

Sulfur isotopes in subduction systems and the global sulfur cycle

Nobumichi Shimizu & Horst Marschall

Models of the global sulfur cycle are afflicted with a lack of knowledge on the efficiency and isotopic effects of subduction processes. Primitive undegassed basalts, as well as sulfide inclusions in mantle xenoliths and in eclogite-type diamonds display a relatively large variation in $\delta^{34}\text{S}$ (Fig.1), providing evidence for significant mantle heterogeneities in S isotopes. It has been speculated that recycling of sulfur in subduction zones is in part responsible for these variations. However, models of the deep mantle sulfur cycle ignore any processes operating during subduction. Estimates on the subduction input into the mantle are reduced to using the compositions of un-metamorphosed oceanic rocks, because little was so far known on the behavior of sulfur and sulfur isotopes during high- P metamorphism and subduction zone devolatilization. This study aimed to start on closing this gap, and investigated the S isotope composition of sulfides in natural high- P rocks.

Sulfur isotope analyses were conducted on pyrite and chalcopyrite *in situ* in thin section or grain mounts by SIMS using the Cameca IMS 1280 at WHOI. A $^{133}\text{Cs}^+$ beam is used with a spatial resolution of $<10\ \mu\text{m}$, and a precision of $\pm 0.7\ \text{‰}$ ($2\sigma_{\text{mean}}$). Instrumental mass fractionation is corrected for using the following international S isotope standards: Balmat pyrite (+15.1 ‰), MVE pyrite (-13.2 ‰), Ruttan pyrite (+1.2 ‰), Norilsk chalcopyrite (+8.0 ‰), Trout Lake chalcopyrite (+0.3 ‰).

Based on petrographic evidence, the sulfides were attributed to formation during two contrasting stages of the subduction-exhumation cycle: (1) sulfides formed prior to or during subduction, and (2) sulfides in revolatilization zones formed during exhumation, probably by fluids released from the subducting slab. The first type bears on the isotopic composition of sulfur in different lithologies subducted to various depths, while the second type complements these data by reflecting the composition of fluids released from the slab.

Conclusions:

The data gathered include both prograde and retrograde sulfide from various localities and present the following picture (Fig.1):

(i) $\delta^{34}\text{S}$ values of prograde pyrite and chalcopyrite in metabasites (blueschists, eclogites) are mainly positive: ~ 0 to $+11\ \text{‰}$, although some individual pyrite grains show moderately negative values down to $-3.4\ \text{‰}$. The grains are typically unzoned in S isotopes.

(ii) $\delta^{34}\text{S}$ values of prograde pyrite and chalcopyrite in oceanic metasediments from the Franciscan formation are very low (appr. -31 and $-19\ \text{‰}$, respectively).

(ii) $\delta^{34}\text{S}$ values of retrograde pyrite show a heterogeneous picture with unzoned grains having positive or negative values. Positive values as high as $+12\ \text{‰}$ are associated with high-pressure mélangé zones dominated by mafic and ultramafic materials (Syros, Catalina), while negative values as low as $-21\ \text{‰}$ were found in the Port-Macquarie mélangé zone, which contains metamorphosed black shales. Some mm-sized grains show core-to-rim zonation with an intra-grain variation of up to ~ 8 permil in $\delta^{34}\text{S}$.

The results obtained to date suggest that altered igneous crust carries a positive $\delta^{34}\text{S}$ signal down to the ultra-high- P eclogite stage, while oceanic sediments carry a very low $\delta^{34}\text{S}$ signal. Evidence for high- $\delta^{34}\text{S}$ fore-arc fluids is found in retrograde pyrite in high- P terrains that are dominated by meta-igneous and mantle-derived rocks. In contrast, retrograde pyrite associated with metamorphosed black shales shows very low $\delta^{34}\text{S}$ values.

Publications from this proposal:

This study was presented at two scientific meetings: the 9th International Eclogite Conference 2011 in Mariánské Lázně, Czech Republic, and the 22nd V.M. Goldschmidt Conference 2012 in Montreal, Canada. The references for the respective abstracts are:

Marschall HR, Shimizu N, Hacker BR, Kylander-Clark ARC (2011) Sulfur isotopes in high-pressure rocks. The 9th International Eclogite Conference Abstracts 43-44.

Marschall HR, Shimizu N (2012) Sulfur isotopes in high-pressure rocks. Goldschmidt Conference Abstracts, #2516.

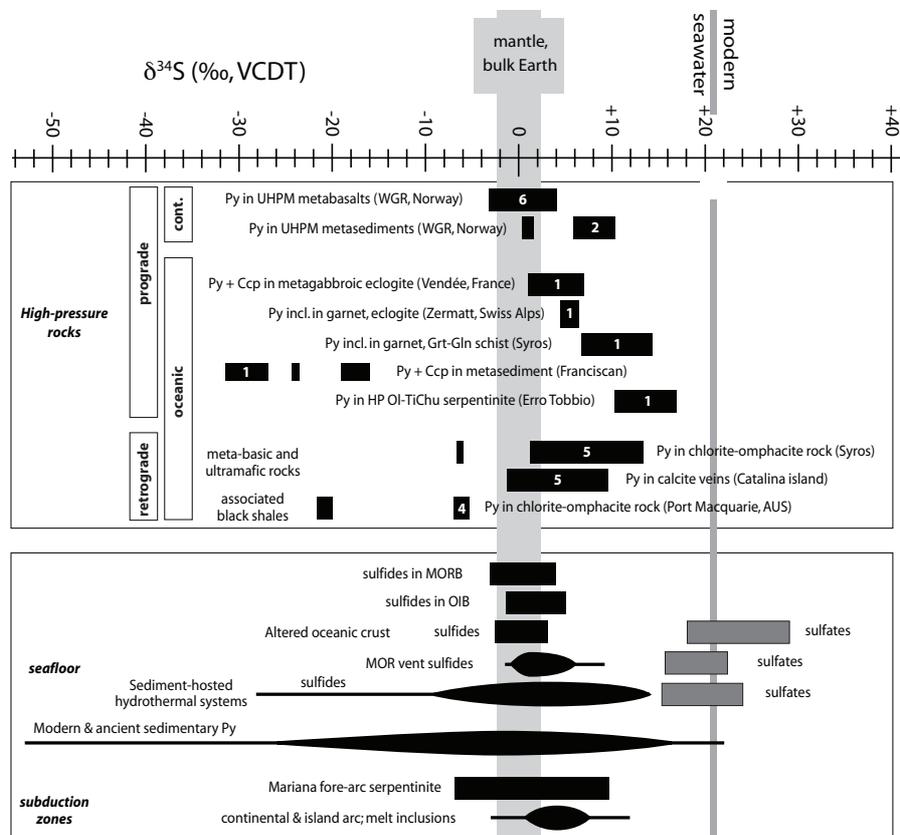


Fig. 1: Results from sulfur isotope analyses conducted in this study. **Top panel:** Sulfur isotopic composition (given as $\delta^{34}\text{S}$ relative to the V-CDT standard) of prograde and retrograde sulfides (pyrite and chalcopyrite) in high-pressure metamorphic rocks from various localities, investigated in this study (except for Catalina island: Bebout 1995, Chem. Geol.). **Lower panel:** Sulfur isotopic composition of seafloor and subduction-related materials. Width of bars relate to the distribution of samples in a specific group.

Future work:

We have extended the technical framework of this project to include other sulfide minerals, pyrrhotite, pentlandite, and heazlewoodite. These minerals occur commonly in serpentized peridotites and their high-pressure recrystallization products, and their sulfur isotopic compositions will become critical information as our work on the deep sulfur cycle in subduction zones continues.

Geochemical behavior of chalcophile elements including Os, Pb, and Tl in mantle-basalt systems is dependent on stability and melting phase relations of sulfide in the mantle. In order to advance our shared interest in geochemistry of these elements and the deep sulfur cycle, we are planning to organize an internal WHOI seminar on the subject with Sune Nielsen and Veronique Le Roux. We hope that the seminar of this type could become a step for new proposals. As our knowledge of sulfur recycling advances, we will be ready for seeking external funding. Sources of funding that we are currently evaluating are not restricted to NSF, but also include the mining industry focused on sulfide deposits in subduction zones (i.e., porphyry deposits).