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

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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‰ (2s) for $\delta^{74/70}\text{Ge}$ values. Using igneous and mantle-derived rocks, the bulk silicate Earth (BSE) $\delta^{74/70}\text{Ge}$ value was re-evaluated to be $0.59 \pm 0.18\text{‰}$ (2s) 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 permis 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 référence 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‰ (2s) pour la mesure du $\delta^{74/70}\text{Ge}$. A partir des roches ignées et dérivées du manteau, la valeur de $\delta^{74/70}\text{Ge}$ de la terre silicatée globale (BSE) a été réévaluée autour de $0.59 \pm 0.18\text{‰}$ (2s) 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 ; matériaux 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 $\delta^{74}\text{Ge}$ values similar to BSE while modern deep-sea sponges and glauconite have $\delta^{74}\text{Ge}$ 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)

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2
3 81 demonstrated that iron meteorites have a $\delta^{74}\text{Ge}$ values heavier than terrestrial samples. The
4
5 82 homogeneous $\delta^{74}\text{Ge}$ values for magmatic iron meteorites, regardless of their oxidation state
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7 83 suggests, in agreement with experimental data (Luais et al., 2009), that core formation
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9 84 processes do not fractionate significantly Ge isotopes in the metal phase with respect to the
10
11 85 primitive material, providing an estimate for Ge isotopic composition of the solar nebula.

12 86 Siebert et al. (2006) reported Ge isotope composition of hydrothermal waters collected
13
14 87 in the Oregon Cascades and in marine settings and found lighter isotope signatures relative to
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16 88 basalts. However, a preliminary intercomparison performed by the authors and colleagues
17
18 89 suggests that the reported Ge-isotope compositions are plagued by calculating errors during
19
20 90 the data reduction scheme (C. Siebert, personal communication), precluding further
21
22 91 comparison with our study.

23 92 The aim of this paper is to compare analytical techniques to obtain Ge-isotope
24
25 93 composition of selected geological reference materials and to intercalibrate Ge-isotope
26
27 94 standards relative to the BSE estimate. We propose the use of a new reference material
28
29 95 NIST3120a to report natural Ge-isotope variations. This approach, together with further
30
31 96 studies of experimental and theoretical fractionation of Ge-isotopes (Galy *et al.* 2003, Luais et
32
33 97 al., 2009, Li *et al.* 2009, Li and Liu 2010) are essential steps toward the development of Ge-
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35 98 isotopes as new geochemical tracer.

36 99

37 100 **Experimental procedures**

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39 101

40 41 102 *Reagents and Germanium standard solutions*

42 103 The hydride generation reagent is composed of 10 g of sodium borohydride powder
43
44 104 (high purity NaBH_4 , Fisher Chemical) and 5 g of sodium hydroxide pellets (analytical grade
45
46 105 NaOH , Acros Organics) dissolved into 1 l of ultra pure water (Milli-Q 18.2M Ω .cm,
47
48 106 Millipore), and is freshly prepared before each analytical session. During chemical
49
50 107 dissolution and purification, we used high purity HNO_3 (distilled grade, CleanAcid, Analab)
51
52 108 and HF (optima grade, Fisher Chemical). Germanium standards used in this study include
53
54 109 NIST3120a (Lot #000411, 1000 $\mu\text{g/g}$); Spex (Lot #11-160GE); Aldrich (Lot #01704KZ;
55
56 110 Luais, 2000, Luais 2007), JMC (Johnson Matthey, Karlsruhe, Lot # 301230S; Luais 2007) and
57
58 111 Aristar (Lot # used in Rouxel et al., 2006 – incorrectly reported as Aldrich standard solution).
59
60 112 We also used Ga (Spex; Lot #12-98Ga; Cat # PLGA2-2Y) and Ga international isotopic
113
114 113 standard (NBS - SRM994, Lot# 680205, Luais et al., 2000; Luais 2007) prepared from Ga
114
114 114 metal as internal standards for instrumental mass bias corrections. Double Spike was prepared

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2
3 115 from Ge metal spikes 73-70 from Isoflex USA Company (Ge-70 #32-01-70-3259 and Ge-73
4 #32-01-73-1405). Each spike was dissolved separately in a mixture HNO₃, sulfuric acid and
5 116
6 trace HF and mixed to obtain a ⁷³Ge/⁷⁰Ge ratio of ~ 0.6.
7 117
8 118

9

10 119 *Geological reference materials and other geological samples*

11
12 Several geological reference materials have been analyzed in this study for
13 intercomparison purposes with previous studies by Rouxel et al. (2006). They include USGS
14 121 standards (Govindaraju 1994) BHVO-2 (Hawaiian basalt), BIR-1 (Icelandic basalt), BCR-1
15 122 (Basalt, Columbia River Group USA), G-2 (Granite, Rhode Island USA), GH (Granite,
16 123 Hoggar, Algeria), DNC-1 (Braggtown Dolerite, North Carolina, USA), DTS-1 (Dunite,
17 124 Hamilton, Washington), PCC-1 (Peridotite- a partially serpentinized harzburgite, California
18 125 USA), AN-G (Anorthosite, Fiskenaeset, Western Greenland), GLO (Glauconite, Normandy
19 126 France), and IF-G (Iron Formation, West Greenland).
20 127

21 128 We also analyzed the Iron meteorite Odessa (IAB group) for which Ge-isotope
22 129 composition has been previously reported by Luais (2003, 2007). We also report Ge-isotope
23 130 composition of hydrothermal sulfides (sphalerite) from volcanogenic sulfide deposits, the
24 131 Navan Zn+Pb ore deposit in Ireland (Blakeman *et al.*, 2002), from continental hydrothermal
25 132 ZnS ores from the St Salvy deposit in France (Luais, 2003, 2007), and from modern seafloor
26 133 hydrothermal systems, the Lucky Strike field (Rouxel *et al.* 2004).
27 134

28

29 135 *Sample dissolution and chromatographic separation*

30 136 A procedure adapted from Rouxel et al. (2006), Luais (2007) and Luais (submitted)
31 137 was applied in this study for Ge purification from siliceous matrices, iron meteorites and
32 138 sulfides. For HG-MC-ICP-MS method (IFREMER and WHOI laboratories), about 50 mg of
33 139 siliceous material was dissolved in ~ 3 ml of 10 mol/l HF in a closed Teflon beaker on a hot
34 140 plate at 70 °C and left to equilibrate overnight with an appropriate addition of double spike
35 141 (spike/natural ratio ~ 1). After appropriate dilution to 1 mol/l HF with ultrapure water, the
36 142 solution was directly purified without evaporation through a chromatographic column
37 143 containing 2 mL of anion exchange resin (AG1-X8 Resin; 100-200 mesh; Chloride Form; Cat
38 144 # 140-1441). The column is cleaned with several washes of 5 ml of 0.28 mol/l HNO₃, distilled
39 145 3 mol/l HNO₃, and ultrapure water. After conditioning with 5 ml of 1 mol/l HF, the sample
40 146 was loaded on the column and germanium strongly adsorbed on the resin. Matrix elements
41 147 such Ca, Fe, Si or Zn were eluted and the resin further cleaned with 5 ml of 1 mol/l HF
42 148 followed by 3 ml of ultrapure water. Ge was then eluted with 10 ml of 3 mol/l HNO₃ and the

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2
3 149 solution evaporated slowly to dryness on a hot plate. The final residue was dissolved in 3 ml
4
5 150 of 0.28 mol/l HNO₃ and ready for isotope analysis. Since the HG sample introduction system
6
7 151 allow complete separation of volatile Ge hydride from the aqueous sample matrix (e.g.
8
9 152 Rouxel et al., 2006), no further purification using cation exchange resin is required.
10
11 153 Procedures for iron meteorite and sulfide dissolution are detailed in Luais et al. (2000) and
12
13 154 Luais (2007). Briefly, it consists of dissolution using 2 mol/l and 14 mol/l HNO₃,
14
15 155 respectively, followed by Ge isolation using AG50X8 cation exchange resin with 0.5 mol/l
16
17 156 HNO₃. Procedures for silicate matrices used at CRPG (Luais, submitted) consist of HNO₃ +
18
19 157 HF dissolution followed by several steps of HF leaching to isolate Ge (\pm matrix) in the
20
21 158 supernatant. After evaporation and subsequent dissolution in 1 mol/l HF, an aliquot of the
22
23 159 sample is loaded on a AG1X8 anion exchange resin. Most of the remaining matrix is eluted
24
25 160 with 1 mol/l HF, and Ge is subsequently collected using 0.2 mol/l HNO₃. Purification of Ge is
26
27 161 then performed on AG50X8 cationic resin similarly developed for iron meteorite matrix. The
28
29 162 efficiency of these procedures including 100 % yield and no isotopic fractionation during all
30
31 163 steps of Ge chemistry is demonstrated by Ge isotopic measurements of various matrices
32
33 164 doped with Ge standard, as well as Ge standard solutions after column separation. Details are
34
35 165 given in Luais (2007) for iron meteorite matrix and in Luais (submitted) and Rouxel et al.
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37 166 (2006) for various silicate matrices from ultra-mafic, mafic to granitic in composition. In all
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39 167 cases, the Ge isotopic composition of these Ge-doped matrices is similar within error to the
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41 168 measured Ge standard solution.

169

170 *MC-ICP-MS isotope ratio measurements:*

171 Germanium isotopes ratios were determined with a Thermo *Neptune* (Thermo Fisher
172 Scientific; Waltham, MA, USA) at the Pôle Spectrométrie Océan (PSO, Brest) at IFREMER
173 (Plouzané, France) and WHOI (Woods Hole, USA) using the hydride generation technique
174 described by Rouxel *et al.* (2006). Pure standard solution and purified sample measurements
175 were also performed on a Nu Plasma MC-ICP-MS at LCABIE laboratory (Pau, France) and
176 Isoprobe (GV) MC-ICP-MS at CRPG laboratory (Nancy, France) (Luais 2007). The Neptune
177 at WHOI and IFREMER was operating at low-mass resolution mode and ⁷⁰Ge, ⁷²Ge, ⁷³Ge
178 and ⁷⁴Ge were measured on L2, C, H1, and H2 cups while ⁶⁸Zn, ⁶⁹Ga, ⁷¹Ga and ⁷⁷Se were also
179 monitored on L4, L3, L1 and H4 cups. The isotope ⁷⁶Ge was not measured due to a major
180 interference of ³⁸Ar₂. For the Nu plasma measurements at LCABIE, we set the cups as H6,
181 H4, H2, and L2 for 74, 73, 72 and 70 at low mass resolution and the Ax and L3 cups for 71
182 and 69 Ga isotopes. For the GV Isoprobe measurements (CRPG), ⁷⁰Ge, ⁷²Ge, ⁷³Ge and ⁷⁴Ge

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2
3 183 were measured on Ax, H2, H3 and H4 cups while ^{68}Zn , ^{69}Ga , and ^{71}Ga were measured on L3,
4 184 L2, and H1 cups.

5
6 185 Several introduction systems were used and include: (1) a cyclonic spray chamber
7 186 (SiS) equipped with PTFE micro concentric nebuliser at 50 $\mu\text{l}/\text{min}$ for WHOI, IFREMER and
8 187 CRPG (Luais 2007) while a Quartz micro concentric nebuliser at 100 $\mu\text{l}/\text{min}$ was used for
9 188 LCABIE measurements; (2) continuous flow hydride generation systems, CETAC HGX-200
10 189 at WHOI and IFREMER (see Rouxel *et al.*, 2006 for instrument settings) and a custom-built
11 190 HG generator at the LCABIE.

12 191 Instrumental mass bias was corrected using several techniques as described in
13 192 previous studies (Galy *et al.* 2003, Luais 2007, Rouxel *et al.* 2006, Siebert *et al.* 2006): (1) a
14 193 sample-standard bracketing (referred to as SSB) technique that involves the measurement of
15 194 the Ge standard solution, before and after each unknown sample (Galy *et al.* 2003, Rouxel *et*
16 195 *al.* 2006); (2) external normalization to Ga-isotopes (referred as Ga-Cor) (Galy *et al.* 2003,
17 196 Hirata 1997, Luais *et al.* 2000, Luais 2007, Siebert *et al.* 2006) and Cu-isotopes. (3) Double
18 197 spike (DS) correction ($73/70$) was performed as described by Siebert *et al.* (2006). The double
19 198 spike solution was mixed with the sample before chemical purification with a spike/natural
20 199 ratio of around 1 (g/g). Data reduction of Ge-isotope ratios was performed using a scheme
21 200 similar to Siebert *et al.* (2001). In some cases, we coupled the hydride generation system with
22 201 the regular cyclonic spray chamber using an extra inlet available on the spray chamber. This
23 202 approach allowed a direct comparison of instrumental mass bias induced by both techniques
24 203 and the calculation of hydride generation yield. It also permitted the use of Ga as an internal
25 204 standard to correct for instrumental mass bias during hydride generation.

26 205

27 206 **Results and discussion**

28 207

29 208 *Notation and data normalization*

30 209 Germanium isotope composition can be reported using several possible notations, such as:

31 210

$$32 211 \delta^x\text{Ge} (\text{‰}) = \left(\frac{({}^x\text{Ge}/{}^{70}\text{Ge})_{\text{sample}}}{({}^x\text{Ge}/{}^{70}\text{Ge})_{\text{STD}}} - 1 \right) \times 1000 \quad (1)$$

33 212

34 213 Where $x = 74, 73$ or 72 and STD corresponds to the normalization to Ge-standard.

35 214 Currently, there is no consensus in the way to report Ge-isotope ratios. Siebert *et al.* (2006)

1
2
3 215 reported $\delta^{74/72}\text{Ge}$ due to the double spike correction using ^{73}Ge and ^{70}Ge spikes. Galy *et al.*
4
5 216 (2003) reported δGe per mass unit while Rouxel *et al.* (2006) and Luais (2003, 2007) reported
6
7 217 $\delta^{74/70}\text{Ge}$ (together with other 73/70 and 72/70 isotope ratios). Due to larger abundances and
8
9 218 minor isobaric interferences, the $^{74}\text{Ge}/^{70}\text{Ge}$ ratio seems to be optimum for reporting Ge-
10
11 219 isotopes. Throughout this study, we reported $\delta^{74}\text{Ge}/^{70}\text{Ge}$ values relative to SRM3120a which
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13 220 is a concentration standard produced in large amount.
14
15 221

16 222 *Isobaric interferences and instrumental mass bias*

17 223 Ge isotope measurements suffer from molecular interferences, such as $^{35}\text{Cl}^{35}\text{Cl}^+$ on
18 224 $^{70}\text{Ge}^+$; $^{40}\text{Ar}^{16}\text{O}_2^+$ and $^{36}\text{Ar}^{36}\text{Ar}^+$ on $^{72}\text{Ge}^+$, $^{58}\text{Ni}^{16}\text{O}^+$ and $^{38}\text{Ar}^{36}\text{Ar}^+$ on $^{74}\text{Ge}^+$ and $^{38}\text{Ar}^{38}\text{Ar}^+$ and
19 225 $^{36}\text{Ar}^{40}\text{Ar}^+$ on $^{76}\text{Ge}^+$. On the Neptune and Nu Plasma coupled to HG, those interferences are
20
21 226 minimized and are generally negligible except for ^{76}Ge , as previously discussed by Rouxel *et*
22
23 227 *al.* (2006). We however observed a ubiquitous interference on $^{70}\text{Ge}^+$ during the early stage of
24
25 228 analytical development on the Neptune, probably from $^{40}\text{Ar}^{14}\text{N}^{16}\text{O}$ due to the use of X-cones
26
27 229 which may induce a higher oxide-level. Therefore, we only used normal cones throughout this
28
29 230 study. On the GV Isoprobe, hydrogen addition in the hexapole collision cell was used to
30
31 231 remove Ar_2 interferences (Luais *et al.* 2000; Luais, 2007).
32

33 232 Ge-isotope measurements, and in particular double-spike correction, may suffer from
34
35 233 potential GeH^+ interference. Therefore, we evaluated the contribution of $^{70}\text{GeH}^+$ on mass 71
36
37 234 by measuring $(^{71}\text{Ga}^+ + ^{70}\text{GeH}^+)/^{69}\text{Ga}^+$ ratios. This approach permits us to evaluate the influence
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39 235 of GeH^+ on the signal, which is around 0.001 ‰ and thus negligible, in agreement with
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41 236 Luais *et al.* (2000).
42

43 237 Isotopic measurements on all instruments were also corrected for Zn interferences on
44
45 238 mass 70 using ^{68}Zn , with a mass bias applied on $^{70}\text{Zn}/^{68}\text{Zn}$ ratios (Luais, 2007).
46

47 239 As germane (GeH_4) formation in the hydride generator may induce isotope
48
49 240 fractionation, we coupled the spray injection system with the HG to evaluate potential mass
50
51 241 bias. This analytical setup allowed a direct comparison of the Ge-isotope ratios of the
52
53 242 standard introduced using conventional spray chamber (“Standard”) vs. hydride generation
54
55 243 (“Sample”) (Figure 1). The SRM3120a Ge standard solution was adjusted to a concentration
56
57 244 of 250 ng/g for spray chamber injection and to 10 ng/g for hydride generation to reach similar
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59 245 intensity for both introduction systems. The results suggest that the difference in mass bias
60
246 between the spray chamber and the HG system is about 0.05 +/- 0.07 ‰ (2s) per mass unit,
247 which suggest that, either Ge-hydride formation does not fractionate Ge-isotopes or that the
248 hydride formation yield is quantitative. Considering that the spray chamber system has an

1
2
3 249 efficiency of Ge transfer into the plasma torch of about 20 % (determined using the volume of
4
5 250 solution taken vs. solution drained in waste), we can determine an overall sensitivity in
6
7 251 abundance of 0.85 pg/V. In comparison, we calculate that hydride generation has a sensitivity
8
9 252 of 0.91 pg/V which suggest that about 100% of germanic acid in solution is reduced to
10
11 253 germane species.

12 254

13 14 255 *Assessment of standard and double-spike isotope composition*

15 256 While Ga is traditionally used to control the mass bias for Ge analyses (Galy *et al.*
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17 257 2003, Hirata 1997, Luais *et al.* 2000, Luais 2007,), we recognize that such approach may not
18
19 258 allow absolute Ge isotope ratio measurement since instrumental mass bias may be different
20
21 259 between elements (e.g. Maréchal *et al.* 1999, Yang and Meija 2010, Meija *et al.* 2009). We
22
23 260 however found that Ga or Cu can be appropriate elements for external mass bias correction
24
25 261 and determination of relative isotopic composition (in delta value) of Ge standards or
26
27 262 samples. The assumption of identical mass bias for analyte and standard however require
28
29 263 identical matrix composition and concentrations. In addition, external mass bias correction
30
31 264 yields identical results in delta values than standard-sample bracketing method or double
32
33 265 spike normalization, as presented in Tables 2 and 3 and discussed below.

34 266 The double-spike composition was defined relative to the NIST 3120a composition
35
36 267 obtained on the Neptune at PSO, Brest (Table 1) using conventional spray chamber
37
38 268 introduction system. In order to calibrate the Ge-isotope ratios of NIST 3120a, we used a
39
40 269 Gallium standard solution (Spex; Lot #12-98Ga) to correct for instrumental mass bias using
41
42 270 $^{69}\text{Ga}/^{71}\text{Ga}$ ratio of 1.50676 (Machlan *et al.*, 1986). This approach was also used to monitor
43
44 271 instrumental mass bias between analyses of pure standard and double spike. It is important to
45
46 272 note that both our double spike and NIST 3120a calibration reported in Table 1 may differ
47
48 273 from the *true* value but this potential bias does not affect the final isotope ratios when using
49
50 274 the delta notation. Although we didn't determine the optimum double spike composition or
51
52 275 spike/natural ratios using error propagation tests, Figure 2 shows that spike/natural ratio
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54 276 between 0.8 to 3.5 yield consistent results with overall precision of 0.15 ‰ (2s). In practice, a
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56 277 ratio between 1 to 2 was routinely used for isotope analysis. This optimal ratio is very similar
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58 278 to the one used by Siebert *et al.* (2006).

59 279

58 280 *Intercomparison of Ge isotope compositions of Ge standard solutions*

59 281 The average compositions of NIST3120a and other standard solutions over multiple
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282 analytical sessions for different instruments and measurement setups are reported in Table 2.

1
2
3 283 *Aristar* and *Spex* solutions show an enrichment in the light isotope of approximately the same
4 proportion ($\delta^{74/70}\text{Ge} = -0.64 \pm 0.18 \text{ ‰}$ (2s) and $-0.71 \pm 0.20 \text{ ‰}$ (2s), respectively). *JMC*
5 284
6 standard also presents an enrichment in the light isotope although in smaller proportion, with
7 285
8 a $\delta^{74/70}\text{Ge}$ value of $-0.32 \pm 0.10 \text{ ‰}$ (2s). The *Aldrich* standard shows the lightest $\delta^{74/70}\text{Ge}$
9 286
10 values at $-2.01 \pm 0.22 \text{ ‰}$ (2s). Several sample introduction systems were tested, using either
11 287
12 spray chamber (SiS) or hydride generation (HG) for different instruments (Neptune, Nu
13 288
14 plasma or Isoprobe) and no systematic differences were found. It is also important to note that
15 289
16 standard-sample bracketing, Ga normalization and double spike corrections yielded similar
17 290
18 results, both in terms of Ge isotope composition and analytical precision.
19 291
20 292

21 293 *Ge isotope composition of geochemical RM and re-evaluation of the bulk silicate Earth value*

22 294 Selected geochemical RM, measured using double spike (this study), sample-standard
23 295
24 bracketing (Rouxel *et al.* 2006), and Ga normalization (Luais 2007) methods are reported in
25 296
26 Table 3. In addition, we report precise Ge concentrations determined by isotope dilution since
27 297
28 the double spike data reduction scheme offers the advantage to also calculate precisely the Ge
29 298
30 concentration of the samples.

31 299 Based on these data, the bulk silicate Earth value has been re-evaluated as $\delta^{74/70}\text{Ge} =$
32 300
33 0.56 ‰ versus NIST SRM3120a. This average is determined from igneous rocks (BHVO-2;
34 301
35 BIR-1; BCR-1) having limited variations (2s = 0.08 ‰). Granitic rocks display significant
36 302
37 deviation from the bulk silicate Earth with G-2 (Rhode Island, USA) having a slightly lighter
38 303
39 composition at $0.40 \pm 0.04 \text{ ‰}$ (2s). Ultramafic rocks, although less concentrated in Ge,
40 304
41 present similar compositions as basaltic rocks. We note that NIST3120a is the standard whose
42 305
43 isotope composition is the closest to the BSE relative to the other standard solutions used
44 306
45 previously (Table 2). As discussed below, iron formation IF-G and marine sediment GL-O
46 307
47 yield heavier $\delta^{74/70}\text{Ge}$ values at $1.03 \pm 0.10 \text{ ‰}$ (2s) and $2.44 \pm 0.14 \text{ ‰}$ (2s) respectively.

48 308 Although Ge concentrations have been widely reported in geochemical reference
49 309
50 materials (Govindaraju 1994), they are only rarely analyzed by isotope dilution and even
51 310
52 more rarely by MC-ICP-MS after chemical purification. In most cases, our new concentration
53 311
54 data in Table 3 are within 5% of previously reported data (e.g. BIR-1, BCR-1, G-2, DNC-1,
55 312
56 AN-G, IF-G) while differences may be up to 10-20% in some cases (e.g. GH, DTS-1, PCC-1,
57 313
58 GL-O).
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60 315 *Ge isotope composition of meteorites, sediments and sulfide deposits*

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2
3 316 As shown in **Figure 3**, the absolute range of $\delta^{74/70}\text{Ge}$ values in rocks and minerals is
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5 317 about 8.05‰ which is comparable or even larger than most non traditional stable isotope
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7 318 systems (e.g. Anbar and Rouxel 2007). The strong heavy isotope depletion in sulfides
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9 319 contrasts strongly with the generally positive Ge isotope values found in many modern and
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11 320 ancient marine sediments (e.g. banded iron formations, glauconite).

12 321 Glauconite (GLO) and Iron Formation (IF-G) are two iron-rich rocks where redox
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14 322 conditions were important in their formation. Glauconite is a secondary clay mineral which is
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16 323 formed in marine sediments during the reduction of Fe(III) to Fe(II), while Archean Iron
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18 324 Formation is believed to have formed in globally anoxic oceans where hydrothermal Fe(II)
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20 325 was partially oxidized and co-precipitated with silica, either biotically or abiotically (e.g.
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22 326 Bekker *et al.*, 2010). In both deposit types, Ge is enriched relative to crustal values with
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24 327 Ge/Si ratios of 6.44×10^{-6} and 2.7×10^{-5} mol/mol for Glauconite and Iron formation,
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26 328 respectively. Since Galy *et al.* (2002) and Li and Liu (2010) suggested that Ge adsorbed onto
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28 329 iron oxyhydroxide is enriched in light isotopes, the positive $\delta^{74/70}\text{Ge}$ values for GLO and IF-G
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30 330 is best explained by the heavy isotope composition of their Ge sources. In this case, the
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32 331 slightly lighter values for IF-G may potentially result from the contribution of hydrothermal
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34 332 Ge to Archean oceans (Hamade *et al.* 2003). Further studies are however required to address
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36 333 this issue.

37 334 Deep sea sponges of the NE Pacific (Rouxel *et al.* 2006) show an average isotope
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39 335 composition at around 2.47 ‰. The relatively high $\delta^{74/70}\text{Ge}$ values obtained for different
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41 336 species at different depths also suggest that sponges likely record the Ge isotope composition
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43 337 of seawater. This value is a lower bound of the Ge isotopic composition of modern seawater
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45 338 because, if sponges fractionate Ge isotopes, they likely discriminate against heavy isotopes as
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47 339 already observed for Si isotopes. More recently, Mantoura (2006) reported $\delta^{74/70}\text{Ge}$ values for
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49 340 cleaned diatom opal from Holocene sediments at around 3.3 ‰. Those results, together with
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51 341 the lack of Ge isotope fractionation observed during Ge uptake by cultured diatoms
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53 342 (Mantoura, 2006), further confirm that seawater is enriched in the heavy Ge isotopes,
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55 343 probably close to 3 ‰.

56 344 Two independent Ge isotope analyses of the non-magmatic iron meteorite Odessa are
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58 345 reported in Table 4 and are in perfect agreement. Also is reported the recalculated Ge isotopic
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60 346 composition of the magmatic iron meteorite Braunau (IIA). It is worthwhile to note that the
347 Ge isotope composition of various types of iron meteorites (magmatic and non-magmatic
348 irons) deviate from BSE in contrast to other heavy stable isotope systems (such as Cu, Zn, Fe;

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3 349 Moynier *et al.* 2007), confirming the complexity of metal-silicate segregation and the
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5 350 importance of volatilization/alteration effects (Luais, 2007).

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7 351 Both sphalerite from ancient Pb-Zn ore deposits (Blakeman *et al.* 2002) and seafloor
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9 352 hydrothermal deposits at Lucky Strike (Rouxel *et al.* 2004) have been analyzed and an
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11 353 average $\delta^{74}\text{Ge}$ value of $-3.53 \pm 0.51\text{‰}$ has been obtained (Table 4). Sphalerite from the single
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13 354 ZnS ore deposit of St Salvy mine (France), precipitated from hydrothermal fluids related to
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15 355 plutonic intrusion, also exhibit negative values with a range of -1 to -2 ‰ (Luais, 2007).
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17 356 These results are interesting because Ge isotopes in sulfides are completely shifted toward
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19 357 negative values by $\sim 4\text{‰}$ relative to BSE. In contrast, preliminary Ge isotope analysis from
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21 358 hydrothermal fluids yield variable $\delta^{74}\text{Ge}$ values around $1.9 \pm 0.5\text{‰}$ (Escoubé *et al.* 2008,
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23 359 Rouxel *et al.* 2008). The recent study by Li *et al.* (2009) estimating equilibrium fractionation
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25 360 factors in the Ge isotope system suggested a very large fractionation toward lighter values (up
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27 361 to 10‰ at 25 °C) in Ge-bearing sulfides relative to 4-coordinated Ge–O compounds (e.g.
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29 362 $\text{Ge}(\text{OH})_4(\text{aq})$ or quartz). Therefore, the large difference between sulfides and BSE is best
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31 363 explained by a strong isotopic fractionation (may be up to 4.5‰) during sulfide precipitation
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33 364 in hydrothermal systems.

34 Conclusion

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36 367 This study permits an intercomparison of germanium isotope measurement techniques
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38 368 as well as a calibration of several geological reference materials and mono-elemental standard
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40 369 solutions used in previous studies. Different methodologies were used during this study: (1)
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42 370 introduction by on-line hydride generation and spray chamber, and (2) mass bias correction
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44 371 by sample-standard bracketing, external mass bias correction using Ga or Cu isotopes and
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46 372 double spike normalization. Even if all methods yield consistent isotope composition with
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48 373 similar precisions ($2s \sim 0.15\text{‰}$), the double spike correction offers the advantage of providing
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50 374 high-precision Ge concentrations and correcting for potential Ge isotope fractionation during
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52 375 sample dissolution and purification.

53
54 376 Using igneous and mantle-derived rocks, the Bulk Silicate Earth (BSE) was re-
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56 377 evaluated to $0.59 \pm 0.18\text{‰}$ ($2s$) relative to NIST3120a. In comparison, Iron meteorites
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58 378 exhibit more positive values of $\delta^{74/70}\text{Ge}$ up to $+1.5\text{‰}$. We report an overall $\delta^{74/70}\text{Ge}$ variation
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60 379 in terrestrial rocks and minerals of about 8‰ . This range is comparable or even larger than
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381 380 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

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3 382 hydrothermal environments, consistent with theoretical calculations (Li *et al.* 2009). This
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5 383 strong isotope depletion in sulfides contrasts drastically with the generally positive Ge isotope
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7 384 values found in many modern and ancient marine sediments (e.g. banded iron formations,
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9 385 glauconite). Large variation in germanium stable isotopes and their reproducible measurement
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11 386 provides new perspectives on the use of Ge as a novel geochemical tracer, in particular for
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13 387 tracing planetary and oceanic processes.
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16 389

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29 396 comments on the manuscript. Adrian Boyce and Yves Fouquet are thanked for providing
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31 397 sulfide samples.
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3 399 **Figure Captions**
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7 401 Figure 1: (A) Comparison between hydride generation (HG) and spray chamber (SiS)
8 402 methods for Ge isotope analysis. A NIST3120a solution was alternatively introduced through
9 403 the HG (square), considered as an “unknown sample” at a concentration of 10 ng/g, and
10 404 through the SiS (Diamond), used as “bracketing standard” at a concentration of 250 ng/g. The
11 405 concentrations were adjusted to obtain the same voltage (graph A). (B) Ge isotope
12 406 composition (in delta values) of the NIST3120a standard determined by HG and normalized
13 407 to SiS values.
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21 409 Figure 2: Ge isotope composition of NIST3120a and Aldrich standards determined using a
22 410 double spike method with different Spike/Sample ratios. While the addition of spike in
23 411 proportions of 0.6-4 relative to sample yielded approximately stable $\delta^{74}\text{Ge}$ values, analyses
24 412 are best performed with Spike/Sample ratios between 1 and 2.
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30 414 Figure 3: Compilation of Ge isotope composition ($\delta^{74/70}\text{Ge}$) of geological reference materials
31 415 and natural samples versus NIST3120a; (a) Luais, 2007; (b) Rouxel et al., 2006; (c) this
32 416 study; (d) Mantoura (2006).
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3 418 **Table Captions**
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7 420 Table 1: Ge isotope compositions of NIST3120a standard and Ge70-73 double spike
8
9 421 determined on the Neptune MC-ICP-MS after internal normalisation to Ga for instrumental
10
11 422 mass bias correction
12

13 423

14 424 Table 2: Intercalibration of Ge isotope composition of standard solutions against NIST 3120a.

15 425

16
17 426 Table 3: Intercomparison study of Ge isotope compositions of geochemical RM versus NIST
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19 427 3120a.
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21 428

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23 429 Table 4: Ge isotope compositions of sulfides and iron meteorites.
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Table 1

Name	$^{74}\text{Ge}/^{70}\text{Ge}$	2s	$^{73}\text{Ge}/^{70}\text{Ge}$	2s	$^{72}\text{Ge}/^{70}\text{Ge}$	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

For Review Only

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Table 2

Lab	Method	nb#	$\delta^{74/70}\text{Ge}$ vs. NIST3120a	2s	$\delta^{73/70}\text{Ge}$ vs. NIST3120a	2s	$\delta^{72/70}\text{Ge}$ vs. NIST3120a	2s	$\delta^{74/72}\text{Ge}$ vs. NIST3120a	2s	
<i>"ARISTAR" standard</i>			<u>-0.64</u>	<u>0.18</u>	<u>-0.54</u>	<u>0.18</u>	<u>-0.38</u>	<u>0.26</u>	<u>-0.28</u>	<u>0.03</u>	
#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	
<i>"JMC" standard</i>			<u>-0.32</u>	<u>0.10</u>	<u>-0.23</u>	<u>0.12</u>	<u>-0.16</u>	<u>0.07</u>	<u>-0.16</u>	<u>0.05</u>	
#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	
<i>"SPEX" standard</i>			<u>-0.71</u>	<u>0.21</u>	<u>-0.56</u>	<u>0.15</u>	<u>-0.37</u>	<u>0.16</u>	<u>-0.31</u>	<u>0.08</u>	
#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	
<i>"ALDRICH" standard</i>			<u>-2.01</u>	<u>0.23</u>	<u>-1.54</u>	<u>0.17</u>	<u>-1.03</u>	<u>0.12</u>	<u>-0.97</u>	<u>0.15</u>	
#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	$\delta^{74/70}\text{Ge}$	2s	reference	Mean $\delta^{74/70}\text{Ge}$	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 Basalt	47.96(e), 47.77(a)	1.5(a); 1.45(b); 1.53(b); 1.49(c); 1.52(d); 1.52(i); 1.40(k)	0.74	0.13	(k)	0.62	0.13
				0.60	0.13	(k)		
				0.56	0.30	(h)		
				0.64	0.33	(g)		
				0.57	0.39	(g)		
				0.61	0.04	(i)		
BCR-1	Columbia River Basalt	54.11(e)	1.5(a); 1.42(b); 1.45(c); 1.36(k)	0.65	0.13	(k)	0.55	0.15
				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); 1.28(k)	0.56	0.13	(k)	0.67	0.19
				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); 1.02(b); 0.92(k)	0.41	0.30	(h)	0.40	0.03
				0.39	0.34	(g)		
GH	Granite	75.8(e)	2.0(a,f); 2.18(c); 1.63(k)	0.74	0.13	(k)	0.68	0.22
				0.74	0.13	(k)		
				0.55	0.28	(g)		
DTS-1	Dunite	40.41(a)	0.88(a); 0.84(c); 0.83(i); 0.75(k)	0.76	0.13	(k)	0.64	0.26
				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); 0.84(k)	0.67	0.13	(k)	0.67	0.01
				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 Formation	41.2(a)	24(a); 22±0.2(f); 21.8(i); 23.06(k)	1.11	0.13	(k)	1.03	0.09
				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	$\delta^{74/70}\text{Ge}$	2s	source
<i>Iron meteorite</i>				
Odessa (IAB)	288 (a)	0.96	0.07	<i>this study</i>
		0.98	0.09	Luais, 2007
Braunau (IIA)	183	1.47	0.24	Luais, 2007
<i>Navan PbZn deposit (b)</i>				
U12473	12	-3.86	0.25	<i>this study</i>
U12474	12	-3.95	0.22	<i>this study</i>
U12487	4	-3.36	0.27	<i>this study</i>
U12487	6	-2.82	0.28	<i>this study</i>
U12499	28	-4.28	0.14	<i>this study</i>
<i>Sphalerite (St Salvy mine, France)</i>				
62W	453	-1.05	0.15	Luais, 2007
64W	1047	-2.06	0.15	<i>Luais, submitted</i>
<i>Seafloor sulfide deposits (c)</i>				
FL-24-02	40	-3.26	0.15	<i>this study</i>
FL-19-08	45	-3.24	0.16	<i>this study</i>
ALV-2604-5-1A	159	-2.98	0.20	<i>this study</i>
FL-18-03/fond	200	-4.00	0.11	<i>this study</i>

Review Only

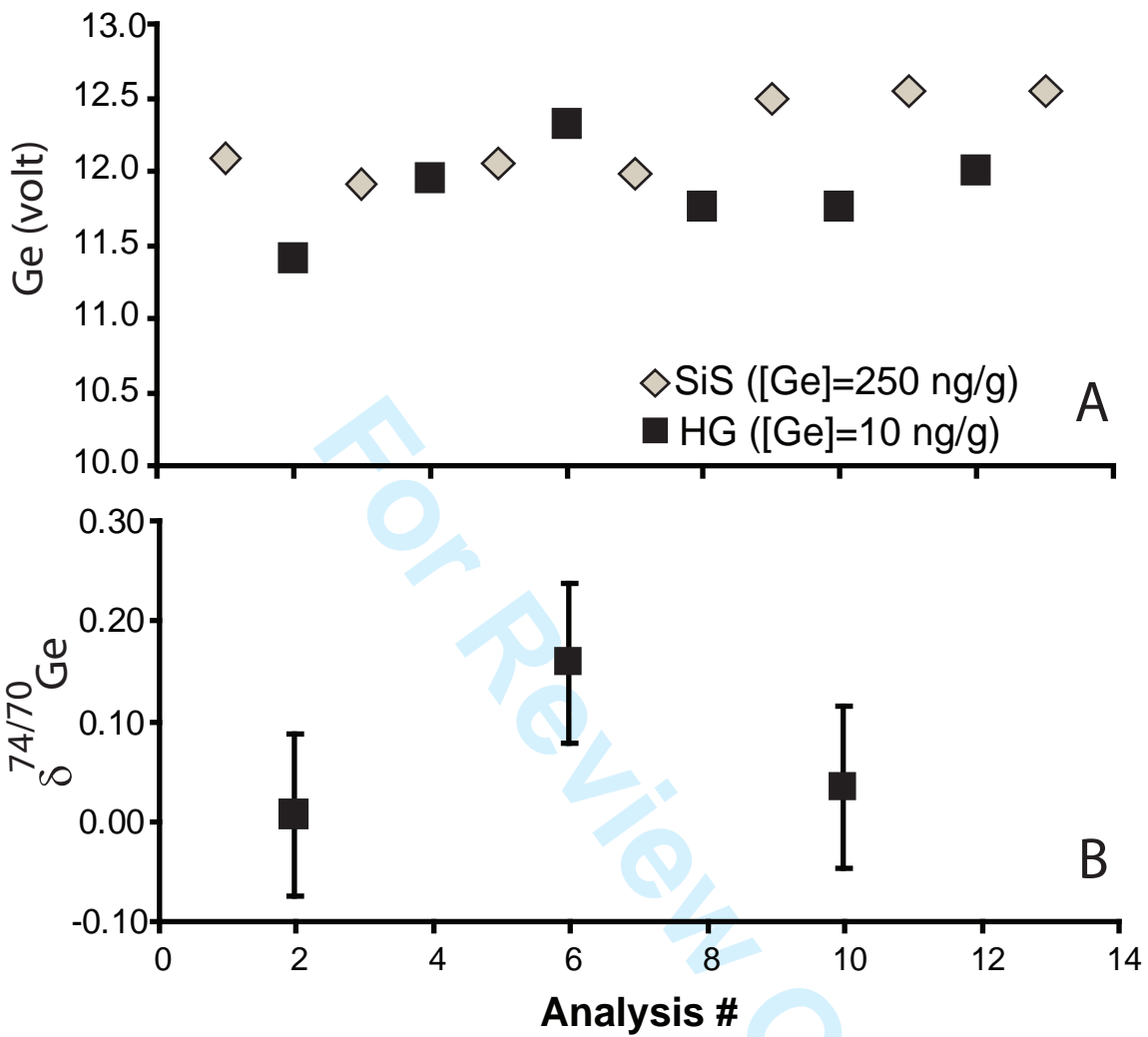


Figure 1

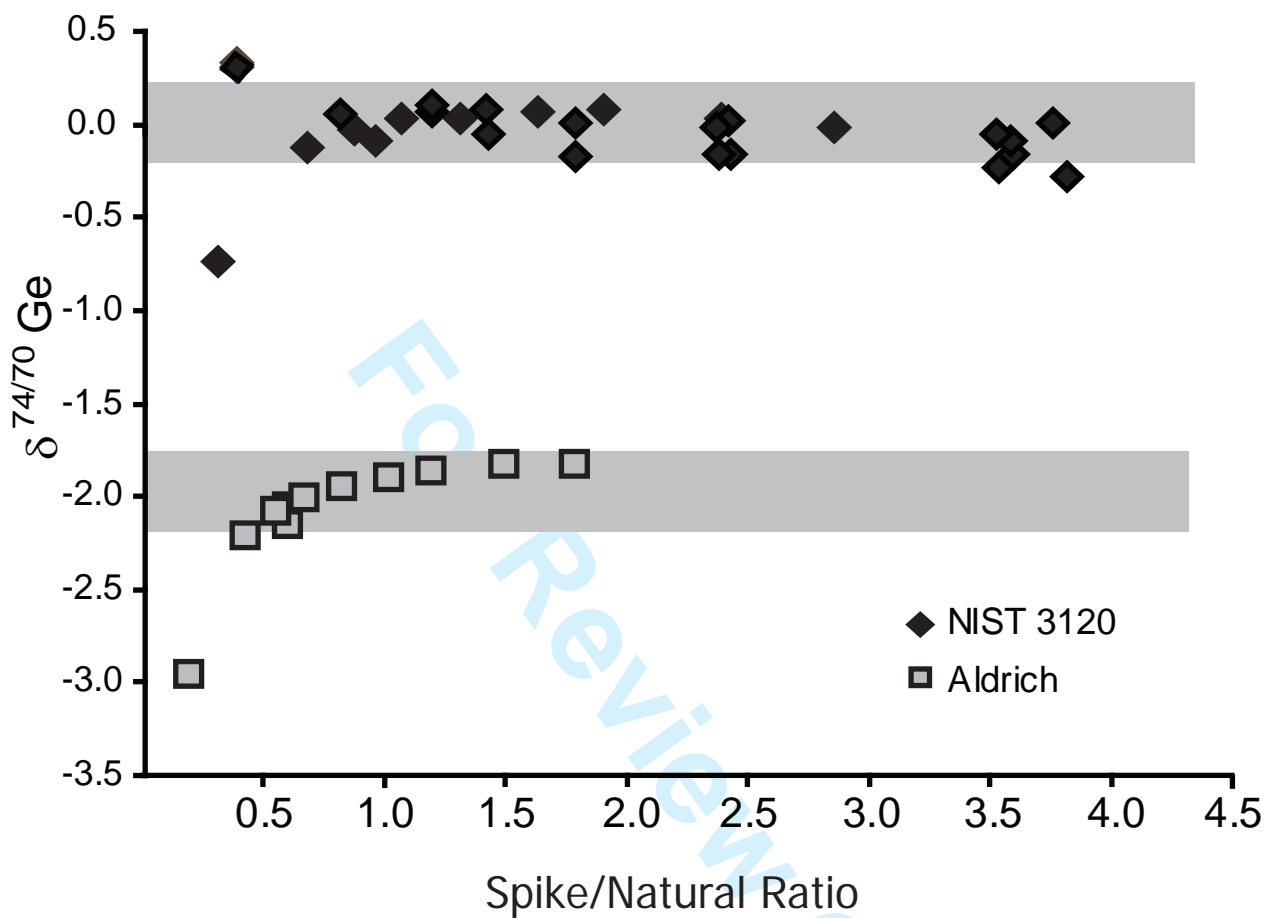


Figure 2

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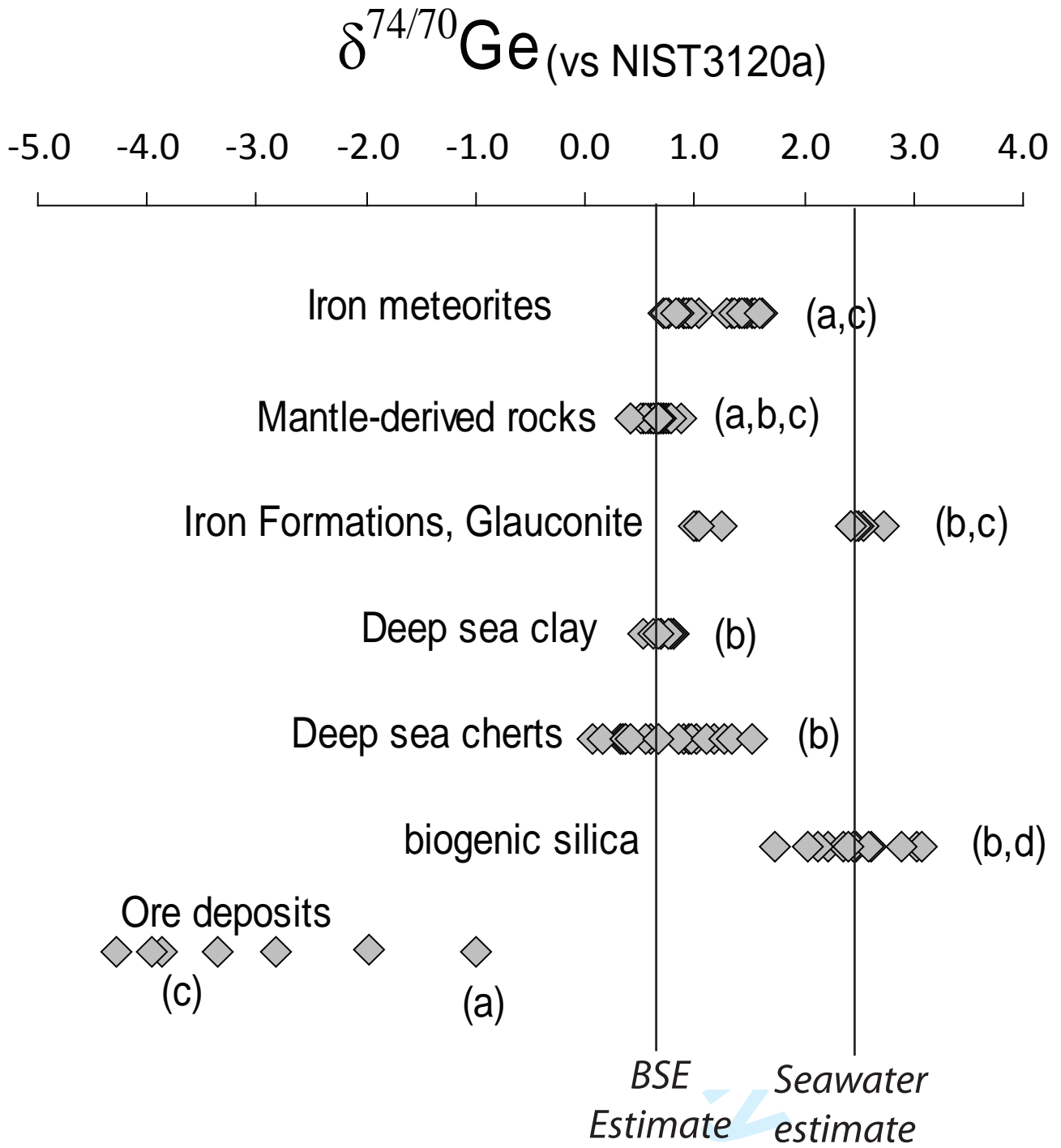


Figure 3