

**FA2-MS01-O1**

**Novel 2:1 Layers Formed by Dehydroxylating (Fe<sup>3+</sup>, Mg)-Rich Dioctahedral Mica.** Toshihiro Kogure<sup>a</sup>, Victor A. Drits<sup>b</sup>. <sup>a</sup>Graduate School of Science, The University of Tokyo, Tokyo, Japan. <sup>b</sup>Russian Academy of Sciences, Moscow, Russia.

E-mail: [kogure@eps.s.u-tokyo.ac.jp](mailto:kogure@eps.s.u-tokyo.ac.jp)

It is known that dioctahedral 2:1 phyllosilicates are topotactically dehydroxylated by heating. This dehydroxylation induces cation migration in the octahedral sheet in several phyllosilicates [1]. For instance, the *cis*-vacant (*cv*) illite transforms to a structure with cation distribution close to the *trans*-vacant (*tv*) structure. On the other hand, it was reported that superstructures within a 2:1 layer are formed in celadonite, *trans*-vacant (Fe<sup>3+</sup>, Mg)-rich dioctahedral mica, by dehydroxylation [2]. The present paper reports the origin and detail of these superstructures by using HRTEM [3].

When celadonite was annealed around 650°C, a primitive *a-b* super-cell formed. HRTEM images indicate that the superstructure is owing to a long-range cation ordering in the octahedral sheet, in agreement with the suggestion by Muller *et al.* [2]. However, the image simulation using the site occupancy they proposed could not completely reproduce the experimental contrast. A new model to explain the contrast is under consideration.

Celadonite annealed at ~800°C shows extra reflections which correspond to a *3a-b* super-cell in the *hk0* electron diffraction pattern [2]. Cross-sectional HRTEM images along the X<sub>1</sub> directions are almost similar to that of natural celadonite. However, the images along the Y<sub>1</sub> directions are completely different from that for normal micas. First of all, the *3a* periodicity is owing to a long-period ordering of the (Fe<sup>3+</sup>, Mg) cations. The most interesting structural feature is that the contrasts corresponding to the two tetrahedral sheets in a 2:1 layer are not staggered at all. Probably cation migration induced lateral shift of ±*a*/3 for the T(tetrahedral sheet)–K(potassium)–T unit. A plausible model to explain the experimental contrasts is shown in Fig. 1. In the model, two third of the spaces surrounded by the two facing hexagonal rings of tetrahedra accommodate three (Fe<sup>3+</sup>, Mg) cations and one third of the spaces is empty. (Fe<sup>3+</sup>, Mg) cations are coordinated by six or five oxygen atoms, forming a trigonal prisms or a square pyramid, respectively.

[1] V.A. Drits, G. Besson and F. Muller, *Clays Clay Miner.*, **1995**, 43, 718-731. [2] T. Kogure, J. Kameda and V.A. Drits, *Am. Mineral.*, **2007**, 92, 1531-1534. [3] F. Muller, V.A. Drits, S.I. Tsipursky and A. Plancon, *Clay Miner.*, **2000**, 35, 505-514.

**Keywords:** layered silicates; HRTEM; micas

**FA2-MS01-O2**

**When the Minerals Become Complex: The Case of the Pearceite-Polybasite Mineral Solid Electrolytes.** Luca Bindi<sup>a</sup>, Michel Evain<sup>b</sup>, Silvio Menchetti<sup>c</sup>. <sup>a</sup>Natural History Museum of Florence, Italy. <sup>b</sup>Institut des Matériaux Jean Rouxel, Univ. Nantes, France. <sup>c</sup>Dipartimento di Scienze della Terra, Univ. Firenze, Italy.

E-mail: [luca.bindi@unifi.it](mailto:luca.bindi@unifi.it)

The minerals belonging to the pearceite-polybasite group - general formula [(Ag,Cu)<sub>6</sub>M<sub>2</sub>S<sub>7</sub>][Ag<sub>9</sub>Cu<sub>4</sub>S<sub>4</sub>] with M = Sb, As - have been recently structurally characterized [1,2,3]. On the whole, their structure can be described as a regular succession of two module layers stacked along the *c* axis: a first module layer (labeled *A*), with general composition [(Ag,Cu)<sub>6</sub>(As,Sb)<sub>2</sub>S<sub>7</sub>]<sup>2-</sup>, and a second module layer (labeled *B*), with general composition [Ag<sub>9</sub>Cu<sub>4</sub>S<sub>4</sub>]<sup>2+</sup>. In the structure, (As,Sb) forms isolated (As,Sb)S<sub>3</sub> pyramids typically occurring in sulfosalts, copper links two sulfur atoms in a linear coordination, and silver occupies sites with coordination ranging from quasi linear to almost tetrahedral. In the *B* layer of the disordered forms, the silver cations are found in various sites corresponding to the most pronounced probability density function locations of diffusion paths.

In this talk it will be presented the state of the art of the crystal chemistry of these minerals on the basis of (1) consideration of the pearceite-polybasite minerals as a family of polytypes, (2) new IMA-approved nomenclature rules, (3) differential scanning calorimetric and complex impedance spectroscopic studies on all the members of the group, (4) study of the ionic phase transitions by high- and low-temperature single-crystal X-ray diffraction and (5) electron diffraction studies.

[1] Bindi L., Evain M., Menchetti S., *Acta Cryst.*, **2006**, B62, 212.

[2] Evain M., Bindi L., Menchetti S., *Acta Cryst.*, **2006**, B62, 447.

[3] Bindi L., Evain M., Menchetti S., *Can. Miner.*, **2007**, 45, 321.

**Keywords:** structural disorder; sulfosalts; polytypism

**FA2-MS01-O3**

**Cation-Cation Interaction (CCIs) in Novel Layered And Framework Uranyl Compounds.** Evgeny V. Alekseev<sup>a</sup>, Sergey V. Krivovichev<sup>b</sup>, Wulf Depmeier<sup>a</sup>. <sup>a</sup>Department of Crystallography, University of Kiel, Germany. <sup>b</sup>Department of Crystallography, St.Petersburg State University, St.Petersburg, Russia.

E-mail: [ea@min.uni-kiel.de](mailto:ea@min.uni-kiel.de)

In higher oxidation states, actinides possess an unique coordination chemistry, owing to their tendency to form linear actinyl ions. One of the interesting points in their crystal chemistry is cation-cation interaction (CCIs) between actinyl ions. CCIs are well-recognized for the Np(V), Pu(V), and Am(V) chemistry, but are rather rare for U(VI). In the frame of our research in the area of uranium crystal chemistry we prepared 9 new uranyl compounds with CCIs, six uranyl arsenates: Li[(UO<sub>2</sub>)<sub>4</sub>(AsO<sub>4</sub>)<sub>3</sub>] (1), Li<sub>5</sub>[(UO<sub>2</sub>)<sub>13</sub>(AsO<sub>4</sub>)<sub>9</sub>(As<sub>2</sub>O<sub>7</sub>)] (2), Li<sub>2</sub>[(UO<sub>2</sub>)<sub>7</sub>(AsO<sub>4</sub>)<sub>5</sub>O] (3), Ag<sub>5</sub>[(UO<sub>2</sub>)<sub>13</sub>(AsO<sub>4</sub>)<sub>9</sub>(As<sub>2</sub>O<sub>7</sub>)] (4), Ba<sub>4</sub>[(UO<sub>2</sub>)<sub>7</sub>(UO<sub>2</sub>)(AsO<sub>4</sub>)<sub>2</sub>O<sub>7</sub>] (5), Ba[(UO<sub>2</sub>)<sub>9</sub>U<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>O<sub>12</sub>] (6), one uranyl molybdate: Li<sub>4</sub>[(UO<sub>2</sub>)<sub>10</sub>O<sub>10</sub>(Mo<sub>2</sub>O<sub>8</sub>)] (7), and two uranyl tungstates: Na<sub>2</sub>Li<sub>8</sub>[(UO<sub>2</sub>)<sub>11</sub>O<sub>12</sub>(WO<sub>5</sub>)<sub>2</sub>] (8), Ag<sub>2</sub>Na<sub>2</sub>Li<sub>6</sub>[(UO<sub>2</sub>)<sub>11</sub>O<sub>12</sub>(WO<sub>5</sub>)<sub>2</sub>] (9). Compounds 1, 2, 3, 4, 5, 6 and 7 have framework structures, whereas phases 8 and 9 are based on double layers. In all these structures the uranyl groups have different equatorial coordination: in the