

# Meteorite Atmospheric Entry Reproduced in Plasmatron II: Iron Oxidation State Change Probed by Xanes

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## Abstract

Heating experiments are one of the approaches used to investigate those changes experienced by meteoroids during their atmospheric entry. In this work, we are going to present the preliminary results from scanning electron microscopy and X-ray Adsorption Spectroscopy, in order to quantify the oxidation state of Fe produced in the VKI Plasmatron.

## 1. Introduction

Atmospheric entry of meteoroids is a complex process that involves melting, evaporation, and redox variations of the original material. Meteorites recovered on the ground are used for constraining the composition and the history of the parent bodies, but atmospheric entry can induce significant changes in microstructures and chemistry that may bias our interpretation. Ablation and heating effects are generally investigated by numerical modeling (e.g., [1]) or by heating experiments, which are however far from reaching the conditions experienced by meteoroids (e.g., [2,3]). Here we present preliminary results from scanning electron microscopy (SEM) and X-ray Adsorption Spectroscopy (XANES), aimed at determining the oxidation state of Fe, on material produced during the first experiments in the VKI Plasmatron. This instrument creates a steady state plasma flow up to 22 mbar pressure, over 10000 K temperature, with a potential heat flux of 16 MW/m<sup>2</sup>, and is commonly used for testing spacecraft heat shields. It represents, therefore, a good approximation of the conditions encountered by any material during the atmospheric entry.

## 2. Methods

Cylinders of ca. 1 cm diameter and 2 cm length were drilled from a specimen of alkali basalt that was chosen as a terrestrial analogue for meteorites. Samples were jacketed in cork or graphite for two series of experiments. Several experimental conditions have been tested at the VKI, varying the pressure (15-220 mbar) and the exposure time (21-51s), keeping constant the heat flux to 3MW/m<sup>2</sup>. After the experiment, droplets of melt flowing over the sample holder and the sample itself (cut in two halves, normal to the flow) were analyzed with  $\mu$ -XRF and SEM, equipped with EDS detector, at the VUB.

Fe K-edge X-ray Absorption Spectroscopy XANES and EXAFS data have been collected at beamline BM08 of the ESRF storage ring (Grenoble, F). Analysis of the pre-edge peak data has been done according to the method reported by [4] on the result of an ablation experiment and on a sample of the starting basalt ground to powder.

## 3. Results

The molten sample clearly shows a change in the bulk chemical composition, with respect to the original material, with a strong depletion in alkali and generally highly volatile elements and an apparent enrichment in refractory elements. Ejection of material is less obvious, but droplets of melt were observed to flow radially on the surface of the sample holder. At the transition between the melt coating, and the unaffected portion of the sample, melt spherules have formed.

Melt spherules have formed and represent the experimental analogue of ablation spherules from meteoroids. The melt exhibits schlieren and flow fabric. Tiny vesicles seem to be coated by iron oxides.

The XAS spectrum of the starting basalt displays values of the edge energy typical of trivalent Fe. As the starting material is a multiphase mixture, it is difficult to determine accurately the Fe oxidation state by means of the pre-edge peak centroid in the absence of constraints on the Fe content in the constituting phases. However, comparison of the pre-edge peak centroid with those of Fe model compounds provides a determination of the  $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$  ratio close to  $0.75 \pm 0.15$ . The edge energy of the melt sample is consistent with the presence of  $\text{Fe}^{2+}$ . Pre-edge peak data allow an accurate evaluation of a  $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$  ratio close to  $0.19 \pm 0.05$ .

## 4. Conclusions

Melting experiments with plasmatron offer a broad range of applications in planetary science, from investigation of meteorite fusion crust and micrometeorite formation to the evolution of impact ejecta. In these preliminary experiments, the change in bulk composition in the melt supports the hypothesis of alkali vaporization during atmospheric entry, based on studies of cosmic spherules (e.g., [5, 6]).

XAS data provide reliable determination of the Fe oxidation state. In this case, the starting material (with mostly trivalent Fe) upon melting has been reduced producing a glass with an  $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$  ratio equal to  $0.19 \pm 0.05$ . The iron reduction could be possibly caused by the extremely high temperature of the experiment. In order to obtain a complete characterization of the oxidation state changes due to atmospheric entry of extraterrestrial material, further analyses of the material produced in experiments performed using equilibrated ordinary chondrites (containing mostly divalent and metallic iron) as starting material are planned.

## References

- [1] Love S.G. and Brownlee D.E. 1991. *Icarus* 89:26-43.
- [2] Greshake A. et al. 1998. *Meteoritics & Planetary Science* 33:267-290.
- [3] Toppani A., et al. 2001. *Meteoritics & Planetary Science* 36:1377-1396.
- [4] Wilke et al., 2001 *American Mineralogist*, 86, 714-730; Giuli et al., 2002, *Geochimica et Cosmochimica Acta*, 66, 4347-4353; Giuli et al., 2011, *American mineralogist*, 96, 631-636.
- [5] Cordier C. et al. 2011. *Geochimica et Cosmochimica Acta* 75:5203-5218.
- [6] Rudraswami N.G. et al. 2012. *Geochimica et Cosmochimica Acta* 99:110-127.