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An Intercomparison Study of the Germanium Isotope Composition of Geological Reference Materials

Raphaelle Escoube[1,2], Olivier J. Rouxel[2,3,4,*], Béatrice Luais[5], Emmanuel Ponzevera[4],
Olivier F.X. Donard[2]

[1] LCABIE, U. Pau et Pays de l'Adour, CNRS UMR 525, Hélioparc 64053 Pau, France
[2] UEB-UBO, European Institute for Marine Studies IUEM, 29280 Plouzané, France
[3] Marine Chemistry and Geochemistry Department, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA
[4] IFREMER, Centre de Brest, DRO/GM, 29280 Plouzané, France
[5] Centre de Recherches Pétrographiques et Géochimiques (CRPG) CNRS – UPR 2300, Nancy-Université, 15 rue Notre Dame des Pauvres, BP 20, 54501 Vandoeuvre-lès-Nancy Cedex, France

*: Corresponding author : Olivier J. Rouxel, email address : orouxel@ifremer.fr

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Abstract :

Recent analytical developments in germanium stable isotope determination by multicollector ICP-MS have provided new perspectives for the use of Ge isotopes as geochemical tracers. Here, we report the germanium isotope composition of the NIST SRM 3120a elemental reference solution that has been calibrated relative to internal isotopic standard solutions used in the previous studies. We also intercalibrate several geological reference materials as well as geological and meteoritic samples using different techniques, including online hydride generation and a spray chamber for sample introduction to MC-ICP-MS, and different approaches for mass bias corrections such as sample–calibrator bracketing, external mass bias correction using Ga isotopes and double-spike normalisation. All methods yielded relatively similar precisions at around 0.1‰ (2*s*) for $\delta^{74/70}$Ge values. Using igneous and mantle-derived rocks, the bulk silicate Earth (BSE) $\delta^{74/70}$Ge value was re-evaluated to be 0.59 ± 0.18‰ (2*s*) relative to NIST SRM 3120a. Several sulfide samples were also analysed and yielded very negative values, down to −4.3‰, consistent with recent theoretical study of Ge isotope fractionation. The strong heavy isotope depletion in ore deposits also contrasts with the generally positive Ge isotope values found in many modern and ancient marine sediments.

Résumé :

De récents développements analytiques ont permit la détermination de la composition isotopique du germanium par ICP-MS multi-collecteur, permettant de nouvelles perspectives dans l'utilisation des isotopes du germanium en tant que traceur géochimique. Dans ce papier, la composition isotopique du germanium de la solution de réference élémentaire NIST SRM 3120a a été calibrée par rapport aux standards utilisés dans les précédentes études. Différents matériaux de références ont été aussi intercalibrés ainsi que des échantillons géologiques et météoritiques en utilisant différentes techniques tels que l'introduction par génération d'hydrure en ligne et par chambre cyclonique, mais aussi différentes approches de correction de biais de masse tels que l'encadrement « échantillon-standard », l'utilisation d'un standard externe avec l'introduction de Ga et la normalisation par double spike. Toutes ces méthodes présentent des précisions relativement similaires autour de 0.1‰ (2*s*) pour la mesure du $\delta^{74/70}$Ge. A partir des roches ingnées et dérivées du manteau, la valeur de $\delta^{74/70}$Ge de la terre silicatée globale (BSE) a été réévaluée autour de 0.59 ± 0.18‰ (2*s*) par rapport au NIST SRM 3120a. Plusieurs échantillons de sulfures ont aussi été analysés et présentent des valeurs très négatives, jusqu'à−4.3‰, ce qui est consistant avec la récente étude théorique sur les fractionnements isotopiques du germanium. De plus, ce fort appauvrissement en isotope lourds dans les dépôts sulfurés contraste avec la tendance positive de la composition isotopique du germanium observée dans les sédiments marins actuels et passé.

Keywords : germanium ; Isotope ; Intercalibration ; reference materials

Mots clés : germanium ; Isotope ; Intercalibration ; materiaux de référence

Introduction

Germanium (Ge) has 5 natural isotopes: ^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge and ^{76}Ge with average relative isotope abundances of 20.84, 27.54, 7.73, 36.28 and 7.61 %, respectively. Early investigations of Ge isotopes using thermal ionization mass spectrometry (TIMS), SIMS and MC-ICP-MS were limited by an uncertainty of several per mil (Green *et al.* 1986, Hirata 1997, Shima 1964), mainly due to the presence of Ar-based interferences (Ar_2^+ and ArO_2^+) at m/z 72, 74, 76, as well as interferences from ^{70}Zn and ^{76}Se. More recently, further analytical developments by MC-ICP-MS have permitted high precision Ge-isotope measurement with repeatability around 0.06 ‰ per mass unit (Galy *et al.* 2003, Luais 2003, 2007, Rouxel *et al.* 2006, Siebert *et al.* 2006, Yang and Meija 2010). Notably, Rouxel et al. (2006) and Siebert et al. (2006) applied a hydride generation (HG) technique coupled to MC-ICP-MS, which allow high-precision Ge-isotope analyses on natural samples for Ge amounts down to ~15 ng.

The analyses of Siebert et al. (2006) were done using a double spike approach while Rouxel et al. (2006) measured isotopic ratios and corrected for instrument fractionation with bracketing standards. In contrast, Luais et al. (2000) and Luais (2003, 2007) used a hexapole-collision cell MC-ICP-MS (Isoprobe GV Instrument) with H_2 gas to remove Ar_2 interferences, and corrected for instrument fractionation by using both Ga-isotopes as an internal normalization standard and by bracketing standards. Despite the obvious success in obtaining high precision measurement of Ge isotopes by MC-ICP-MS in a range of terrestrial and meteoritic materials, those previous studies have used a large diversity of techniques, standards, normalization ratios and instrumentations which preclude a straightforward comparison of published values. Thus, the concept of metrological traceability has not been applied.

Rouxel et al. (2006) obtained a crude estimate of the Ge isotopic composition of the Bulk Silicate Earth (BSE) by the analysis of various igneous rocks such as tholeiitic glasses from mid-ocean ridges, continental basalts and volcanic island basalts. Deep sea clays have δ^{74}Ge values similar to BSE while modern deep-sea sponges and glauconite have δ^{74}Ge values heavier than BSE. Considering that Ge isotope fractionation during biogenic opal and glauconite may favour enrichment in light isotopes in the forming product, it has been suggested that the Ge isotopic composition of the ocean is enriched in heavy isotopes relative to BSE (Rouxel *et al.* 2006). In addition, Mantoura (2006) carried out laboratory experiments indicating that cultured diatoms do not fractionate Ge isotopes. Luais (2003, 2007) demonstrated that iron meteorites have a δ^{74}Ge values heavier than terrestrial samples. The homogeneous δ^{74}Ge values for magmatic iron meteorites, regardless of their oxidation state suggests, in agreement with experimental data (Luais et al., 2009), that core formation processes do not fractionate significantly Ge isotopes in the metal phase with respect to the primitive material, providing an estimate for Ge isotopic composition of the solar nebula.

Siebert et al. (2006) reported Ge isotope composition of hydrothermal waters collected in the Oregon Cascades and in marine settings and found lighter isotope signatures relative to basalts. However, a preliminary intercomparison performed by the authors and colleagues suggests that the reported Ge-isotope compositions are plagued by calculating errors during the data reduction scheme (C. Siebert, personal communication), precluding further comparison with our study.

The aim of this paper is to compare analytical techniques to obtain Ge-isotope composition of selected geological reference materials and to intercalibrate Ge-isotope standards relative to the BSE estimate. We propose the use of a new reference material NIST3120a to report natural Ge-isotope variations. This approach, together with further studies of experimental and theoretical fractionation of Ge-isotopes (Galy *et al.* 2003, Luais et al., 2009, Li *et al.* 2009, Li and Liu 2010) are essential steps toward the development of Ge-isotopes as new geochemical tracer.

Experimental procedures

Reagents and Germanium standard solutions

The hydride generation reagent is composed of 10 g of sodium borohydride powder (high purity $NaBH_4$, Fisher Chemical) and 5 g of sodium hydroxide pellets (analytical grade NaOH, Acros Organics) dissolved into 1 l of ultra pure water (Milli-Q 18.2MΩ.cm, Millipore), and is freshly prepared before each analytical session. During chemical dissolution and purification, we used high purity HNO_3 (distilled grade, CleanAcid, Analab) and HF (optima grade, Fisher Chemical). Germanium standards used in this study include NIST3120a (Lot #000411, 1000µg/g); Spex (Lot #11-160GE); Aldrich (Lot #01704KZ; Luais, 2000, Luais 2007), JMC (Johnson Mattey, Karlsruhe, Lot # 301230S; Luais 2007) and Aristar (Lot # used in Rouxel et al., 2006 – incorrectly reported as Aldrich standard solution). We also used Ga (Spex; Lot #12-98Ga; Cat # PLGA2-2Y) and Ga international isotopic standard (NBS - SRM994, Lot# 680205, Luais et al., 2000; Luais 2007) prepared from Ga metal as internal standards for instrumental mass bias corrections. Double Spike was prepared from Ge metal spikes 73-70 from Isoflex USA Company (Ge-70 #32-01-70-3259 and Ge-73 #32-01-73-1405). Each spike was dissolved separately in a mixture HNO_3, sulfuric acid and trace HF and mixed to obtain a $^{73}Ge/^{70}Ge$ ratio of ~ 0.6.

Geological reference materials and other geological samples

Several geological reference materials have been analyzed in this study for intercomparison purposes with previous studies by Rouxel et al. (2006). They include USGS standards (Govindaraju 1994) BHVO-2 (Hawaiian basalt), BIR-1 (Icelandic basalt), BCR-1 (Basalt, Columbia River Group USA), G-2 (Granite, Rhode Island USA), GH (Granite, Hoggar, Algeria), DNC-1 (Braggtown Dolerite, North Carolina, USA), DTS-1 (Dunite, Hamilton, Washington), PCC-1 (Peridotite- a partially serpentinized harzburgite, California USA), AN-G (Anorthosite, Fiskenaesset, Western Greenland), GLO (Glauconite, Normandy France), and IF-G (Iron Formation, West Greenland).

We also analyzed the Iron meteorite Odessa (IAB group) for which Ge-isotope composition has been previously reported by Luais (2003, 2007). We also report Ge-isotope composition of hydrothermal sulfides (sphalerite) from volcanogenic sulfide deposits, the Navan Zn+Pb ore deposit in Ireland (Blakeman *et al.*, 2002), from continental hydrothermal ZnS ores from the St Salvy deposit in France (Luais, 2003, 2007), and from modern seafloor hydrothermal systems, the Lucky Strike field (Rouxel *et al.* 2004).

Sample dissolution and chromatographic separation

A procedure adapted from Rouxel et al. (2006), Luais (2007) and Luais (submitted) was applied in this study for Ge purification from siliceous matrices, iron meteorites and sulfides. For HG-MC-ICP-MS method (IFREMER and WHOI laboratories), about 50 mg of siliceous material was dissolved in ~ 3 ml of 10 mol/l HF in a closed Teflon beaker on a hot plate at 70 °C and left to equilibrate overnight with an appropriate addition of double spike (spike/natural ratio ~ 1). After appropriate dilution to 1 mol/l HF with ultrapure water, the solution was directly purified without evaporation through a chromatographic column containing 2 mL of anion exchange resin (AG1-X8 Resin; 100-200 mesh; Chloride Form; Cat # 140-1441). The column is cleaned with several washes of 5 ml of 0.28 mol/l HNO_3, distilled 3 mol/l HNO_3, and ultrapure water. After conditioning with 5 ml of 1 mol/l HF, the sample was loaded on the column and germanium strongly adsorbed on the resin. Matrix elements such Ca, Fe, Si or Zn were eluted and the resin further cleaned with 5 ml of 1 mol/l HF followed by 3 ml of ultrapure water. Ge was then eluted with 10 ml of 3 mol/l HNO_3 and the solution evaporated slowly to dryness on a hot plate. The final residue was dissolved in 3 ml of 0.28 mol/l HNO_3 and ready for isotope analysis. Since the HG sample introduction system allow complete separation of volatile Ge hydride from the aqueous sample matrix (e.g. Rouxel et al., 2006), no further purification using cation exchange resin is required. Procedures for iron meteorite and sulfide dissolution are detailed in Luais et al. (2000) and Luais (2007). Briefly, it consists of dissolution using 2 mol/l and 14 mol/l HNO_3, respectively, followed by Ge isolation using AG50X8 cation exchange resin with 0.5 mol/l HNO_3. Procedures for silicate matrices used at CRPG (Luais, submitted) consist of HNO_3 + HF dissolution followed by several steps of HF leaching to isolate Ge (± matrix) in the supernatant. After evaporation and subsequent dissolution in 1 mol/l HF, an aliquot of the sample is loaded on a AG1X8 anion exchange resin. Most of the remaining matrix is eluted with 1 mol/l HF, and Ge is subsequently collected using 0.2 mol/l HNO_3. Purification of Ge is then performed on AG50X8 cationic resin similarly developed for iron meteorite matrix. The efficiency of these procedures including 100 % yield and no isotopic fractionation during all steps of Ge chemistry is demonstrated by Ge isotopic measurements of various matrices doped with Ge standard, as well as Ge standard solutions after column separation. Details are given in Luais (2007) for iron meteorite matrix and in Luais (submitted) and Rouxel et al. (2006) for various silicate matrices from ultra-mafic, mafic to granitic in composition. In all cases, the Ge isotopic composition of these Ge-dopped matrices is similar within error to the measured Ge standard solution.

MC-ICP-MS isotope ratio measurements:

Germanium isotopes ratios were determined with a Thermo *Neptune* (Thermo Fisher Scientific; Waltham, MA, USA) at the Pôle Spectrométrie Océan (PSO, Brest) at IFREMER (Plouzané, France) and WHOI (Woods Hole, USA) using the hydride generation technique described by Rouxel *et al.* (2006). Pure standard solution and purified sample measurements were also performed on a Nu Plasma MC-ICP-MS at LCABIE laboratory (Pau, France) and Isoprobe (GV) MC-ICP-MS at CRPG laboratory (Nancy, France) (Luais 2007). The Neptune at WHOI and IFREMER was operating at low-mass resolution mode and ^{70}Ge, ^{72}Ge, ^{73}Ge and ^{74}Ge were measured on L2, C, H1, and H2 cups while ^{68}Zn, ^{69}Ga, ^{71}Ga and ^{77}Se were also monitored on L4, L3, L1 and H4 cups. The isotope ^{76}Ge was not measured due to a major interference of $^{38}Ar_2$. For the Nu plasma measurements at LCABIE, we set the cups as H6, H4, H2, and L2 for 74, 73, 72 and 70 at low mass resolution and the Ax and L3 cups for 71 and 69 Ga isotopes. For the GV Isoprobe measurements (CRPG), ^{70}Ge, ^{72}Ge, ^{73}Ge and ^{74}Ge

were measured on Ax, H2, H3 and H4 cups while ^{68}Zn, ^{69}Ga, and ^{71}Ga were measured on L3, L2, and H1 cups.

Several introduction systems were used and include: (1) a cyclonic spray chamber (SiS) equipped with PTFE micro concentric nebuliser at 50 µl/min for WHOI, IFREMER and CRPG (Luais 2007) while a Quartz micro concentric nebuliser at 100 µl/min was used for LCABIE measurements; (2) continuous flow hydride generation systems, CETAC HGX-200 at WHOI and IFREMER (see Rouxel *et al.*, 2006 for instrument settings) and a custom-built HG generator at the LCABIE.

Instrumental mass bias was corrected using several techniques as described in previous studies (Galy *et al.* 2003, Luais 2007, Rouxel *et al.* 2006, Siebert *et al.* 2006): (1) a sample-standard bracketing (referred to as SSB) technique that involves the measurement of the Ge standard solution, before and after each unknown sample (Galy *et al.* 2003, Rouxel *et al.* 2006); (2) external normalization to Ga-isotopes (referred as Ga-Cor) (Galy *et al.* 2003, Hirata 1997, Luais et al. 2000, Luais 2007, Siebert *et al.* 2006) and Cu-isotopes. (3) Double spike (DS) correction (73/70) was performed as described by Siebert *et al.* (2006). The double spike solution was mixed with the sample before chemical purification with a spike/natural ratio of around 1 (g/g). Data reduction of Ge-isotope ratios was performed using a scheme similar to Siebert *et al.* (2001). In some cases, we coupled the hydride generation system with the regular cyclonic spray chamber using an extra inlet available on the spray chamber. This approach allowed a direct comparison of instrumental mass bias induced by both techniques and the calculation of hydride generation yield. It also permitted the use of Ga as an internal standard to correct for instrumental mass bias during hydride generation.

Results and discussion

Notation and data normalization

Germanium isotope composition can be reported using several possible notations, such as:

$$\delta^{x}Ge\ (‰)=\left(\frac{(^{x}Ge/^{70}Ge)_{sample}}{(^{x}Ge/^{70}Ge)_{STD}}-1\right)\times1000 \qquad (1)$$

Where x = 74, 73 or 72 and STD corresponds to the normalization to Ge-standard. Currently, there is no consensus in the way to report Ge-isotope ratios. Siebert *et al.* (2006)

reported $\delta^{74/72}$Ge due to the double spike correction using ^{73}Ge and ^{70}Ge spikes. Galy *et al.* (2003) reported δGe per mass unit while Rouxel *et al.* (2006) and Luais (2003, 2007) reported $\delta^{74/70}$Ge (together with other 73/70 and 72/70 isotope ratios). Due to larger abundances and minor isobaric interferences, the ^{74}Ge/^{70}Ge ratio seems to be optimum for reporting Ge-isotopes. Throughout this study, we reported δ^{74}Ge/^{70}Ge values relative to SRM3120a which is a concentration standard produced in large amount.

Isobaric interferences and instrumental mass bias

Ge isotope measurements suffer from molecular interferences, such as $^{35}Cl^{35}Cl^+$ on $^{70}Ge^+$; $^{40}Ar^{16}O_2^+$ and $^{36}Ar^{36}Ar^+$ on $^{+72}Ge^+$, $^{58}Ni^{16}O^+$ and $^{38}Ar^{36}Ar^+$ on $^{74}Ge^+$ and $^{38}Ar^{38}Ar^+$ and $^{36}Ar^{40}Ar^+$ on $^{76}Ge^+$. On the Neptune and Nu Plasma coupled to HG, those interferences are minimized and are generally negligible except for ^{76}Ge, as previously discussed by Rouxel *et al.* (2006). We however observed a ubiquitous interference on $^{70}Ge^+$ during the early stage of analytical development on the Neptune, probably from $^{40}Ar^{14}N^{16}O$ due to the use of X-cones which may induce a higher oxide-level. Therefore, we only used normal cones throughout this study. On the GV Isoprobe, hydrogen addition in the hexapole collision cell was used to remove Ar_2 interferences (Luais et al. 2000; Luais, 2007).

Ge-isotope measurements, and in particular double-spike correction, may suffer from potential GeH^+ interference. Therefore, we evaluated the contribution of $^{70}GeH^+$ on mass 71 by measuring ($^{71}Ga^+$+$^{70}GeH^+$)/$^{69}Ga^+$ ratios. This approach permits us to evaluate the influence of GeH^+ on the signal, which is around 0.001 ‰ and thus negligeable, in agreement with Luais et al. (2000).

Isotopic measurements on all instruments were also corrected for Zn interferences on mass 70 using ^{68}Zn, with a mass bias applied on ^{70}Zn/^{68}Zn ratios (Luais, 2007).

As germane (GeH_4) formation in the hydride generator may induce isotope fractionation, we coupled the spray injection system with the HG to evaluate potential mass bias. This analytical setup allowed a direct comparison of the Ge-isotope ratios of the standard introduced using conventional spray chamber (“Standard”) vs. hydride generation (“Sample”) (Figure 1). The SRM3120a Ge standard solution was adjusted to a concentration of 250 ng/g for spray chamber injection and to 10 ng/g for hydride generation to reach similar intensity for both introduction systems. The results suggest that the difference in mass bias between the spray chamber and the HG system is about 0.05 +/- 0.07 ‰ (2s) per mass unit, which suggest that, either Ge-hydride formation does not fractionate Ge-isotopes or that the hydride formation yield is quantitative. Considering that the spray chamber system has an efficiency of Ge transfer into the plasma torch of about 20 % (determined using the volume of solution taken vs. solution drained in waste), we can determine an overall sensitivity in abundance of 0.85 pg/V. In comparison, we calculate that hydride generation has a sensitivity of 0.91 pg/V which suggest that about 100% of germanic acid in solution is reduced to germane species.

Assessment of standard and double-spike isotope composition

While Ga is traditionally used to control the mass bias for Ge analyses (Galy *et al.* 2003, Hirata 1997, Luais et al. 2000, Luais 2007,), we recognize that such approach may not allow absolute Ge isotope ratio measurement since instrumental mass bias may be different between elements (e.g. Maréchal *et al.* 1999, Yang and Meija 2010, Meija et al. 2009). We however found that Ga or Cu can be appropriate elements for external mass bias correction and determination of relative isotopic composition (in delta value) of Ge standards or samples. The assumption of identical mass bias for analyte and standard however require identical matrix composition and concentrations. In addition, external mass bias correction yields identical results in delta values than standard-sample bracketing method or double spike normalization, as presented in Tables 2 and 3 and discussed below.

The double-spike composition was defined relative to the NIST 3120a composition obtained on the Neptune at PSO, Brest (Table 1) using conventional spray chamber introduction system. In order to calibrate the Ge-isotope ratios of NIST 3120a, we used a Gallium standard solution (Spex; Lot #12-98Ga) to correct for instrumental mass bias using $^{69}Ga/^{71}Ga$ ratio of 1.50676 (Machlan et al., 1986). This approach was also used to monitor instrumental mass bias between analyses of pure standard and double spike. It is important to note that both our double spike and NIST 3120a calibration reported in Table 1 may differ from the *true* value but this potential bias does not affect the final isotope ratios when using the delta notation. Although we didn't determine the optimum double spike composition or spike/natural ratios using error propagation tests, Figure 2 shows that spike/natural ratio between 0.8 to 3.5 yield consistent results with overall precision of 0.15 ‰ (2s). In practice, a ratio between 1 to 2 was routinely used for isotope analysis. This optimal ratio is very similar to the one used by Siebert et al (2006).

Intercomparison of Ge isotope compositions of Ge standard solutions

The average compositions of NIST3120a and other standard solutions over multiple analytical sessions for different instruments and measurement setups are reported in Table 2.

Aristar and *Spex* solutions show an enrichment in the light isotope of approximately the same proportion ($\delta^{74/70}$Ge = -0.64 +/- 0.18 ‰ (2s) and -0.71 +/- 0.20 ‰ (2s), respectively). *JMC* standard also presents an enrichment in the light isotope although in smaller proportion, with a $\delta^{74/70}$Ge value of -0.32 +/- 0.10 ‰ (2s). The *Aldrich* standard shows the lightest $\delta^{74/70}$Ge values at -2.01 +/- 0.22 ‰ (2s). Several sample introduction systems were tested, using either spray chamber (SiS) or hydride generation (HG) for different instruments (Neptune, Nu plasma or Isoprobe) and no systematic differences were found. It is also important to note that standard-sample bracketing, Ga normalization and double spike corrections yielded similar results, both in terms of Ge isotope composition and analytical precision.

Ge isotope composition of geochemical RM and re-evaluation of the bulk silicate Earth value

Selected geochemical RM, measured using double spike (this study), sample-standard bracketing (Rouxel *et al.* 2006), and Ga normalization (Luais 2007) methods are reported in Table 3. In addition, we report precise Ge concentrations determined by isotope dilution since the double spike data reduction scheme offers the advantage to also calculate precisely the Ge concentration of the samples.

Based on these data, the bulk silicate Earth value has been re-evaluated as $\delta^{74/70}$Ge = 0.56 ‰ versus NIST SRM3120a. This average is determined from igneous rocks (BHVO-2; BIR-1; BCR-1) having limited variations (2s = 0.08 ‰). Granitic rocks display significant deviation from the bulk silicate Earth with G-2 (Rhode Island, USA) having a slightly lighter composition at 0.40 +/- 0.04 ‰ (2s). Ultramafic rocks, although less concentrated in Ge, present similar compositions as basaltic rocks. We note that NIST3120a is the standard whose isotope composition is the closest to the BSE relative to the other standard solutions used previously (Table 2). As discussed below, iron formation IF-G and marine sediment GL-O yield heavier $\delta^{74/70}$Ge values at 1.03 +/- 0.10 ‰ (2s) and 2.44 +/- 0.14 ‰ (2s) respectively.

Although Ge concentrations have been widely reported in geochemical reference materials (Govindaraju 1994), they are only rarely analyzed by isotope dilution and even more rarely by MC-ICP-MS after chemical purification. In most cases, our new concentration data in Table 3 are within 5% of previously reported data (e.g. BIR-1, BCR-1, G-2, DNC-1, AN-G, IF-G) while differences may be up to 10-20% in some cases (e.g. GH, DTS-1, PCC-1, GL-O).

Ge isotope composition of meteorites, sediments and sulfide deposits

As shown in **Figure 3**, the absolute range of $\delta^{74/70}$Ge values in rocks and minerals is about 8.05‰ which is comparable or even larger than most non traditional stable isotope systems (e.g. Anbar and Rouxel 2007). The strong heavy isotope depletion in sulfides contrasts strongly with the generally positive Ge isotope values found in many modern and ancient marine sediments (e.g. banded iron formations, glauconite).

Glauconite (GLO) and Iron Formation (IF-G) are two iron-rich rocks where redox conditions were important in their formation. Glauconite is a secondary clay mineral which is formed in marine sediments during the reduction of Fe(III) to Fe(II), while Archean Iron Formation is believed to have formed in globally anoxic oceans where hydrothermal Fe(II) was partially oxidized and co-precipitated with silica, either biotically or abiotically (e.g. Bekker et al., 2010). In both deposit types, Ge is enriched relative to crustal values with Ge/Si ratios of 6.44 x 10^{-6} and 2.7 x10^{-5} mol/mol for Glauconite and Iron formation, respectively. Since Galy *et al.* (2002) and Li and Liu (2010) suggested that Ge adsorbed onto iron oxyhydroxide is enriched in light isotopes, the positive $\delta^{74/70}$Ge values for GLO and IF-G is best explained by the heavy isotope composition of their Ge sources. In this case, the slightly lighter values for IF-G may potentially result from the contribution of hydrothermal Ge to Archean oceans (Hamade *et al.* 2003). Further studies are however required to address this issue.

Deep sea sponges of the NE Pacific (Rouxel *et al.* 2006) show an average isotope composition at around 2.47 ‰. The relatively high $\delta^{74/70}$Ge values obtained for different species at different depths also suggest that sponges likely record the Ge isotope composition of seawater. This value is a lower bound of the Ge isotopic composition of modern seawater because, if sponges fractionate Ge isotopes, they likely discriminate against heavy isotopes as already observed for Si isotopes. More recently, Mantoura (2006) reported $\delta^{74/70}$Ge values for cleaned diatom opal from Holocene sediments at around 3.3 ‰. Those results, together with the lack of Ge isotope fractionation observed during Ge uptake by cultured diatoms (Mantoura, 2006), further confirm that seawater is enriched in the heavy Ge isotopes, probably close to 3 ‰.

Two independent Ge isotope analyses of the non-magmatic iron meteorite Odessa are reported in Table 4 and are in perfect agreement. Also is reported the recalculated Ge isotopic composition of the magmatic iron meteorite Braunau (IIA). It is worthwhile to note that the Ge isotope composition of various types of iron meteorites (magmatic and non-magmatic irons) deviate from BSE in contrast to other heavy stable isotope systems (such as Cu, Zn, Fe;

Moynier *et al.* 2007), confirming the complexity of metal-silicate segregation and the importance of volatilization/alteration effects (Luais, 2007).

Both sphalerite from ancient Pb-Zn ore deposits (Blakeman *et al.* 2002) and seafloor hydrothermal deposits at Lucky Strike (Rouxel *et al.* 2004) have been analyzed and an average δ^{74}Ge value of -3.53 ± 0.51‰ has been obtained (Table 4). Sphalerite from the single ZnS ore deposit of St Salvy mine (France), precipitated from hydrothermal fluids related to plutonic intrusion, also exhibit negative values with a range of -1 to -2 ‰ (Luais, 2007). These results are interesting because Ge isotopes in sulfides are completely shifted toward negative values by ~4 ‰ relative to BSE. In contrast, preliminary Ge isotope analysis from hydrothermal fluids yield variable δ^{74}Ge values around 1.9 ± 0.5 ‰ (Escoube *et al.* 2008, Rouxel *et al.* 2008). The recent study by Li *et al.* (2009) estimating equilibrium fractionation factors in the Ge isotope system suggested a very large fractionation toward lighter values (up to 10 ‰ at 25 °C) in Ge-bearing sulfides relative to 4-coordinated Ge–O compounds (e.g. $Ge(OH)_4$(aq) or quartz). Therefore, the large difference between sulfides and BSE is best explained by a strong isotopic fractionation (may be up to 4.5 ‰) during sulfide precipitation in hydrothermal systems.

Conclusion

This study permits an intercomparison of germanium isotope measurement techniques as well as a calibration of several geological reference materials and mono-elemental standard solutions used in previous studies. Different methodologies were used during this study: (1) introduction by on-line hydride generation and spray chamber, and (2) mass bias correction by sample-standard bracketing, external mass bias correction using Ga or Cu isotopes and double spike normalization. Even if all methods yield consistent isotope composition with similar precisions (2s~0.15‰), the double spike correction offers the advantage of providing high-precision Ge concentrations and correcting for potential Ge isotope fractionation during sample dissolution and purification.

Using igneous and mantle-derived rocks, the Bulk Silicate Earth (BSE) was re-evaluated to 0.59 +/- 0.18 ‰ (2s) relative to NIST3120a. In comparison, Iron meteorites exhibit more positive values of $\delta^{74/70}$Ge up to +1.5 ‰. We report an overall $\delta^{74/70}$Ge variation in terrestrial rocks and minerals of about 8 ‰. This range is comparable or even larger than most non-traditional stable isotope systems (e.g., Fe). This large range of compositions is mainly due to the extreme value (down to -4.3 ‰) for sulfide samples originating from hydrothermal environments, consistent with theoretical calculations (Li *et al.* 2009). This strong isotope depletion in sulfides contrasts drastically with the generally positive Ge isotope values found in many modern and ancient marine sediments (e.g. banded iron formations, glauconite). Large variation in germanium stable isotopes and their reproducible measurement provides new perspectives on the use of Ge as a novel geochemical tracer, in particular for tracing planetary and oceanic processes.

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Figure Captions

Figure 1: (A) Comparison between hydride generation (HG) and spray chamber (SiS) methods for Ge isotope analysis. A NIST3120a solution was alternatively introduced though the HG (square), considered as an “unknown sample” at a concentration of 10 ng/g, and through the SiS (Diamond), used as “bracketing standard” at a concentration of 250 ng/g. The concentrations were adjusted to obtain the same voltage (graph A). (B) Ge isotope composition (in delta values) of the NIST3120a standard determined by HG and normalized to SiS values.

Figure 2: Ge isotope composition of NIST3120a and Aldrich standards determined using a double spike method with different Spike/Sample ratios. While the addition of spike in proportions of 0.6-4 relative to sample yielded approximately stable δ^{74}Ge values, analyses are best performed with Spike/Sample ratios between 1 and 2.

Figure 3: Compilation of Ge isotope composition ($\delta^{74/70}$Ge) of geological reference materials and natural samples versus NIST3120a; (a) Luais, 2007; (b) Rouxel et al., 2006; (c) this study; (d) Mantoura (2006).

Table Captions

Table 1: Ge isotope compositions of NIST3120a standard and Ge70-73 double spike determined on the Neptune MC-ICP-MS after internal normalisation to Ga for instrumental mass bias correction

Table 2: Intercalibration of Ge isotope composition of standard solutions against NIST 3120a.

Table 3: Intercomparison study of Ge isotope compositions of geochemical RM versus NIST 3120a.

Table 4: Ge isotope compositions of sulfides and iron meteorites.

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Table 1

Name	$^{74}Ge/^{70}Ge$	2s	$^{73}Ge/^{70}Ge$	2s	$^{72}Ge/^{70}Ge$	2s
DS (^{70}Ge;^{73}Ge)	0.07614	0.00010	0.60707	0.00008	0.05626	0.00008
NIST3120a	1.76094	0.00005	0.37335	0.00003	1.32901	0.00004

Table 2

Lab	Method		nb#	$\delta^{74/70}$Ge	2s	$\delta^{73/70}$Ge	2s	$\delta^{72/70}$Ge	2s	$\delta^{74/72}$Ge	2s
				vs. NIST3120a		vs. NIST3120a		vs. NIST3120a		vs. NIST3120a	
"ARISTAR" standard				-0.64	0.18	-0.54	0.18	-0.38	0.26	-0.28	0.03
#1	HG	SSB	11	-0.58	0.12	*nd*		-0.30	0.09	-0.28	0.04
#1	HG	Ga	11	-0.57	0.08	*nd*		-0.30	0.05	-0.28	0.07
#2	SiS	SSB	4	-0.59	0.02	-0.47	0.04	-0.33	0.01	-0.26	0.01
#2	SiS	DS	4	-0.61	0.11	-0.46	0.08	-0.31	0.06	-0.30	0.06
#3	SiS	Ga	6	-0.76	0.28	-0.61	0.20	-0.41	0.17	*nd*	
#3	SiS	SSB	6	-0.75	0.28	-0.63	0.20	-0.63	0.17	*nd*	
"JMC" standard				-0.32	0.10	-0.23	0.12	-0.16	0.07	-0.16	0.05
#1	HG	SSB	*4*	*-0.33*	*0.33*	*nd*		*-0.15*	*0.27*	*-0.18*	*0.06*
#1	HG	Ga	*4*	*-0.31*	*0.29*	*nd*		*-0.14*	*0.25*	*-0.17*	*0.06*
#2	SiS	SSB	4	-0.23	0.02	-0.14	0.04	-0.11	0.03	-0.12	0.03
#2	SiS	DS	4	-0.32	0.07	-0.24	0.05	-0.16	0.04	-0.16	0.04
#3	SiS	Ga	8	-0.37	0.04	-0.25	0.02	-0.19	0.07	*nd*	
#3	SiS	SSB	8	-0.37	0.16	-0.28	0.14	-0.20	0.06	*nd*	
"SPEX" standard				-0.71	0.21	-0.56	0.15	-0.37	0.16	-0.31	0.08
#1	HG	SSB	1	-0.59	nd	*nd*		-0.28	nd	-0.31	nd
#1	HG	Ga	1	-0.60	nd	*nd*		-0.28	nd	-0.31	nd
#1	HG	SSB	*5*	*-0.84*	*0.16*	*nd*		*-0.48*	*0.10*	*-0.36*	*0.08*
#1	HG	Ga	*5*	*-0.81*	*0.11*	*nd*		*-0.46*	*0.09*	*-0.35*	*0.04*
#2	SiS	SSB	3	-0.61	0.04	-0.51	0.09	-0.33	0.03	-0.28	0.05
#2	SiS	DS	4	-0.63	0.13	-0.48	0.10	-0.32	0.06	-0.31	0.06
#3	SiS	Ga	10	-0.81	0.19	-0.62	0.24	-0.41	0.11	*nd*	
#3	SiS	SSB	10	-0.79	0.18	-0.62	0.16	-0.41	0.12	*nd*	
#4	SiS	SSB	14	-0.64	0.42	*nd*		*nd*	0.00	-0.23	0.26
#4	SiS	Ga	14	-0.79	0.18	*nd*		*nd*	0.00	-0.31	0.04
"ALDRICH" standard				-2.01	0.23	-1.54	0.17	-1.03	0.12	-0.97	0.15
#2	SiS	SSB	4	-1.88	0.03	-1.46	0.07	-0.97	0.02	-0.92	0.03
#2	SiS	DS	4	-2.14	0.06	-1.61	0.05	-1.08	0.03	-1.05	0.03
#2	HG	DS	6	-1.90	0.10	-1.44	0.08	-0.96	0.05	-0.94	0.05
#3	SiS	Ga	84	-2.08	0.26	-1.61	0.20	-1.08	0.16	*nd*	
#3	SiS	SSB	84	-2.05	0.22	-1.60	0.20	-1.06	0.14	*nd*	

Table 3:

Sample Name	Sample Type	SiO_2 % (m/m)	Ge ug/g	$\delta^{74/70}$Ge	2s	reference	Mean $\delta^{74/70}$Ge	2s
BHVO-1	Hawaiian	49.9(a)	1.64(a); 1.55(c)	0.55	0.15	(g)	0.55	0.15
BHVO-2	Basalt	49.9(e)	1.53(k)	0.55	0.13	(k)	0.51	0.10
				0.54	0.13	(k)		
				0.52	0.13	(k)		
				0.43	0.19	(h)		
				0.53	0.15	(h)		
BIR-1	Icelandic	47.96(e),	1.5(a); 1.45(b);	0.74	0.13	(k)	0.62	0.13
	Basalt	47.77(a)	1.53(b); 1.49(c);	0.60	0.13	(k)		
			1.52(d); 1.52(i);	0.56	0.30	(h)		
			1.40(k)	0.64	0.33	(g)		
				0.57	0.39	(g)		
				0.61	0.04	(i)		
BCR-1	Columbia	54.11(e)	1.5(a); 1.42(b);	0.65	0.13	(k)	0.55	0.15
	River Basalt		1.45(c); 1.36(k)	0.54	0.19	(h)		
				0.47	0.39	(h)		
				0.54	0.22	(g)		
DNC-1	Dolerite	47.15(e), 47.04(a)	1.3(a); 1.26(b);	0.56	0.13	(k)	0.67	0.19
			1.28(k)	0.76	0.13	(k)		
				0.74	0.31	(g)		
				0.61	0.42	(g)		
G-2	Granite	69.1(a)	1.14(a); 0.94(b);	0.41	0.30	(h)	0.40	0.03
			1.02(b); 0.92(k)	0.39	0.34	(g)		
GH	Granite	75.8(e)	2.0(a,f); 2.18(c);	0.74	0.13	(k)	0.68	0.22
			1.63(k)	0.74	0.13	(k)		
				0.55	0.28	(g)		
DTS-1	Dunite	40.41(a)	0.88(a); 0.84(c);	0.76	0.13	(k)	0.64	0.26
			0.83(i); 0.75(k)	0.50	0.06	(i)		
				0.65	0.28	(g)		
PCC-1	Peridotite	41.71(a)	0.94(a); 0.82(k)	0.69	0.13	(k)	0.66	0.13
				0.64	0.13	(k)		
				0.59	0.30	(h)		
				0.74	0.13	(g)		
AN-G	Anorthosite	46.3(a)	0.8(a); 0.93(c);	0.67	0.13	(k)	0.67	0.01
			0.84(k)	0.66	0.13	(g)		
Mean Bulk Silicate Earth							**0.60**	**0.18**
GL-O	Glauconite	50.9(a)	4.5(a); 4.02(k)	2.49	0.13	(k)	2.44	0.15
				2.34	0.21	(h)		
				2.51	0.55	(g)		
				2.42	0.26	(g)		
IF-G	Iron	41.2(a)	24(a); 22±0.2(f);	1.11	0.13	(k)	1.03	0.09
	Formation		21.8(i); 23.06(k)	1.03	0.13	(k)		
				1.01	0.25	(j)		
				1.00	0.27	(j)		
				1.01	0.17	(i)		

Table 4:

Sample Name	Ge ug/g	$\delta^{74/70}$Ge	2s	source
Iron meteorite				
Odessa (IAB)	288 (a)	0.96	0.07	*this study*
		0.98	0.09	Luais, 2007
Braunau (IIA)	183	1.47	0.24	Luais, 2007
Navan PbZn deposit (b)				
U12473	12	-3.86	0.25	*this study*
U12474	12	-3.95	0.22	*this study*
U12487	4	-3.36	0.27	*this study*
U12487	6	-2.82	0.28	*this study*
U12499	28	-4.28	0.14	*this study*
Sphalerite (St Salvy mine, France)				
62W	453	-1.05	0.15	Luais, 2007
64W	1047	-2.06	0.15	*Luais, submitted*
Seafloor sulfide deposits (c)				
FL-24-02	40	-3.26	0.15	*this study*
FL-19-08	45	-3.24	0.16	*this study*
ALV-2604-5-1A	159	-2.98	0.20	*this study*
FL-18-03/fond	200	-4.00	0.11	*this study*

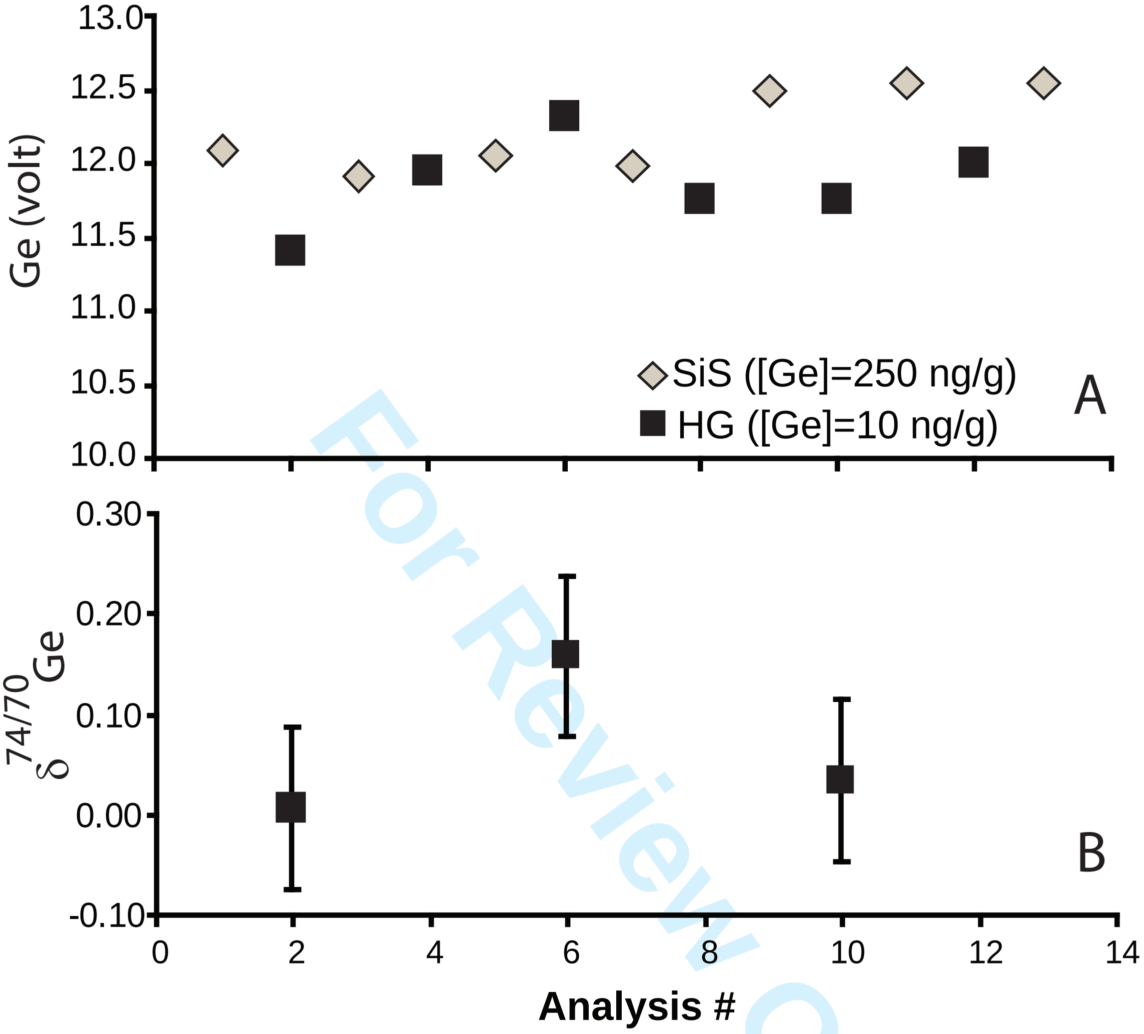
13.0
12.5
12.0
11.5
11.0
10.5
10.0
Ge (volt)
SiS ([Ge]=250 ng/g)
HG ([Ge]=10 ng/g)
A
0.30
0.20
0.10
0.00
-0.10
δ74/70Ge
B
0
2
4
6
8
10
12
14
Analysis #

Figure 1

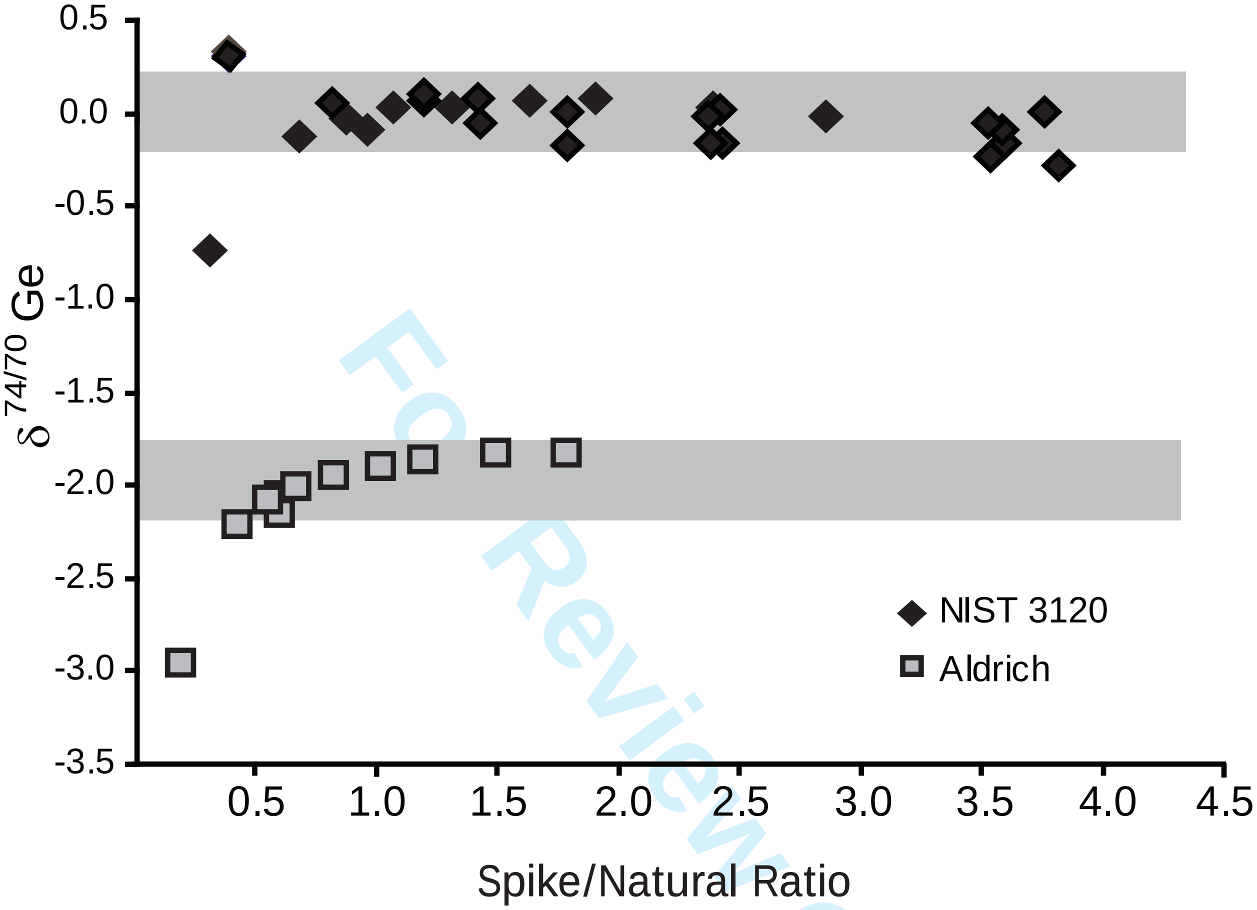
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
$\delta^{74/70}$Ge
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Spike/Natural Ratio
◆ NIST 3120
▣ Aldrich

Figure 2

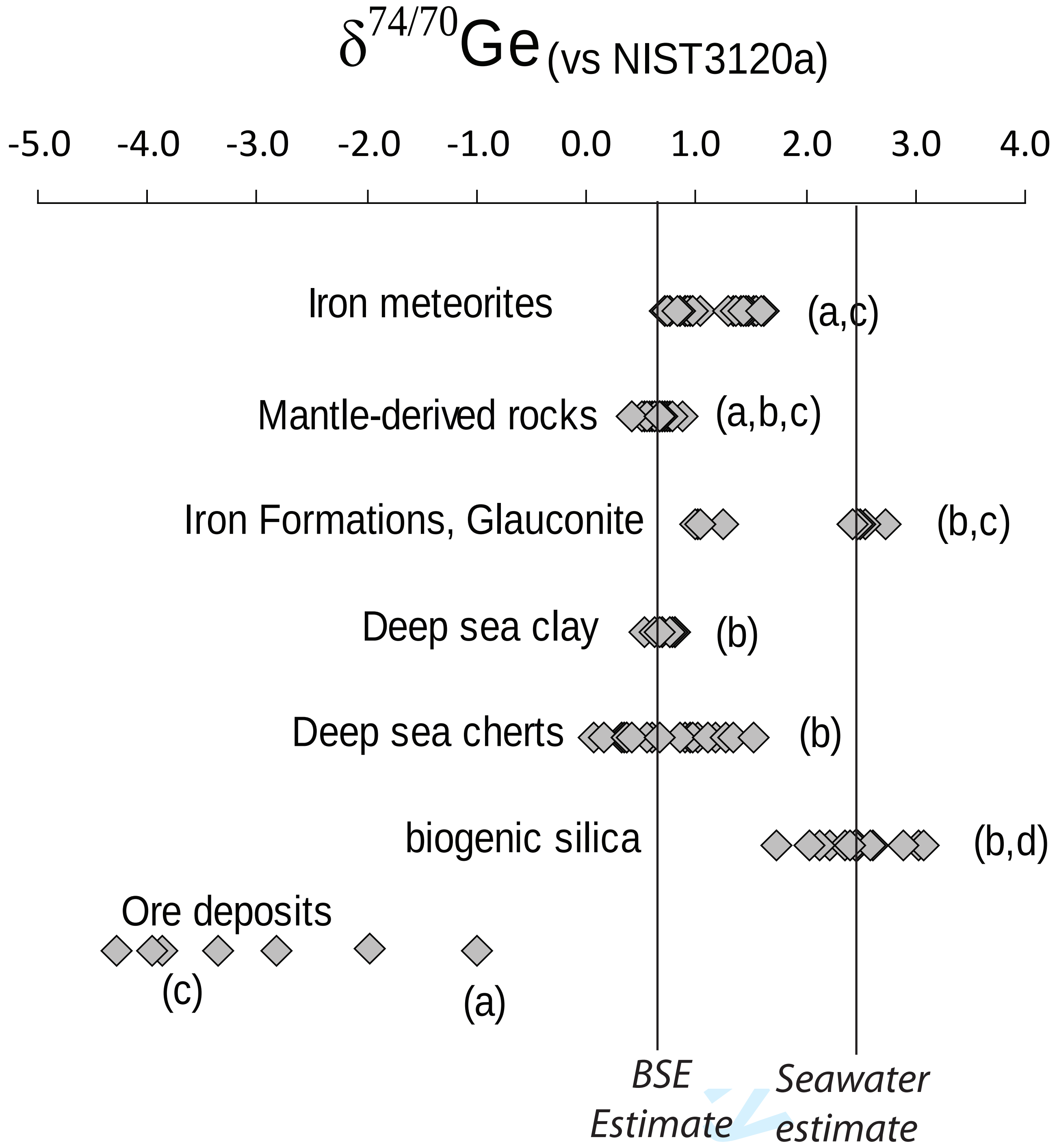
$\delta^{74/70}$Ge (vs NIST3120a)
-5.0
-4.0
-3.0
-2.0
-1.0
0.0
1.0
2.0
3.0
4.0
Iron meteorites
(a,c)
Mantle-derived rocks
(a,b,c)
Iron Formations, Glauconite
(b,c)
Deep sea clay
(b)
Deep sea cherts
(b)
biogenic silica
(b,d)
Ore deposits
(c)
(a)
BSE Estimate
Seawater estimate

Figure 3