Theoretical determination of some important Ge isotope fractionations

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This study provides some geologically important equilibrium fractionation factors for Ge isotope in water (including seawater), quartz-like material and several Ge-bearing organic complexes. Such information could be useful to explore the unclear world for the Ge isotope [1, 2].

Urey model or Bigeleisen-Mayer equation based theoretical method and the "super-molecule" way has been used to calculate the fractionation factors between $Ge(OH)_4$, $GeO(OH)_3^-$, $GeO(OH)_3$-Na, $GeO_4(Si(OH)_3)_4$ and Ge-bearing organic complexes. All calculations are at the B3LYP/6-311+G** level. Supermolecules are built by using 30 water molecules surrounding the central Ge species. We also used 4 different conformers for each of the supermolecules to prevent possible error resulting from the diversity of conformations.

The dominant Ge species in water is $Ge(OH)_4$ and $GeO(OH)_3^-$.The fractionation $\Delta_{Ge(OH)4-GeO(OH)3-}$ is small (0.6‰) at 25°C in terms of $^{74}Ge/^{70}Ge$. In the seawater, this fractionation will become even smaller (~0.2‰). It suggests no matter what species is removed from the seawater, the Ge isotopic composition of seawater won't be changed much. The Ge in quartz-like structure will be the most enriched of Ge heavy isotopes. The $\Delta_{quartz-Ge(OH)4}$=1.0‰. Comparing to the small fractionations between inorganic compounds, the fractionations between Ge in quartz-like structure and all the 6-coordinated organic complexes are very large (~5.8‰), suggesting a new way to distinguish the possible bio-interferences.

[1] Rouxel *et al.* (2006) *GCA* **70,** 3387-3400. [2] Siebert *et al.* (2006) *GCA* **70,** 3986-3995.

Formation mechanism of banded iron formation and atmosphere and ocean of early Earth

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Isotopic compositions of S, Si and O of BIFs at the Northern China Craton are investigated systematically. The ^{30}Si values of quartz in BIFs of different types and ages (2.3-3.5Ga) are from -2.0‰ to -0.3‰, similar to those of modern submarine black smoker and sinter. The $\delta^{30}Si$ values of quartz contained in magnetite layer are lower than those of neighboring siliceous layer, while this goes the other way round for $\delta^{18}O$. This kind of regular variety of Si and O isotopic compositions may reflect the original feature at the sediment stage of BIFs but not the outcome of later metamorphism. The isotopic component of Si and O imply that BIF was formed by submarine exhalation, whatever the Algoma-type or the Superior-type. SiO_2 was precipitated at first to form the siliceous layer during the marine exhalation process due to the abrupt temperature drop, subsequently Fe^{2+} was gradually oxygenized and deposited to form the magnetite layer. A set of rhythmic layering stands for once marine exhalation activity and the periodic marine exhalations form regular rhythmic layers.

The $\Delta^{33}S$ values in the sulfides of BIFs vary from -0.89‰ to +1.2‰, showing an obvious mass independent fractionation. $\Delta^{33}S$ usually displays a negative value at the Algoma-type BIF closely related to volcanic activities, whereas a positive Δ33S value appears at Superior-type BIF distant from volcanic activity center. The widespread BIFs and S isotope mass independent fractionation indicate a extremely low oxygen concentration in atmosphere and soluble sulfate concentration in ocean, intense marine exhalation activities, high temperature of sea water and concentration of SiO_2 and Fe^{2+}, low pH value.