

## The redox state of iron in primitive, aqueously altered, and thermally metamorphosed chondrites by XANES.

A. Garenne<sup>1</sup>, P. Beck<sup>1</sup>, G. Montes-Hernandez<sup>2</sup>, L. Bonal<sup>1</sup>, E. Quirico<sup>1</sup>, B. Schmitt<sup>1</sup>, O. Proux<sup>3</sup>, JL Hazemann<sup>4</sup>, <sup>1</sup>UJF-Grenoble 1 / CNRS-INSU, Institut de Planétologie et d'Astrophysique de Grenoble (IPAG) UMR 5274, Grenoble, F-38041, France, alexandre.garenne@obs.ujf-grenoble.fr. <sup>2</sup>UJF-Grenoble 1 / CNRS-INSU, Institut des Sciences de la Terre (ISTerre), Grenoble, France. <sup>3</sup>Observatoire des Sciences de l'Univers de Grenoble (OSUG) CNRS UMS 832, 414 rue de la piscine 38400 Saint Martin d'Hères, France. <sup>4</sup>Institut Néel, 25 av. des Martyrs, 38042, Grenoble, France.

**Introduction:** Chondrites are primitive meteorites originating from undifferentiated asteroids. Their mineralogy record presolar, nebular and asteroidal histories. On their parent body, they may have experienced important physico-chemical modifications through geological events, such as thermal metamorphism and aqueous alteration, transforming primary minerals into secondary phases [1-3].

Iron is a major chemical element in planetary materials and its various valence states can be used to fingerprint geological processes [4]. Iron in fresh meteorites can exist as Fe<sup>0</sup> in Fe-Ni metal, Fe<sup>2+</sup> in silicates and sulfides and Fe<sup>3+</sup> in phyllosilicates and magnetite. During fluid/rock interaction, iron as Fe<sup>0</sup> and Fe<sup>2+</sup> are transformed into Fe<sup>3+</sup>-rich phases. In the other hand, during thermal events, a reduction of iron is likely to occur.

X-ray Absorption Near-Edge Spectroscopy (XANES) is a very sensitive method to constrain redox states and local coordination environment of iron in natural materials including meteorites [5]. This valence state can also be used to follow the origin of D/H fractionation in aqueously altered meteorites and ultimately of terrestrial water [6].

In the present study, we performed XANES on 90 chondrites belonging to 6 different families, and on 10 terrestrial standards with well-known redox state. Clear variations in the redox state of iron and its crystallographic environment are observed and the Fe<sup>3+</sup>/Fe<sup>total</sup> ratio could be quantified. These results are discussed in the light of parent body processes.

**Methods:** The bulk redox state of iron was determined by synchrotron K-edge Fe-XANES at beamline BM30b (CRG-FAME) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Typically 5 mg of meteorites were ground in a mortar before being mixed with 45 mg of boron nitride powder and subsequently pressed into pellets of 5 mm diameter. The spectra were measured in transmission mode from 7004 eV to 7385 eV with energy steps of 0.2 eV near the K-edge and a resolution around 0.35 eV in the farthest part. The beam size was around 300 x 100 μm<sup>2</sup> (HxV, FWHM). The beamline energy was calibrated by setting the maximum of the derivative of a Fe<sup>0</sup> foil spectrum to 7112 eV. A minimum of 3 spectra were measured for each meteorite at different positions on

the pellet in order to probe the inhomogeneity and variability of the preparation.

For each sample, an average spectrum was calculated before performing a baseline correction and normalization (0 at the minimum pre-edge intensity and 1 at the average post-edge intensity).

**Results and discussion:** Figure 1 presents 5 “typical” spectra of 5 different families of chondrites (CI, CM, CR, CV and LL). This figure shows the variability of the pre-edge intensity, of the edge position and of the energy of the first maximum for these different chondrites. Position, intensity and spectral shape can be used to constrain the Fe state. Also, following Wilke et al. (2001) [4], the pre-edge peak was analysed to quantify the Fe<sup>3+</sup>/Fe<sup>total</sup> ratio. After baseline subtraction, the energy of the pre-edge centroid was calculated as well as its integrated intensity (Fig. 2 and Fig. 3).

The valence state between falls and finds among CM chondrites is compared on Fig. 2. It allows to assess the possible consequences/impact of terrestrial residence. When comparing the pre-edge features of 25 Antarctica CM chondrites and 11 fall CM chondrites, an overlap is observed rather than an increased oxidation for the finds. This implies similar Fe<sup>3+</sup>/Fe<sup>total</sup> ratio for all CM finds and falls. Thus, terrestrial oxidation did not significantly modify the redox state of Fe in Antarctic finds.

Figure 3 presents the energy at maximum intensity for the different groups of chondrites. This diagram reveals a clear dichotomy between chondrites having experienced hydrothermal alteration (CR, CI, CM) and thermal metamorphism (CV, LL). Some exceptions are present within each family of meteorites. Among CMs, PCA 02010 and PCA 02012 are distinct and present a reduced mineralogy (Fig. 3). Both have been considered as thermally metamorphosed [7-8]. Among CRs, RBT 04133 and GRA 06100 appears different. Both have been considered as anomalous in comparison to other CRs, and evidence of thermal metamorphism has been found for GRA 06100 [9-11].

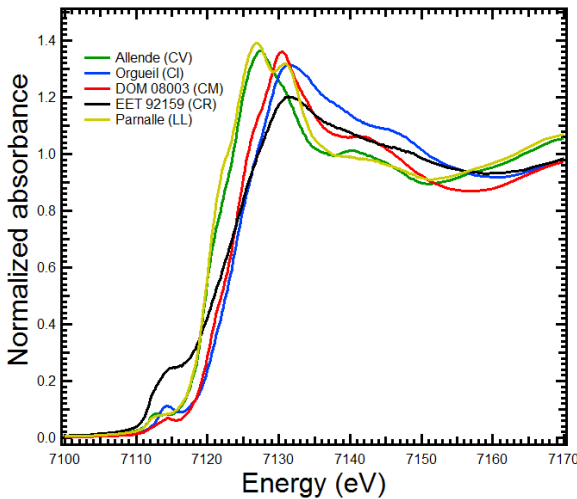
Kaba appears different from the other CVs, by a significant amount of Fe<sup>3+</sup>. In our dataset, it is the only relatively low metamorphosed (3.1) oxidised CV

chondrite [12]. In the case of LL chondrites, MET 00452 appears unusual with a high-amount of  $\text{Fe}^{3+}$ .

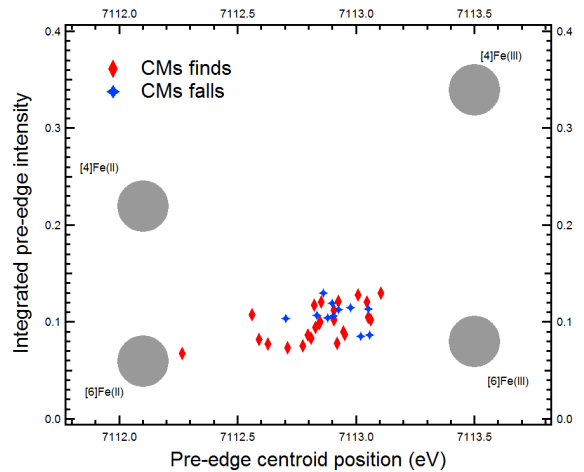
**Conclusion:** Fe K-edge XANES is an efficient method to characterize the redox state of iron atoms in chondritic meteorites. Our dataset reveals a clear dichotomy between the aqueously altered and the thermally processed meteorites. This dichotomy might be related to the thermal buffer effect of water phase transitions on the parent body. The relation with other geochemical indicator is currently under deep investigation (H and O isotopes).

**References:**

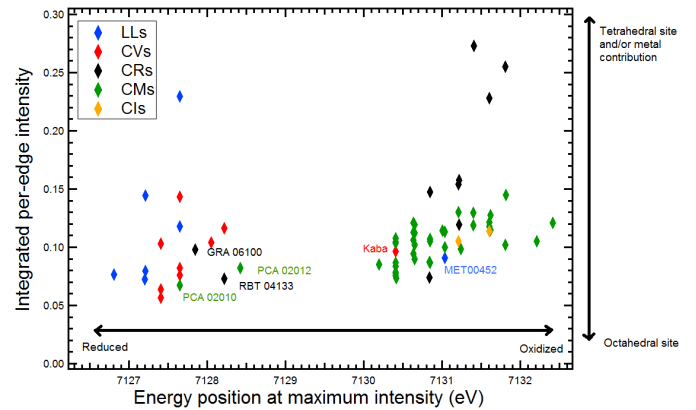
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**Fig. 1 :** XANES spectra of 5 types of chondrites



**Fig. 2 :** The pre-edge feature of CMs (finds and falls) plotted in the Wilke et al. (2001) diagram.



**Fig. 3 :** Maximum energy position of K-edge for the different family of chondrites