

Determining the nitrogen isotopic composition of geoporphyryns by the denitrifier method

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Values of $\delta^{15}\text{N}$ of sedimentary porphyryns can reveal the nutrient dynamics of modern and ancient oceans. Intact porphyryns record the isotopic composition of the nitrogen supply to the surface ocean. Such information will help to decipher oceanic responses to past climatic events and will provide critical predictive power as the Earth faces future shifts in the biogeochemistry of the ocean-atmosphere system. We have developed a fast and robust methodology for measuring values of porphyryn- $\delta^{15}\text{N}$: our technique involves separation of porphyryn-enriched lipid fractions by high-performance liquid chromatography, wet oxidation of the nitrogen to nitrate, and isotopic measurement of this nitrate-N using the denitrifier method [1]. Using a Rayleigh fractionation model, at the measured oxidation efficiencies of $\geq 80\%$, $< 1\text{‰}$ (generally $< 0.5\text{‰}$) of fractionation is expressed due to the analytical process. This method allows us to measure the nitrogen isotopic composition of very small samples in triplicate by requiring < 100 nmol of total porphyryn-N to be purified. In our primary method development sample, the Devonian New Albany Shale deposit (~380Ma; 10% total organic carbon (TOC)), this yield typically has corresponded to a starting quantity of < 0.2 g of rock powder. Further work on samples from Cretaceous Ocean Anoxic Event 2 has yielded sufficient porphyryns for analysis from < 5 g of samples containing 1% TOC. The resulting data promises to reconstruct nitrogen dynamics from past ocean events with sufficient throughput for high-resolution profiling.

[1] Sigman, D.M. *et al.* (2001) *Analytical Chemistry* **73**, 4145-4153.

Metal/olivine partition coefficients and the cooling rates of pallasites

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Introduction

Current estimates for the cooling rates of pallasites, based on zoning profiles in olivines [1], differ by as much as four orders of magnitude from metallographic cooling rates [2]. Calculations using chemical zonations in olivines assume a constant metal/olivine partition coefficient (D) during the cooling episode. This cannot be correct. Partitioning of a trace element between metal and olivine is dependent on temperature (T), pressure (P), composition (X) and $f\text{O}_2$. To date, only two direct measurements of metal/olivine partition coefficients for Ni (D_{Ni}), at pressure of interest, appear in the literature [3]. So as to better understand the controls on metal/olivine Ni and Co partitioning in pallasites, we are performing experiments under suitable P, T, X and $f\text{O}_2$. For a more detailed description of experimental and analytical conditions please refer to [4]. We report here on progress to date.

Results and Discussion

Concentrations of Co in olivines from our experiments are close to the electron microprobe's (EMP) detection limit. The associated large uncertainties mean we must rely on SIMS to obtain good D_{Co} values. Nickel concentrations are an order of magnitude higher, however, the uncertainty on the counting statistics is typically $\geq 10\%$ resulting in relatively large propagated errors for $\ln D_{\text{Ni}}$. The presence of a high concentration of Ni next to the olivine results in considerable fluorescence, thus hampering analysis of the experimental products. We have overcome this issue by running experiments of sufficient duration for equilibrium to be attained beyond the area of fluorescence in the olivine. Based on our results, it is possible to make some first observations regarding the effects of composition and $f\text{O}_2$ on D_{Ni} . We find that Ni concentration in olivine increases with increasing $f\text{O}_2$. As in a closed system the relative $f\text{O}_2$ decreases with decreasing T, we would expect metal/olivine D_{Ni} to increase during the cooling history of the pallasite parent body.

[1] Tomiyama & Huss (2006) *LPSC XXXVII* (2132) **40**, A156.
[2] Buseck & Goldstein (1969) *Geol. Soc. Amer. Bull.* **80**, 2141-2158. [3] Ehlers, Grove, Sisson, Recca & Zervas (1992) *Geochim. Cosmochim. Acta* **56**, 3733-3743. [4] Hill, Domanik & Drake (2008) *LPSC XXXIX* (1415).