

Visualizing Iron Oxidation State in a Possible Cometary Clast from Carbonaceous Meteorite LAP 02342

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Meteorites originate from asteroids, which formed by accretion of various clasts, dust, and ice present in the solar nebula. Meteoriticists learn more about these ancient nebular components by studying primitive meteorites that do not contain evidence for alteration by asteroidal processing mechanisms (e.g., thermal metamorphism or saturation by aqueous fluid derived from melted ice). The carbonaceous chondrite LAP 02342 belongs to the CR group, one of the most primitive classes of carbonaceous meteorites. One of the carbonaceous clasts in this sample is unusual, in that it contains ~70% C and a higher presolar grain abundance than the surrounding fine-grained matrix material [1]. Similar characteristics are found in ultracarbonaceous Antarctic micrometeorites, which are thought to originate from comets [2].

Previous STEM observation of this carbonaceous clast indicates the presence of extremely primitive components, such as GEMS grains, but also evidence of aqueous alteration, like calcite and Ca sulfates [3]. Thus, the degree of fluid processing in this particular clast is highly heterogeneous and probably related to the local ice and carbon abundance. Since chemical homogenization develops as a result of processing on the parent asteroid, the distribution of oxidation states in Fe-bearing minerals can be used to visualize the redox conditions of the fluids that altered a given clast.

Four TEM lamellae were prepared from LAP 02342 with an FEI Nova 600 FIB-SEM—Two lamellae from within the carbonaceous clast; one lamella from a region of the clast that is unusually depleted in ¹⁶O; one lamella from nearby fine-grained matrix outside the clast. Multiple Fe X-ray absorption images (ranging from 695–740 eV at a variable energy step as small as 0.2 eV at peak absorption) were acquired with the scanning-transmission X-ray microscope on beamline 5.3.2.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory. Peak X-ray absorption in this energy range is shifted depending on the oxidation state of Fe (707.8 eV for Fe²⁺ to 709.5 eV for Fe³⁺) [4]. After image registration and calibration of background intensity, X-ray absorption near-edge structure (XANES) spectra can be extracted from the hyperspectral image stack by reading pixel intensity along the energy axis. For each spectrum that contains an Fe absorption edge, the peak intensity is fit with three fixed Gaussian peaks (707.8 eV, 709.5 eV, and 711.6 eV), allowing peak intensity *I* and width σ to vary. Following the method of Van Aken [4], the oxidation state of Fe, as quantified by Fe³⁺/ΣFe, is proportional to $I_{707.8}/\Sigma I$:

$$\text{Fe}^{3+}/\Sigma\text{Fe} = A_{\text{fit}}(I_{707.8}/\Sigma I) + B_{\text{fit}}$$

The calibration parameters A_{fit} and B_{fit} are determined from endmember representative spectra that match known oxidation states in silicate minerals. We converted these values to average Fe valence by $\text{Fe}^{3+}/\Sigma\text{Fe} + 2$ (Figure 1). Metal grains were identified and removed by their broader XANES peak ($\sigma > \sim 1.0$). The remaining Fe-bearing minerals are various sulfides (Fe²⁺), oxides (Fe³⁺ and mixed valence), and silicates (mixed valence).

Fine-grained material outside the carbonaceous clast is dominated by Fe³⁺-bearing minerals (Figure 1),

consistent with oxidation of initially-reduced primary components, due to low levels of aqueous alteration. In contrast, material within the clast shows a much broader range of Fe valence, with a prominent abundance of minerals with a valency of $\text{Fe}^{2.8+}$ (Figure 1). This broader valence distribution indicates that the aqueous fluids that altered the clast was not as oxidizing as the carbonaceous clast as in the surrounding meteorite matrix, indicating that much of the fluid was generated from within the clast itself. The ^{16}O -depleted region, which is located on the border of the carbonaceous clast, has a more complicated distribution of Fe valence, in part because it contains more sulfide grains than any of the other FIB lamellae. However, the prevalence of Fe^{3+} -bearing material in this lamella may suggest some infiltration by and reaction with asteroidal water that did not penetrate further into the clast.

References:

- [1] CE Moyano-Camero *et al*, Lunar and Planetary Science Conference XLVII (2016), abstract 2537.
 [2] E Dobrică *et al*, *Geochimica et Cosmochimica Acta* **76** (2012), p. 68.
 [3] RM Stroud *et al*, 79th Annual Meeting of the Meteoritical Society (2016), abstract 6360.
 [4] PA Van Aken & B Liebscher, *Physics and Chemistry of Minerals* **29** (2002), p. 188.
 [5] The authors acknowledge funding from the NASA Origins and Emerging Worlds Programs.

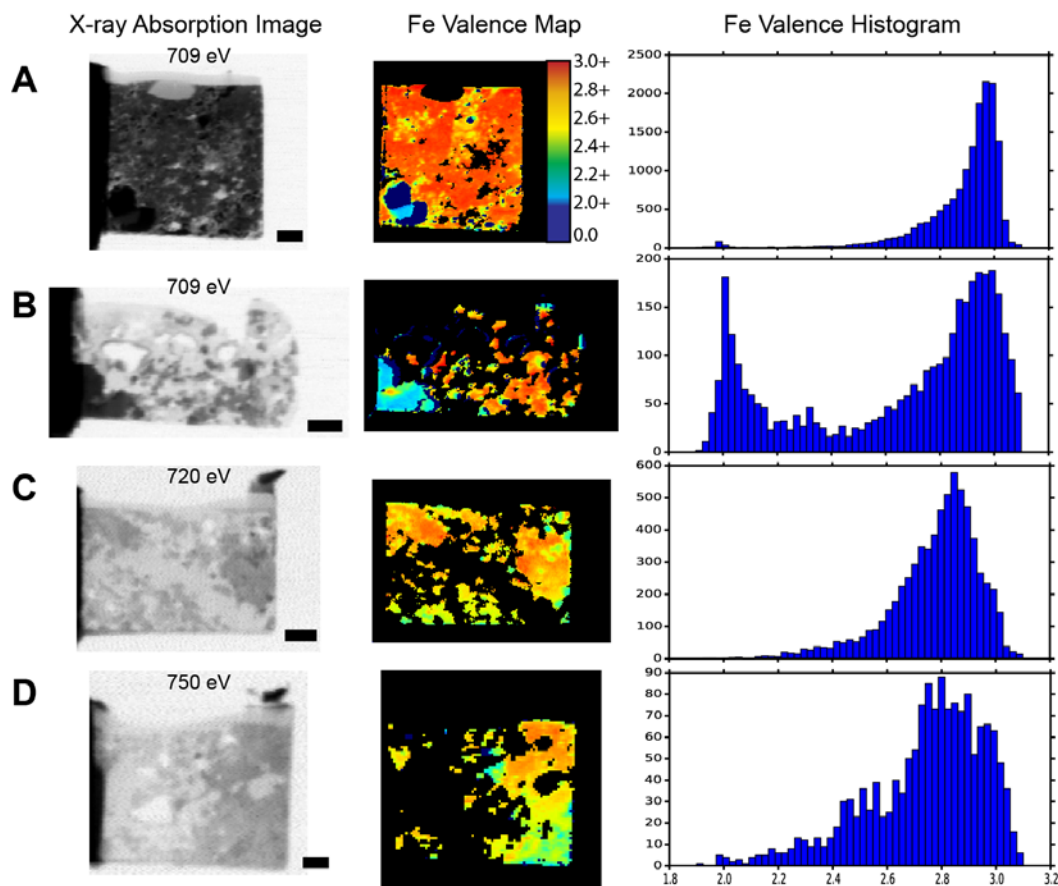


Figure 1. X-ray absorption images, Fe valence maps, and histograms of Fe valence in FIB lamellae from meteorite LAP 02342. (A) Fine-grained matrix material. (B) ^{16}O -depleted region on the edge of the carbonaceous clast. (C-D) Regions from the interior of the carbonaceous clast. Scale bars are 1 μm .