# The fate of sulfur in late-stage magmatic processes: Insights from quadruple sulfur isotopes

NICOLE S. KELLER[1,2], SHUHEI ONO[2]
AND ALISON M. SHAW[1]

[1]Woods Hole Oceanographic Institution, Woods Hole, MA 02543, U.S.A (nkeller@whoi.edu)
[2]EAPS, MIT, Cambridge, MA 02139, U.S.A

Arc volcanism plays a major role in the global sulfur cycle, yet the sulfur mass balance at convergent margins is poorly constrained. This is partly due to the fact that late-stage processes are challenging to quantify and lead to large uncertainties in the global output fluxes. Here, we take advantage of the fact that the ascent of volcanic gases through a hydrothermal system causes complex isotopic fractionation. Through combined use of multiple sulfur isotopes ($^{32}$S, $^{33}$S, $^{34}$S and $^{36}$S) such fractionations can be used to unravel the various modifying processes. $\delta^{34}$S is thought to trace the source of sulfur as well as magma degassing; at equilibrium, $\delta^{33}$S follows a mass-dependent fractionation relationship such that two phases in equilibrium with each other have equal $\Delta^{33}$S ($\equiv \ln(\delta^{33}\text{S}+1) - 0.515*\ln(\delta^{34}\text{S}+1)$) values. Disequilibrium $\Delta^{33}$S values can indicate isotope mixing and other fluid-rock interactions [1]. Thus, quadruple sulfur isotopes provide a powerful tool to untangle the convoluted history of volcanic systems. Here we report the first quadruple sulfur isotopic values for $H_2S$, $SO_2$ and native sulfur from arc volcanoes.

Fumarolic gases (~100°C) and sulfur sublimates were collected from Poas and Turrialba, two actively degassing volcanoes in Costa Rica. The gases were bubbled *in situ* through chemical traps to separate $H_2S$ from $SO_2$: $H_2S$ was reacted to form ZnS, and $SO_2$ to form $BaSO_4$. Sulfur was chemically extracted from the solid phases and precipitated as $Ag_2S$, which was fluorinated to $SF_6$ and analysed by IRMS. Poas and Turrialba have $H_2S/SO_2$ ~1 and 0.01, respectively. $\delta^{34}S_{H2S}$ and $\delta^{34}S_{SO2}$ are similar to gases measured at other arcs [2], -7.9‰ and 0.6‰ for Poas, and -8.5‰ and +9‰ for Turrialba, likely reflecting a mixture of mantle ($\delta^{34}$S = 0‰) and slab sources which have been degassed to variable degrees. Sulfur sublimate values are similar to those for $H_2S$.

$\Delta^{33}$S values are different within each $H_2S/SO_2$ pair ($\Delta^{33}S_{H2S}$ and $\Delta^{33}S_{SO2}$ are -0.01‰ and -0.02‰ for Poas, 0‰ and -0.07‰ for Turrialba), indicating that the two gas species are not in isotopic equilibrium at Turrialba. Reaction of the gases with mineral phases, such as sulfur-bearing alteration products in the volcanic edifice (e.g., alunite, anhydrite, sulfides) may explain these differences.

[1] Ono *et al*. (2007), *GCA* **70** 1170-1182, [2] Taylor (1986), *RiM* **16** 185-225

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# Altered oceanic crust in the western Pacific and its consequences for crust and mantle evolution

KATHERINE A. KELLEY

Graduate School of Oceanography, Univ. of Rhode Island, Narragansett, RI 02882, USA (kelley@gso.uri.edu)

The oceanic crust experiences hydrothermal alteration during its lifetime near the earth's surface, which fundamentaly changes the element distribution and the bulk composition of the crust through time. Some of the oldest oceanic crust resides in the western Pacific, where it forms an essential component of the crustal package being actively subducted into the mantle in this region. The subduction of altered oceanic crust (AOC) has been linked to specific geochemical signatures apparent in arc magmas and to certain isotopic heterogeneities in the earth's mantle (i.e., HIMU). Its careful geochemical characterization is thus an essential component for testing models of crustal and mantle evolution.

Recent ocean drilling efforts at two sites of old, fast-spreading Pacific crust (ODP Sites 801 [~170 Ma] and 1149 [~135 Ma]) penetrated deeply into the upper oceanic crust (470 m and 133 m, respectively) and generated two important reference sites. Samples from these drill sites provide valuable end-member constraints on the influence of hydrothermal alteration as a function of crustal age, structure, and spreading rate for comparison with other well-studied deep drill sites (e.g., 417/418, 504, 1256), and also provide essential data on the geochemical fluxes from AOC entering the Mariana and Izu-Bonin subduction zones.

Composite sample analyses and averages of discrete sample data for Sites 801 and 1149 reveal similar patterns of element redistribution and enrichment. Both sites show significant bulk enrichments in U (2-5x) and the alkalis (Li [2x], K [4x], Rb [9-10x], Cs [7-12x]) over pristine glass, and indicate that Pb is redistributed locally during alteration without a significant net change to the bulk crustal concentration. These data permit a quantitative examination of how certain element systems behave as the AOC is subducted. The U-Th-Pb system, for example, provides particularly useful tracers of these processes because each element behaves differently in water, but they are all linked through radioactive decay. Mass balance constraints using Site 801 AOC and arc lava compositions from the Marianas show that subduction processing drives Pb and U from the subducted plate at different depths, and that the residual slab at the end of this process is an appropriate starting material for generating mantle HIMU Pb isotopic signatures.