Petersite-(La), a new mixite-group mineral from Ohgurusu, Kiwa, Kumano City, Mie Prefecture, Japan

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Petersite-(La) is a new mineral of the petersite series in the mixite group with an ideal formula of Cu₅La (PO₄)₃(OH)₃H₂O from Ohgurusu, Kiwa-cho, Kumano City, Mie Prefecture, Japan. The mixite-group minerals occur in small cavities coated by chrysocolla developed along quartz veins. Four members from different cavities have been identified: petersite-(La), petersite-(Ce), petersite-(Y), and agardite-(La). Petersite-(La) occurs as a radial aggregate formed by acicular to hexagonal columnar crystals of yellowish green color. Crystals are elongated along [001] and the prismatic face is probably formed by {001} and {110} or {110}. It is non-fluorescent in UV light. Crystals are brittle, cleavage and parting are non-existent, and fracture is uneven. These characteristics are common in other mixite-group minerals. The calculated density of petersite-(La) is 3.33 g/cm³, based on the empirical formula and powder XRD data. It is optically uniaxial positive with \( \omega = 1.680(3) \) and \( \epsilon = 1.767(3) \) (white light), and pleochroism varies from light green to yellowish green. Based on the WDS analysis, the empirical formula of petersite-(La) calculated on the basis of \( P + As + Si = 3 \) is \( (Cu_{0.692}Fe_{0.010})_{2.702}La_{0.148}Ce_{0.122}Nd_{0.117}Y_{0.086}Sm_{0.022}P_{0.498}O_{4.372}H_3O_7.680 \cdot 3H_2O \).

Petersite-(La) is hexagonal (P63/m) with \( a = 13.367(2) \) Å, \( c = 5.872(2) \) Å, and \( V' = 906.7(4) \) Å³ (Z = 2). The eight strongest lines of petersite-(La) in the powder XRD pattern \( [d in \{hkl\}(hkil)] \) are 11.578(100) (100), 3.377(28) (210 + 120), 3.509(18) (211 + 121), 3.211(10) (310 + 130), 2.898(14) (221, 400), 2.656(10) (320 + 230), 2.526(11) (410 + 140), and 2.438(25) (212 + 122). Petersite-(La) is the third defined member in the petersite series and corresponds to the La-dominant analogue of petersite-(Y) and petersite-(Ce).

**Keywords:** Petersite-(La), Petersite series, Mixite group, New mineral, Mie Prefecture

**INTRODUCTION**

The mixite-group minerals have a general formula \( Cu^2+[(TO_6,TO_3)OH]_3(OH)_3H_2O \) in which \( A = REE^{3+} \) (lanthanoids + Y), \( Bi^{3+}, Al^{3+}, Ca^{2+}, \) or \( Pb^{2+} \), and \( T = As^{5+} \) or \( P^{5+} \), and the root name is classified on the basis of the occupancy of the \( A \) and \( T \) sites. Mixite \( (A = Bi, T = As) \) was first found in Jáchymov, Czech Republic in 1880 AD (Schauf, 1880), and eleven species have been found to be members of the group so far. Among them, agardite \( (T = As) \) and petersite \( (T = P) \) are series based on \( A = REE \). The mineral petersite was first found in Laurel Hill, USA and named after Thomas and Joseph Peters, curators of minerals at the Paterson Museum, New Jersey and the American Museum of Natural History, New York, respectively (Peacock and Dunn, 1982). Since this petersite was mainly composed of \( Y \), it was later renamed petersite-(Y) according to the Levinson rule (Levinson, 1966; Bayliss and Levinson, 1988; Nickell and Grice, 1998). Recently, the Ce-dominant analogue of petersite-(Y) was found in the Cherry Creek district, Arizona, USA and described as a new mineral, petersite-(Ce) (Morrison et al., 2016). Before this work, the only minerals in the petersite series were petersite-(Y) and petersite-(Ce).

The crystal structure of petersite series was refined only petersite-(Ce), which is isomorphous with agardite series (Hess, 1983; Aruga and Nakai, 1985; Morrison et al.,...
Figure 1. The structural model for petersite-(REE) (a) and an expanded view (b) based on the structure of Hess (1983) drawn with VESTA 3 (Momma and Izumi, 2011). Color version is available online from https://doi.org/10.2465/jmps.191211b.

The mixite-group minerals widely occur in the oxidized zone of ore deposits, while the occurrence of the phosphates such as the petersite series is generally very rare compared to arsenates. In Japan, petersite-(Y) is the most abundant mixite-group mineral and is found in the oxidized zones of copper deposits from several localities (e.g., Ohori and Kobayashi, 1996; Miyawaki et al., 2000). As a phosphate, only petersite-(Y) is known to occur, from the Haiyama quarry, Shiga Prefecture (Okamoto et al., 1988). To date, no mixite-group minerals have been found on the Kii Peninsula, where copper deposits are widely developed, while one of the authors (S.I.) first collected mixite-group minerals from Ohgurusu, Kiwa-cho, Kumano City, Mie Prefecture. As a result of mineralogical investigation, we succeeded in identifying a new mineral, petersite-(La), as the La-dominant analogue of petersite-(Y) and petersite-(Ce). Both the mineral and its name have been approved by the International Mineralogical Association, Commission on New Minerals, Nomenclature and Classification (no. 2017-089). A typical specimen was deposited in the collections of the National Museum of Nature and Science, Japan, specimen number NSM-M45621. Here we describe a new mineral, petersite-(La), and its related mixite-group minerals.

OCCURRENCE AND APPEARANCE

The Miocene sedimentary complex, known as the Kumano Group, and the Middle Miocene igneous complex, called the Kumano acidic rocks, are widely distributed in the southeast part of the Kii Peninsula (e.g., Tanai and Mizuno, 1954; Aramaki and Hada, 1965). The Kumano Group consists mainly of mudstone and sandstone, and the hydrothermal-vein type copper deposits formed by the Kii copper mineralization are widely developed along the contact area associated with the Kumano acidic rocks (e.g., Saeki and Koto, 1972). These large-scale ore deposits were vigorously mined in the Kishu mine and Myoho mine, while small-scale mineralization zones also occur

2013, 2016). Figure 1 shows a representative structural model for petersite-(REE). The structure is based on chains of edge-shared CuO₅ pyramids along the c-axis. These chains are connected with REEO₉ polyhedra and PO₄ tetrahedra in the ab plane. The polyhedra are arranged in a hexagonal array to form the walls of channels along c-axis that are large enough to accommodate free water molecules. The hydroxyls are accompanied by O4 and O5 sites. O4 is shared by the CuO₅ pyramids and the REEO₉ polyhedron, and O5 is shared by the CuO₅ pyramids. An extra hydroxyl in association with the REE³⁺–Ca²⁺H⁺ substitution is thought to occur around the O3 site, according to the results of structural refinement of Ca-rich agardite-(Y) (Aruga and Nakai, 1985), which is located at the tip of the CuO₅ pyramid and shared by the REEO₉ polyhedron and the PO₄ tetrahedron. The position of hydroxyl associated with the P(As)⁵⁺–Si⁴⁺H⁺ substitution is still unclear.

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widely in the Kumano Group. We conducted a geological survey in the Kumano Group, and then the first sample was obtained as a boulder from the confluence of the Detani River and its tributaries, Ohgurusu, Kiwa, Kumano City, Mie Prefecture (33°52′57″N 135°53′46″E). The boulder was composed of highly weathered sandstones, and chalcopyrite with supergene minerals were also found inside it. During a subsequent geological survey, one of the authors (S.I.) found an outcrop of sandstone with a quartz vein containing chalcopyrite and supergene minerals upstream of the tributary. Although the minerals reported in this study were obtained from boulders, those probably originated their outcrop.

Sandstones along quartz veins have many cavities and cracks by quartz crystals within which supergene minerals develop. The cavities vary in size and shape, ranging from less than 1 mm to a maximum of about 1 cm in spherical to irregular shapes. The mixite–group minerals also occur in cavities coated by chrysocolla, and the chemical compositions are different for each cavity. We named four representative cavities according to the compositional features of the mixite–group minerals. For example, petersite–(La), petersite–(Ce), petersite–(Y), and agardite–(La) were dominant in #LaP, #CeP, #YP, and #LaA cavities, respectively. These all occurred as radial aggregates formed by acicular to hexagonal columnar crystals of light green to yellowish green color (Fig. 2). In the #LaP and #CeP cavities, the mixite–group minerals coexisted with spherical pseudomalachite and radial malachite. Brochantite and pyromorphite also occur in cavities, although they did not coexist with the mixite–group minerals. The mixite–group minerals such as petersite–(La) are probably the rare products in an oxidizing and hydrous environment involving the leaching of copper at a low temperature during weathering. The composition of the solution in which each mineral precipitate and the stage of its formation may be different.

The physical and optical properties as petersite–(La) were obtained using the crystals from the #LaP cavity. Petersite–(La) occurs as yellowish–green acicular to hexagonal columnar crystals, up to 200 µm long and 5 µm in diameter. The mineral forms commonly as a radial aggregate with silky luster. Crystals are elongated along [001] and the prismatic face is probably formed by {001} and {100} or {110} (Fig. 3). It is non–fluorescent in UV light. The Mohs hardness is thought to be ~3 by analogy with other mixite–group minerals. Crystals are brittle, cleavage and parting are non–observed, and fracture is uneven. The calculated density is 3.33 g/cm³ based on the empirical formula and powder X-ray diffraction (pXRD) data. The refractive indices were measured using a diiodomethane solution in which a small amount of sulfur was dissolved. It is optically uniaxial positive with \( \alpha = 1.680(3) \) and \( \epsilon = 1.767(3) \) (white light), and pleochroism varies from light green to yellowish green. Crystals from the #LaP cavity exhibited some compositional variations (Table 1), but errors in optical parameters were small. The compatibility \( \chi(Kp/Kc) = -0.007 \) (superior) using the oxide \( k \) values for CuO (Mandarino, 1981).

**RAMAN SPECTROSCOPY**

Raman spectroscopic analysis was performed with a HORIBA HR320 spectrometer using a 514.5 nm argon laser. Measurement was performed with 500, 900, 1500, 3000, and 3500 cm⁻¹ as the center wavelength. The sample was collected from the #LaP cavity as a radial aggregate. It was mounted on a glass slide by epoxy and then polished (Fig. 3b). The sample was also analyzed by EDS before Raman spectroscopy. Figure 4 shows the Raman spectra of petersite–(La). As tentative assignments based on Fröst et al. (2006a, 2006b) and Morrison et al. (2016), the peaks in the region 2800 to 3700 cm⁻¹ are attributed to O–H stretching vibrations associated with H₂O and OH groups. Weak peaks for H–O–H bending vibrations are found in the range 1400 to 1700 cm⁻¹. The peaks at 900 to 1200 cm⁻¹ and 450 to 650 cm⁻¹ are PO₄ stretching and bending vibrations, respectively. Other peaks could not be assigned in this study, but Morrison et al. (2016) assumed that the Raman band below 400 cm⁻¹ are attributed to CuO₂ stretching, PO₄ rotations, CuO₃ bending, CeO₃ interaction, and other lattice modes in the case of petersite–(Ce).

**CHEMICAL COMPOSITION**

Chemical analyses were performed for the mixite–group minerals from four representative cavities. Analyses for the new mineral petersite–(La) were carried out using a JEOL JXA–8105 electron microprobe (WDS mode, 15 kV, 5 nA, 1 µm beam diameter) at Kyoto University, and the ZAF method was used for data correction. The chemical analyses for petersite–(La) and the mixite–group minerals were also carried out using a JEOL IT–100 scanning electron microprobe (EDS mode, 15 kV, 0.8 nA, 1 µm beam diameter) at the Institute for Solid State Physics, the University of Tokyo, and the ZAF method was used for data correction. Detectable REE by WDS were Y, La, Ce, Nd, and Sm, while Sm was undetectable by EDS. The standards for WDS were the REEP₅O₁₄ (REE and P), quartz (Si), InAs (As), diopside (Ca), hematite (Fe), and cuprite (Cu). The standards for EDS were the REEP₅O₁₄ (REE excluding Y and P), yttrium metal (Y), quartz (Si), InAs (As), diopside (Ca), hematite (Fe), cu-
The empirical formula of the mixite-group mineral has been calculated on the basis of $O = 12$ and $OH = 6$, $\Sigma$cation $= 10$, or $P + As + Si = 3$ (e.g., Olmi et al., 1991; Miyawaki et al., 2000; Walenta and Theye, 2005; Pekov et al., 2011; Morrison et al., 2016). The formula based on $O = 12$ and $OH = 6$ is, on the other hand, unstable for Ca- and Si-bearing systems which involve hydrogen. The calculations based on $\Sigma$cation $= 10$ often lead to excess especially in the $T$ site (e.g., Olmi et al., 1991; Miyawaki et al., 2000). This is presumably because vacancy may exist at the Cu and $A$ sites. Thus, we adapt the basis of $P + As + Si = 3$ for calculation of the empirical formula. $H_2O$ wt% was calculated from the $P(As)^{5+}$–$Si^{4+}$H$^+$ and $REE^{3+}$–Ca$^{2+}$H$^+$ substitutions based on the stoichiometry of the mixite-group mineral.

**Petersite-(La)**

WDS and EDS analytical data for crystals collected from the #LaP cavity are given in Table 1 and Table 2, respectively. Although compositional zoning in an aggregate could not be visually recognized from the BSE image as shown in Figure 3b, the compositions are distributed in a certain range. The
compositional variation with its average is plotted in Figure 5a. Data were plotted in the P–As–Si and REE–Ca–Pb ternary systems, respectively. Although the REE content is somewhat intermediate in the La–Ce–Nd ternary system, most and mean values were in the La-dominated area. Thus, the mineral can be identified as petersite–(La). Based on the WDS analysis, the empirical formula of petersite–(La) calculated on the basis of P + As + Si = 3 is (Cu5.692Fe0.010)Σ5.702[(La0.148Ce0.122Nd0.117Y0.086Sm0.022)Σ0.495Ca0.372Σ0.866(P1.890As0.799Si0.311)Σ3O10.320(OH)7.680·3H2O. The empirical formula based on the EDS analysis is (Cu5.678Fe0.011)Σ5.689[(La0.153Nd0.125Ce0.119Y0.114)Σ0.511Sm0.022]Σ0.865(P1.786As0.884Si0.330)Σ3O10.290(OH)7.710·3H2O. The simplified formula is Cu4La3(PO4)3(OH)6·3H2O, which requires P2O5 22.15, La2O3 16.95, CuO 49.65, H2O 11.25, total 100 wt%.

### Table 1. Mean chemical composition data (n = 5) for petersite–(La) from the #LaP cavity by WDS analysis

| Element | wt% Mean (Min.-Max.) | wt% Ideal |
|---------|----------------------|-----------|
| CuO     | 50.35 (49.13-51.55)  | 49.65     |
| FeO     | 0.08 (0.01-0.13)     | FeO       |
| CaO     | 2.32 (2.22-2.44)     | CaO       |
| Y2O3    | 1.08 (0.63-1.58)     | Y2O3      |
| La2O3   | 2.68 (2.53-3.06)     | La2O3 16.95|
| Ce2O3   | 2.22 (1.87-2.54)     | Ce2O3     |
| Nd2O3   | 2.18 (1.77-2.42)     | Nd2O3     |
| Sm2O3   | 0.42 (0-1.04)        | Sm2O3     |
| P2O5    | 14.92 (14.65-15.22)  | P2O5 22.15|
| As2O5   | 10.21 (9.74-11.06)   | As2O5     |
| SiO2    | 2.08 (1.94-2.51)     | SiO2      |
| H2O     | 13.70                | H2O       |
| Total   | 102.24               | Total     |

*Calc. apfu

| Element | apfu |
|---------|------|
| Cu      | 5.692 |
| Fe      | 0.010 |
| Σ       | 5.702 |
| Ca      | 0.372 |
| Y       | 0.086 |
| La      | 0.148 |
| Ce      | 0.122 |
| Nd      | 0.117 |
| Sm      | 0.022 |
| Σ       | 0.866 |
| P       | 1.890 |
| As      | 0.799 |
| Si      | 0.311 |
| Σ       | 3.03  |
| OH      | 7.680 |
| O       | 10.320|
| H2O**   | 3     |

** Fixed parameter.

### Figure 4. Raman spectra of petersite–(La).

Other mixite-group minerals

EDS analytical data for mixite-group minerals collected from other cavities (#CeP, #YP, and #LaA) are given in Ta-
The chemical variation is also shown in Figures 5b–5d. The chemical analyses indicated that the sorts of A and T cations in the mixite-group minerals differed from one cavity to another. The empirical formula from the #CeP cavity is $(\text{Cu}_{5.388}\text{Fe}_{0.012})\Sigma_{5.400}[(\text{Ce}_{0.157}\text{La}_{0.132}\text{Nd}_{0.122}\text{Y}_{0.104})\Sigma_{0.516}\text{Ca}_{0.312}\text{Pb}_{0.016}\Sigma_{0.844}](\text{P}_{1.754}\text{As}_{0.849}\text{Si}_{0.398})\Sigma_{3}\text{O}_{9.606}(\text{OH})_{8.394} \cdot 3\text{H}_{2}\text{O}$, which corresponds to petersite–(Ce). The empirical formula from the #YP cavity is $(\text{Cu}_{5.682}\text{Fe}_{0.010})\Sigma_{5.692}[(\text{Y}_{0.522}\text{La}_{0.074}\text{Nd}_{0.044}\text{Ce}_{0.007})\Sigma_{0.648}\text{Ca}_{0.198}\text{Pb}_{0.056}\Sigma_{0.901}](\text{P}_{1.957}\text{As}_{0.843}\text{Si}_{0.200})\Sigma_{3}\text{O}_{10.633}(\text{OH})_{7.367} \cdot 3\text{H}_{2}\text{O}$, which corresponds to petersite–(Y). The empirical formula from the #LaA cavity is $(\text{Cu}_{5.486}\text{Fe}_{0.012})\Sigma_{5.498}[(\text{La}_{0.186}\text{Nd}_{0.120}\text{Ce}_{0.080}\text{Y}_{0.011})\Sigma_{0.504}\text{Ca}_{0.357}\text{Pb}_{0.011}\Sigma_{0.871}](\text{As}_{1.272}\text{P}_{1.235}\text{Si}_{0.494})\Sigma_{3}\text{O}_{7.750}(\text{OH})_{8.250} \cdot 3\text{H}_{2}\text{O}$, which corresponds to agardite–(La).

**Table 2.** Mean chemical composition data for the mixite-group minerals from four cavities (#LaP, #CeP, #YP, and #LaA) by EDS analyses

| Cation | #LaP (n=58) | #CeP (n=33) | #YP (n=20) | #LaA (n=15) |
|--------|-------------|-------------|------------|-------------|
| CuO    | 48.74 (46.11-53.50) | 46.95 (43.84-49.24) | 48.46 (44.26-51.73) | 47.43 (45.86-48.70) |
| FeO    | 0.09 (0-0.35) | 0.10 (0-0.36) | 0.08 (0-0.31) | 0.10 (0-0.38) |
| CaO    | 2.12 (1.75-2.49) | 1.92 (1.43-2.25) | 1.19 (0.90-1.52) | 2.17 (1.78-2.59) |
| PbO    | 0.08 (0-0.49) | 0.38 (0.04-0.73) | 1.34 (0.84-1.78) | 0.26 (0-0.62) |
| $Y_2O_3$ | 1.39 (0.91-2.04) | 1.28 (0.72-1.98) | 6.32 (5.70-6.91) | 1.45 (0.45-2.13) |
| LaO    | 2.70 (1.74-3.60) | 2.36 (1.77-3.40) | 1.30 (0.58-1.80) | 3.30 (2.82-4.12) |
| CeO    | 2.11 (0.82-3.31) | 2.83 (1.88-3.81) | 0.13 (0-0.76) | 1.43 (0.96-1.95) |
| NdO    | 2.27 (1.40-2.78) | 2.26 (1.18-3.77) | 0.79 (0.57-1.57) | 2.19 (1.28-3.05) |
| P$_2$O$_5$ | 13.68 (10.89-15.62) | 13.63 (11.43-16.79) | 14.89 (13.02-16.70) | 9.52 (8.62-10.08) |
| As$_2$O$_3$ | 10.96 (8.85-14.42) | 10.68 (8.22-13.71) | 10.39 (9.20-12.04) | 15.88 (15.06-16.63) |
| SiO$_2$ | 2.14 (1.61-3.27) | 2.62 (2.10-3.35) | 1.29 (0.89-1.79) | 5.22 (2.79-3.58) |

\[ \text{H}_2\text{O}^{*} \]

| Total | 99.61 | 99.21 | 99.08 | 100.90 |

\[ \text{Calc.} \]

| Cation | apfu |
|--------|------|
| Cu     | 5.678 |
| Fe     | 0.011 |
| $\Sigma$ | 5.689 |
| Ca     | 0.350 |
| Pb     | 0.003 |
| Y      | 0.114 |
| La     | 0.153 |
| Ce     | 0.119 |
| Nd     | 0.125 |
| $\Sigma$ | 0.865 |
| P      | 1.786 |
| As     | 0.884 |
| Si     | 0.330 |
| $\Sigma^{**}$ | 3 |
| OH     | 7.710 |
| O      | 10.290 |

\[ \text{H}_2\text{O}^{**} \]

\[ \text{** Fixed parameter.} \]

**CRYSTALLOGRAPHY**

**X-ray diffraction**

Single-crystal X-ray diffraction investigation was attempted, but diffraction spots for determining the unit cell parameters could not be detected owing to the small grain size. Therefore, the crystallography was studied by powder XRD (pXRD) method. Subsequent to the above chemical analysis, samples for pXRD were separated from thin sections. The obtained samples were placed on Kapton tape and pXRD data were collected using a synchrotron X-ray source on the NE1 beam line at the Photon Factory Advanced Ring (PF-AR) institute, KEK,
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Japan. This source provided a 30 µm diameter collimated beam of monochromatized X-ray (λ = 0.4178 Å). The pXRD spectra were collected by the Debye–Scherrer method, recorded via an imaging plate detector, and then converted to conventional one-dimensional profiles using the IPAnalyzer and PDindexer software packages by Seto et al. (2010).

The pXRD patterns for petersite-(La) are shown in Figure 6, and the resulting data are also summarized in Table 3. The eight strongest lines of petersite-(La) in the powder XRD pattern \( d \) in Å \((hkl)\) are 11.578(100), 4.377(28)(210 + 120), 3.509(18)(211 + 121), 3.211(10)(310 + 130), 2.898(14)(221, 400), 2.656(10)(320 + 230), 2.526(11)(410 + 140), and 2.438(25)(212 + 122). Based on powder data, petersite-(La) can be indexed to the hexagonal \( P6_3/m \) space group, and the unit cell parameters refined by least squares method are \( a = 13.367(2) \) Å, \( c = 5.872(2) \) Å, and \( V = 908.7(4) \) Å³ (\( Z = 2 \)). The \( c/a \) ratio calculated from the obtained unit cell parameters is 0.439.

Other mixite-group minerals were also investigated by pXRD with the same procedure. The XRD patterns and the data are shown in Figure 6 and Table 3, respectively. The \( hkl \) indices of the strongest lines were common to all the mixite-group minerals (Fig. 6). The resulting unit cell parameters were slightly different depending on the chemical composition, while the \( c/a \) ratio (≈ 0.44) was common to all the minerals.

**RELATION TO OTHER SPECIES**

The mixite-group minerals are summarized in Table 4. All members occur in radial aggregates of prismatic to acicular crystals with yellowish to bluish green in color and are formed as a secondary mineral in the oxidized zone in the copper-based deposit. They are optically uniaxial and show the range of \( \omega = 1.67–1.73 \) and \( \epsilon = 1.75–1.81 \). The minerals are thought to have identical structures with the \( P6_3/m \) space group. Petersite-(La) becomes the twelfth new member of the mixite group. Among the mixite-group minerals, the petersite series \([A = \text{REE} \text{ and } T = \text{P} \text{ in Cu}_2^2A(T_2O_4,T_3O_3OH)_3(OH)_6\cdot3H_2O]\) are rather rare, and only petersite-(Y) and petersite-(Ce) have been known so far. Petersite-(La) is the third in the petersite series and corresponds to the La-dominant analogue of petersite-(Y) and petersite-(Ce). Considering compositional variation for #LaP and #CeP, several analytical points fall into the Nd-dominant area (Figs. 5a and 5b). It is thought that Nd-dominant petersite, as in the agardite series, may also exist in nature. Furthermore, the compositions of our petersite-(La) and -(Ce) and other previous petersite series (e.g., Sejkora et al., 2005) lie on the intermediate regions between REE-dominant and Ca-domin-
inant endmembers. So far, no minerals with compositions between REE–dominant and Ca–dominant (calciopetersite) endmembers have been reported, but they might be naturally formed in a wide range of environments.

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SUPPLEMENTARY MATERIALS

Color versions of Figures 1, 2, and 5 are available online from https://doi.org/10.2465/jmps.191211b.

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| Table 4. Comparison of the mixite group minerals |
|-----------------------------------------------|
| Ideal Formula | a (Å) | c (Å) | c/a | ω | ε | Reference |
|----------------|-------|------|-----|---|---|-----------|
| Petersite-(Y)  | Cu6Y(PO4)3(OH)6·3H2O | 13,329 | 5.862 | 0.440 | - | - | 1 |
| Petersite-(La)  | Cu6La(PO4)3(OH)6·3H2O | 13,288 | 5.877 | 0.442 | 1.666 | 1.747 | 2 |
| Petersite-(Ce)  | Cu6Ce(PO4)3(OH)6·3H2O | 13,367 | 5.872 | 0.439 | 1.680 | 1.767 | 1 |
| Calciopetersite | Cu6Ca(PO4)3(PO3OH)3(OH)6·3H2O | 13,220 | 5.859 | 0.443 | - | - | 3 |
| Agardite-(Y)  | Cu6Y(AsO4)3(OH)6·3H2O | 13,506 | 5.890 | 0.436 | 1.701 | 1.782 | 5, 6 |
| Agardite-(La)  | Cu6La(AsO4)3(OH)6·3H2O | 13,424 | 5.877 | 0.438 | - | - | 1 |
| Agardite-(Ce)  | Cu6Ce(AsO4)3(OH)6·3H2O | 13,586 | 5.931 | 0.437 | 1.715 | 1.794 | 7, 8 |
| Agardite-(Nd)  | Cu6Nd(AsO4)3(OH)6·3H2O | 13,605 | 5.917 | 0.435 | 1.725 | 1.810 | 9, 10 |
| Zálesíte      | Cu6Ca(AsO4)3(AsO4)3(OH)6·3H2O | 13,548 | 5.894 | 0.435 | 1.709 | 1.775 | 11 |
| Plumboagardite | Cu6Pb(AsO4)3(AsO4)3(OH)6·3H2O | 13,770 | 5.940 | 0.431 | 1.726 | 1.805 | 13 |
| Goudeyite     | Cu6Al(AsO4)3(OH)6·3H2O | 13,472 | 5.902 | 0.438 | 1.704 | 1.765 | 14 |
| Mixite        | Cu6Bi(AsO4)3(AsO4)3(OH)6·3H2O | 13,633 | 5.913 | 0.434 | 1.750 | >1.8 | 15 |

* Description as Pb analogue of zálesíte because of the unbalanced charge of CNMNC approved formula.

Reference: 1: This study; 2: Peacor and Dunn (1982); 3: Morrison et al. (2016); 4: Sejkora et al. (2005); 5: Morrison et al. (2013); 6: Dietrich et al. (1969); 7: Kunov et al. (2002); 8: Olmi et al. (1991); 9: Hess (1983); 10: Walenta and Theye (2004); 11: Pekov et al. (2011); 12: Sejkora et al. (1999); 13: Walenta and Theye (2005); 14: Wise (1978); 15: Miletich et al. (1997).
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