

Sulfur isotopes in high-pressure rocks

HORST R. MARSCHALL^{1*}, NOBUMICHI SHIMIZU¹

¹WHOI, Woods Hole, MA, USA, hmarschall@whoi.edu (* presenting author), nshimizu@whoi.edu

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 $\delta^{34}\text{S}$ (Seal, 2006) 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 is known on the behavior of sulfur and sulfur isotopes during high-*P* metamorphism and subduction zone devolatilization. This study aims to close this gap, and investigates the S isotope composition of sulfides in natural high-*P* rocks.

Sulfur isotope analyses were conducted by SIMS on pyrite and chalcopyrite. 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.

Preliminary data from various samples investigated so far include both types of sulfide from various localities (Cycladic blueschist belt, Greece; Zermatt-Saas Fee, Italian Alps; Western Gneiss Region, Norway; New England Fold belt, Australia; Franciscan fm., California) and present the following picture:

(i) $\delta^{34}\text{S}$ values of prograde pyrite and chalcopyrite in eclogites are mainly positive: ~ 0 to $+14$ ‰, although some individual pyrite grains show negative values down to -3.4 ‰. The grains are typically unzoned in S isotopes.

(ii) prograde pyrite and chalcopyrite from a high-*P* metasediment shows grains unzoned in $\delta^{34}\text{S}$ with values as low as -31 ‰.

(iii) $\delta^{34}\text{S}$ values of retrograde pyrite show a heterogeneous picture with unzoned grains having negative (as low as -21 ‰) or positive values, as well as mm-sized grains with ~ 8 permil $\delta^{34}\text{S}$ core-to-rim zonation.

The results obtained to date suggest that altered igneous crust carries a positive $\delta^{34}\text{S}$ signal down to the UHP eclogite stage, while sediments are probably depleted in ^{34}S . Evidence for high- $\delta^{34}\text{S}$ fore-arc fluids is found in retrograde pyrite. However, some retrograde pyrite shows very low $\delta^{34}\text{S}$ values, which may be related to metasedimentary sources in the slab. High-*P* serpentinites and harzburgites will be one of the future foci of this ongoing study into the subduction zone sulfur cycle.

[1] Seal RR (2006) Sulfur isotope geochemistry of sulfide minerals. MSA Reviews in Mineralogy and Geochemistry, 61: 633–677.

Warm Arctic Peatlands – Future Methane Factories?

CHRIS MARSHALL^{*1}, DAVID J LARGE¹, WILL MEREDITH¹, COLIN E SNAPE¹, BARUCH F SPIRO² AND MALTE JOCHMANN^{3*}

¹Chemical & Environmental Engineering, University of Nottingham, enxcm3@nottingham.ac.uk

²Natural History Museum, London
baruch.spiro@gmail.com

³Store Norske Grubekompani AS Longyearbyen
Malte.Jochmann@snsk.no (* presenting author)

Palaeocene Arctic coal represents a unique terrestrial record of peatland processes and carbon storage during the last period of Arctic warmth. Modern high latitude warming is accelerated when compared to global averages [1] indicating future Arctic peatlands may bear closer resemblance to Palaeocene peatlands than those seen at the present time. The Svalbard coals formed around 60Ma at latitude 68°N. Previous studies of mid-latitude Paleocene coals, [2] provide evidence of significant methanogenic communities within peatlands before and during the PETM event. Modern high latitude methane fluxes have been linked to polar stratospheric cloud formation [3] and accelerated Arctic warming. This study aims to use organic petrology and geochemistry to find evidence of such methane fluxes in Palaeocene, Svalbard and study the implications for modern peatlands

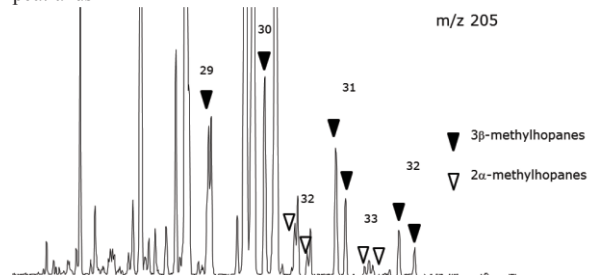


Figure 1: M/z 205 gas chromatograms showing 2 & 3 Methylhopanes in Svalbard coal extracts.

Total hopane concentrations (bacterial biomarkers) in Svalbard coals are 45–125mg/g extract indicating the coals are massively enriched in microbial lipids compared to other source rocks (<2 mg/g extract [4]). High detrovitrinite contents in the Svalbard coals also indicate high levels of biodegradation for the latitude. This is probably a feature of high peatland seasonality with winter productivity lowered but temperatures sufficient, to allow continued biodegradation.

Methanotrophic biomarkers, 3-methyl hopanes (figure 1) are enriched (1.26mg/g extract) significantly compared to other source rocks (<300 µg/g extract, [4]). This increase is thought associated with the general increases in biodegradation shown by the hopanes. This is reflected by 3Me/Total Hopane ratios of 2-3%, which are consistent with other source rocks [4]. Consequently, if future Arctic peatlands evolve similarly, biodegradation would be expected to increase rapidly, increasing the Arctic terrestrial carbon flux and accelerating subsequent high latitude warming.

[1] Holland & Bitz (2003) *Climate Dynamics* 2, 221-232 [2] Pancost et al. (2007) *Nature* 449, 332-335. [4] Sloan & Pollard (1998) *Geophysical Research Letters* 25, 3517-3520 [4] Farrimond et al. (2004) *Geochimica et Cosmochimica Acta* 68, 3873-3882.