

Isotopic composition of dissolved Mg in natural waters

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Multiple collector inductively coupled mass spectrometry (MC-ICPMS) has experienced a big increase in technique and application development over the past few years. Variations in the stable isotopic composition of elements rarely studied, such as Mg, Cu, Zn, Fe or Mo are now attainable. Using this technique, natural variations in the isotopic composition of terrestrial Mg have been already found in carbonate, silicate and biological material. Here, I present preliminary results on the variation of the isotopic composition of dissolved Mg in natural waters.

27 natural waters from various geological settings (Open Ocean, continental spring, karst, lagoon, lake, and sediment) were studied. The overall variation is 4 ‰ and 2 ‰ in $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$, respectively. This is more than 30 times the uncertainty of the measurements and clearly demonstrates that the isotopic composition of dissolved Mg is not unique.

The four seawater samples have indistinguishable $\delta^{26}\text{Mg}_{\text{SRM980}}$ of +2.54‰. This result is consistent with the long residence time of Mg in the oceans. Upon the twelve continental waters, only one has a heavier isotopic composition than seawater. On the other side, all the seven water coming from coastal lagoon, lake and pore-water in sediments deposited in these environments are enriched in heavy isotopes.

The isotopic composition of a dissolved element is primarily affected by 1) source/sink isotopic composition and 2) isotopic fractionation associated to dissolution/precipitation reactions. The initial source of Mg in coastal lagoon is likely to be the seawater. The positive relationship between [Mg] or Mg/Ca and the isotopic composition of the Mg left in the water is likely the result of a Mg isotopic fractionation during the precipitation of minerals. This suggests that minerals should be enriched in light isotopes and has been established for Low-Mg calcite. In coastal environment, the isotopic of dissolved Mg is primarily controlled by its uptake and associated isotopic fractionation.

Given that silicate rocks are enriched in heavy isotopes by comparison to carbonate, the few data obtained on spring water from known aquifers suggest that the Mg-isotopes in continental water may reflect the source (silicate vs. carbonate) of the dissolved Mg.

References

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Ge-isotopic fractionation during its sorption on goethite: an experimental study

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Ge is generally believed to behave like Si in aqueous solution. However, unlike Si, Ge can form strong surface complexes with organic acids and iron oxides in which it increases its coordination number from 4 to 6 (Pokrovski and Schott, 1998). As a result, Ge isotopic fractionation could be associated with this process (Ge has five naturally occurring isotopes, ⁷⁰Ge, ⁷²Ge, ⁷³Ge, ⁷⁴Ge, and ⁷⁶Ge.) and used for better understanding and quantifying weathering processes. —To check this, a set of Ge sorption experiments on goethite were performed at 25°C and constant ionic strength (0.001 M) as a function of pH and Ge/goethite ratio and resulted in a fraction of adsorbed Ge ranging from 0.1 to 0.95.

The variation in the isotopic composition of Ge has been obtained by multiple collector inductively coupled mass spectrometry (MC-ICPMS). Following the method developed for Mg, solutions are introduced through into the MC-ICPMS (Nu Instruments) via a Cetac Aridus nebulizer. Isobaric interference from Ar has only been found on ⁷⁶Ge. Using this standard-sample bracketing technique, the external reproducibility of the MC-ICPMS obtained on pure Ge solution is 0.05‰/amu (2σ, n=20) on the three investigated ratios ⁷⁴Ge/⁷⁰Ge, ⁷³Ge/⁷⁰Ge, and ⁷²Ge/⁷⁰Ge.

Measured against its initial composition, the Ge left in solution after adsorption is systematically enriched in heavy isotope (up to 0.75‰/amu). In addition, the Ge-isotopic defines a single mass fractionation curve on three-isotope plots. When reported against the proportion of adsorbed Ge, all the data can be modelled by a single Rayleigh distillation.

These results have been modelled within the framework of a surface complexation approach that postulates the interaction of neutral Ge hydroxocomplexes with >FeOH^o and >FeO⁻ sites of goethite.

These preliminary data suggest that isotopic fractionation of Ge occur during its adsorption on goethite. Since goethite is a common mineral produced during weathering, Ge-isotopic composition in rivers and groundwater will be partly controlled by these adsorption mechanisms. Similar fractionation is expected to occur during Ge sorption on organic matter.

References

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