Progress in understanding of sulfur in subduction zone magmas

C. MANDEVILLE[1]*, N. SHIMIZU[2], K. KELLEY[3], N. METRICH[4], A. FIEGE[5] AND H. BEHRENS[5]

[1]US Geological Survey (cmandeville@usgs.gov)
[2]Woods Hole Oceanographic Institution (nshimizu@whoi.edu)
[3]University of Rhode Island (kelley@gso.uri.edu)
[4]Institut de Physique du Globe de Paris (metrich@ipgp.fr)
[5]Univ. of Hannover (a.fiege@mineralogie.uni-hannover.de)

Progress in developing a better understanding of sulfur's behavior and origin in subduction zone magmas has now been facilitated through new *in situ* analytical techniques and recent conduction of high pressure and temperature (P-T) partitioning and isotopic fractionation experiments. Development of an *in situ* secondary ionization mass spectrometry (SIMS) technique for measurement of $^{34}S/^{32}S$ ratios in silicate glasses now allows for direct measurements of experimental glasses and melt inclusions from mafic arc magmas. Complementary SIMS calibrations for sulfur isotope ratio measurements of pyrrhotite and anhydrite now allow for investigation of S isotopic fractionation between sulfur-bearing melt and condensed sulfur phases at magmatic temperatures. Conventional and SIMS analysis of run products from high (P-T) decompression experiments investigating S partitioning between vapor and melt (Fiege *et al*. [1]) provide direct measurement of isotopic fractionations that can now be compared to estimates derived from previous extrapolations of data from lower temperature experiments, analogue materials and/or theoretical models [2]. Advances in S and Fe micro-X-ray Absorption Near Edge Structure Spectroscopy (XANES) has allowed for determination of the oxidation state of S and Fe in both natural and experimental samples.

Measured $^{34}S/^{32}S$ ratios via SIMS in olivine-hosted basaltic melt inclusions (MI's) from Krakatau and Galunggung volcanoes in Indonesia and Augustine volcano, Alaska yield $\delta^{34}S$ values from -2.8‰ to 17.2‰. Highest $\delta^{34}S$ values of 9.6‰ to 17.2‰ were measured in MI's from a Pleistocene basalt from Augustine volcano that have high disolved volatiles of 8.0 wt.% H_2O, 2624 to 5100 ppm S, 3900 ppm Cl, and sulfur XANES spectra with prominent peaks at 2482 eV indicating 100% SO_4^{2-} species in melt. Melt inclusions from the 1982 eruption of Galunggung yield $\delta^{34}S$ of -2.8‰ to 9.6‰. Melt inclusions from Krakatau pre-1883 basaltic scoria yield $\delta^{34}S$ values of 1.6‰ to 8.7‰. $A^{34}S$-enriched material is present in these magma source regions.

[1] Fiege *et al*. (2011) *MinMag*, this volume. [2] Mandeville *et al*. (2009) *GCA* **73**, 2978–3012.

Mn-crusts record deep ocean ventilation changes

AUGUSTO MANGINI

Heidelberger Akademie der Wissenschaften, INF 229, D-69120 Heidelberg (amangini@iup.uni-heidelberg.de)

The end of glacial stages is accompanied by an increase of atmospheric CO_2. During the last Termination this increase goes along with a drastic drop of atmospheric ^{14}C by about 190‰. The probable explanation assumes the release of old carbon stored from a poorly ventilated glacial Ocean. This period was addressed by Broecker as the 'Mystery Interval' due to lacking higher glacial Benthic-Planktic foraminifera ages. However, the mystery could be an artefact of the tool applied, as benthic foraminifera cannot survive in an anoxic ocean.

More than 20 years ago we had measured profiles of ^{230}Th in the top mm of two Mn-crusts from the Central Pacific, from 4, 400 m and 1, 500 m water depth at a resolution of 20μm. In both samples growth rates during the past 300, 000 years were faster in Interglacials than in Glacials. We attributed the extremely slow growth rate during stage 2, and, especially, stops of growth during glacial stages 6 and 8 to periods of anoxia of the deep ocean, impeding formation of Mn-oxides. However, these conclusions were ignored, arguing that the occurrence of benthic forams and the lack of peaks of uranium in sediments contradicted periods of anoxia. In the meantime, however, there are a number of indications that the deep glacial Pacific Ocean was less ventilated than at present and that the shut down of N. Atlantic deep water formation during Heinrich 1 could have led to a short anoxic period in the deep Pacific. Reconsidering the data from the Mn crusts may help to solve the mystery.