

Redox reactions in meteoroid atmospheric entry reproduced in plasma experiments

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Abstract

Atmospheric entry of meteoroids has been reproduced in a high enthalpy facility, with basalt as a meteorite analog and an ordinary chondrite, to investigate the redox reactions triggered by interaction between the newly formed melt and the atmospheric gases under high temperature. The resulting material has been analyzed by electron microprobe, LA-ICP-MS, and X-ray Adsorption Spectroscopy (the latter to determine the oxidation state of Fe). The observations on the experimentally produced melt perfectly match those from natural meteorite fusion crusts.

1. Introduction

Melting, evaporation, ablation, and redox variations occurring during the atmospheric entry of extraterrestrial material may affect microstructures of and induced chemical changes in the recovered meteorites and cosmic spherules, inducing a bias in our interpretation. This problem is generally approached by numerical modeling (e.g., [1]) or heating experiments, which however are far from reaching the conditions experienced by meteoroids (e.g., [2,3]). In the VKI Plasmatron, an induction-heated plasma wind tunnel creates a steady state plasma flow up to 2200 Pa pressure, 10,000 K temperature, and a potential heat flux of 16 MW/m². It operates with N₂, CO₂, and Ar as plasma gases, is commonly used for testing spacecraft heat shields and, therefore, represents a good approximation of the conditions encountered by any material during the atmospheric entry. Recently, a plasma tube has been used for similar experiments but with a different set-up [4]. Here we present the results of a series of experiments, testing different material and experimental conditions, which produced features that are very close to those observed in natural samples [5,6] and that shed light on the environmental

conditions and the redox reactions occurring during the process.

2. Methods

Cylinders of ca. 1 cm diameter and 2 cm length were drilled from a specimen of a coarse-grained, alkali- and water-rich basalt, specifically selected to investigate volatilization of light elements, and used here as analog for meteorites, and from a sample of the H5 El Hamammi ordinary chondrite meteorite. Two types of sample holders, in cork and graphite, were used, as they have different thermal properties. Several experimental conditions have been tested (Table 1). The recovered material after the experiments has been embedded in epoxy, cut in two halves, and mechanically polished for detailed characterization. Preliminary analyses include micro-XRF and SEM, equipped with EDS detector, at the VUB, followed by EMPA at the NHM-Vienna, LA-ICP-MS at Ghent University (Belgium), and Fe K-edge X-ray Absorption Spectroscopy XANES and EXAFS at beamline BM08 of the ESRF storage ring in Grenoble (France) according to the method described in [7-9].

Table 1: Melting experiments

Exp no.	Sample holder	Heat flux (MW/m ²)	P (Pa)	Duration (s)
B 1.1	cork	3.04	1500	41
B 1.2	graph	3.12	1500	21
B 2.1	cork	1.01	20000	12
OC 2.1	cork	1.01	20000	21

3. Results

During the experiment, fragments of unmelted basalt were ejected and droplets of melt were observed to

flow radially on the surface of the sample holder. The recovered quenched material exhibits a strong depletion in alkali and generally highly volatile elements, with an apparent enrichment in refractory elements. Spectroscopic analysis during the experiments shows that Na, K, Mg, and Ca, ordered for decreasing concentration, are ablated. On a second order, Fe and Ti are also volatilized. The surface temperature, measured with a pyrometer and calculated with the Planck curve, was ca. 2100-2300 K. Despite the rapid cooling to ambient temperature, evidence of devitrification is noted in all samples. The melt exhibits *schlieren* and flow fabric. Tiny vesicles are coated by iron oxides. Locally, melt spherules have formed, representing the experimental analog of meteoroid ablation spherules.

The resulting melt is clearly depleted in the alkali metals and significantly enriched in Ti and Mg (both refractory elements), but plotting the elements according to their volatility does not reveal any clear trends. The spherules are enriched in SiO_2 with respect to the original basalt. In experiments using a graphite sample holder, at the contact with the graphite some Fe-Si metal alloys have crystallized, and the material exhibits a further enrichment in Ni (20 times higher than the preserved basalt) and Cr. In both experiments, the melt appears to be enriched in the REE (normalized on CI) and in the moderately siderophile elements with respect to the preserved basalt. The XAS spectrum of the starting basalt displays values of the edge energy that are 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, by comparison with values of Fe model compounds, $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio is evaluated close to 0.75 ± 0.15 . The edge energy of the melt sample is consistent with the presence of 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 ± 0.05 .

The melt resulting from experiments on the ordinary chondrite presents widespread vesiculation and is internally largely crystallized. Similar to natural samples [5,6], the transition between the unaffected material and the melt is marked by fractures minerals and by trails of metal-rich inclusions along. The crystallized phase that dominates in the melt is olivine, sub-euhedral to skeletal, including hopper shape [10]. Locally, rounded olivine fragments are preserved, suggesting incipient melting. New olivine has

overgrown on these fragments, exhibiting a progressive change in composition towards more Fe-rich terms, after an initial apparent enrichment in Mg, exactly as in natural samples [6]. Locally, new olivine is enriched in Ca, Cr, and Ni (the latter is almost absent in the original olivine), and depleted in Mn. In the groundmass, opaque phases crystallized, either skeletal (magnetite) or botryoidal (Fe, Ni, and related oxides). The melt is enriched in TiO_2 , FeO , and Cr_2O_3 , all relatively highly siderophile. The rare earth elements are also enriched in the melt with respect to the bulk meteorite.

4. Conclusions

The sample holder has a strong influence on the redox environment recorded by the final product. Interestingly, all experiments, independently from the used jacket, show enrichment of the melt in moderately siderophile elements, whose partitioning in the melt depends on the fO_2 [11]. The experiment with the ordinary chondrite has reproduced the same features observed in a natural meteorite fusion crust coating a similar type of meteorite. In summary, both XANES and microanalysis suggest possible reduction rather than oxidation of the quenched melt, but in a dynamic environment with complex redox reactions, leading to a non-unequivocal interpretation of the process.

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