MAPPING THE IRON DISTRIBUTION AND VALENCE STATE IN PRIMITIVE METEORITES BY SYNCHROTRON MOSSBAUER SPECTROSCOPY.
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Introduction: Chondritic meteorites contain, at the micron-scale, heterogeneous iron-bearing phases with the 3 oxidation states, that are thus not in thermodynamical equilibrium. The ubiquity of iron makes it a tracer of initial condensation, recrystallization. Furthermore, during and after their accretion, thermal metamorphism and aqueous alteration triggered a partial textural and chemical recrystallization. As a consequence the initial state of the different components are poorly known. In this context, the study of the Fe valence state and mineralogy is of crucial importance. First because the valence state is very sensitive to the redox conditions that prevailed during the formation of iron-bearing phases and second because aqueous alteration efficiently changes this valence state. But if a detailed mineralogy of iron is the key to understand the formation and evolution of small bodies, the origin of its heterogeneity is hardly debated and lacks from a comprehensive mapping at the sample scale. Here, we use the unique Synchrotron Mossbauer Spectroscopy (SMS) developed at the Advanced Photon Source to produce these maps. This development will be crucial to analyze returned samples from the next space missions (Hayabusa 2 and Osiris Rex).

Analytical methods: The issue with iron as a chemical proxy is analytical in essence. First, chemical analysis of minerals hardly provides a quantification of the valence state because a fraction of silicates are amorphous or poorly crystallized and also because some of these minerals can accept both divalent and trivalent iron cations. Second, other spectroscopic methods such as XANES and STXM may in principle be used to image the valence state of iron at the nanoscale. However, these methods require complicated cross calibration and are poorly adapted to quantify and characterize metallic phases.

In this context, Synchrotron-based Nuclear Resonant Scattering techniques, such as SMS are much more relevant but were hardly available until recently. These methods involve nuclear resonant transitions of Mössbauer nuclei excited by a synchrotron radiation. These techniques are sensitive to the chemical environment of Mössbauer isotopes. The Mössbauer microscopy developed at Sector 3ID allows imaging samples at the micrometer spatial resolution. This microscopy collects coherent nuclear resonant scattering signal and yields information based on hyperfine interactions of the nuclei in the solid. It leads to quantitative and absolute information about the magnetic, valence and spin state of the system, and local atomic symmetry for all the possible valence state of iron. In other words, this microscopy alleviates all the caveats of other available methods. Some proof-of-principle experiments were carried out employing the instruments at beamline 3-ID at the Advanced Photon Source (APS). Excellent signal-to-noise ratio was achieved, a resolution to 5 microns has been achieved, and sub-micrometer is envisioned.

Results: In an effort to develop this method to characterize meteorite samples, we mapped six samples of well-known carbonaceous chondrites (Orgueil, CI; Paris, CM3.0; Murchison, CM2.5; QUE 97990, CM2.0; PCA 91008, heated CM). The area scanned are as large as a millimeter square, consisting of 40000 data points. Maps of Fe distribution were first collected and then local analyses were performed. This spatial mapping enables to locate region of interest for further analysis. In the case of PCA 91008, it was possible to distinguish matrix silicates (Fig. 1, green spectra) from a large oxide grain with probable hyperfine splitting (Fig. 1, blue spectra). When comparing measurement obtained on matrix area from the series of CM, similarities are found among CM chondrites (Murchison, QUE 97990, Paris). The SMS spectra of PCA91008 matrix seems distinct (counts minima at 50 and 80 ns), possibly related to the thermal process experienced by this sample. Overall all SMS spectra obtained on these suite of CM are in agreement with silicates (including phyllosilicates) being the major host of iron. On the contrary, the spectra of Orgueil is clearly different with a lot of structure in agreement with Fe being majorly present within magnetite. Detailed fitting of this data is underprocess and should reveal the fine crystallographic environment of iron in this suite of samples.

Figure 1 (left): Typical SMS spectra of olivine (green), and magnetite, (blue).

Figure 2 (right): Typical SMS spectra of the matrices of studied meteorites with some reference spectra of single minerals. The spectral variations reflects the relative proportions of iron-bearing minerals in these matrices.