## Ambrinoite (K,NH<sub>4</sub>)<sub>2</sub>(As,Sb)<sub>8</sub>S<sub>13</sub>·H<sub>2</sub>O, the first natural (K,NH<sub>4</sub>)-hydrated sulfosalt, from Signols (Piedmont, Italy)

Bonaccorsi, E.<sup>1</sup>, Biagioni, C.<sup>1</sup>, Moëlo, Y.<sup>2</sup>, Pasero, M.<sup>1\*</sup> & Bersani, D.<sup>3</sup>

<sup>1</sup>Dipto. di Scienze della Terra, Università di Pisa, Italy (\*pasero@dst.unipi.it) <sup>2</sup>Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, France

<sup>3</sup>Dipto di Fisica, Università di Parma, Italy

Ambrinoite, ideally  $(K,NH_4)_2(As,Sb)_8S_{13}$ -H<sub>2</sub>O, occurs as a rare mineral species in Triassic evaporitic rocks from Signols, Susa Valley, Piedmont, Italy. It is associated with sulfur and orpiment; in the same occurrence galkhaite was also identified, together with enargite and stibnite. Ambrinoite is red in colour, with a vitreous to resinous lustre. Electron microprobe analyses give (wt.%): K 4.57, Na 0.05, Tl 0.13, N 0.48, As 35.69, Sb 21.69, S 34.69, O 1.52, sum 98.81. With N and O as NH<sub>4</sub> and H<sub>2</sub>O, respectively, this gives the following chemical formula:  $[K_{1.44}(NH_4)_{0.48}Na_{0.03}Tl_{0.01}][As_{6.00}Sb_{2.00}]S_{13.39}$ -1.20H<sub>2</sub>O.

With the data below this gives a calculated density of 3.305 g cm<sup>-3</sup>. The presence of H<sub>2</sub>O and NH<sub>4</sub> was confirmed by micro-Raman spectroscopy (O-H and N-H stretching and bending vibrations).

Ambrinoite is triclinic, space group  $P\overline{1}$ , with *a* 9.704(1), *b* 11.579(1), *c* 12.102(2) Å,  $\alpha$  112.82(1),  $\beta$  103.44(1),  $\gamma$  90.49(1)°, *V* 1211.6(3) Å<sup>3</sup>, *Z* 2. The strongest X-ray powder diffraction lines [*d* in Å, (*I*), (*hkl*)] are: 10.78 (100) (001), 5.79 (55) (0 $\overline{2}$  1), 4.23 (35) (102), 5.31 (34) ( $\overline{1}$  02), 5.39 (32) (002).

The crystal structure of ambrinoite was solved by direct methods and refined to R = 0.035 for 2554 reflections with  $F_0 > 4\sigma(F_0)$ . It is based on MS<sub>3</sub> polyhedra (M = As, Sb) sharing corners to form double chains running along [100]; within each chain, trigonal pyramids arranged in M<sub>3</sub>S<sub>5</sub> triangular groups alternate with single MS<sub>3</sub> pyramids. (K,NH<sub>4</sub>) and H<sub>2</sub>O are hosted in channels along [010]; K-S bonds crosslink the double MS<sub>3</sub> chains. H<sub>2</sub>O molecules are coordinated to two K ions, but the latter are coordinated only by one H<sub>2</sub>O molecule, plus seven or nine S atoms.

According to modular analysis, the crystal structure of ambrinoite corresponds to the stacking along *c* of two kinds of layer, with common parameters a = 9.7 and b = 11.6 Å, and different widths. The chemical compositions of the two layers are  $[(As,Sb)_8S_{13}]^{2-}$  and  $[K_2(H_2O)]^{2+}$ , respectively. OD theory allowed one to derive two possible MDO polytypes, one triclinic (corresponding to the crystal studied), and the other monoclinic with symmetry  $P2_1/c11$ .

Ambrinoite belongs to the hutchinsonite merotypic series [1] and is closely related to gillulyite,  $Tl_2(As,Sb)_8S_{13}$  [2], and gerstleyite,  $Na_2(Sb,As)_8S_{13}$ ·2H<sub>2</sub>O [3].

The new mineral has been approved by the IMA CNMNC (2009-071). The name is after Pierluigi Ambrino, a mineral collector.

[1] Makovicky, E. (1997) *EMU Notes Mineral.*, **1**, 237-271. [2] Makovicky, E. & Balić-Žunić, T. (1999) *Am. Mineral.*, **84**, 400-406. [3] Nakai, I. & Appleman, D.E. (1981) *Chem. Letters*, 1327-1330.

## Tancaite-(Ce), a new molybdate from Italy

Bonaccorsi, E.<sup>\*</sup> & Orlandi, P.

Dipto. di Scienze della Terra, Università di Pisa, Italy (\*elena@dst.unipi.it)

Tancaite-(Ce), ideally FeCe( $MoO_4$ )<sub>3</sub>·3H<sub>2</sub>O, is a new mineral species occurring within cavities in the quartz veins which cut the granite at Su Senargiu, Sarroch (CA), Sardinia, Italy. It is a secondary mineral formed in the oxidation zone of a sulphide ore vein. Associated minerals are quartz, muscovite, molybdenite, pyrite and mendozavilite.

Tancaite-(Ce) is red or pale brown in colour, with a vitreous to adamantine lustre. Electron microprobe analyses give (wt.%): SiO<sub>2</sub> 0.34, CaO 0.09, Fe<sub>2</sub>O<sub>3</sub> 11.29, SrO 0.02, La<sub>2</sub>O<sub>3</sub> 5.04, Ce<sub>2</sub>O<sub>3</sub> 10.35, Pr<sub>2</sub>O<sub>3</sub> 1.07, Nd<sub>2</sub>O<sub>3</sub> 3.66, Sm<sub>2</sub>O<sub>3</sub> 0.19, ThO<sub>2</sub> 2.58, UO<sub>2</sub> 0.17, MoO<sub>3</sub> 58.62, H<sub>2</sub>O 7.43, sum 100.85. It gives the formula: Fe<sup>3+</sup><sub>1.03</sub>(Ce<sub>0.46</sub>La<sub>0.23</sub>Nd<sub>0.16</sub>Pr<sub>0.05</sub>Sm<sub>0.01</sub>U<sub>0.01</sub>Th<sub>0.07</sub>)<sub>Σ=0.99</sub>(Mo<sub>2.96</sub> Si<sub>0.04</sub>)<sub>Σ=3.00</sub>O<sub>12</sub>·3H<sub>2.00</sub>O, which can be simplified as Fe<sup>3+</sup>(REE)(MoO<sub>4</sub>)<sub>3</sub>·3H<sub>2</sub>O. The calculated density is 3.834 g/cm<sup>3</sup>. The presence of H<sub>2</sub>O was confirmed by micro-Raman spectrometry (stretching and bending vibrations of O-H).

The X-ray diffraction pattern of tancaite-(Ce) is characterised by a set of strong reflections, which indicate a cubic unit cell, with a = 6.80 Å and space group  $Pm \overline{3}m$ , plus a set of weaker reflections. By measuring only the strong reflections with a 4-circle diffractometer, it was possible to solve and refine the "average structure" of tancaite (R = 0.032for 149 unique reflections). The crystal structure consists of FeO<sub>6</sub> octahedra (in violet, Fig. 1a) centred at the origin of the cubic cell and linked together through MoO<sub>4</sub> tetrahedra by corner sharing (Fig. 1b). The molybdate tetrahedra are statistically distributed in four symmetry-related positions, with 1/4 occupancy. In the centre of the unit cell the REE cations exhibit 6+3 coordination, bonding six oxygen atoms and three H<sub>2</sub>O molecules.



**Fig. 1:** Crystal structure of tancaite-(Ce) in space group  $Pm \ 3 \ m$ ; (a) the REE cation lies within the yellow polyhedron; Fe<sup>3+</sup>-centred octahedra are indicated in violet; partially occupied Mo, O and H<sub>2</sub>O sites are indicated, respectively, by black, red and white spheres; (b) the molybdate groups (light blue tetrahedra) are statistically distributed over four possible and mutually exclusive positions.

The refined structure is clearly an average structure, characterised by statistical disorder which involves the Mo cations, the H<sub>2</sub>O molecules and the ligands of the REE cations at the centre of the unit cell. Two intensity data collections were performed in order to measure the weaker reflections and to solve the real crystal structure of tancaite-(Ce). The former was performed at the synchrotron facility Elettra, at the XRD1 beamline; the latter was carried out by means of a CCD-equipped Oxford diffractometer, operating with MoKa radiation. Both sets of data indicated a larger super-cell with respect to the previous cubic cell with a = 6.80 Å. One of the possible super-cells showed rhombohedral symmetry, with a = 19.2, c = 47.4 Å in the hexagonal setting. The new mineral has been approved by the IMA CNMNC (# 2009-097). The name is after Giuseppe Tanca, mineral collector.