| | Experiment title: Magnetism and crystal-chemistry of cronstedtite, a terrestrial and extra-terrestrial iron rich sheet silicate | Experiment number: HE-3013 |
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| **Beamline**: ID12 | **Date of experiment**: from: 08/07/2009 to: 14/07/2009 | **Date of report**: 21/07/2010 |
| **Shifts:** 18 | **Local contact(s)**: Andreï Rogalev, Alevtina Smekhova, Fabrice Wilhelm | *Received at ESRF:* |

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## Report:

Cronstedtite is a sheet silicate containing up to 60 wt% iron, and which structure consists in the stacking of layers built from a plane of $(Fe^{III},Si)O_4$ tetrahedra (T) and a plane of $(Fe^{II},Fe^{III})O_2(OH)_4$ octahedra (O). This mineral makes up to 50% of the mass of CM2 type carbonaceous chondrites, which are among the most pristine samples from the Solar System. In these extra-terrestrial objects, this mineral testifies of early (>3 Gy) interactions between water and rocks that occurred mostly on the parent body of the meteorites (Zolensky et al., 2008). The determination of the conditions of aqueous alteration would yield a better understanding of the formation of small Solar System bodies that might have significantly contributed to the terrestrial water budget, as reviewed by Albarède (2009). The mixed valence of iron in cronstedtite makes it a potential marker of the redox power of the growth fluid (Kogure et al., 2002; Zega et al., 2003). Deciphering the crystal-chemistry of iron in cronstedtite by means of XMCD at the Fe K-edge, which is our main goal, would thus bring essential clues to the conditions of formation of the parent body of these meteorites. For achieving this goal, we performed XMCD experiments on a meteorite as well as on reference minerals, for which we measured both the angular dependence of XMCD and XLD at the Fe K-edge, in order to be able to take the crystallographic and magnetic anisotropy into account in the determination of the valence and site occupancy of iron, using ligand field multiplet calculations at the pre-edge of the Fe K-edge.
Reference cronstedtite samples consist in two plate-like crystals of cronstedtite having their c axis perpendicular to the surface of the samples. Their structural formula are ${}^{O}\left[Fe^{2+}_{2.22}Fe^{3+}_{0.78}\right]^{T}\left[Si_{1.22}Fe^{3+}_{0.78}\right]O_5(OH)_4$ (Kisbanya sample) and ${}^{O}\left[Fe^{2+}_{2.16}Fe^{3+}_{0.84}\right]^{T}\left[Si_{1.16}Fe^{3+}_{0.84}\right]O_5(OH)_4$ (Salsigne sample). Prior to the experiments, a series of XAS scans at the Fe K-edge were performed on a polycrystalline sample of cronstedtite, using circularly polarized light, in order to check for potential radiation damages. No modification of the spectra was observed after performing 10 scans of about 500 s each, demonstrating that no significant radiation damage occurred.
We measured the X-ray Linear Dichroism of Kisbanya and Salsigne samples at the Fe K-edge, at room temperature, and for 4 angles between the direction of the x-ray beam and the c axis: 0°, 22.5°, 45° and 67.5°. The two crystals yield a strong dichroism that reaches 20% of the isotropic absorption at the edge, and 15% at the pre-edge (Figure 1). The angular dependence of the XLD explored during this experiment will yield information about both the electric dipole and quadrupole contributions to the x-ray absorption spectra.

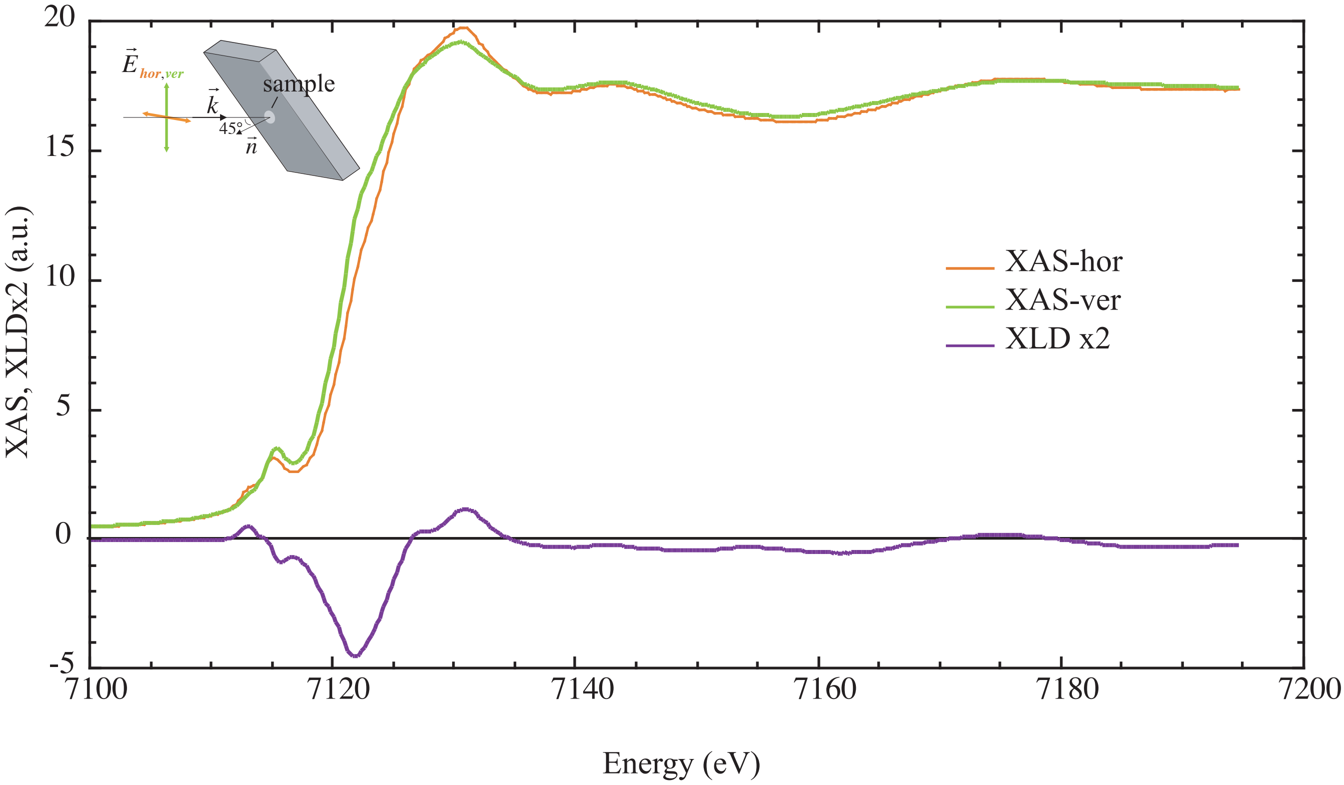


Figure 1: Fe K-edge XAS and XLD spectra of cronstedtite from Kisbanya, room temperature. The c axis is along the surface normal, and at 45° from k.

We measured the XAS and XMCD spectra of the same two samples at the Fe K-edge, at a temperature of about 10 K and using a magnetic induction of ±6 T. The XAS and XMCD spectra were recorded at two or three angles of both the x-ray beam and applied magnetic field, with the c axis: 0°, 25° (Salsigne sample only) and 49°. A marked angular dependence of XAS and XMCD at the pre-edge is observed. The smallest, yet sizeable, signal is obtained for the magnetic field applied parallel to the c axis, which is consistent with bulk magnetometry, which has shown that the induced magnetization is about 5 times lower than that acquired when **B**⊥c . Apart from differences in amplitude, the spectra obtained for Salsigne sample with a magnetic field applied at 25° or 49° to the c axis are similar, with, in the pre-edge region, the succession of a large negative feature at 7113.0 eV, a small positive one around 7114.7 eV, and a negative one at 7115.7 eV. The spectra obtained for the magnetic field applied parallel to c (Salsigne and Kisbanya samples) does not contain the large negative peak at 7713.0 eV but a small positive one instead, at the same energy. These results will bring new insights into the microscopic origin of the strong magnetic anistropy of cronstedtite.
The XAS and XMCD spectra of Murchison meteorite at the Fe K-edge were recorded on a pressed pellet containing about half weight of meteorite powder and half boron nitride. The normal to the surface of the pellet was oriented at 56° from the applied magnetic field. A sizeable XMCD signal was measured, bearing three distinctive features, analogous to those observed in Salsigne sample (Figure 2).

Next, reproducing the XMCD signal of the powder meteorite sample using XMCD spectra of crystals in different orientations will be one of our task. Ligand field mutiplet calculations at the pre-edge of the XMCD spectra of the meteorite and the references (Arrio et al., 2000), using the crystallographic information gained by XLD and the angular dependence of the XMCD of reference crystals, will then allow for the attribution of the XMCD peaks and are expected to yield determination of both the iron valence and site distribution in meteoritic cronstedtite.

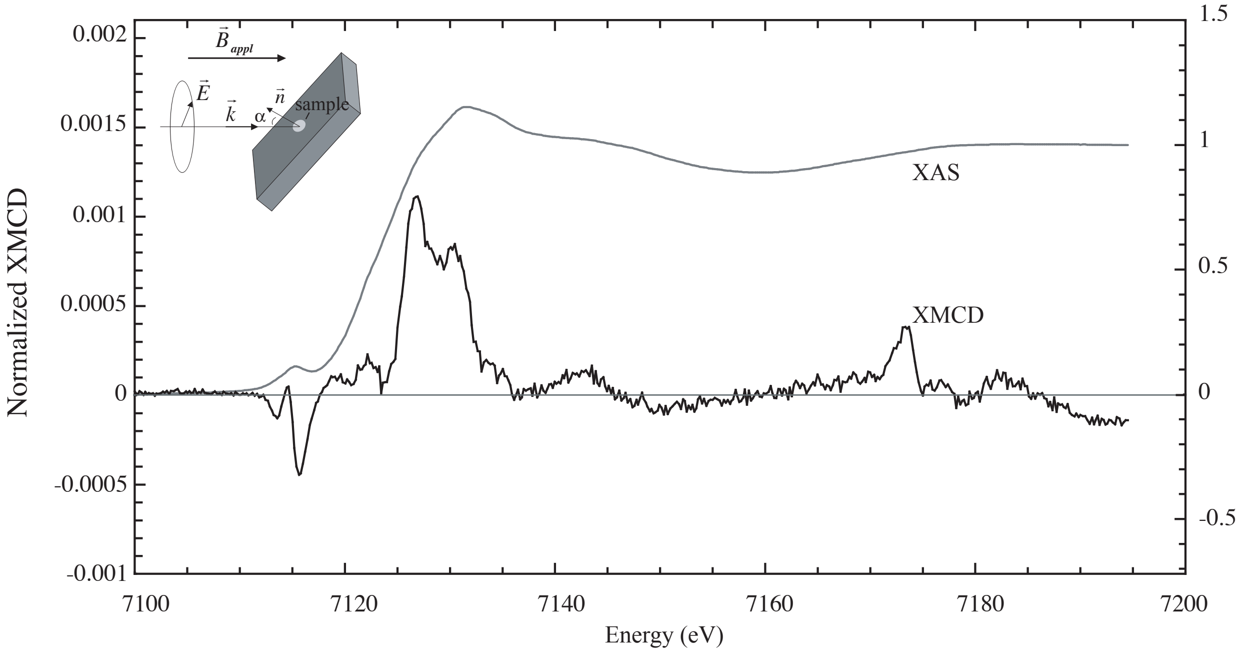


Figure 2: Fe K-edge XAS and XMCD spectra of Murchison meteorite (α=56°). T=10K, B=±6T.

**References**


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