that of other members of the mixite group. Pleochroism is strong, E ≫ O, with E = green, O = light yellowish green. Calculation of the Gladstone–Dale relationship, using the constants of Mandarino (1976) yields K_C = 0.191 and K_P = 0.203, providing good agreement between physical and chemical data. There is no discernible fluorescence under ultraviolet radiation.

Chemistry

Petersite was chemically analyzed using an ARL–SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μA, standardized on brass. The standards used were synthetic olivenite (Cu), fluorapatite (P), hornblende (Fe, Ca), and the Drake rare earth glasses for REE. The data were corrected using a modified version of the MAGIC-4 program of the Geophysical Laboratory. The resultant analysis yields: P_2O_5 23.1, CuO 52.1, CaO 2.4, FeO 0.8, Y_2O_3 2.5, Ce_2O_3 2.5, Nd_2O_3 1.2, Sm_2O_3 1.2, La_2O_3 1.0 with H_2O 12.3 weight percent by difference, sum = 100.0 percent. (Pr, Gd, Eu, Tm, Ho were present as traces; Pb, Sr, Er, Dy, Ba, Yb and S were sought but not found). The accuracy of the data is estimated to be ±3% of the amount present for Ca, Fe, Cu and P; ±7% of the amount present for REE. Fe was assigned to Fe^{2+} on the basis of a microchemical test. The unit cell contents for petersite, calculated on the basis of P = 6 atoms, are:

$$Y_{0.41}Ce_{0.28}Nd_{0.23}Sm_{0.13}La_{0.11}Fe^{2+}_{0.20}Ca_{0.79})_{\Sigma 2.15}\ Cu_{12.07}(PO_4)_{6.00}\ (OH)_{11.60}\cdot 6.78H_2O$$

or, ideally, $(Y,REE,Ca)_2Cu_{12}(PO_4)_6(OH)_{12}\cdot 6H_2O$ with the sum of REE > Ca and with Y as the dominant rare earth. A wavelength-dispersive microprobe scan indicated the absence of any other elements with atomic number greater than 9 including Al, As and Bi, elements found in other members of the mixite group. There is too little material for the direct determination of water. It was therefore calculated by difference. The resulting OH and H_2O contents are in reasonable agreement with those for other members of the mixite group.

Because the chemical analysis indicates that no single element occupies more than half of the site occupied in part by rare earth elements, there is some problem with nomenclature. Peter Modreski of the United States Geological Survey, Denver, (personal communication and paper in preparation) has considered such factors in rare earth arsenate equivalents of petersite and notes that the name agardite–(La) has been approved for such a mineral having only 0.23 La as the dominant element in that site. Similar considerations may eventually have to be applied to phosphate solid-solution equivalents of petersite, but until such minerals have actually been discovered we need not be concerned with such factors. Petersite is defined simply as a phosphate isostructural with members of the mixite group, and having rare earth elements dominant over Ca.

The substitution of Ca^{2+} in a site occupied principally by cations having a charge of +3 requires some discussion, as the charge-balanced, end-member formula requires that no cations of charge +2 be in that site. The mutual solid solution of Ca for REE occurs in many phases. However, it requires coupling with some other substitution mechanism in order to maintain charge balance. One possible substitution is $3Ca^{2+} \rightarrow 2M^{3+} + \square$. However, the crystal structure of mixite and isostructural phases is not known, so we cannot hypothesize the existence of a site for such an addition solid solution mechanism. There is some indication of such a mechanism in that there is a slight excess (0.15) of Y, REE, Fe and Ca over the value of 2.0 per unit cell. A second possible substitution mechanism could be $Ca^{2+} + \square$ (or H_2O) $\rightarrow M^{3+}\ (OH)^{1-}$. There is also some indication for this mechanism in the observed deficiency (0.4) of OH relative to the ideal structure, coupled with an excess of H_2O. The two postulated substitution mechanisms account for much of the Ca^{2+} and Fe^{2+}. However, such interpretations are beyond the limits of the precision of the available chemical data. Definition of the actual substitution mechanisms requires additional analytical data on other phases, preferably those with a higher content of calcium.

Occurrence

Petersite was found by Mr. Nicholas Facciolla in early 1981 at the traprock quarry operated by the Gallo Asphalt Company at Laurel Hill (known locally as big Snake Hill), in Secaucus, Hudson Co., New Jersey. When the significance of the mineral was known, Mr. Facciolla, together with Mr. Thomas Peters and Mr. Russell Titus of the Paterson Museum, revisited the locality and obtained additional material for study.

The geology of Laurel Hill was described by Darton *et al.* (1908), who noted that it consists of a plug of diabase cutting Triassic sediments, which originally were ferruginous sediments, now metamorphosed into a biotite–plagioclase hornfels. A review of the geology of Laurel Hill and a discussion of the diabase and included magnetite veins was given by Puffer and Peters (1974). A detailed review of the minerals of Laurel Hill has been privately published by Facciolla (1981).

Petersite occurs wholly within the hornfels located approximately 30–60 m from the northern contact with the diabase stock. The hornfels has been extensively brecciated in places and subjected to secondary mineralization. The occurrence for the type material has been "mined-out" and thus chances of finding additional samples are poor. Petersite occurs in minute cavities between brecciated hornfels fragments where approximately a dozen hand-sized samples were recovered. Petersite must be considered a rare mineral because of the limited occurrence.

Petersite occurs in several assemblages. The originally discovered material occurs on a matrix of severely altered chalcopyrite, which is coated with an amorphous dark red mineral similar to pitticite, but more likely near diadochite in composition, given the geochemistry of the occurrence. This in turn is coated with abundant malachite and chrysocolla, coated with hematite and a thin, desiccated layer of light bluish amorphous opal. The final mineralization was of malachite, in small mammilary aggregates, coated sparingly with tiny clusters of petersite crystals. Although petersite occurs in other assemblages, the best formed and largest crystals occur within this altered sulfide assemblage. Petersite encrusts both the opal and the malachite.

A second assemblage consists of white albite with or without chlorite, malachite and anatase, the latter in bright euhedral crystals. These minerals are coated with light blue opal and, lastly, petersite. Petersite may form on any of these minerals but it is usually found on the light blue opal. Other samples occur in slightly varied assemblages with cloudy albite which gives a grayish appearance to the matrix. In these samples, the opaline coating is more glassy and chalcedonic as compared with the desiccated appearance of the previously described assemblages.

Petersite appears to be a supergene mineral with copper derived from the altered chalcopyrite. The origin of the rare earth elements and phosphorus is problematical. However, allanite and apatite are known to occur at the locality and alteration of these minerals may well have provided the rare earths.

Acknowledgments

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