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Novel 2:1 Layers Formed by Dehydroxylating (Fe^{3+}, Mg)-Rich Dioctadedral Mica.

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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^{3+}, 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 3***a***-***b*** super-cell in the *hk*0 electron diffraction pattern [2]. Cross-sectional HRTEM images along the X_i directions are almost similar to that of natural celadonite. However, the images along the Y_i directions are completely different from that for normal micas. First of all, the 3***a*** periodicity is owing to a long-period ordering of the (Fe^{3+}, 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^{3+}, Mg) cations and one third of the spaces is empty. (Fe^{3+}, Mg) cations are coordinated by six or five oxygen atoms, forming a trigonal prisms or a square pyramid, respectively.

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Keywords: layered silicates; HRTEM; micas

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When the Minerals Become Complex: The Case of the Pearceite-Polybasite Mineral Solid Electrolytes.

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The minerals belonging to the pearceite-polybasite group - general formula $[(Ag,Cu)_6M_2S_7][Ag_9CuS_4]$ 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 $[(Ag,Cu)_6(As,Sb)_2S_7]^{2-}$, and a second module layer (labeled *B*), with general composition $[Ag_9CuS_4]^{2+}$. In the structure, (As,Sb) forms isolated $(As,Sb)S_3$ 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.

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Keywords: structural disorder; sulfosalts; polytypism

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Cation-Cation Interaction (CCIs) in Novel Layered And Framework Uranyl Compounds.

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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: $Li[(UO_2)_4(AsO_4)_3]$ (1), $Li_5[(UO_2)_{13}(AsO_4)_9(As_2O_7)]$ (2), $Li_2[(UO_2)_7(AsO_4)_5O]$ (3), $Ag_5[(UO_2)_{13}(AsO_4)_9(As_2O_7)]$ (4), $Ba_4[(UO_2)_7(UO_4)(AsO_4)_2O_7]$ (5), $Ba[(UO_2)_9U_2(AsO_4)_2O_{12}]$ (6), one uranyl molybdate: $Li_4[(UO_2)_{10}O_{10}(Mo_2O_8)]$ (7), and two uranyl tungstates: $Na_2Li_8[(UO_2)_{11}O_{12}(WO_5)_2]$ (8), $Ag_2Na_2Li_6[(UO_2)_{11}O_{12}(WO_5)_2]$ (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 structures of 1, 2, 3, 4, 5, 7 it is tetragonal and pentagonal (deformed octahedra and pentagonal bipyramids, respectively), in the structure of 6 uranium atoms have UO_8 and UO_7 coordination, and in the structures of 8 and 9 three different uranyl ion coordinations – tetragonal, pentagonal and hexagonal are realized (actually, this is the first actinide compounds with the actinyl cation in three different coordinations). The configuration of the CCIs in these structures differ: dimers in 1 and 3, two types of trimers in 2, 4 and 5, pentamers in 8 and 9, in the structure of 6 circular hexamers are realized, and in the structure of 7 observes a one-dimensional array of two- and three-center cation-cation bonds. The configurations of CCIs realized in the structures of 5, 6, 7 and 8 have been observed for the first time. It should be mentioned that all compounds except 1 and 3 crystallized in new structure types.

Keywords: uranium compounds; crystallography inorganic; crystallochemistry

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The Tobermorite-Like Layer in Non-Tobermorite Minerals.

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The tobermorite-like layer (TLL) is a characteristic feature in all the structures of the natural and synthetic compounds of the tobermorite group [1]. In those structures eptahedra of calcium cations, characterized by ‘a pyramidal part on one side and a dome part on the other side joining the equatorial oxygen atoms’, form columns through edge sharing; the columns are connected each other, once again through edge sharing, and adjacent columns present the pyramidal apical ligands on opposite sides of the resulting infinite layers. These layers, decorated with wollastonite chains on both sides, build up the ‘complex layers’ which are the basic structural module in all the phases of the tobermorite group (Fig. 1).

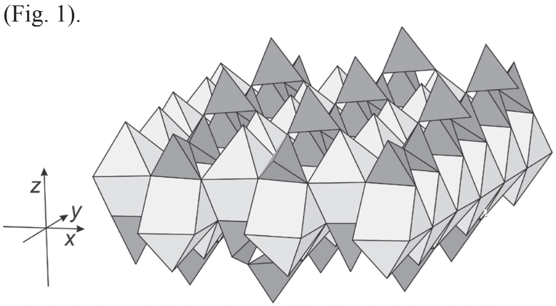

Fig. 1. The tobermorite-like layer decorated with wollastonite chains on both sides, as it appears in the structures of the natural and synthetic compounds of the tobermorite group.

TLL is a recurrent feature in several natural phases belonging to distinct mineral groups. In the structures of the compounds of the rinkite group the TLL is decorated on both sides by disilicate groups and is accompanied by an infinite ‘octahedral’ layer in building up the structural arrangement. Dovyrenite [2] and roumaite [3] are closely related to the minerals of the rinkite group and differ only in the way of decoration of the TLL by the disilicate groups. Fukalite [4] too presents the TLL, decorated on both sides by four-repeat silicate chains and carbonate groups; tilleyite-type polyhedral layers are also present as distinct modules in building up the structural arrangement. The ubiquitous occurrence of TLL is related to its chemical and structural flexibility: the chemical and geometrical variations of the TLL in the different structures are described and discussed.

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Byzantievite, the First Silicate-Borate-Phosphate Mineral.

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Byzantievite, ideally $Ba_5(Ca,REE,Y)_{22}(Ti,Nb)_{18}(SiO_4)_4[(PO_4),(SiO_4)]_4(BO_3)_9O_{22}[(OH),F]_{43}(H_2O)_{1.5}$, is the only mineral which contains three different oxyanions: (BO_3), (SiO_4) and (PO_4). They occur in the ratio 9:5:3. Byzantievite occurs in the moraine of the Dara-i-Pioz glacier, the Alai mountain ridge, Tien-Shan Mountains, northern Tajikistan. Byzantievite has no natural or synthetic analogues. The crystal structure of byzantievite, a 9.1202(2), c 102.145(5) Å, γ 120°, V 7357.9(5)$Å^3$, sp. gr. *R*3, Z=3, D_{calc} 4.151 g/cm^3, was solved by direct methods and refined to an R index of 13.14%. In the crystal structure, there are fifty cation sites. Twenty-three sites are fully occupied and twenty-seven sites are characterized by partial occupancy: six sites are more than 50% occupied and twenty-one sites are less than 50% occupied. In the crystal structure of byzantievite, there are two distinct parts that alternate along the c axis. Part one is characterized mainly by fully occupied cation sites and part two, mainly by partially occupied cation sites. Part one has a local inversion centre whereas part two does not. Hence the crystal structure of byzantievite lacks an inversion centre. For better understanding of this framework structure, we describe it as sheets of polyhedra stacked along [001]. Sheet a is composed of [12]-coordinated Ba atoms. Ti-dominant octahedra and B-triangles share common vertices to form sheet b. [8]-coordinated (Ca,REE, Y) polyhedra and B triangles share common vertices and edges to form sheet c. Sheet d is composed of [10]-coordinated (Ca,REE, Y) polyhedra and P tetrahedra. Sheet e is formed by [8]-coordinated (Ca,REE, Y) polyhedra, Si tetrahedra and B