

Iron and Osmium Isotopes from Stony Micrometeorites and Implications for the Os Budget of the Ocean. C. Chen¹, S. Taylor², and M. Sharma¹, ¹Dartmouth College, Department of Earth Sciences, Hanover, NH 03755, Cynthia.Chen@dartmouth.edu, Mukul.Sharma@dartmouth.edu, ²Cold Regions Research and Engineering Laboratory, 72 Lyme Road, Hanover, NH 03755 Susan.Taylor@erdc.usace.army.mil.

Introduction: The Os isotopic composition of seawater and continental crust require that between 20 to 30% Os is unradiogenic and potentially derived from either hydrothermal alteration of mid-ocean ridge basalts or from dissolution of cosmic dust [1]. Our recent results evaluating the Os flux from mid-ocean ridges indicate that ridge crest hot springs and off-ridge warm/cold springs are not a significant source of Os dissolved in the oceans. Thus, most Os appears to be derived from the dissolution of cosmic dust in seawater. The present study examines the mechanism through which Os might be getting dissolved in seawater by measuring Os and Fe concentrations and Fe isotopic composition of the most common silicate spherules, which appear to have undergone melting.

Most micrometeorites experience significant mass loss due to heating during entry through the atmosphere [2]. The volatilization of micrometeorites is not completely understood and experimental details of volatilization mechanisms are lacking at present. There are different models on how micrometeorites lose material during entry. Material might be lost as a series of metal nuggets or a continuous vapor. The manner in which loss occurs is controlled by the velocity and angle at which the micrometeorite enters the atmosphere which would affect the heating history of the micrometeorite. The heating history of micrometeorites ultimately determines how the elements and minerals in micrometeorites are incorporated into the terrestrial environment. For example, volatilization could influence the particle size of micrometeorites that fall to the earth surface. If micrometeorite mass loss is mainly in discrete events like relatively large and dense metallic nuggets, the latter would fall quickly through the water column and be incorporated into ocean sediment. However, if micrometeorites lose mass mainly as continuous nanoparticulate vapor, the resulting nanoparticles could remain in the water column for a long period of time and may get dissolved in the seawater. The primary purpose of this study is to throw light on the ratio of Os dissolved to that incorporated in the sediment. Understanding the mechanism by which micrometeorites lose their mass during entry through the atmosphere is thus important to understanding the contribution of cosmic dust to the osmium budget of the oceans.

Samples and Methods: Individual stony micrometeorites collected from the South Pole Water Well were dissolved and analyzed for osmium and/or iron

concentrations and isotopes. Three different types of stony micrometeorites, one calcium aluminum titanium rich micrometeorite (CAT), one brown glass micrometeorite (SMK) and three barred olivine (BO) micrometeorites were analyzed. Among the stony micrometeorites, BO is the most common followed by SMK and then CAT. The progression from BO through SMK to CAT indicates increasing iron loss which is manifested in the loss of color in the samples.

Each sample was photographed and weighed prior to dissolution. Two methods for dissolution were used, one using a combination of HNO₃, HF and CrO₃ (for osmium analysis) and the other using HCl and HNO₃. The second method was developed without the use of CrO₃, to allow the simultaneous extraction of iron and osmium from the same sample. Chromium interferes with Fe isotope measurements.

Samples were weighed, spiked for osmium (¹⁹⁰Os) and iron (⁵⁴Fe-⁵⁸Fe double spike), following which liquid bromine and acid added to the sample for dissolution. The ⁵⁴Fe-⁵⁸Fe double spike was used to precisely measure the Fe isotopic composition by correcting the mass dependent isotope variations with the double spike. Samples were then placed in a sealed beaker and put on a hotplate overnight at 80°C. The osmium is partitioned into the liquid bromine which is then carefully removed and placed into hydrobromic acid resulting in an osmium fraction. The residual liquid after the liquid bromine extraction contains the iron fraction of the sample. Prior to running on the TIMS (thermal ionization mass spectrometer), the samples need to be further purified. The osmium split of the samples is cleaned using CrO₃ in a microdistillation unit. The iron fraction of the sample is separated out by passing it through an anion exchange column. Osmium is measured as a negative ion on the TIMS while iron is run as a positive ion. The yields were consistently high (>90%) and the blanks are low for the entire procedure thus allowing the analysis of individual micrometeorite grains. We are continuing work to improve sample recovery and detection limits.

Results: The results are given in Table 1 and displayed in Figure 1. Concentration of osmium in chondrites, the likely precursors of most micrometeorites, is on the order of 500 µg Os/g. The samples analyzed using different methods for osmium extraction range from 0.3 - 1.5 µg Os/g. Clearly, the bulk of osmium (about 99.5%) has been lost from the micrometeorites. Analysis of iron isotopes indicates that up to 90% of

the total iron may be lost due to heating during entry; however, iron loss varies considerably between meteorite classes. By examining the extent of fractionation in the iron isotopes, we can constrain the type of mass loss undergone by the micrometeorite. Fe loss due to nanoparticle vaporization resembles Rayleigh fractionation in that Fe isotopic composition becomes increasingly heavier as the volatilization proceeds [3, 4]. In contrast, if mass loss is in the form of a nugget, no fractionation should occur because all the iron or osmium would be lost at once, not allowing fractionation to occur [5]. Fe (and Os) may be lost in stages whereby some Fe loss occurs through nugget formation and its extraction following which the loss is through nanoparticle volatilization. If so, we should find spherules with fractionated Fe isotopes but with Fe concentrations that are not in sync with Rayleigh fractionation calculations.

All of the samples analyzed for iron isotopes show an enrichment of ^{57}Fe over ^{56}Fe indicating fractionation. Figure 1 suggests that volatilization occurs according to Rayleigh fractionation. This is in contrast to the findings by other groups who measure Fe isotopes and concentrations with ion probe. The lower the iron concentration (greater iron loss) found in the sample the greater the fractionation. The CAT sample had the lowest iron concentration and had the greatest fractionation of iron (Table 1). A sample that has a large fractionation could have experienced a nugget loss followed by subsequent heating. Since most of the material has been lost, any heating causing fractionation would have a large effect since there is not much material left. Another possibility for a sample showing large fractionation is that it experienced a long period of continuous vapor loss. If a sample does not show large fractionation but has experienced iron loss, then it must have lost its iron as a nugget without suffering

much heating after the loss. This appears to be the case for our barred olivine samples.

Conclusions: As all samples fall on the theoretical Rayleigh fractionation curve, the simplest interpretation is that that iron and osmium are mainly being lost from micrometeorites as nanoparticles. Given that barred olivine is the most common (about 70%) type of stony micrometeorite [6] these particles should contribute significantly to dissolved Os in the ocean. Fe would be significant in the High Nutrient Low Chlorophyll regions of the oceans. Isotopic analysis on these nuggets would give further insights as to how mass loss is occurring in micrometeorites.

References: [1] Sharma, M. et al. (1997) *GCA*, 61, 3287-3299. [2] Love, S. G. and Brownlee, D. E. (1991) *Icarus*, 89, 26-43. [3] Alexander, C. M. O. et al. (2002) *GCA*, 66, 173-183. [4] Davis, A. M. et al. (1991) *LPS XXII*, 281-282. [5] Taylor, S. et al. (2005) *GCA*, in press. [6] Taylor S. et al. (1997) *CRREL Report*, 97-1, 1-35.

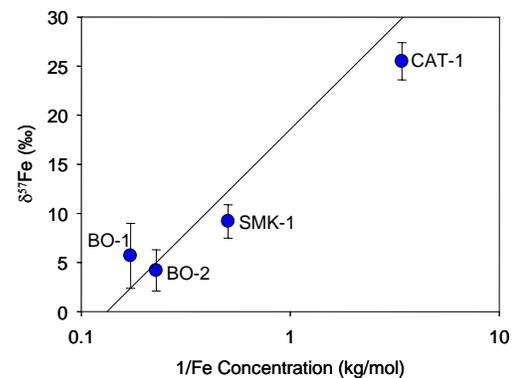


Figure 1: Iron fractionation compared to the iron content. The line describes the predicted iron loss according to Rayleigh fractionation.

Table 1. Osmium and iron concentrations and isotopic composition data for stony micrometeorites.

Sample	Sample Wt (μg)	Fe Conc (mol/kg)	$\delta^{57}\text{Fe}$	Os Conc (10^{-6} mol/kg)	Fe/Os	$1-f^1$
BO-1	18	5.81	5.7 ± 3	8.12	$7.16\text{E}+05$	0.47
BO-2	17	4.38	4.2 ± 2	3.63	$1.21\text{E}+06$	0.38
CAT-1	37	0.29	25.5 ± 2	1.48	$1.97\text{E}+05$	0.94
SMK-1	34	1.98	9.2 ± 2	1.67	$1.18\text{E}+06$	0.65
274 ²	25	-	-	5.08	-	-

¹f is the fraction of Fe remaining in the micrometeorite. f is calculated from

$$\Phi = \frac{\delta^{57}\text{Fe}}{\text{mass}57 - \text{mass}56} = \frac{f^{\left(\frac{1}{\alpha}-1\right)}}{\text{mass}57 - \text{mass}56} \times 1000 \quad \text{and} \quad \alpha = \sqrt{\frac{\text{mass}57}{\text{mass}56}} = 1.0089$$

²This sample consisted of two barred olivine type objects. Iron analysis was not performed on this sample. CrO_3 was used for the extraction of Os from the sample.