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Ge/Si and Ge isotope systematic in marine sediments

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Ge is a trace element in seawater whose biogeochemistry is dominated by its Si-like behaviour. Glacial-interglacial variations in oceanic Ge/Si, as recorded in biogenic opal, have been interpreted as reflecting periodic changes in past continental weathering processes [1]. However, the use of Ge/Si as a paleoceanographic tool remains uncertain as Ge may be removed from the ocean in iron-rich reducing sediments independently of Si [2].

Because Ge incorporation into iron oxides fractionates Ge-Si ratios but also Ge isotopes [3], we investigated the Ge isotope systematic in marine sediment to better understand past and present Ge oceanic cycle as well as high- and low-temperature weathering processes.

A new technique for the precise and accurate determination of Ge stable isotope compositions has been developed and applied to silicate, sulfide, hydrothermal fluid and biogenic material. The analyses were performed using a continuous flow hydride generation system coupled to a Nu Instrument MC-ICPMS. Samples have been purified through anion and cation exchange resins to separate Ge from matrix elements and potential interferences. Variations of $^{74}Ge/^{70}Ge$ ratios are expressed as $\delta^{74}Ge$ values relative to our internal standard and the long-term external reproducibility of the data is better than 0.2‰ for sample size as low as 10ng of Ge.

Igneous rocks have been analysed and define a Bulk Silicate Earth reservoir with a $\delta^{74}Ge$ of 1.05±0.25‰. Deep sea sediments do not deviate from this baseline but Mesozoic deep-sea cherts (opal CT and Quartz) have $\delta^{74}Ge$ values ranging from 0.5‰ to 1.7‰. Modern deep-sea sponges have $\delta^{74}Ge$ values clustered at 2.8‰ and are in marked contrast with marine chert values. This suggests either (1) distinct biological fractionation by siliceous organisms (2) change of seawater $\delta^{74}Ge$ values through time or (3) diagenetic fractionation during opal-A, opal CT, Quartz transformation.

Preliminary study of Ge/Si and $\delta^{74}Ge$ systematic during oceanic crust alteration (seafloor basalt weathering and hydrothermal systems at mid-oceanic ridges) is very promising and a total range of $\delta^{74}Ge$ values of 6‰ is observed. We suggest that Ge sequestration in sulfides, iron oxides, and potentially hydrothermal quartz are among key processes to produce such large variations in Ge isotopes.

References

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4.2.45

Using non-traditional stable isotopes as tracers: What do Tl isotopes tell us about hydrothermal water fluxes?

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The hydrothermal circulation that occurs at mid-ocean ridges and in older ocean crust has profound effects on the chemical budgets of the oceans but our understanding of the relevant fluxes is incomplete. The emerging non-traditional stable isotope systems of heavy elements provide new means to investigate oceanic budgets and fluxes. Here, we use Tl isotope data for hydrothermal fluids and rocks from ODP Hole 504B to obtain independent estimates of the high- and low-temperature (T) hydrothermal water fluxes at ridges and ridge flanks.

High-T hydrothermal fluids from ridges display Tl isotope compositions of $\varepsilon^{205}Tl = -2\pm1$, indistinguishable from "normal" unaltered mantle rocks ($\varepsilon^{205}Tl = 10^4 \times (^{205}Tl/^{203}Tl_{sample} - ^{205}Tl/^{203}Tl_{std}) / ^{205}Tl/^{203}Tl_{std}$). The correlation of Tl and Cl contents indicate an average Tl concentration of 10-25 nmol/kg for high-T endmember fluids, significantly higher than seawater (65 pmol/kg). The low-T alteration of the upper volcanic zone of ODP Hole 504B is associated with Tl-uptake from seawater ($\varepsilon^{205}Tl \approx -6$). The isotope fractionation that occurs during the uptake generates Tl-rich rocks that have $\varepsilon^{205}Tl$ as low as –15. The sheeted dike complex appears to have low Tl contents due to leaching of the dikes by high-T hydrothermal fluids.

These observations indicate that high-T hydrothermal fluids do not acquire significant Tl from the Tl-rich rocks of the volcanic section. Given this constraint, the high-T axial water flux is calculated, assuming that Tl is leached with an efficiency of 90-100% from 1.2-1.4 km of sheeted dikes and upper gabbros, which have a Tl concentration of 3 ppb. For hydrothermal fluids with 10-15 nmol/kg Tl, this requires a high-T water flux of 1-2 x 10^{13} kg/yr, equivalent to a heat flux of 0.5 to 1.0 TW. If the total axial hydrothermal power output is about 2 TW, our result is indicative of significant heat loss at mid-ocean ridges by diffuse low-T fluid flow.

The Tl isotope compositions of volcanic zone rocks are in accord with large losses of Tl from circulating seawater (up to 80%). Assuming that 35 ppb of Tl are added to the top 600 m of ocean crust, an extraction efficiency of 80% from seawater equates to a low-T water flux of 1.8 x 10^{16} kg/yr. This flux is in accord with the observed heat flow anomaly only for average fluid exit temperatures of less than about 8°C.