



## Measurement of Germanium isotope composition in marine samples by hydride generation coupled to MC-ICP-MS

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Germanium (Ge) is a trace metalloid in seawater that is of particular interest in marine biogeochemistry because of its strong chemical similarity to silicon. In addition, Ge stable isotope ratios in biogenic silica may have strong potential as paleoceanography proxies. Recently, Rouxel *et al.* (2006) reported Ge-isotope composition of igneous rocks and deep-sea clays and defined a bulk Earth  $\delta^{74/70}\text{Ge}$  value of 0.5‰ (relative to NIST3120a). Based on  $\delta^{74}\text{Ge}$  values of modern marine sponges, it has been suggested that Ge-isotope composition of seawater is enriched in heavy isotopes relative to the crust ( $\delta^{74}\text{Ge}$  around 2.2‰). Despite this initial study, the distribution of Ge isotopes in seawater is presently unknown due to analytical challenges to measure Ge-isotope composition of Ge species, respectively  $\text{Ge}_i$  (inorganic Ge), methyl Ge and dimethyl Ge at low concentrations ( $\text{Ge}_i \sim 20 \text{ ng/L}$ ).

Here, we report the development of a new technique to pre-concentrate  $\text{Ge}_i$  from seawater.  $\text{Ge}_i$  and other ultra-trace elements such as Fe are co-precipitated with magnesium present in seawater by addition of  $\text{NH}_4\text{OH}$  (final pH~9-10). Mg precipitates are filtered and dissolved in 0.25N  $\text{HNO}_3$ . The samples are then analyzed using a continuous flow hydride generation system coupled to a MC-ICP-MS (Thermo-Finnigan Neptune) operating at WHOI. The instrumental mass bias was corrected by the "standard-sample bracketing" method. Mass-bias correction using  $^{71}\text{Ga}/^{69}\text{Ga}$  ratios was also evaluated but did not result in improved accuracy of the measurements.

The Mg co-precipitation method was evaluated by processing 1L of acidified surface seawater spiked with our Ge standard to a concentration 50ng/L. We obtained preliminary  $\delta^{74}\text{Ge}$  values of  $0.26 \pm 0.25\%$ , ( $1\sigma$ ) for 5 repeated tests with a yield of  $80 \pm 17\%$  suggesting minor fractionation during chemical procedure. Procedural blanks are estimated at less than 0.4ng/L.

We also measured Ge-isotope composition of Ge-rich hydrothermal system samples without any pre-concentration but after a purification step with cation-exchange resin. Preliminary results on Ge isotopic composition of Ge-rich seafloor hydrothermal fluids from Loihi Seamount in the Pacific Ocean show systematically positive  $\delta^{74}\text{Ge}$  values  $\sim 1.5\%$ . In contrast,  $\delta^{74}\text{Ge}$  values of associated hydrothermal deposits, composed essentially of Fe-oxyhydroxides, range from -0.7 to 0.6%. The enrichment of light Ge-isotopes in Fe-oxyhydroxide precipitates at Loihi relative to the fluid (up to 2.5%) is consistent with previous experimental study of Ge-isotope fractionation during Ge-sorption onto Fe-oxyhydroxides (goethite) (Galy *et al.*, 2002). These results suggest that seafloor hydrothermal fluids may represent a source of isotopically heavy Ge in the ocean and that this isotope signature may be affected by Ge precipitation upon mixing with seawater. Additional studies will focus on Ge-isotope systematics in rivers and deep seawater in order to establish a reliable isotope mass balance of Ge in the ocean.