

**MS15-P22** Rumseyite,  $[\text{Pb}_2\text{OF}]\text{Cl}$ -fluoroxychloride mineral with the parent crystal structure for layered lead oxychlorides. Oleg I. Siidra,<sup>a</sup> Rick W. Turner,<sup>b</sup> Sergey V. Krivovichev,<sup>a</sup> John Spratt<sup>c</sup> <sup>a</sup>Department Crystallography, Saint-Petersburg State University, University emb. 7/9, St.Petersburg, 199034, Russia. <sup>b</sup>The Drey, Allington Track, Allington, Salisbury SP4 0DD, Wiltshire, UK. <sup>c</sup>Department of Mineralogy, Natural History Museum, Cromwell Road, London SW7 5BD, UK.  
E-mail: [siidra@mail.ru](mailto:siidra@mail.ru)

The structure of rumseyite contains one symmetrically unique Pb position. The  $\text{Pb}^{2+}$  cation is coordinated by four O/F atoms and four Cl atoms. In agreement with previous results on Pb oxychlorides, the general feature of the  $\text{Pb}^{2+}$  coordination in rumseyite is the presence of several short Pb-O bonds located in one coordination hemisphere of the  $\text{Pb}^{2+}$  cation. In the opposite hemisphere, the  $\text{Pb}^{2+}$  cation forms four long Pb-Cl bonds. This distortion is usually interpreted as the influence of the stereoactivity of  $s^2$  lone electron pairs on the  $\text{Pb}^{2+}$  cations. Cl atoms have cubic coordination, whereas O/F atoms have tetrahedral coordination, thus being central for anion-centered (O/F) $\text{Pb}_4$  tetrahedra. The presence of fluorine in the crystal structure of rumseyite is confirmed by the Pb-(O/F) bond length of 2.41 Å. The crystal structure of rumseyite is based on alternation of continuous  $[\text{OFPb}_2]$  layers of edge-sharing  $\text{XPb}_4$  tetrahedra (X = O, F) and sheets of chlorine ions. The  $[\text{OFPb}_2]$  layers are of the type observed in the structure of tetragonal modification of  $\text{PbO}$ .

The type of structure observed in rumseyite is characteristic for a number of minerals, including symesite,  $\text{Pb}_{10}(\text{SO}_4)\text{O}_7\text{Cl}_4(\text{H}_2\text{O})$ , mereheadite,  $\text{Pb}_{47}\text{O}_{24}(\text{OH})_{13}\text{Cl}_{25}(\text{BO}_3)_2(\text{CO}_3)$ , kombatite,  $(\text{Pb}_{14}(\text{VO}_4)_2\text{O}_9\text{Cl}_4)$ , sahlinite,  $(\text{Pb}_{14}(\text{AsO}_4)_2\text{O}_9\text{Cl}_4)$ , parkinsonite  $(\text{Pb}_7\text{MoO}_9\text{Cl}_2)$ , hereroite,  $[\text{Pb}_{32}(\text{O})_{21}](\text{AsO}_4)_2((\text{Si},\text{As},\text{V},\text{Mo})\text{O}_4)_2\text{Cl}_{10}$  and vladkrivovichevite,  $[\text{Pb}_{32}\text{O}_{18}][\text{Pb}_4\text{Mn}_2\text{O}]\text{Cl}_{14}(\text{BO}_3)_8 \cdot 2\text{H}_2\text{O}$ . Obviously rumseyite is in close relationship with these minerals. However, all of these minerals contain different types of vacancies in their  $\text{PbO}$ -like sheets, these sheets invariably being formed by edge- and corner-sharing  $\text{OPb}_4$  oxocentered tetrahedra and/or halogen layers. For instance the defects in the  $\text{PbO}$ -like layers in the structure of symesite have a square form. In mereheadite, additional Pb atoms are inserted in the chlorine layer. This observation lets us to consider the crystal structure of rumseyite as a defect-free parent for all of the minerals in the growing class of layered lead oxychlorides. Rumseyite is also the first example of a mineral crystal structure containing mixed O/F anion-centered tetrahedra. Fluorine plays an important role as a charge compensating agent.

[1] Turner, R.W., Siidra, O.I., Krivovichev, S.V., Stanley, C.J. & Spratt, J. M. (2012) *Mineral. Mag.* accepted.

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**MS15-P23** In situ high temperature study of structural transformation of cronstedtite-1T. Serena C. Tarantino,<sup>a</sup> Michele Zema,<sup>a</sup> Agnès Elmaleh,<sup>b</sup> <sup>a</sup>Department of Earth and Environmental Sciences, University of Pavia, Italy, <sup>b</sup>Institut de Minéralogie et de Physique des Milieux Condensés, UPMC/CNRS, Paris, France  
E-mail: [serenachiara.tarantino@unipv.it](mailto:serenachiara.tarantino@unipv.it)

Cronstedtite,  $(\text{Fe}_2^{2+}\text{Fe}^{3+})(\text{SiFe}^{3+})\text{O}_5(\text{OH})_4$ , is a trioctahedral 1:1 layer silicate of the serpentine group. It presents spin-glass like properties [1], contrasting with the long-range magnetic order observed in other Fe-serpentine [2]. A deficiency in tetrahedral iron with respect to the ideal formula is often reported, giving a  $\text{Si}:\text{Fe}^{3+}$  ratio in tetrahedra as high as 2:1. Mg is also known to substitute for iron in octahedral coordination in natural samples. In this mineral, an extraordinary amount of variation in the stacking sequence is possible and a variety of polytypes has been reported. The crystal structures of several polytypes of cronstedtite have been refined [3-5], and coexistence and intergrowths of different polytypes have also been reported [e.g., 6,7].

Thermal transformations of cronstedtite have been described on the basis of ex situ treatments and oscillation and Weissenberg photographs [8].

The thermal behaviour of a Mg-bearing cronstedtite-1T from Prizbram (Czech Republic) has been analysed by *in situ* high-temperature single-crystal X-ray diffraction. No oxygen buffering was applied. The evolution of the unit-cell parameters has been followed from RT to 800°C at temperature intervals of 25°C. Up to dehydroxylation, which occurs at ca. 300°C and causes an abrupt decrease of unit-cell parameters and volume, cronstedtite-1T shows a fairly anisotropic dilatation with thermal expansion coefficients  $\alpha_c:\alpha_a$  ratio of ca. 2. With increasing temperature, a broadening and weakening of reflections is first observed, and then the observed diffraction pattern shows quite sharp reflections with cubic symmetry. No powder rings are observed after the transformation. Diffraction intensity data were collected at different temperatures in order to evaluate changes in the geometry of the crystal structure and unravel the mechanisms of dehydroxylation associated to Fe-oxidation.

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