

Natural Variations of Selenium Isotopes Determined by Multicollector Plasma Source Mass Spectrometry: Application to Seafloor Hydrothermal Systems

Olivier Rouxel (rouxel@crpg.cnrs-nancy.fr)¹, John Ludden (ludden@crpg.cnrs-nancy.fr)¹, Yves Fouquet (fouquet@ifremer.fr)² & Jean Carignan (carignan@crpg.cnrs-nancy.fr)

¹ CRPG-CNRS, B.P. 20, 54501 Vandoeuvre-les-Nancy Cedex, France

² IFREMER, BP 70 - 29280 Plouzané Cedex, France

Introduction

Selenium (Se) has six stable isotopes, 74, 76, 77, 78, 80 and 82 with abundances of approximately 1, 9.0, 7.5, 23.5, 50.0 and 9.0%. Chemically similar to sulphur, Se occurs as +6, +4, 0 and -2 valences in a variety of organic compounds and geological settings. This makes the study of Se stable isotope ratios a potential indicator of geological and biological processes. For a decade, numerous workers have focused their studies on Se biogeochemistry in polluted soils and the marine environment but, largely due to the analytical difficulties, Se isotope fractionation has received little attention. Se isotopes were first determined in the early 60's (Krouse and Thode, 1962) and recently, a new method for measurement of natural Se isotope ratio has been developed by N-TIMS (Johnson et al., 1999). These results showed that the $^{82}\text{Se}/^{76}\text{Se}$ ratio varied by as much as 15‰ and indicates that reduction of soluble oxyanions is the dominant cause of Se isotope fractionation. Se follows sulphur in magmatic cycles and is concentrated in magmatic-hydrothermal ores, being richer in the high-temperature deposits. We show here that analyses of Se concentration and isotope compositions performed in conjunction with sulphur isotopes provide a powerful tool for resolving some fundamental processes in hydrothermal systems, such as the redox state of the source reservoir, the near-surface hydrothermal reaction processes and the evolution of depositional processes in the chimney environment.

Methodology

We present in this study the measurements of Se isotopes by MC-ICP-MS (Micromass Isoprobe). The analytic procedure has been developed following the study of (1) background and interference correction on Se isotopes (2) instrumental mass fractionation correction, (3) matrix effects (4) Se purification on natural samples. Three approaches, namely Sr-doping, double spike and "sample-standard bracketing" have been evaluated. We used here the "sample-standard bracketing" technique which offers rapid, simple and sufficiently precise isotope measurement. Se isotopes are measured relative to an Se internal standard (MERCK Titrisol solution) and are given in delta notation $\delta^{82}\text{Se}/^{80}\text{Se}$ and $\delta^{83}\text{Se}/^{76}\text{Se}$. The external analytical precision after

Se separation is better than 0.3‰ for the $^{82}\text{Se}/^{80}\text{Se}$ ratio and 0.8‰ for the $^{82}\text{Se}/^{76}\text{Se}$ ratio.

Results and discussion

Massive sulphides and active chimneys from different hydrothermal fields along the mid atlantic ridge (MAR) have been examined to determine their mineralogical, chemical, sulphur and Se isotope characteristics. Se isotope data are reported in Figure 1 and for all data, the relation $\delta^{82}\text{Se}/^{76}\text{Se} = 3 * \delta^{80}\text{Se}/^{82}\text{Se}$ was observed as predicted theoretically. We have determined the Se meteoritic value obtained in Bella Roca troilite. The Lucky Strike hydrothermal field is located near the Azores Triple Junction and, based on vent structures, mineral abundance and zonation, 2 main types of hydrothermal deposits were identified. The $\delta^{34}\text{S}$ (between 1.5-4.5‰) and Se values (up to 2000 ppm) of Cu-rich sulphides suggest a high temperature undepleted hydrothermal fluid with a dual source of sulphur, sulphur leached from magmatic rocks, and sulphur from the reduction of seawater sulphate. Pyrite and marcasite have lower $\delta^{34}\text{S}$ within the range of magmatic values (0 to 1‰) and are characterized by a depleted concentration of Se of less than 10 ppm. The overall variations of Se isotopes are large, with variation up to 7‰ in $^{76}\text{Se}/^{82}\text{Se}$ ratios. No systematic relationships between sulphur and Se isotopes have been observed. However, the variations in Se isotopes display some interesting correlation with Se content in sulphides showing that mechanisms responsible for Se depletion in sulphides may strongly fractionate Se isotopes. Such mechanisms include reservoir Rayleigh-type fractionation during sulphide precipitation and fluid transport and pH-f₂ changes.

The natural variations of Se isotopes obtained in this study demonstrate the potential for using Se as a tracer in hydrothermal systems. Additional data on igneous rocks and sediments will be presented to determine the isotopic composition of potential sources of selenium in hydrothermal systems. The new capability for Se isotopes measurements by MC-ICP-MS is expected to have a major impact in disciplines ranging from cosmochemistry to biogeochemistry.

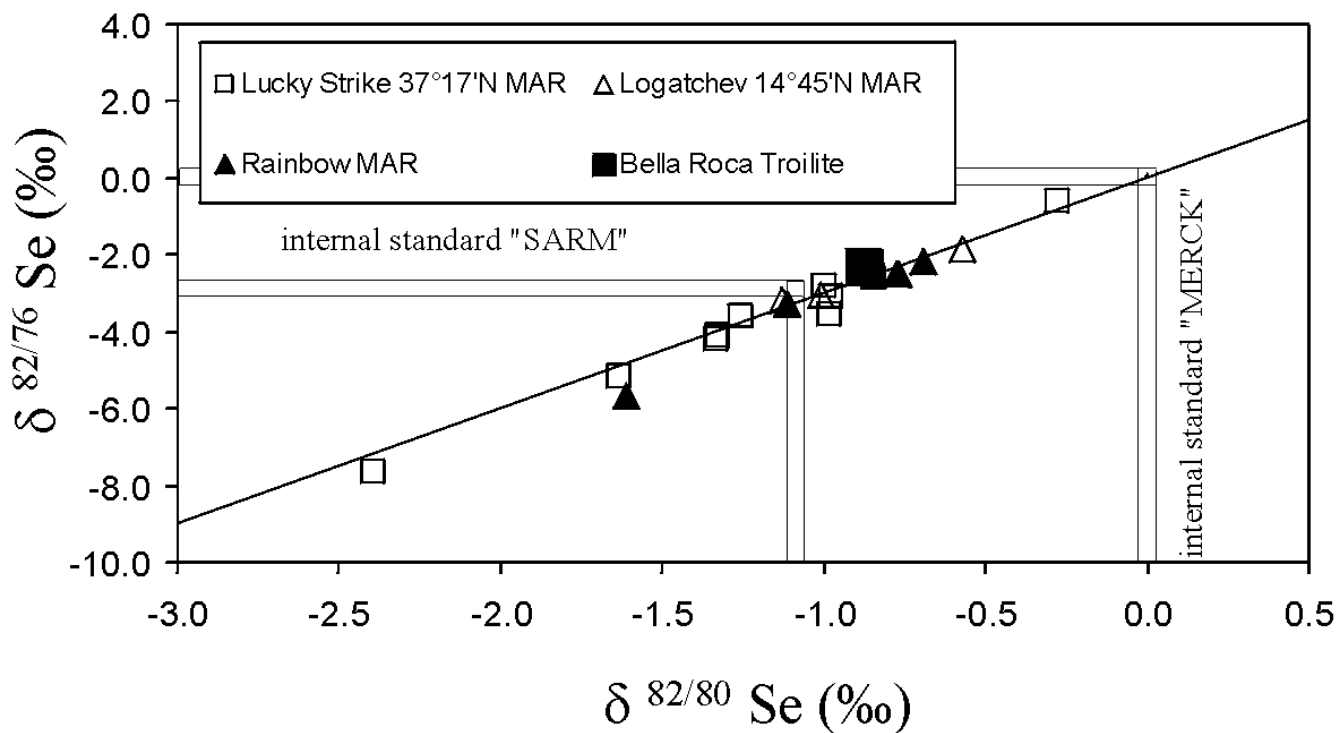


Figure1: Se isotope data of sulphides (chalcopyrite, pyrite and marcasite) from different hydrothermal fields along the Mid Atlantic Ridge

Johnson, T.M., Herbel, M.J., Bullen, T.D. and Zawislanski, P.T., *Geochimica et Cosmochimica Acta*, **63**, 2775-2783, (1999).

Krouse, H.R. and Thode, H.G., *Canadian Journal of Chemistry*, **40**, 367-375, (1962).