

## Crystal Structure of Almeidaite, a New Mineral of the Crichtonite Group

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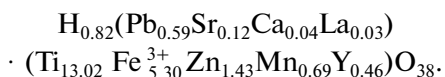
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The crichtonite group combines minerals with the general formula  $X^{II}A^{VI}B^{IV}T_2^{VI}C_{18}O_{38}$ , where  $A = \text{Ba, K, Pb, Sr, La, Ce, Na, Ca}$ ;  $B = \text{Mn, Y, U}^{4+}, \text{Fe, Zr, Sc}$ ;  $T = \text{Fe, Mn, Mg, Zn}$ ;  $C = \text{Ti}^{4+}, \text{Fe}^{3+}, \text{Cr, Nb, V}^{5+}, \text{Mn}^{3+}$ , or Al (the Roman numerals indicate the coordination numbers) and comprises 13 approved mineral species and an inadequately studied mineral with high uranium content, which crystallize in the rhombohedral systems, space group  $R\bar{3}$ .

Almeidaite<sup>1</sup> is a new mineral of the crichtonite group found in the dumps of an old mine near Novo Horizonte, Bahia, Brazil, in association with quartz, rutile, anatase, hematite, and xenotime-(Y). This mineral differs from other members of the crichtonite group by simultaneously high contents of zinc and lead.

The empirical formula of the mineral was determined from local X-ray spectral analysis data and gas chromatography of the annealing products:



According to the IR spectrum, the mineral contains OH groups, which are detected by a weak peak at  $3340\text{ cm}^{-1}$ . According to Mössbauer spectroscopy, almost all iron is in the trivalent state.

<sup>1</sup> The mineral and its name were approved on June 1, 2013, by the Commission on New Minerals, Nomenclature, and Classification of the International Mineralogical Association IMA No. 2013-020.

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The X-ray diffraction experiment was performed in the full sphere of the reciprocal space on a Xcalibur Oxford Diffraction diffractometer with a CCD detector. Some of the reflections are blurred. In view of the trace amounts of thorium, this can be attributed to the metamict character of the crystal due to its partial radiation damage. The crystal data and X-ray experiment details are presented in Table 1.

**Table 1.** Crystal data and X-ray experiment details for almeidaite

Chemical formula	$(\text{Pb}_{0.6}\text{Sr}_{0.1})(\text{Fe}^{3+}, \text{Fe}^{2+})_{4.9}\text{Ti}_{13.4} \cdot \text{Zn}_{1.5}(\text{Mn}^{2+}, \text{Mn}^{3+})_{0.8}\text{Y}_{0.4}(\text{O}, \text{OH})_{38}$
$a$ , Å	10.4359(2)
$c$ , Å	21.0471(4)
$V$ , Å <sup>3</sup>	1985.10(7)
$M$	1774.1
Symmetry, space group, $Z$	Trigonal, $R\bar{3}$ , 3
$\mu$ , mm <sup>-1</sup>	13.1
$D_x$ , g/cm <sup>3</sup>	4.62
Crystal size, mm	0.2 × 0.25 × 0.45
Diffractometer	Xcalibur Oxford Diffraction (CCD-detector)
Radiation	$\text{MoK}\alpha$
Scan mode	$\omega$
$\theta_{\text{max}}$ , deg	56.16
Ranges of $h, k, l$	$-21 < h < 23, -19 < k < 22, -39 < l < 36$
Number of reflections: measured/independent with $ F  > 3\sigma(F)$ , $R_{\text{int}}$	5880/2110, 9.7
Method of refinement	Least-squares method on $F^2$
Weighting scheme	$w = 1/(\sigma^2(F) + 0.0009F^2)$
$R/wR$	3.9/4.19
GOF	0.64
Calculation software	Jana 2006 [1]

**Table 2.** Coordinates, equivalent atom displacement parameters ( $U_{eq}$ ) and site multiplicity ( $Q$ ) and occupancy ( $q$ )

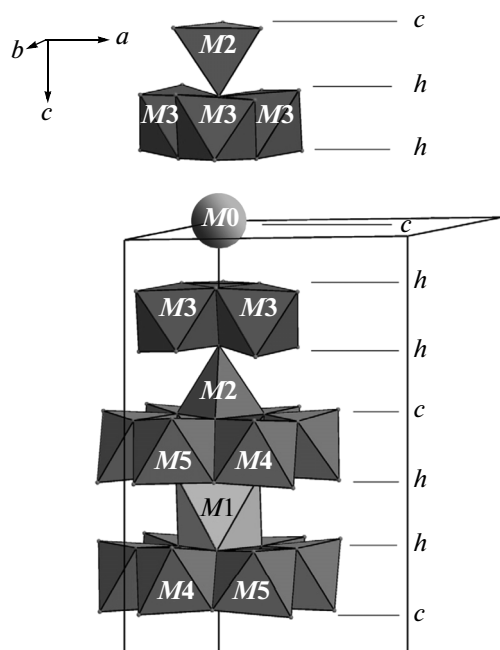
Site	$x/a$	$y/b$	$z/c$	$U_{eq}, \text{\AA}^2$	$Q$	$q$
<i>M0</i>	0	0	0	0.0495(3)	3	0.7
<i>M1</i>	-0.6667	-0.3333	0.1667	0.0100(1)	3	1.0
<i>M2</i>	0	0	0.3093(1)	0.0098(1)	6	0.75
<i>M3</i>	-0.1457(1)	0.0379(1)	0.1655(1)	0.0106(1)	18	1.0
<i>M4</i>	-0.4229(1)	-0.0137(1)	0.0656(1)	0.0098(1)	18	1.0
<i>M5</i>	0.0882(1)	0.3379(1)	0.0589(1)	0.0109(1)	18	1.0
<i>M6</i> *	0	0	0.3681(3)	0.021(1)	6	0.25
<i>O1</i>	-0.3075(2)	-0.0755(2)	0.2264(1)	0.0078(3)	18	1.0
<i>O2</i>	-0.3000(3)	-0.0648(3)	0.0064(1)	0.0111(6)	18	1.0
<i>O3</i>	-0.2582(2)	0.1052(2)	0.1164(1)	0.0087(5)	18	1.0
<i>O4</i>	0.0459(2)	0.1735(2)	0.1098(1)	0.0088(5)	18	1.0
<i>O5</i>	-0.4785(3)	-0.2009(2)	0.1029(1)	0.0120(6)	18	1.0
<i>O6</i>	0.0517(2)	0.1974(3)	0.3361(1)	0.0098(5)	18	1.0
<i>O7</i> **	0	0	0.2150(2)	0.0091(6)	6	1.0

\* The designation corresponds to [14].

\*\* The site contains OH group.

The structural model of the mineral was obtained by the “charge flipping” method using the JANA program [1]. The cations were distributed among the sites based on the chemical composition data taking into account the correspondence of the atom displacement

parameter to the sort of the cation and of the cation size to the standard crystal chemical characteristics of the polyhedra. The results were checked by calculation of the local valence balance on the anions. In some structural positions, mixed atomic scattering curves were used.



**Fig. 1.** General view of the almeidaite structure along the 3-axis.

The refinement of positional and atom displacement parameters by the least-squares method in the anisotropic approximation with allowance for isomorphic substitution resulted in the  $R$  value of 3.9%. The final coordinates, atom displacement parameters, and site occupancies are summarized in Table 2, and characteristics of the polyhedra are given in Table 3.

Topologically, the structure of the new mineral is similar to the structures of other members of the group. The structure is based on the framework of the anionic close packing in which one can distinguish nine layers alternating along the longer axis  $c \approx 21 \text{ \AA}$  in the sequence  $chhchh...$  (Figs. 1 and 2). The  $A$  cations occupy one of the anionic sites in the cubic layer ( $M0$ ). It accommodates large Pb and Sr cations with average  $M0-O$  distances of  $2.84 \text{ \AA}$ . Due to the incomplete occupancy (0.7) of the mixed site, the atom displacement parameter in this site is much higher compared to other atoms of the structure.

The smallest  $Zn^{2+}$  cation occupies the  $M2$  tetrahedron with the  $Zn-O$  distance of  $1.95 \text{ \AA}$ . The other four sites are occupied by cations in octahedral coordination. The distribution of cations among these sites is

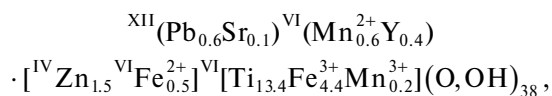
complicated by the fact that they differ little in size (the ionic radii were taken from [2]) and atomic mass and the average cation–anion distance in the octahedra varies over a narrow range from 2.0 to 2.2 Å.

The largest octahedron is occupied by the  $\text{Mn}^{3+}$  cations ( $r_{\text{Mn}} = 0.67 \text{ \AA}$ ) and Y ( $r_{\text{Y}} = 0.9 \text{ \AA}$ ), which occur in a *M1* polyhedron with the maximum average distance of 2.2 Å. The *C*-cations with smaller ion radii,  $r_{\text{Fe}^{3+}} = 0.55 \text{ \AA}$ ,  $r_{\text{Ti}^{4+}} = 0.605 \text{ \AA}$ , are grouped in *M3*–*M5* octahedra. In view of the fact that the Ti most often shifts from the octahedron center to one of the apical sites, being located at a shortened distance from this site, we placed this atom into *M4* and *M5* sites with cation–anion distances of 1.87–2.2 and 1.88–2.1 Å, respectively. The *M3* site with more uniform distribution of the central atom to oxygen bonds and an average cation–anion distance of 2.0 Å is mainly occupied by Fe with admixture of remaining titanium atoms and some manganese(III) atoms.

In the structure of this mineral, unlike other members of the crichtonite family (Tables 3 and 4) we have found an additional (*M6*) site occupied by a small amount of Fe atoms with an average Fe–O distance of 2.1 Å. This site occurs at a short distance (1.26 Å) from *M2* in the tetrahedron, resulting in statistical occupation of both sites by Fe and Zn atoms, respectively.

A similar site was found, among three other sites, in the structure of the uranium-enriched variety of senaite [12]. Octahedra *M6*–*M9* share faces with *M0*–*M5* polyhedra, and cations cannot occupy them simultaneously due to short cation–cation distances. In the authors' opinion, two domains, the main and the additional (10% occupancy) ones, are statistically present in the mineral structure within one close packing of O atoms.

The main features of the composition and structure of almeidaite are reflected in its crystal chemical formula. According to the general formula including cations *A*, *B*, *T*, and *C*, it can be written as follows ( $Z = 3$ ):



where Roman numerals indicate the coordination numbers of cations. The presence of OH groups in the vertex of the Zn tetrahedron common with the *M3* octahedron was established based on the valence balance for the anion at incomplete occupancy of the tetrahedron.

The data of structural studies of crichtonite group minerals are summarized in Table 4, which shows the distribution of cations over six structural sites designated by *M0*–*M5*, the identity of minerals being determined by the cations that predominate in these sites. As can be seen from this table, zinc is present in the

**Table 3.** Site distribution of cations, site composition ( $Z = 3$ ), and interatomic distances (Å)

Site	Composition	Atom	Interatomic distance
<i>M0</i>	$\text{Pb}_{0.6}\text{Sr}_{0.1}$	O4	$2.835(2) \times 6$
		O2	$2.843(3) \times 6$ (2.839)
<i>M1</i>	$\text{Mn}_{0.6}\text{Y}_{0.4}$	O5	$2.216(2) \times 6$ (2.216)
<i>M2</i>	$\text{Zn}_{1.5}$	O6	$1.939(3) \times 3$
		O7	2.001(4) (1.954)
<i>M3</i>	$\text{Fe}_{4.4}^{3+}\text{Ti}_{1.4}\text{Mn}_{0.2}^{3+}$	<i>M6</i>	1.265(4)
		O3	1.943(2)
		O1	1.972(2)
		O4	1.972(2)
		O7	2.031(2)
		O3	2.048(2)
		O4	2.132(2) (2.016)
		<i>M4</i>	$\text{Ti}_6$
O5	1.895(2)		
O1	1.939(2)		
O6	2.010(2)		
O2	2.038(2)		
O6	2.204(2) (1.993)		
<i>M5</i>	$\text{Ti}_6$	O4	1.884(2)
		O1	1.968(2)
		O2	1.972(2)
		O5	1.999(2)
		O2	2.081(3)
		O6	2.078(2) (1.997)
<i>M6</i>	$\text{Fe}_{0.5}^{2+}$	O6	$1.983(2) \times 3$
		O5	$2.244(3) \times 3$ (2.114)
		<i>M2</i>	1.265(4)

tetrahedral *M2* site in several minerals together with iron, the latter being predominant, in particular, in senaite. However, only in landauite and almeidaite, is this site zinc-dominant. The similarity between almeidaite and landauite also follows from the composition of other sites, except *M0*, which is occupied by sodium with minor of lead in landauite, while in almeidaite, this site is mainly occupied by lead with strontium admixture.

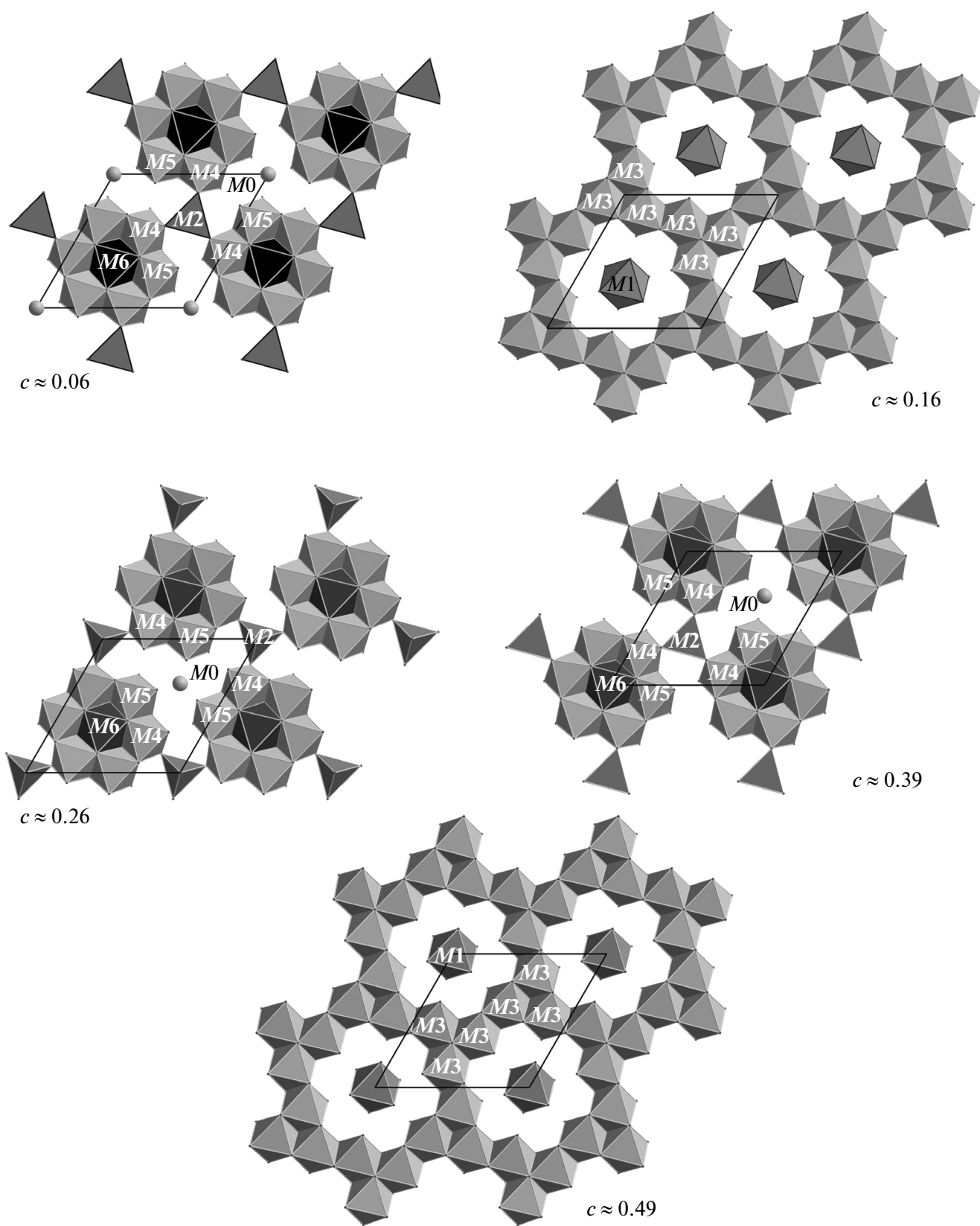


Fig. 2. Polyhedral layers of the structure projected on (001) at 0.06 to 0.49 levels.

**Table 4.** Crichtonite group minerals and elements predominating in their structural sites ( $Z = 3$ )

Mineral	Site						Ref.
	$M0(A)$	$M1(B)$	$M2(T)$	$M3-M5(C)$	$X^*$	$M6-M9$	
Landauite	Na, Pb	Mn, Y	Zn <sub>2</sub>	(Ti, Fe, Nb) <sub>18</sub>	O, OH		[3]
Loveringite	Ca, REE	Zr, Fe	(Mg, Fe) <sub>2</sub>	(Ti, Fe, Cr, Al) <sub>18</sub>	O		[4]
Lindsleyite	Ba, K	Zr, Fe	(Mg, Fe) <sub>2</sub>	(Ti, Cr, Fe) <sub>18</sub>	O		[5]
Mathiasite	K, Na, Ba, Sr	Zr, Fe	(Mg, Fe) <sub>2</sub>	(Ti, Cr, Fe) <sub>18</sub>	O		[6]
Davidite-(La)	La, Ce, Ca	Y, REE, U	(Fe, Mg) <sub>2</sub>	(Ti, Fe, Cr, V) <sub>18</sub>	O, OH		[7]
Davidite-(Ce)	Ce, La	Y, REE, U	(Fe, Mg) <sub>2</sub>	(Ti, Fe, Cr, V) <sub>18</sub>	O, OH		[7]
Crichtonite	Sr, Ba, Pb	Mn	(Fe, Zn) <sub>2</sub>	(Ti, Fe) <sub>18</sub>	O		[8]
Dessauite-(Y)	Sr, Pb	Y, U	(Fe, Zn) <sub>2</sub>	(Ti, Fe <sup>3+</sup> ) <sub>18</sub>	O		[9]
Senaite	Pb, Sr	Mn	(Fe, Zn) <sub>2</sub>	(Ti, Fe) <sub>18</sub>	O, OH		[10]
Gramaccioliite-(Y)	Pb, Sr	Y, Mn	(Fe, Zn) <sub>2</sub>	(Ti, Fe) <sub>18</sub>	O		[11]
Cleusonite	Pb, Sr	U <sup>4+</sup> , U <sup>6+</sup>	(Fe <sup>2+</sup> , Zn) <sub>2</sub>	(Ti, Fe <sup>2+</sup> , Fe <sup>3+</sup> ) <sub>18</sub>	O, OH		[12]
Paseroite	Pb, Sr	Mn <sup>2+</sup>	(Mn, Fe <sup>2+</sup> ) <sub>2</sub>	(V, Ti, □, Fe <sup>3+</sup> ) <sub>18</sub>	O		[13]
U-senaite	(Pb, O) <sub>0.25</sub>	U <sub>0.48</sub>	Met <sub>1.34</sub> **	(Met <sub>0.78</sub> Ti <sub>0.93</sub> Ti <sub>0.9</sub> ) <sub>6</sub>	O	Met <sub>3,3</sub>	[14]
Almeidaite	Pb <sub>0.6</sub> Sr <sub>0.1</sub> □ <sub>0.3</sub>	Mn <sub>0.6</sub> Y <sub>0.4</sub>	Zn <sub>1.5</sub>	Ti <sub>13.4</sub> Fe <sub>4.4</sub> <sup>3+</sup> Mn <sub>0.2</sub> <sup>3+</sup>	O, OH	Fe <sub>0.5</sub> <sup>2+</sup>	This work

\*  $X = 38$  for all representatives of the crichtonite group.

\*\* Designation of the metal cation in [14].

Thus, almeidaite is the Zn analog of senaite and the Pb analog of landauite, while the  $M6$  site found in its structure makes it similar to “U-senaite.”

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#### REFERENCES

- Petricek, V., Dusek, M., and Palatinus, L., Structure Determination Software Programs, Inst. of Physics, Praha, 2006.
- Shannon, R., *Acta Crystallogr. Sect. A*, 1976, vol. 32, pp. 751–767.
- Grey, I.E. and Gatehouse, B.M., *Can. Mineral.*, 1978, vol. 16, pp. 63–68.
- Gatehouse, B.M., Grey, I.E., Campbell, I.H., and Kelly, P.R., *Am. Mineral.*, 1978, vol. 63, pp. 28–36.
- Zhang, J., Ma, J., and Li, L., *Geol. Rev.*, 1988, vol. 34, pp. 132–144.
- Gatehouse, B.M., Grey, I.E., and Smyth, J.R., *Acta Crystallogr. Sect. C*, 1983, vol. 39, pp. 421–422.
- Gatehouse, B.M., Grey, I.E., and Kelly, P.R., *Am. Mineral.*, 1979, vol. 64, pp. 1010–1017.
- Grey, I.E., Lloyd, D.J., and White, J.S., *Am. Mineral.*, 1976, vol. 61, pp. 1203–1212.
- Orlandi, P., Pasero, M., Duchi, G., and Olmi, F., *Am. Mineral.*, 1997, vol. 82, pp. 807–811.
- Grey, I.E. and Lloyd, D.J., *Acta Crystallogr. Sect. B*, 1976, vol. 32, pp. 1509–1513.
- Orlandi, P., Pasero, M., Rotiroti, N., et al., *Eur. J. Mineral.*, 2004, vol. 16, pp. 171–175.
- Wulser, P.A., Meisser, N., Brugger, J., et al., *Eur. J. Mineral.*, 2005, vol. 17, pp. 933–942.
- Mills, S.J., Bindi, L., Cadoni, M., et al., *Eur. J. Mineral.*, 2012, vol. 24, pp. 1061–1067.
- Armbruster, Th. and Kunz, M., *Eur. J. Mineral.*, 1990, vol. 2, pp. 163–170.

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