

## PETERSITE-(Ce), $\text{Cu}^{2+}_6\text{Ce}(\text{PO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ , A NEW MIXITE GROUP MINERAL FROM YAVAPAI COUNTY, ARIZONA, USA

SHAUNNA M. MORRISON<sup>§</sup>, KENNETH J. DOMANIK, HEXIONG YANG, AND ROBERT T. DOWNS

*Department of Geosciences, University of Arizona, 1040 E 4th Street, Tucson, Arizona 85721-0077, USA*

### ABSTRACT

A new mineral, petersite-(Ce), ideally  $\text{Cu}^{2+}_6\text{Ce}(\text{PO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$  (IMA2014-002), has been found in the Cherry Creek District of Yavapai County, Arizona, USA. It is a secondary alteration mineral associated with malachite, chlorite, a biotite phase, quartz, albite, orthoclase, hematite, chalcocopyrite, and an uncharacterized hisingerite-like mineral. Petersite-(Ce) occurs as sprays of yellowish-green, acicular crystals approximately  $20 \times 20 \times 50 \mu\text{m}$  in size. It has a white streak with vitreous luster. The mineral is brittle and has a Mohs hardness of  $\sim 3.5$ ; no cleavage or parting was observed. The calculated density is  $3.424 \text{ g/cm}^3$ . An electron microprobe analysis resulted in an empirical chemical formula of  $\text{Cu}_{6.05}(\text{Ce}_{0.18}\text{Y}_{0.16}\text{La}_{0.12}\text{Nd}_{0.09}\text{Gd}_{0.03}\text{Pr}_{0.02}\text{Dy}_{0.01}\text{Sm}_{0.01}\text{Ca}_{0.42})_{\Sigma 1.04}[(\text{PO}_4)_{2.54}(\text{SiO}_4)_{0.14}(\text{PO}_3\text{OH})_{0.32}(\text{OH})_6] \cdot 3.65\text{H}_2\text{O}$ .

Petersite-(Ce) is hexagonal, with space group  $P6_3/m$  and unit-cell parameters  $a$  13.2197(18) Å,  $c$  5.8591(9) Å, and  $V$  886.8(4) Å<sup>3</sup>,  $Z = 2$ . It is the Ce analogue of petersite-(Y) and exhibits the mixite structure type. The mixite group can be expressed by the general formula  $\text{Cu}^{2+}_6A(\text{TO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ , where nine-coordinated  $A$  is a rare earth element, Al, Ca, Pb, or Bi, and  $T$  is P or As. The structure of petersite-(Ce) is characterized by chains of edge-sharing  $\text{CuO}_5$  square-pyramids along  $c$ . These chains are connected in the  $a$ - $b$  plane by edge-sharing  $\text{CeO}_9$  polyhedra and corner-sharing  $\text{PO}_4$  tetrahedra. Hydroxyl groups occupy each corner of the  $\text{CuO}_5$  polyhedra not shared by a neighboring P or Ce atom. Each  $\text{CeO}_9$  polyhedron is surrounded by three zeolitic channels. The walls of the channels, parallel to  $c$ , are six-membered, hexagonal rings composed of  $\text{CuO}_5$  and  $\text{PO}_4$  polyhedra in a ratio of 2:1, respectively, and contain  $\text{H}_2\text{O}$  molecules. In our model of petersite-(Ce), we defined one distinct  $\text{H}_2\text{O}$  site positioned to form a ring inside the channel, although there are many statistically possible locations.

**Keywords:** petersite-(Ce),  $\text{Cu}^{2+}_6\text{Ce}(\text{PO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ , petersite-(Y), mixite, crystal structure, X-ray diffraction, Raman spectra.

### INTRODUCTION

The mixite structural group has the general formula  $\text{Cu}^{2+}_6A(\text{TO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ , where nine-coordinated  $A$  is a rare earth element (REE), Al, Ca, Pb, or Bi, and  $T$  is P or As (Table 1). Due to the small crystal size and acicular habit, only mixite (Mereiter & Preisinger 1986), zálesiite (Aruga & Nakai 1985), agardite-(Ce) (Hess 1983), and agardite-(Y) (Morrison *et al.* 2013) have reported crystal structures. Interestingly, the mixite group has a structural feature in common with zeolites: a channel large enough to take in free water molecules. These channels are of interest due to their potential industrial and environmental applications.

A new mineral, petersite-(Ce), ideally  $\text{Cu}^{2+}_6\text{Ce}(\text{PO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ , was found on a micromount

specimen from the Cherry Creek District of Yavapai County, Arizona, USA. The specimen was donated to the Mineral Museum of the University of Arizona by Dr. Arthur Roe, Professor of Chemistry and Director of the Radioisotope laboratory at the University of North Carolina. Petersite-(Ce) is named for its chemistry as the Ce-dominant analogue of petersite-(Y) (Hatert & Burke 2008). “Petersite” [now recognized by the IMA as “petersite-(Y)”] was named after brothers Thomas and Joseph Peters, curators of the Paterson Museum in Paterson, New Jersey and the American Museum of Natural History in New York, respectively (Peacor & Dunn 1982). The Peters brothers were well known for their contribution to the mineralogy of New Jersey and provided the sample of petersite-(Y) described in Peacor & Dunn (1982).

<sup>§</sup> Corresponding author e-mail address: shaunnamm@email.arizona.edu

TABLE 1. COMPARISON OF PETERSITE-(Ce) TO OTHER MEMBERS OF THE MIXITE STRUCTURAL GROUP

Mineral	Chemical Formula	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )
plumboagardite [1]	Cu <sub>6</sub> (Pb,La,Nd,Ce,Ca)(AsO <sub>4</sub> ) <sub>3</sub> (OH) <sub>6</sub> ·3H <sub>2</sub> O	13.770	5.940	975.4
agardite-(La) [2]	Cu <sup>2+</sup> <sub>6</sub> La(AsO <sub>4</sub> ) <sub>3</sub> (OH) <sub>6</sub> ·3H <sub>2</sub> O	13.700	5.880	955.8
mixite [3]	Cu <sup>2+</sup> <sub>6</sub> Bi(AsO <sub>4</sub> ) <sub>3</sub> (OH) <sub>6</sub> ·3H <sub>2</sub> O	13.633	5.913	951.7
agardite-(Ce) [4]	Cu <sup>2+</sup> <sub>6</sub> Ce(AsO <sub>4</sub> ) <sub>3</sub> (OH) <sub>6</sub> ·3H <sub>2</sub> O	13.605	5.917	948.5
zálesite [5]	Cu <sub>6</sub> Ca(AsO <sub>4</sub> ) <sub>2</sub> (AsO <sub>3</sub> OH)(OH) <sub>6</sub> ·3H <sub>2</sub> O	13.571	5.880	937.8
agardite-(Nd) [6]	Cu <sup>2+</sup> <sub>6</sub> Nd(AsO <sub>4</sub> ) <sub>3</sub> (OH) <sub>6</sub> ·3H <sub>2</sub> O	13.548	5.894	937.0
agardite-(Y) [7]	Cu <sup>2+</sup> <sub>6</sub> Y(AsO <sub>4</sub> ) <sub>3</sub> (OH) <sub>6</sub> ·3H <sub>2</sub> O	13.506	5.890	930.5
goudeyite [8]	Cu <sub>6</sub> Al(AsO <sub>4</sub> ) <sub>3</sub> (OH) <sub>6</sub> ·3H <sub>2</sub> O	13.472	5.902	927.7
calciopetersite [9]	Cu <sub>6</sub> Ca(PO <sub>4</sub> ) <sub>2</sub> (PO <sub>3</sub> OH)(OH) <sub>6</sub> ·3H <sub>2</sub> O	13.284	5.902	902.0
petersite-(Y) [10]	Cu <sub>6</sub> Y(PO <sub>4</sub> ) <sub>3</sub> (OH) <sub>6</sub> ·3H <sub>2</sub> O	13.288	5.877	898.6
petersite-(Ce) [11]	Cu <sup>2+</sup> <sub>6</sub> Ce(PO <sub>4</sub> ) <sub>3</sub> (OH) <sub>6</sub> ·3H <sub>2</sub> O	13.220	5.859	886.8

1: Walenta & Theye (2005); 2: Kunov *et al.* (2002); 3: Miletich *et al.* (1997); 4: Hess (1983); 5: Sejkora *et al.* (1999); 6: Pekov *et al.* (2011); 7: Morrison *et al.* (2013); 8: Wise (1978); 9: Sejkora *et al.* (2005); 10: Peacor & Dunn (1982); 11: This work.

The new mineral, petersite-(Ce), and its name have been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA2014-002). The holotype sample has been deposited at the Mineral Museum of the University of Arizona (Catalogue # 19801) and the RRUFF Project (deposition # R050541). This paper describes the structure and composition of petersite-(Ce) as determined by single-crystal X-ray diffraction, electron microprobe, and Raman spectroscopy.

#### SAMPLE DESCRIPTION AND EXPERIMENTAL METHODS

##### *Occurrence, physical and chemical properties, and Raman spectra*

Petersite-(Ce) occurs as a rare secondary mineral in the highly weathered Bradshaw granite of an unnamed

prospecting pit in the Cherry Creek District, Yavapai County, Arizona, USA (34° 34' N 112° 5' W). Mined for gold and silver in the early 1900's (Wilson *et al.* 1967), veins of milky quartz with a small amount of tourmaline run through this area of the shattered, oxidized Bradshaw granite (Lindgren 1926). Associated minerals include malachite, chlorite, a biotite phase, quartz, albite, orthoclase, hematite, chalcopyrite, and a hisingerite-like phase.

Petersite-(Ce) forms in radial clusters of acicular crystals (approximately 20 × 20 × 50 μm) (Fig. 1). It is yellowish green, translucent, and has a white streak and vitreous luster. It is brittle and has a Mohs hardness of ~3.5. No cleavage or parting was observed and its fracture is uneven. The calculated density is 3.42(2) g/cm<sup>3</sup> based on the empirical chemical formula. Optical properties were not measured due to the small size of the crystals.

Chemical analyses (seven points) of petersite-(Ce) were carried out with a CAMECA SX100 electron microprobe (WDS mode, 25 kV, 20 nA, and <1 μm beam diameter) (Table 2). The standards used were wollastonite for Si and Ca, chalcopyrite for Cu, YAG for Y, REE glasses (Drake & Weill 1972) for other REE, and synthetic fluorapatite for P. H<sub>2</sub>O was calculated by difference. Previous studies have accurately accounted for the H<sub>2</sub>O and OH in minerals of the mixite group (Miletich *et al.* 1997, Frost *et al.* 2005a). The electron microprobe analysis resulted in an average composition (wt.%) of SiO<sub>2</sub> 0.92(23), CaO 2.53(8), P<sub>2</sub>O<sub>5</sub> 21.67(51), CuO 51.49(62), Y<sub>2</sub>O<sub>3</sub> 1.99(13), La<sub>2</sub>O<sub>3</sub> 2.18(13), Ce<sub>2</sub>O<sub>3</sub> 3.10(9), Nd<sub>2</sub>O<sub>3</sub> 1.58(8), Pr<sub>2</sub>O<sub>3</sub> 0.36(6), Sm<sub>2</sub>O<sub>3</sub> 0.27(5), Gd<sub>2</sub>O<sub>3</sub> 0.62(2), Dy<sub>2</sub>O<sub>3</sub> 0.19(3), H<sub>2</sub>O+ 13.12 (by difference), yielding a total of 100% and an empirical chemical

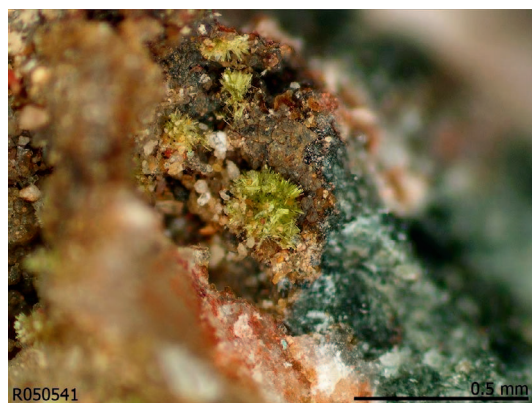


FIG. 1. Photograph of acicular petersite-(Ce) crystals.

TABLE 2. CHEMICAL COMPOSITION OF PETERSITE-(Ce)

	1	2	3	4	5	6	7	Average
wt. %								
SiO <sub>2</sub>	0.623	0.705	0.777	0.954	1.240	1.054	1.092	0.921
Ce <sub>2</sub> O <sub>3</sub>	3.007	3.077	3.006	3.044	3.169	3.255	3.122	3.097
Y <sub>2</sub> O <sub>3</sub>	2.124	2.118	2.098	2.019	1.847	1.877	1.830	1.988
La <sub>2</sub> O <sub>3</sub>	2.364	2.301	2.206	2.206	2.067	2.074	2.017	2.176
Pr <sub>2</sub> O <sub>3</sub>	0.460	0.351	0.388	0.318	0.342	0.274	0.393	0.361
Nd <sub>2</sub> O <sub>3</sub>	1.730	1.604	1.580	1.479	1.531	1.567	1.533	1.575
Sm <sub>2</sub> O <sub>3</sub>	0.283	0.235	0.189	0.317	0.241	0.332	0.279	0.268
Gd <sub>2</sub> O <sub>3</sub>	0.655	0.623	0.630	0.618	0.604	0.608	0.578	0.617
Dy <sub>2</sub> O <sub>3</sub>	0.221	0.245	0.151	0.189	0.171	0.160	0.191	0.190
CuO	52.269	52.360	51.456	51.357	51.191	51.176	50.615	51.489
CaO	2.405	2.426	2.504	2.610	2.607	2.569	2.573	2.528
P <sub>2</sub> O <sub>5</sub>	21.760	21.728	21.050	22.480	21.767	20.992	21.917	21.671
Total	87.900	87.773	86.036	87.592	86.778	85.939	86.140	86.880
H <sub>2</sub> O*	12.100	12.227	13.964	12.408	13.222	14.061	13.860	13.120

\* The amount of H<sub>2</sub>O was calculated by difference. Empirical chemical formula calculated on the basis of three *T*-site cations (P and Si) per formula unit.

formula, based on 3 *T*-site cations (P and Si), of Cu<sub>6.05</sub>(Ce<sub>0.18</sub>Y<sub>0.16</sub>La<sub>0.12</sub>Nd<sub>0.09</sub>Gd<sub>0.03</sub>Pr<sub>0.02</sub>Dy<sub>0.01</sub>Sm<sub>0.01</sub>Ca<sub>0.42</sub>)Σ1.04[(PO<sub>4</sub>)<sub>2.54</sub>(SiO<sub>4</sub>)<sub>0.14</sub>(PO<sub>3</sub>OH)<sub>0.32</sub>(OH)<sub>6</sub>]·3.65H<sub>2</sub>O. The ideal formula is Cu<sub>6</sub>Ce(PO<sub>4</sub>)<sub>3</sub>(OH)<sub>6</sub>·3H<sub>2</sub>O.

The Raman spectrum of petersite-(Ce) (Fig. 2) was collected from a randomly oriented crystal at 40% of 150 mW with a Thermo Almega microRaman system, using a 532 nm solid-state laser, confocal Olympus optics with a 10× objective, and a thermoelectrically cooled CCD detector. The laser was partially polarized with 4 cm<sup>-1</sup> resolution and a spot size of 1 μm.

#### X-ray crystallography

Powder X-ray diffraction data were calculated from the determined petersite-(Ce) structure using the XPOW program (Downs *et al.* 1993) because the limited amount of available material precluded a measurement. In Table 3, the calculated powder X-ray diffraction pattern of petersite-(Ce) is compared to the pattern of petersite-(Y) measured by Peacor & Dunn (1982). Single-crystal X-ray studies were carried out with a 4-circle Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromized

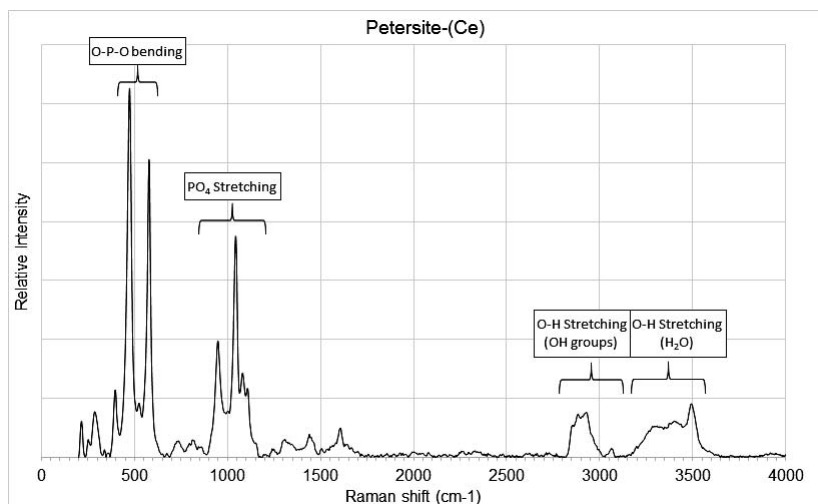


Fig. 2. The Raman spectrum of petersite-(Ce) with tentative Raman band assignments.

TABLE 3. POWDER X-RAY DIFFRACTION (Å) DATA FOR PETERSITE-(Ce) AND PETERSITE-(Y)

<i>l</i>	petersite-(Ce)	petersite-(Y)	<i>hkl</i>
	<i>d</i> <sub>calc</sub> (Å)	<i>d</i> <sub>obs</sub> (Å) [1]	
100	11.449	11.6	100
1	6.610		110
3	5.724		200
1	5.216		101
2	4.385		111
13	4.327		120
7	4.327	4.36	210
1	4.095	4.12	201
2	3.481		121
2	3.481	3.49	211
12	3.305	3.32	220
2	3.198		301
5	3.175	3.19	310
3	2.930		002
7	2.879		221
9	2.862	2.877	400
4	2.792		131
2	2.627	2.634	320
7	2.627		230
4	2.498	2.509	410
10	2.426		122
4	2.426	2.433	212
1	2.298		141
1	2.192	2.197	222
1	2.056		150
3	2.047		402
2	1.956		232
2	1.956	1.961	322
2	1.901		412
1	1.761	1.767	332
2	1.740		242
3	1.683		152
2	1.653	1.659	440
1	1.516	1.523	710
3	1.439	1.444	442
1	1.387		124

[1] Peacor & Dunn (1982)

MoK $\alpha$  radiation. All reflections were indexed on the basis of a hexagonal unit-cell (Table 4) using SAINT software (Bruker 2004). The crystal structure was solved and refined using SHELX97 (Sheldrick 2008). The positions of all atoms were refined with anisotropic displacement parameters (Table 5). Due to similar X-ray scattering power, all REE were treated as Ce. Cerium and Ca were allowed to share the *A* site and their abundances were refined assuming full occupancy. Various models were used in refining the water position, including site-splitting models. However, one distinct H<sub>2</sub>O (WAT) site forming a ring

TABLE 4. SUMMARY OF CRYSTAL DATA AND REFINEMENT RESULTS FOR PETERSITE-(Ce)

Ideal chemical formula	Cu <sup>2+</sup> <sub>6</sub> Ce(PO <sub>4</sub> ) <sub>3</sub> (OH) <sub>6</sub> ·3H <sub>2</sub> O
Crystal symmetry	Hexagonal
Space group	<i>P</i> 6 <sub>3</sub> / <i>m</i>
<i>a</i> (Å)	13.2197(18)
<i>c</i> (Å)	5.8591(9)
<i>V</i> (Å <sup>3</sup> )	886.8(4)
<i>Z</i>	2
<i>P</i> <sub>calc</sub> (g/cm <sup>3</sup> )	3.424
$\lambda$ (Å, MoK $\alpha$ )	0.71073
$\mu$ (mm <sup>-1</sup> )	8.97
2 $\theta$ range for data collection	≤65.21°
No. of reflections collected	4508
No. of independent reflections	1167
No. of reflections with <i>I</i> > 4 $\sigma$ ( <i>I</i> )	754
No. of parameters refined	56
<i>R</i> (int)	0.0745
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> factors [ <i>I</i> > 4 $\sigma$ ( <i>I</i> )]	0.0424
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> factors (all data)	0.0855
Goodness-of-fit	1.005

inside the channel was the only model that converged. The large isotropic displacement parameter for WAT is expected, as the site represents a free molecule in a large channel. Selected bond distances are given in Table 6.

## DISCUSSION

Petersite-(Ce) is isostructural with mixite-group minerals (Table 1) and is characterized by chains of edge-sharing CuO<sub>5</sub> square-pyramids along *c*. These chains are connected in the *a*-*b* plane by edge-sharing CeO<sub>9</sub> polyhedra and corner-sharing PO<sub>4</sub> tetrahedra (Fig. 3). Hydroxyl groups occupy each corner of the CuO<sub>5</sub> polyhedra not shared by a neighboring P or Ce atom. Each CeO<sub>9</sub> polyhedron is surrounded by three zeolitic channels. The walls of the channels, parallel to *c*, are constructed of six-membered, hexagonal rings composed of CuO<sub>5</sub>- and PO<sub>4</sub>-polyhedra in a ratio of 2:1, respectively, and contain H<sub>2</sub>O molecules. In our model of petersite-(Ce), we defined the free H<sub>2</sub>O molecule as one distinct site that, by symmetry, forms a ring inside the channel, although there are many statistically possible locations (Fig. 3). Miletich *et al.* (1997) demonstrated that the water in the mixite structure does not contribute to the stability of the structure by observing a very low value of activation energy for dehydration, which indicates that the H<sub>2</sub>O molecules are not bonded to any cation. Furthermore, Miletich *et al.* (1997) and Frost *et al.* (2005a) performed thermogravimetric analysis to determine

TABLE 5. ATOM COORDINATES AND DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ ) FOR PETERSITE-(Ce)

Atom	$x/a$	$y/b$	$z/c$	$U_{\text{iso}}$	$U_{11}$
Ce**	2/3	1/3	1/4	0.0092(3)	0.0097(3)
Cu	0.4120(1)	0.3149(1)	0.5033(1)	0.0112(2)	0.019(3)
P	0.4931(1)	0.1487(1)	3/4	0.0067(3)	0.0079(8)
O1	0.3904(4)	0.4042(4)	1/4	0.012(1)	0.015(2)
O2	0.4179(4)	0.2105(4)	3/4	0.0106(9)	0.017(2)
O3	0.5667(3)	0.1784(3)	0.5355(5)	0.0127(7)	0.015(2)
OH1	0.3641(4)	0.3747(4)	3/4	0.0095(9)	0.014(2)
OH2	0.4447(5)	0.2480(4)	1/4	0.015(1)	0.030(3)
WAT***	0.132(2)	0.160(3)	0.124(5)	0.2723(17)	
Ce**	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Cu	0.0097(3)	0.0082(5)	0.0048(2)	0	0
P	0.0147(3)	0.0054(3)	0.0128(3)	0.0006(3)	0.0003(2)
O1	0.0065(7)	0.0052(8)	0.0033(6)	0	0
O2	0.016(2)	0.008(2)	0.010(2)	0	0
O3	0.011(2)	0.008(2)	0.010(2)	0	0
OH1	0.012(2)	0.012(2)	0.008(1)	0.004(1)	0.001(1)
OH2	0.017(2)	0.003(2)	0.012(2)	0	0
WAT***	0.019(3)	0.004(2)	0.017(2)	0	0

H positions were not located. OH groups were determined from bond valence calculations.

\*\* The Ce site also contains Ca and other REE (Y, La, Nd, Gd, Pr, Dy); occupancy: 0.564(5)Ce and 0.436(5)Ca. \*\*\* O of a water molecule.

the nature of the channel  $\text{H}_2\text{O}$  molecules and the OH groups in mixite-group minerals. Both studies found that approximately three  $\text{H}_2\text{O}$  are driven off as the temperature reaches 373 K. Dehydroxylation occurs at 523 K, causing the mixite structure to decompose, thus indicating that the H of the OH groups, unlike  $\text{H}_2\text{O}$ , are critical to the stability of the structure. Minerals with channels large enough to accommodate water molecules are of industrial and environmental importance due to their potential for use as catalysts (Miletich *et al.* 1997, Frost *et al.* 2005a) or in the sorption of toxic chemicals (Leone *et al.* 2013).

Raman spectroscopy has been used to study the structural features of mixite-group minerals (Frost *et al.* 2005b, 2006, Morrison *et al.* 2013). Based on these

previous studies, tentative assignment of major Raman bands for petersite-(Ce) are shown in Figure 2. The Raman bands at 3499, 3411, and 3292  $\text{cm}^{-1}$  are O–H stretching modes associated with  $\text{H}_2\text{O}$ . The 3072, 2934, 2873, and 2862  $\text{cm}^{-1}$  bands are O–H stretching modes of OH groups.  $\text{PO}_4$  stretching modes are observed at 1095, 1084, 1043, and 945  $\text{cm}^{-1}$ , while O–P–O bending modes of  $\text{PO}_4$  are at 580, 528, and 472  $\text{cm}^{-1}$ . The Raman band at 393  $\text{cm}^{-1}$  is associated with  $\text{CuO}_5$  stretching. Bands  $<350 \text{ cm}^{-1}$  are attributed to  $\text{PO}_4$  rotations,  $\text{CuO}_5$  bending,  $\text{CeO}_9$  interactions, and other lattice modes.

#### ACKNOWLEDGMENTS

We are grateful to Dr. Arthur Roe, Professor of Chemistry and Director of the Radioisotope laboratory at the University of North Carolina, for providing the specimen used in this study to the Mineral Museum of the University of Arizona. Funding support of this study is from the Arizona Science Foundation, the National Science Foundation, ChevronTexaco, P.E.O. International, and NASA NNX11AP82A, Mars Science Laboratory Investigations. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Aeronautics and Space Administration.

TABLE 6. SELECTED BOND DISTANCES ( $\text{\AA}$ ) IN PETERSITE-(Ce)

Ce–O3 $\times 6$	2.459(3)	Cu–O1	2.004(3)
Ce–O5 $\times 3$	2.563(5)	Cu–O2	2.025(3)
Avg.	2.492(1)	Cu–O3	2.307(3)
P–O1	1.570(5)	Cu–O4	1.902(2)
P–O2	1.575(4)	Cu–O5	1.893(3)
P–O3 $\times 3$	1.514(3)	Avg.	2.026(1)
Avg.	1.543(2)		

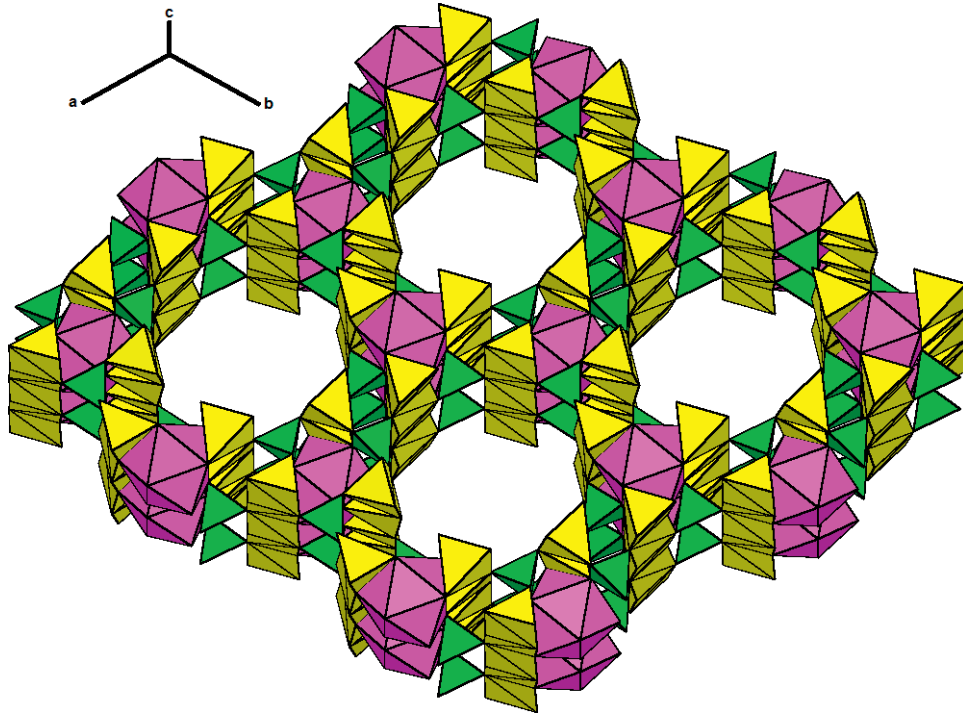


FIG. 3. The structure of petersite-(Ce). Yellow square pyramids, green tetrahedra, and pink polyhedra represent  $\text{CuO}_5$ ,  $\text{PO}_4$ , and  $\text{CeO}_9$  units, respectively. Water site omitted for clarity. Image creating using *The American Mineralogist* Crystal Structure Database (Downs & Hall-Wallace 2003).

#### REFERENCES

- ARUGA, A. & NAKAI, I. (1985) Structure of Ca-rich agardite  $(\text{Ca}_{0.40}\text{Y}_{0.31}\text{Fe}_{0.09}\text{Ce}_{0.06}\text{La}_{0.04}\text{Nd}_{0.01})\text{Cu}_{6.19}[(\text{AsO}_4)_2.42(\text{HAsO}_4)_{0.49}](\text{OH})_{6.38}\cdot 3\text{H}_2\text{O}$ . *Acta Crystallographica C* **41**, 161–163.
- BRUKER (2004) *APEX2, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, United States.
- DOWNES, R.T. & HALL-WALLACE, M. (2003) The American Mineralogist Crystal Structure Database. *American Mineralogist* **88**, 247–250.
- DOWNES, R.T., BARTELMERHS, K.L., GIBBS, G.V., & BOISEN, M.B., JR. (1993) Interactive software for calculating and displaying X-ray or neutron powder diffractometer patterns of crystalline materials. *American Mineralogist* **78**, 1104–1107.
- DRAKE, M.J. & WEILL, D.F. (1972) New rare earth element standards for electron microprobe analysis. *Chemical Geology* **10**, 179–181.
- FROST, R.L., ERICKSON, K.L., WEIER, M.L., MCKINNON, A.R., WILLIAMS, P.A., & LEVERETT, P. (2005a) Thermal decomposition of agardites (REE) - relationship between dehydroxylation temperature and electronegativity. *Thermochimica Acta* **427**, 167–170.
- FROST, R.L., WEIER, M., & MARTENS, W.N. (2005b) Raman microscopy of synthetic goudeyite  $(\text{YCu}_6(\text{AsO}_4)_2(\text{OH})_6\cdot 3\text{H}_2\text{O})$ . *Spectrochimica Acta: Part A* **63**, 685–689.
- FROST, R.L., WEIER, M., & MARTENS, W.N. (2006) Using Raman spectroscopy to identify mixite minerals. *Spectrochimica Acta: Part A* **63**, 60–65.
- HATERT, F. & BURKE, E.A.J. (2008) The IMA-CNMNC dominant-constituent rule revisited and extended. *Canadian Mineralogist* **46**, 717–728.
- HESS, H. (1983) Die Kristallstruktur des Chlorotils,  $\text{SECu}_6(\text{AsO}_4)_2(\text{OH})_6\cdot 3\text{H}_2\text{O}$  (SE = seltene Erdmetalle). *Neues Jahrbuch für Mineralogie - Monatshefte* **1983**, 385–392.
- KUNOV, A.Y., NAKOV, R.A., & STANCHEV, C.D. (2002) First agardite-(Y), -(Nd), -(La) find in Bulgaria. *Neues Jahrbuch für Mineralogie Monatshefte* **2002**, 107–116.
- LEONE, V., CANZANO, S., IOVINO, P., SALVESTRINI, S., & CAPASSO, S. (2013) Sorption of organic pollutants onto zeolitic tuff: isosteric and standard enthalpy. *Chemosphere* **91**, 415–420.

- LINDGREN, W. (1926) Ore deposits of the Jerome and Bradshaw Mountains quadrangles, Arizona. *United States Geological Survey Bulletin* **782**, 102–107.
- MEREITER, K. & PREISINGER, A. (1986) Kristallstrukturdaten der Wismutminerale atelestit, mixit und pucherit. *Oesterreichische Akademie der Wissenschaften, Mathematisch-Naturwissenschaftliche Klasse, Sitzungsberichte* **123**, 79–81.
- MILETICH, R., ZEMANN, J., & NOWAK, M. (1997) Reversible hydration in synthetic mixite,  $\text{BiCu}_6(\text{OH})_6(\text{AsO}_4)_3 \cdot n\text{H}_2\text{O}$  ( $n \leq 3$ ): Hydration kinetics and crystal chemistry. *Physics and Chemistry of Minerals* **24**, 411–422.
- MORRISON, S.M., DOMANIK, K.J., ORIGLIERI, M.J., & DOWNS, R.T. (2013) Agardite-(Y),  $\text{Cu}^{2+}_6\text{Y}(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ . *Acta Crystallographica* **E69**, i61–i62.
- PEACOR, D.R. & DUNN, P.J. (1982) Petersite, a REE and phosphate analog of mixite. *American Mineralogist* **67**, 1039–1042.
- PEKOV, I.V., CHUKANOV, N.V., ZADOV, A.E., VOUDOURIS, P., MAGGANAS, A., & KATERINOPOULOS, A. (2011) Agardite-(Nd),  $\text{NdCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ , from the Hilarion Mine, Lavrion, Greece: mineral description and chemical relations with other members of the agardite–zálesiite solid-solution system. *Journal of Geosciences* **57**, 249–255.
- SEJKORA, J., RIDKOŠIL, T., & ŠREIN, V. (1999) Zálesiite, a new mineral of the mixite group, from Zálesi, Rychlebské hory Mts., Czech Republic. *Neues Jahrbuch für Mineralogie Abhandlungen* **175**, 105–124.
- SEJKORA, J., NOVOTNÝ, P., NOVÁK, M., ŠREIN, V., & BERLEPSCH, P. (2005) Calciopetersite from Domašov nad Bystricí, Northern Moravia, Czech Republic, a new mineral species of the mixite group. *Canadian Mineralogist* **43**, 1393–1400.
- SHELDRIK, G.M. (2008) A short history of *SHELX*. *Acta Crystallographica* **A64**, 112–122.
- WALENTA, K. & THEYE, T. (2005) Plumboagardite, a new mineral of the mixite group from an occurrence in the Southern Black Forest. *Neues Jahrbuch für Mineralogie Abhandlungen* **181**, 219–224.
- WILSON, E.D., CUNNINGHAM, J.B., & BUTLER, G.M. (1967) Arizona lode gold mines and gold mining. *Arizona Bureau of Geology and Mineral Technology Geological Survey Branch Bulletin* **137**, 28–29.
- WISE, W.S. (1978) Parnauite and goudeyite, two new copper arsenate minerals from the Majuba Hill Mine, Pershing County, Nevada. *American Mineralogist* **63**, 704–708.

Received April 21, 2015. Revised manuscript accepted May 5, 2016.