

**FA2-MS01-P01**

**Layered Silicates: Polysomatic Macaulayite-burckhardtite Series.** Olga V. Yakubovich<sup>a</sup>, Werner Massa<sup>b</sup>, Nikita V. Chukanov<sup>c</sup>. <sup>a</sup>*Department of Geology, Moscow State Lomonosov University, Russia.* <sup>b</sup>*Department of Chemistry, Philipps-University of Marburg, Germany.* <sup>c</sup>*Institute of Problems of Chemical Physics, Chernogolovka, Russia.*  
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The macaulayite-burckhardtite family [1] of layered silicates is discussed along in terms of the modular concept. The characterization of a new mineral britvinitite  $[\text{Pb}_7(\text{OH})_3\text{F}(\text{BO}_3)_2(\text{CO}_3)]_n[\text{Mg}_{4.5}(\text{OH})_3(\text{Si}_5\text{O}_{14})]_{2n}$  [2,3] allowed considering this mineral group as a polysomatic series with a TOT-“pyrophyllite” block as one end-member. Along *c* axis of the unit cells these three-layered blocks alternate with lamellar modules of different size and composition, such as oxide, oxide-carbonate, oxide-carbonate-sulfate, ect. The group involves among britvinitite the minerals macaulayite, lourencewalsite, burckhardtite, kegelite, surite, ferrisurite, and niksergievite. In the absence of data of precision structure investigations, the preliminary inferences regarding their structures were made using the results of chemical, spectroscopic, and X-ray powder diffraction analyses and, in a number of cases, microdiffraction experiments.

Tetrahedral fragments of the britvinitite crystal structure built from 12-membered rings are topologically identical to tetrahedral nets in zeophyllite  $\text{Ca}_{13}(\text{F},\text{OH})_{10}[\text{Si}_5\text{O}_{14}]_2 \cdot 6\text{H}_2\text{O}$  [4, 5] and synthetic  $\text{Rb}_6\text{Si}_{10}\text{O}_{23}$  [6] structures. These tetrahedral  $(\text{Si}_5\text{O}_{14})_{\infty}$  layers differ only by the direction of apical vertices of  $\text{SiO}_4$  tetrahedra, and can be presented as  $(\text{UUU} \dots)_{\infty}$  in britvinitite,  $(\text{UUUDUUUD} \dots)_{\infty}$  in zeophyllite, and  $(\text{UDUDUD} \dots)_{\infty}$  in  $\text{Rb}_6\text{Si}_{10}\text{O}_{23}$ . In the crystal structures of orthorhombic and hexagonal modifications of  $\text{Rb}_6\text{Si}_{10}\text{O}_{23}$ , neighboring tetrahedral layers share oxygen vertices with formation of a tetrahedral 3D framework  $(\text{Si}_{10}\text{O}_{23})_{\infty}$ .

Two types of blocks alternate along the *c* axis in the britvinitite crystal structure. Blocks of the first type are built from brucite-like layers of edge-sharing octahedra bounded on both sides by networks of Si tetrahedra in three-layer sandwiches of  $\{\text{Mg}_{4.5}(\text{OH})_3(\text{Si},\text{Al})_5\text{O}_{14}\}_{\infty}$  composition. Blocks of the second type are complex defect seven-layer packs described by the formula  $[\text{Pb}_{7.1}(\text{OH})_{2.7}\text{F}(\text{CO}_3)(\text{BO}_3)_{1.7}(\text{SiO}_4)_{0.3}]_{\infty}$ . Observed diffuse streaks along the *c\** direction of the reciprocal lattice of britvinitite were interpreted as diffuse scattering from lead atoms associated with one-dimensional disorder. The translational Si<sub>10</sub>O layers parallel to the *ab* plane and containing ordered vacancies in Si positions, are displaced with respect to the neighboring Pb layer. Thus, the “vacant” tetrahedra and, hence, the Pb atoms appear to be displaced in the second and third superposed equivalent layers (stacking disorder).

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**Keywords:** layered silicates; britvinitite crystal structure; polysomatic series

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**Fettelite,  $[\text{Ag}_6\text{As}_2\text{S}_7][\text{Ag}_{10}\text{HgAs}_2\text{S}_8]$ : Structure, Twinning, and Revised Chemical Formula.** Silvio Menchetti<sup>a</sup>, Luca Bindi<sup>b</sup>, Frank N. Keutsch<sup>c</sup>, Carl A. Francis<sup>d</sup>. <sup>a</sup>*Dipartimento di Scienze della Terra, Univ. Firenze, Italy.* <sup>b</sup>*Natural History Museum of Florence, Italy.* <sup>c</sup>*Department of Chemistry, Univ. Wisconsin-Madison, USA.* <sup>d</sup>*Harvard Mineralogical Museum, Cambridge, USA.*  
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The crystal structure of the rare mineral fettelite [1] was solved using intensity data collected from a twinned crystal from Chañarcillo, Copiapó Province, Chile. The study revealed that, in spite of the strong hexagonal pseudosymmetry, the structure is monoclinic (space group C2) with  $a = 26.0388(10)$ ,  $b = 15.0651(8)$ ,  $c = 15.5361(8)$  Å,  $\beta = 90.48(1)^\circ$  and  $V = 6094.2(5)$  Å<sup>3</sup>. The refinement of an anisotropic model led to an *R* index of 0.0656 for 7143 observed reflections [ $I > 2\sigma(I)$ ] and 0.0759 for all 17447 independent reflections [2]. Fettelite is intimately twinned with six twin domains. The structure consists of the stacking of two module layers along [001]: an *A* module layer with composition  $[\text{Ag}_6\text{As}_2\text{S}_7]^{2-}$  and a *B* module layer with composition  $[\text{Ag}_{10}\text{HgAs}_2\text{S}_8]^{2+}$ . The As atoms form isolated  $\text{AsS}_3$  pyramids typical of sulfosalts, Hg links two sulfur atoms in a linear coordination, and Ag occupies sites with coordination ranging from quasi linear to almost tetrahedral. The *A* module layer found for fettelite is identical to that described for the minerals belonging to the pearceite-polybasite group. On the basis of information gained from this characterization the crystal chemical formula was revised according to the structural results, yielding  $[\text{Ag}_6\text{As}_2\text{S}_7][\text{Ag}_{10}\text{HgAs}_2\text{S}_8]$  ( $Z = 8$ ).

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**Keywords:** sulfosalts; twinning; mineralogical crystallography

**FA2-MS01-P03**

**Ordering of the Al Cation Distribution in the Octahedral Sheets Related to the Ordering of Al in the Tetrahedral Sheets of Phlogopite Investigated by 2D CPMAS NMR and Monte Carlo Simulations.** Ramona Langner<sup>a</sup>, Michael Fechtelkord<sup>a</sup>, Erika Palin<sup>b</sup>, Alberto Garcia<sup>c</sup>, Javier López-Solano<sup>d</sup>. <sup>a</sup>*Institut fuer Geologie, Mineralogie und Geophysik, Ruhr-Universitaet Bochum, Germany.* <sup>b</sup>*Department of Earth Sciences, University of Cambridge, UK.* <sup>c</sup>*ICMAB-CSIC, Institut de Ciencia de Materials de*

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This work is part of the ORION-project (Ordering of Ions in Minerals) within the EuroMinSci programme of the ESF which aims at the elucidation of ionic ordering by combining experimental investigations and theoretical calculations. Previous solid state NMR spectroscopic investigations of phlogopite, a trioctahedral 2:1 layer silicate, indicated a non-statistical distribution of cations and anions in the octahedral sheets: F prefers sites coordinated by three Mg, whereas OH prefers sites with Al as next-nearest-neighbours [1]. Further investigations were carried out on phlogopites with various Al-contents and synthesized at different temperatures. Cross-polarization (CP)  $\{^1\text{H}\}$   $^{29}\text{Si}$  CPMAS NMR experiments were performed to clarify whether the degree of ordering in the octahedral sheets is related to that in the tetrahedral layers. These experiments clearly indicate a direct neighbourhood of aluminium in the tetrahedral sheets to aluminium in the octahedral sheets and, thus, a relationship between the ordering of ions in both sheets. Support for these conclusions comes also from atomistic simulations of ordering using the so-called "J formalism" in which total-energy calculations with interatomic potentials are used to generate a set of pair interaction parameters which are then employed in Monte Carlo (MC) simulations [2,3]. In phlogopite we have considered the OH-rich extreme and performed MC simulations for several overall concentrations of Al in the range  $0 < x < 1$ , finding significant segregation of the Al atoms with a strong spatial correlation between the Al-rich domains in the two layers.

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**Keywords:** NMR in solids; ordering clustering; micas

#### FA2-MS01-P04

##### X-Ray Powder Diffraction of Synthetic Al-rich Phlogopites: Lattice Parameters, Polytypes, Stacking Faults, and Implication of Modulations.

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X-ray powder diffraction experiments of synthetic Al-rich phlogopites synthesized at 800 °C and 2 kbar were carried out. The grain size of the synthetic phlogopites ranges between particle diameters of 3 to 5 µm. The samples

have already been well characterized by solid state NMR spectroscopy, and thus, possible impurity phases have been assigned. As for all micas, the phlogopite structure can be described in terms of the OD-theory, where 2-d periodic layers can be stacked in different ways without changing the transition from one layer to the adjacent one [1]. One aim of the experiments was to study the change of lattice parameters with increasing F- and Al-content. Previous investigations have already shown that the c-lattice parameter decreases strongly with increasing F-content [2]. From combined powder XRD and TEM investigations we expect to get detailed information on the polytypes which were formed during synthesis and on stacking faults in the mica structure. Up to now, many natural phlogopite single-crystals and synthetic powder samples have been characterized using XRD techniques. The most common polytype is the one-layer monoclinic polytype (1M) with space group symmetry C2/m. The other two possible polytypes, 2M<sub>1</sub> (space group symmetry C2/c) and 3T (space group symmetry P3<sub>1</sub>12) are far less abundant [3]. Our first refinements indicate that all phlogopite samples consist of polytype 2M<sub>1</sub>. However, there may also be a mixture of polytype 2M<sub>1</sub> and polytype 1M, leading to inelastic X-ray scattering. In some powder patterns with better resolution, satellite reflections surrounding hkl-reflections occur, which have not yet been reported and imply the presence of a modulated structure. While solid-state NMR spectroscopic investigations offer an insight into the local structure of the nuclei, the powder XRD patterns refinements may give new information about the long-range order of the tetrahedral and octahedral sheets. Combined with the TEM investigations, the results will contribute to a better understanding of stacking faults in the mica structure. Furthermore, this information may clarify the presence and type of modulations in the structure.

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#### FA2-MS01-P05

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The structure and lattice parameters of the tantalum and tantalum oxides phases were determined by temperature X-ray diffraction under vacuum and low pressure carbone monoxide between 293 and 2278K. We show that the metallique phase structure is stabilized by inclusion of oxygen into the metal octahedral hole. We determined the crystalline characteristics at high temperatures for Ta and Ta<sub>2</sub>O<sub>5</sub> phases.