Germanium isotope geochemistry: analysis, fractionation mechanisms and geochemical tracing

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Introduction

Since Ge isotope is a new nontraditional isotope, the accumulated Ge isotope literatures are quite limited. The available researches mainly focused on two aspects: (1) the measurement of Ge isotopic compositions of geological and extraterrestrial materials, such as igneous rocks, marine sediments, seafloor hydrothermal fluids, hydrothermal Fe-oxyhydroxides, terrestrial high-temperature geothermal fluids, sphalerite, and iron meteorites; and (2) theoretical prediction of germanium isotope fractionation. Here we report two cases on the analysis, fractionation mechanisms and geochemical tracing of Ge isotope of Ge-rich coal and Pb-Zn sulfides from Southwest China.

Sample preparation and analysis

About 50 to 150 mg sphalerite, galena, pyrite and chalcopyrite samples were digested by concentrated HNO_3 and HF, and Ge was separated and purified by AG1-X8 anion-exchange resin. The recovery of Ge of whole sample preparation procedures was evaluated by standard-addition method. Then the Ge isotope compositions of all samples were determined by MC-ICP-MS coupled with hydride generation system (HG-MC-ICP-MS). Duplicate measurements of NIST SRM3120a during 8-month yielded a long-term reproducibility of about ± 0. 19‰ (2s) for δ^{74}Ge. Repeated analysis of Spex and Merck standard solutions yielded an average δ^{74}Ge value of −0. 70± 0. 19‰ (2s, n=27) and −0. 36 ± 0. 08‰ (2s, n = 26), respectively.

The matrix effects of several elements were investigated by doping experiments. The concentrations of possible matrix elements in the final solutions of purified natural sulfide samples are distinctly lower than the concentration levels of these elements that can lead to significantly biases of Ge isotopic compositions. The δ^{74}Ge values of sphalerite GBW-07270 doped with various amounts of Spex solution strictly follow the predicted mixing line between sphalerite GBW-07270 and Spex standard solution. These facts demonstrate that there is no Ge isotope fractionation during the whole purification and analysis process (Meng et al. , 2015).

Germanium isotopic sytsematics in Ge-rich coal from the Lincang Ge deposit (LGD) , Yunnan, Southwestern China

Ge-rich lignite samples exhibit large Ge isotopic fractionation (δ^{74}Ge values range from −2. 59‰ to 4.

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72‰), and their δ^{74}Ge values negatively correlate with Ge concentrations. Along stratigraphic sections, Ge is mainly concentrated in the top or the bottom of the coal seam, such that high values of δ^{74}Ge are usually found in the middle part of the coal seam.

Simulative calculation approves that Rayleigh fractionation and mixing processes in an open system control the overall variations of Ge isotope fractionation of various samples; Ge-bearing coal and hydrothermal chert derives from a same source with δ^{74}Ge values ranging from 1. 84‰ to 1. 97‰. Low temperature ashing (600°C) cannot lead to obvious Ge isotope fractionation, however, high temperature coal combustion fractionates Ge isotopes. The simultaneously enrichment of potential hazardous elements (i. e. , Pb, Cd, Tl and As) and light Ge isotope (^{70}Ge) in soot implies that Ge isotopes can be possibly used as tracers of the sources of anthropogenic heavy metal pollution in the environment (Qi et al. , 2011).

Germanium isotopic variations in Pb-Zn sulfides from Southwestern China

Nature sulfide separates (sphalerite, galena, and pyrite) with sizes of 20 to 60 mesh were obtained by crushing the Pb–Zn ores from the Jinding (JD), Shanshulin (SSL) and Tianqiao (TQ) Pb–Zn deposits in Southwestern China and handpicking under a binocular microscope. Germanium isotopic compositions of these separates were then obtained using the proposed method.

Sulfides from these Pb–Zn deposits have δ^{74}Ge values of −4. 94‰ to +2. 07‰. The paragenetic sequence of sulfides from the Shanshulin and Tianqiao Pb–Zn deposits is pyrite, sphalerite and galena from early to late. Sulfides from the same ore show a trend of $\delta^{74}Ge_{pyrite} < \delta^{74}Ge_{sphalerite} < \delta^{74}Ge_{galena}$, which may be controlled by the kinetic or Rayleigh fractionation (Meng et al. , 2015).

Final Remark

The above researches have revealed an overall range of 9. 66 per mil for δ^{74}Ge (δ^{74}Ge values vary from −4. 94‰ to 4. 72‰) in all Ge-rich coal samples and Pb-Zn ores from low temperature hydrothermal deposits, however, unlike any other radiogenic isotopes (such as Sr and Nd isotope), the variations of Ge isotopes among different samples do not distinctly show any special source or end-member. How to connect the variation of Ge isotope with ore-forming process or the evolution of hydrothermal fluid will be the key issues for Ge isotope studies in the future.

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