

## Constraints on the deep water cycle based on volcanic and hydrothermal gas emissions

Tobias Fischer  
University of New Mexico

Fluids discharging from hydrothermal and volcanic systems through fumaroles, hot springs and geothermal wells are dominated by water (> 90%), CO<sub>2</sub>, sulfur (SO<sub>2</sub> and H<sub>2</sub>S), and chlorine. In addition to these major components, N<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, CO, HF and the noble gases generally contribute the gas composition. Helium, with two isotopes is an excellent tracer for mantle (upper and lower) and crustal contributions to the overall helium budget of volcanic and hydrothermal gases; combined with stable isotopes and abundances of C and N<sub>2</sub>, the provenance of these gas species can be evaluated. Work over the past two decades has utilized the technique of combining helium with stable isotope systems to estimate the relative contributions of C and N from the mantle, the subducting slab, and from atmospheric and crustal sources. This work has provided valuable insights into the recycling of volatiles from the Earth's surface to the interior through subduction as well as the evolution of the volatile composition of the deep mantle.

While the sources of C and N in these systems are relatively well constrained in terms of mantle wedge, slab and crust; the ultimate sources of water and sulfur remain somewhat more enigmatic. It has been shown that the isotopic composition of O and H<sub>2</sub> of steam discharging from high temperature (>400°C) fumaroles located on volcanoes in subduction zone settings has a characteristic positive shift of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  relative to the local meteoric water line. Global fumarole data suggests the existence of an end-member in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  space that is related to water derived from the devolatilization of the subducting slab. In the crust or close to the surface this "arc-type" water mixes with meteoric water resulting in isotopic compositions that lie along mixing lines extending from the meteoric water end-member to the arc-type water end-member. The end-member composition of arc-type water has been confirmed by  $\delta\text{D}$  measurements of H<sub>2</sub>O in melt inclusions from volcanic arcs, supporting the idea of a unique slab-derived water end-member. The issue, however, with such an end-member is that there is rarely a correlation of  $\delta\text{D}$  with the total H<sub>2</sub>O content of the gas discharges and that some samples have  $\delta\text{D}$  values suggesting almost 100% of the discharging steam to be of magmatic/slab-derived origin. Similarly, there is no correlation between the water content of melt inclusions and the  $\delta\text{D}$  values. One, therefore, may argue that the arc-type stable isotopic composition is the result of a fractionation process of meteoric water in the crust rather than an end-member phenomenon. If indeed, water discharging from high temperature fumaroles is mainly of meteoric rather than mantle or slab origin, it would have profound implications for the global water cycle.

Application of <sup>85</sup>Kr, <sup>39</sup>Ar/<sup>40</sup>Ar measured in high temperature volcanic emissions that have stable isotope signatures of slab-derived water, combined with other geochemical tracers (C, N, He isotopes and abundance ratios), would provide unprecedented insights into the ultimate source and age of the fluids transporting these gases. Such a study should be

combined with investigations of gas discharges from fumaroles in volcanic rift and hot spot settings to constrain the composition of upper mantle water without any slab influence. In this way, fractionation and shallow contamination processes could be distinguished from source characteristics, which would significantly advance our understanding of the global deep water cycle and its effect on the water budget and recycling efficiency of Earth.