ESRF	**Experiment title:** Selective study of iron occupancy in tetrahedral and octahedral sites in the layer silicate cronstedtite-$2H_2$ by application of the Anomalous Diffraction and Diffraction Anomalous Near-edge Structure (DANES)	**Experiment number:** CH-683
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Report:

Recently structures of several polytypes of cronstedtite, a trioctahedral 1:1 layer silicate close of serpentinite - kaolinite group were refined: 3*T* (Smrčok et al., 1994), 1*T* (Hybler et al., 2000), $2H_2$ (Hybler, 1997, Hybler et al., in prep.). In these structures the cation-coordinating oxygen octahedra and tetrahedra form distinct layers are held together by hydrogen bonds. The formula of cronstedtite is usually reported as $(Fe^{2+}_{3-x}\ Fe^{3+}_{x})\ [Si_{2-x}\ Fe^{3+}_{x}\ O_5](OH)_4$ (where $0 < x < 1$). The Fe^{2+} occupies octahedral while Si tetrahedral positions. The excessive Fe which is supposed to be trivalent can partially replace the Si in tetrahedral sites. Presumably a corresponding proportion of trivalent Fe^{3+} in octahedral sites balances the replacement of tetravalent Si by trivalent Fe^{3+} in tetrahedral sites.

The refinement of the relatively rare hexagonal polytype $2H_2$ from Wheal Maudlin, England (WM) and Příbram, Czech Republic (PB) (in a hexagonal cell, a=5.500, c=14.163 Å, space group $P6_3$) revealed an exceptional feature. There are two tetrahedral (T1, T2) and one octahedral sites (M) in the structure of this polytype. The electron density in the site T1 is about 1.4 times larger than in T2 while the T1-O distances are considerably smaller than T2-O ones. The problem with the sizes of the tetrahedra also appeared in the earlier refinement of $2H_2$ polytype (Geiger et al. 1983). The observed phenomenon violates the dependence of the Si/Fe - O distances on the Si/Fe ratio (Inorganic Crystal Structure Database, Bergerhoff 1983).

The electron density in the T1 site could be expressed by occupation of Si and Fe in the ratio 0.41:0.59(WM) and 0.44:0.56 (PB), whereas the electron density of the second tetrahedral site T2 corresponded to the full occupancy by Si. The T1-O distances are reasonable - 1.696 Å (WM), 1.690 Å (PB) (Hybler 1997) in contrast to T2: the average T2-O distance is 1.739 Å (WM, PB) while the typical value for Si-O is ~ 1.62 Å. Crystals were refined to values R(obs)=0.0402 (PB) R(obs)=0.0299 (WM). The problems with the electron density *vs.* T-O distances persisted in all structural models.

One possible explanation of this disaccord is that the the T2 site in cronstedtite-$2H_2$ might be partially vacant. The vacancies, if present, affect the composition as: $(Fe^{2+}_{y0}\ Fe^{3+}_{y1})[(\ Si_{x1}Fe^{3+}_{y1})(\ Si_{x2}Fe^{3+}_{y2}\ \square_{z})]\ [(O_5)(OH)_4]$.

The aim of the study is to determine the exact distribution of Fe^{2+}/Fe^{3+} in the octahedral and occupation of Fe in tetrahedral sites with aid of the anomalous diffraction and DAFS across the FeK edge and confirm or refuse possibility of vacancies in T2. We also intended to test possibility of DAFS studies of real crystals of minerals.

We have performed preliminary calculations to find reflections sensitive to contribution from M, T1 and T2 sites. This has been done by a series of simulated runs of the refinement program of the package JANA98 (Petříček & Dušek, 1998). The occupancies of respective sites were intentionally changed and reflections affected by these changes were selected from the output file by an auxiliary program. These calculations revealed existence of many reflections sensitive entirely to M site. On the other hand, the reflections sensitive to T1 or T2 sites were always simultaneously sensitive to other sites. There were two reflections (1 1 10 and 205) sensitive merely to oxygen atoms.

One of previously studied specimens, an acicular crystal of hexagonal cross-section from Příbram of size 0.080 ×0.089×0.638 mm^3 (PB specimen) was mounted on the seven circle diffractometer at the BM02 beamline. After the centering of the crystal and determination of the orientation matrix, the DAFS scans of 17 reflections were taken. The following reflections were selected for this study: 1 1 10, 115, 026, 306, 3 -1 0, 205, -1 5 0, 114, 4 -2 0, 140, 2 2 10, 038, 020, 220, 106, 200, and 4 -2 5. The DAFS scans of 038 and 020 reflections were remeasured in equivalent positions (the 038 reflection twice) because of presence of "glitches" affecting the profile. Each reflections was recentered at three energies prior to the DAFS scan. The conditions were following: Energy range from 6.900 to 7.300 keV, step 0.08 keV in ranges 6.900-7.050 and 7.180-7.300 keV, 0.001 keV in the range 7.050-7.180 keV. Simultaneously the fluorescence signal was measured at each energy point.

The last day, an anomalous diffraction study of another layer silicate, iron bearing mica celladonite-$2M_1$ from Mt.Ruker, Antarctica was performed. The formula of celladonite is $K_2(Fe_3\ Mg)(Si_{7.5}Al_{0.5})O_{20}(OH)_4$, lattice parameters are: a=5.252, b=9.105, c=20.06 Å, β=95.12space group is *C*2/*c*. The study comprised registration of diffraction profiles of selected reflections at 7.00, 7.05, 7.08, 7.10, and 7.20 keV. The following reflections were registered: 0 2 15, 0 0 8, 0 0 10, 0 0 12, 0 0 14, 0 0 16, 2 0 10, 0 2 10, 0 4 15, 1 5 11, 1 3 12, 1 3 10, 2 2 13, 2 2 12, 2 2 11, 1 1 12, 1 1 17, 3 1 12, 3 1 10, -1 1 18, 2 4 14, 2 4 13, 2 4 12, 4 2 12, 2 2 14, 2 2 16, and 0 0 18.

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