



# Reliable Determination of Ge in Solid Environmental Samples Using a Chemical Preparation Procedure Developed for Si Isotopes and ICP-MS Analysis

Camille Delvigne, Abel Guihou, Bernard Angeletti, Isabelle Basile-Doelsch, Jean-Dominique Meunier

## ► To cite this version:

Camille Delvigne, Abel Guihou, Bernard Angeletti, Isabelle Basile-Doelsch, Jean-Dominique Meunier. Reliable Determination of Ge in Solid Environmental Samples Using a Chemical Preparation Procedure Developed for Si Isotopes and ICP-MS Analysis. *Geostandards and Geoanalytical Research*, 2018, 42 (1), pp.139 - 149. 10.1111/ggr.12197 . hal-01695926

**HAL Id: hal-01695926**

**<https://hal.science/hal-01695926>**

Submitted on 18 May 2018

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



**Reliable determination of Ge using the silicon isotopes  
chemical preparation and ICP-MS analysis for solid  
environmental samples.**

Journal:	<i>Geostandards and Geoanalytical Research</i>
Manuscript ID:	GGR-0514.R1
Manuscript Type:	Original Article
Date Submitted by the Author:	n/a
Complete List of Authors:	Delvigne, Camille; Centre Europeen de Recherche et d'Enseignement des Geosciences de l'Environnement, Guihou, Abel; Centre Europeen de Recherche et d'Enseignement des Geosciences de l'Environnement Angeletti, Bernard; Centre Europeen de Recherche et d'Enseignement des Geosciences de l'Environnement Basile-Doelsch, Isabelle; Centre Europeen de Recherche et d'Enseignement des Geosciences de l'Environnement Meunier, Jean-Dominique; Centre Europeen de Recherche et d'Enseignement des Geosciences de l'Environnement
Keywords:	germanium, ICP-MS, reference materials, soils, plants, sample digestion, cation exchange purification

1 Reliable determination of Ge using the silicon isotopes chemical preparation and  
2 ICP-MS analysis for solid environmental samples.

3  
4  
5 Camille Delvigne (1) \*, Abel Guihou (1), Bernard Angeletti (1), Isabelle Basile-Doelsch (1), Jean-  
6 Dominique Meunier (1)  
7 (1) Aix-Marseille Univ, CNRS, IRD, Coll. de France, INRA, CEREGE, Europôle Méditerranéen de  
8 l'Arbois BP 80 13545 Aix-en-Provence, cedex 4, France

9  
10 \*Corresponding author. Email : [delvigne@cerege.fr](mailto:delvigne@cerege.fr)

11  
12  
13  
14 Keywords: germanium, ICP-MS, reference materials, soils, plants, sample digestion, cation exchange  
15 purification

16 Mots clés: germanium, ICP-MS, matériaux de référence, sols, plantes, digestion d'échantillon,  
17 purification cationique par résine échangeuse d'ions

18

## 19 Abstract

20 Germanium (Ge) exists at trace levels in the Earth's crust and is a powerful geochemical  
21 tracer of the silicon (Si) cycle. This study proposes a simple and reliable method for  
22 determining Ge contents in environmental samples using ICP-MS. As Si and Ge have very  
23 similar chemical properties, we investigated the applicability of the chemical preparation  
24 procedure developed for Si isotopes to the analysis of Ge in environmental samples.  
25 Advantages of this procedure are: (1) efficient removal of the matrix and main interferences  
26 affecting Ge analyses by ICP-MS; (2) a low limit of detection ( $6 \text{ ng l}^{-1}$ ); (3) relative  
27 repeatability of approximately 3% obtained on  $^{74}\text{Ge}$ ; and (4) robustness and accuracy based  
28 on agreement within errors with the published Ge concentrations for rock standards (BHVO-  
29 2, AGV-2 and BCR-2). This procedure allows revising the Ge concentrations for 3 soils  
30 standards ( $1.67 \pm 0.09 \text{ } \mu\text{g g}^{-1}$ ;  $2.41 \pm 0.18 \text{ } \mu\text{g g}^{-1}$ ;  $1.89 \pm 0.10 \text{ } \mu\text{g g}^{-1}$  for GBW 07401, GBW 07404  
31 and GBW 07407 respectively) and proposing a value for the ERM-CD281 plant standard  
32 ( $0.06 \pm 0.01 \text{ } \mu\text{g g}^{-1}$ ). This method provides a convenient procedure for determining Ge  
33 concentrations in environmental samples and opens the possibility of coupling two tracers of  
34 the Si biogeochemical cycle with a single analytical procedure.

35

36    Résumé

37    Le germanium (Ge), présent à des teneurs en trace dans la croûte terrestre, est un traceur  
38    géochimique performant du cycle du silicium (Si). Cette étude propose une méthode simple,  
39    rapide et fiable pour déterminer les concentrations en Ge dans les échantillons  
40    environnementaux par ICP-MS. Vu les propriétés géochimiques très similaires entre Ge et Si,  
41    nous avons investigué la pertinence de la procédure de mise en solution et de purification  
42    développée pour les isotopes du silicium à l'analyse du Ge dans des échantillons  
43    environnementaux. Les avantages de cette technique sont : (1) une élimination efficace de la  
44    matrice et des interférences principales affectant l'analyse du Ge par ICP-MS ; (2) une limite  
45    de détection de  $6 \text{ ng l}^{-1}$  ; (3) une répétabilité relative de 3% obtenue sur l'isotope  $^{74}\text{Ge}$ ; (4) une  
46    bonne fiabilité et justesse basées sur la concordance entre les valeurs de Ge publiées pour les  
47    standards de roche (BHVO-2, AGV-2 et BCR-2) aux incertitudes près. Cette méthode a  
48    permis de réévaluer les concentrations en Ge de 3 standards de sol ( $1.67 \pm 0.09 \text{ } \mu\text{g g}^{-1}$ ;  
49     $2.41 \pm 0.18 \text{ } \mu\text{g g}^{-1}$ ;  $1.89 \pm 0.10 \text{ } \mu\text{g g}^{-1}$  pour GBW 07401, GBW 07404 et GBW 07407  
50    respectivement) et de proposer une valeur pour le standard de plante ERM-CD281 ( $0.06 \pm 0.01$   
51     $\mu\text{g g}^{-1}$ ). Cette méthode présente aussi le grand avantage de coupler deux traceurs du cycle du  
52    silicium (à savoir les isotopes stables du silicium et le rapport Ge/Si), en une préparation  
53    chimique unique.

## 1. Introduction

Germanium (Ge) exists at trace levels in the Earth's crust and is a powerful geochemical tracer of the silicon (Si) cycle. Like Si, Ge is a Group IV element. Both elements have identical outer electronic configurations and similar covalent radii (Ge: 1.22Å and Si 1.17Å; Höll et al., 2007). The geochemistry of Ge is dominated by its propensity to substitute for Si in silicate minerals, and thus closely follows Si through its biogeochemical cycle.

Fundamentals of high and low-temperature geochemistry of Ge are reviewed in Rouxel and Luais (2017). To summarize, the Ge/Si ratio has been employed as a tracer of weathering processes (*e.g.*, Kurtz and Derry, 2004; Scribner et al., 2006; Opfergelt et al., 2010; Lugolobi et al., 2010), hydrothermal and geothermal activity (*e.g.*, Mortlock et al., 1993; Evans and Derry, 2002), biological processes (*e.g.*, Ellwood and Maher, 2003; Derry et al., 2005; Sutton et al., 2010), and flow paths (*e.g.*, Kurtz et al., 2011) in modern environments but also in paleo-environmental studies (*e.g.*, Filippelli et al., 2000; Hammond et al., 2004). The use of Ge/Si has recently been extended to the study of the Archean Si cycle (*e.g.*, Hamade et al., 2003; Frei and Polat, 2007; Delvigne et al., 2012; 2016). Another facet of Ge environmental research focuses on the potential economic resource of Ge in soils and plants as the Ge demand for new technologies is exploding while Ge is rare in natural environments (Rosenberg, 2009; Wiche et al., 2017). However, Ge content is often overlooked in the array of analyzed elements. This arises from the analytical difficulties to obtain reliable data because Ge concentrations in environmental samples are generally below the limit of detection of many modern analytical methods. In addition, Ge suffers from various interferences on its isotopes with ICP-MS techniques (mainly  $^{56}\text{Fe}^{16}\text{O}$  on  $^{72}\text{Ge}$ ,  $^{57}\text{Fe}^{16}\text{O}$  and  $^{56}\text{FeH}^{16}\text{O}$  on  $^{73}\text{Ge}$ , and  $^{74}\text{Se}$  and  $^{58}\text{Ni}^{16}\text{O}$  on  $^{74}\text{Ge}$ ). Interferences due to iron oxides are particularly problematic because some samples contain a few tenths of a percent of Fe while Ge is present at a  $\mu\text{g g}^{-1}$  level. The  $^{58}\text{Ni}^{16}\text{O}$  interference is also an issue as it combines the

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

79 most abundant Ni and O isotopes ( $^{58}\text{Ni}=68\%$ ;  $^{16}\text{O}=99\%$ ). In addition, Ar-based molecular  
80 interferences ( $^{40}\text{Ar}^{16}\text{O}_2$ ,  $^{36}\text{Ar}^{36}\text{Ar}$  and  $^{38}\text{Ar}^{36}\text{Ar}$  on  $^{72}\text{Ge}$ ,  $^{73}\text{Ge}$  and  $^{74}\text{Ge}$ , respectively) should  
81 also be monitored. Germanium is then often qualified as a “tricky” element to analyze and is  
82 not routinely determined in environmental samples.

83 The majority of studies published so far on Ge have been carried out using the isotope-  
84 dilution hydride-generation ICP-MS technique (ID-HG-ICP-MS) developed by Mortlock and  
85 Froelich (1996) (Fillipelli et al., 2000; Kurtz et al., 2002; Evans and Derry, 2002; Derry et al.,  
86 2005; Wheat and McManus, 2005; Ellwood et al., 2006; Scribner et al., 2006; Blecker et al.,  
87 2007; Makishima and Nakamura, 2009; Lugolobi et al., 2010; Sutton et al., 2010). This is  
88 probably the most reliable and precise technique for Ge determination, although it requires a  
89 hydride generation system, which is not widespread in laboratories. Alternative techniques  
90 are: (1) graphite furnace atomic absorption spectrometry (GF-AAS) (McMahon et al., 2006);  
91 (2) ICP-MS analysis with or without high resolution (Hamade et al., 2003 ; Delvigne et al.,  
92 2009; Cornelis et al., 2010; Tribouvillard et al., 2011); (3) laser ablation ICP-MS analysis  
93 (Hamade et al., 2003; Shen et al., 2011; Belissont et al., 2014; Dong et al., 2015;); and (4) X-  
94 ray fluorescence spectrometer analysis (Frei and Polat, 2007). While valid for most geological  
95 samples, these techniques are working close to their limits of detection for environmental  
96 samples, such as plants that commonly range from 0.07 to 20 ng g<sup>-1</sup> (Derry et al., 2005;  
97 Blecker et al., 2007; Delvigne et al., 2009; Cornelis et al., 2010; Lugolobi et al., 2010). One  
98 option is to preconcentrate samples in order to reach concentrations above the detection  
99 limits. This was investigated by Soylak and Yigit (2015), who suggested a separation-  
100 preconcentration procedure using a polysulfone membrane filter combined with  
101 spectrophotometric measurements. This method has the disadvantage of requiring specific  
102 materials. For natural water samples, ID-HG-ICP-MS remains the only reliable technique  
103 thanks to its high precision and unequaled low detection limits.

1  
2  
3 104 The objective of this study is to propose a simple and reliable alternative method determining  
4  
5 105 Ge contents in solid environmental samples, with a notable focus on soils and plants using  
6  
7 106 ICP-MS, a common instrument found in geochemistry laboratories. As silicon isotopes and  
8  
9 107 Ge/Si ratios are complementary tracers of the Si biogeochemical cycle, we investigate the  
10  
11 108 applicability of the chemical preparation procedure developed for silicon isotopes (Georg et  
12  
13 109 al., 2006) to the analysis of Ge in solid environmental samples.

## 110 2. Experimental

### 111 2.1. Material analyzed

112 Reference materials with the recommended values for Ge concentrations are scarce. Three  
113 international geological USGS reference materials have been chosen in this study for  
114 intercomparison with previous studies: BHVO-2 (basalt), AGV-2 (andesite), and BCR-2  
115 (basalt). Despite certified values not being available for these standards, an increasing number  
116 of published data provide constraints on Ge concentrations (Table 1). A considerable  
117 compilation effort was undertaken by Jochum et al. (2016), which provides reference values  
118 (or informative values) determined following ISO guidelines and IAG Certification Protocol  
119 using data published between 1995 and 2015. In addition, to better fit the matrix of targeted  
120 samples of soils and plants, we selected three soil standards from the Institute of Geophysical  
121 and Geochemical Exploration (IGGE, Langfang, China) (GBW 07401, GBW 07404 and  
122 GBW 07407, also known as GSS-1, GSS-4 and GSS-7) and a plant standard from European  
123 Reference Material (ERM-CD281). Certified Ge concentrations are available for the soils  
124 standards, but with low precision (Table 1), while no Ge data is provided for ERM-CD281.  
125 Recently, additional data have been made available for GBW 07401-07408 standards (Liu et  
126 al., 2014) (Table 1).



	Sample type	Provider	Published value	rsd (2σ)	n	References
BHVO-2	basalt	USGS	<b>1.62±0.04</b> μg g <sup>-1</sup>	2%	10	Jochum et al., 2016
			1.53 μg g <sup>-1</sup>	0.2%	n.s.	Escoube et al., 2012
			1.59±0.04 μg g <sup>-1</sup>	3%	3	Scribner et al., 2006
AGV-2	andesite	USGS	1.20±0.08 μg g <sup>-1</sup>	7%	6	Jochum et al., 2016
BCR-2	basalt	USGS	1.46±0.26 μg g <sup>-1</sup>	18%	6	Jochum et al., 2016
GBW 07401	soil	IGGE	1.50±0.04 μg g <sup>-1</sup>	3%	6	Liu et al., 2014
			<b>1.34±0.2</b> μg g <sup>-1</sup>	15% *	at least 8	Wang et al., 2013
GBW 07404	soil	IGGE	2.10±0.02 μg g <sup>-1</sup>	1%	6	Liu et al., 2014
			<b>1.9±0.3</b> μg g <sup>-1</sup>	16% *	at least 8	Wang et al., 2013
GBW 07407	soil	IGGE	<b>1.6±0.3</b> μg g <sup>-1</sup>	19% *	at least 8	Wang et al., 2013
ERM-CD281	plant	ERM	no data	-	-	-

**Table 1.** Reference materials analyzed in this study with their Ge concentrations and associated uncertainties. Values in bold are certified values while others are informative values. \* refers to an uncertainty of 3σ instead of 2σ; n.s.= not specified.

2.2. Sample digestion

Samples were digested following the procedure developed for silicon isotopes using a solid sodium hydroxide (NaOH) flux (Georg et al., 2006). Between 10-20 mg (200 mg up to 600 mg for ERM-CD281, the plant standard) of powdered samples were weighed directly into silver crucibles after drying for at least 24h at 105°C. Prior to the fusion, calcination steps were carried out to ensure the combustion of organic matter into CO<sub>2</sub>. Calcinations were performed at 450°C with a 1 h stage at 250°C to ensure slow temperature increase. The 450°C calcination step lasted for at least 1 hour for soils, and 16 h for plants. In the case of plants, the total calcination procedure lasted at least 24 h. Qi et al., (2011) showed that calcination at 600°C does not induce Ge loss. Ashes were mixed with approximately 200 mg of NaOH and placed in a furnace at 720°C for 10 minutes. Fusion cakes were then allowed to dissolve overnight in ultrapure water with a brief ultrasonic bath to favor dissolution. Solutions were then quantitatively transferred into pre-cleaned HDPE bottles and acidified to pH ~2 with HNO<sub>3</sub>. Due to the volatile behavior of Ge in the presence of halogens (HCl, HClO<sub>4</sub>), only

1  
2  
3 145 HNO<sub>3</sub> could be used (Luais, 2007; 2012). Acidification to pH~2 was important for Fe-rich  
4  
5 146 samples to ensure a complete dissolution of Fe-oxides as well as ensuring a complete  
6  
7 147 recovery during the following cationic purification (Fitoussi et al., 2009). At this pH, the  
8  
9 148 dominant Ge species is the Ge(OH)<sub>4</sub><sup>0</sup> form (Pokrovski and Schott, 1998).

### 12 149 2.3. Sample purification

15 150 To overcome matrix effects and various interferences, which are complex to correct for,  
16  
17 151 purification of samples appears to be an ideal approach. Perhaps more importantly, the  
18  
19 152 elimination of matrix elements prior to analysis allows a substantial reduction in the dilution  
20  
21 153 factor, which is of great interest for samples with low Ge contents. In addition, performance  
22  
23 154 of ICP-MS can be fully exploited, as the sampling interface and the ion optics are not  
24  
25 155 deteriorated due to salt depositions. A cation-free solution was obtained by passing the  
26  
27 156 solution through a cation exchange column. This allowed for testing of the resin used for  
28  
29 157 germanium isotopes chemical preparation, AG50W-X8 (100-200 mesh in H<sup>+</sup> form; Bio-Rad)  
30  
31 158 (Luais, 2007, 2012) using the column chemistry routine of silicon isotopes (Georg et al.,  
32  
33 159 2006). Sample solutions were loaded on a Bio-Rad type column filled with 1.8 ml of  
34  
35 160 AG50W-X8 cation-exchange resin, pre-cleaned with several rinsing with HCl, HNO<sub>3</sub> as  
36  
37 161 detailed in the study of Georg et al., (2006) (Table 2). Before loading the sample on the resin,  
38  
39 162 ultrapure water was passed into the resin to remove acids (Georg et al., 2006). The matrix  
40  
41 163 (sodium from fusion and other cations from the sample itself) was retained on the resin, while  
42  
43 164 anionic and neutral species (*e.g.*, Ge(OH)<sub>4</sub><sup>0</sup> and Si(OH)<sub>4</sub><sup>0</sup>) passed through. To minimize the  
44  
45 165 dilution due to elution, the sample volume was maximized (here ~ 10 ml of fused solution)  
46  
47 166 while the volume of eluent was kept to a minimum of one resin bed volume (~ 2 ml) (Table  
48  
49 167 2). Since the Si and Ge species do not interact with the resin, the eluent is simply ultrapure  
50  
51 168 water. Ge was collected in a ~ 12 ml cation-free solution. Recovered solutions were weighed  
52  
53 169 to minimize uncertainties inherent to the imprecise volumes recovered. Regarding the  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 170 removal of matrix element, Na is potentially the more difficult element to eliminate as it is the  
4  
5 171 most abundant and resin shows a weak relative selectivity for Na. To warrant a good  
6  
7 172 purification, resin is largely in excess based on expected resin capacity and fused sample  
8  
9 173 concentrations. Indeed, a 10 ml fused solution (typically 0.5 meq) saturates the resin  
10  
11 174 approximately 15% of its exchange capacity. Complete removal of ambient cationic species  
12  
13  
14 175 and especially problematic cations (*i.e.*, Fe, Ni, Zn) and Na was checked with ICP-MS.  
15  
16

BioRad AG50W-X8, 1.8 ml resin bed		
Separation stage	Solution matrix	Volume (ml)
Pre-cleaning	3N HCl	3 ml
Pre-cleaning	6N HCl	3 ml
Pre-cleaning	7N HNO <sub>3</sub>	3 ml
Pre-cleaning	10N HCl	3 ml
Pre-cleaning	6N HCl	3 ml
Pre-cleaning	3N HCl	3 ml
Rinse	ultrapure water	6 ml
Sample load	Acidified fused sample	10 ml
Elution	ultrapure water	2 ml

17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29 176  
30  
31  
32 177 **Table 2.** Column chemistry routine of the preparation of a solid sample fused with NaOH flux  
33  
34 178 adapted from Georg et al., 2006.  
35

36  
37 179 2.4.Sample introduction and mass spectrometry

38  
39 180 Ge concentrations were measured using an ICP-MS Nexion 300X (Perkin Elmer) using a PFA  
40  
41 181 nebulizer, a quartz cyclonic spray chamber and a SC-FAST DX-4 automated introduction  
42  
43 182 system. Operating conditions are detailed in Table 3. A series of five standard solutions with  
44  
45 183 different concentrations (50, 100, 250, 500, 1000 ng l<sup>-1</sup>) were used to calibrate Ge  
46  
47 184 concentrations. These calibration solutions were made from single element Ge standard 1000  
48  
49 185 mg l<sup>-1</sup> solution (Chem Lab, Plasma HIQU, 2-5% HNO<sub>3</sub>). To correct for instrumental drift,  
50  
51 186 rhodium (Chem Lab, Plasma HIQU, 2-5% HNO<sub>3</sub>) was introduced to sample solutions through  
52  
53 187 a cross flow line injection resulting in a Rh concentration of 1.58 µg l<sup>-1</sup> in the analyzed  
54  
55 188 solution. Ge isotopes 72, 73 and 74 were analyzed and provided consistent values, proving the  
56  
57  
58  
59  
60

robustness of the method. However, Ge contents were determined using the  $^{74}\text{Ge}$  isotope, the most abundant isotopes (36.28%), given higher sensitivity and lower detection limits compared to other isotopes. In the sequence, 400 ng l<sup>-1</sup> Ge standard solutions were measured after every 15 samples to check for instrumental drift and evaluate reproducibility.

<b>Plasma power</b>	1600 W
<b>Torch</b>	Quartz glass torch
<b>Plasma Ar gas flow rate</b>	15 l min <sup>-1</sup>
<b>Auxiliary Ar gas flow rate</b>	1.2 l min <sup>-1</sup>
<b>Nebuliser Ar gas flow rate</b>	0.95 - 1.05 l min <sup>-1</sup> (optimized to minimize $^{140}\text{Ce}^{16}\text{O}^+ / ^{140}\text{Ce}^+ < 0.025$ and $^{70}\text{Ce}^{++} / ^{140}\text{Ce}^+ < 0.03$ )
<b>Nebuliser</b>	PFA 0.4 ml min <sup>-1</sup>
<b>Spray chamber</b>	cyclonic (quartz)
<b>Sample uptake rate</b>	0.337 ml min <sup>-1</sup>
<b>Interfaces cones</b>	Nickel
<b>Resolution</b>	700
<b>Typical <math>^{74}\text{Ge}</math> sensitivity</b>	~ 12000 cps $\mu\text{g}^{-1}$ l
<b>Typical <math>^{103}\text{Rh}</math> sensitivity</b>	~ 680000 cps $\mu\text{g}^{-1}$ l

**Table 3.** Instrumental operating conditions for ICP-MS Nexion 300X

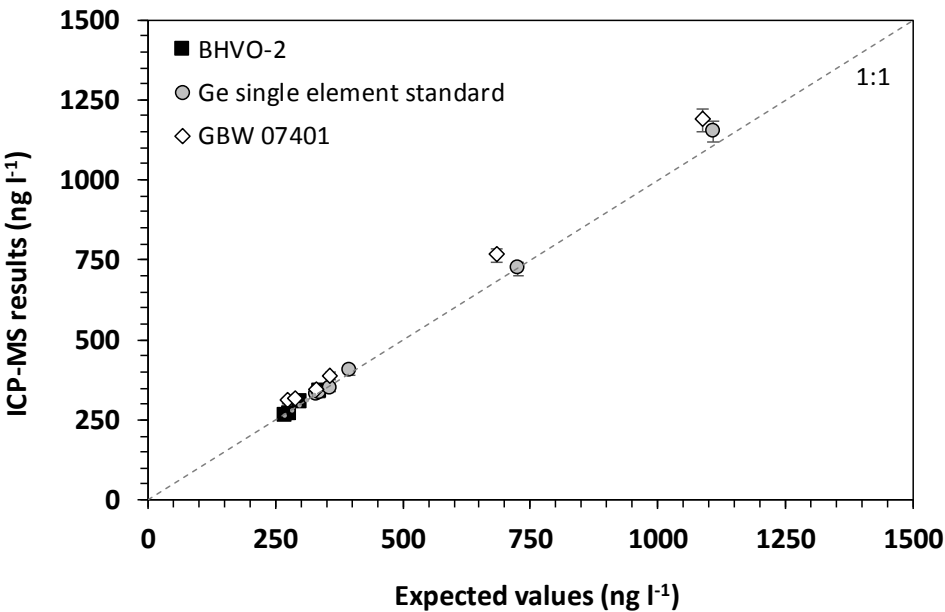
### 3. Results and discussion

#### 3.1. Assessment of Ge recovery yields during chemical procedure

As the dominant Ge species after fusion is the  $\text{Ge}(\text{OH})_4^0$ , no affinity for cation exchange resin is expected and thus Ge should be quantitatively recovered through the chromatographic procedure. A complete Ge recovery (102±2%; n=6) during sample purification through cationic resin was obtained with single element Ge standard solution at different Ge concentrations (330 to 1100 ng l<sup>-1</sup>; Fig. 1). To take into account matrix effects, recovery yields for BHVO-2 and GBW 07401 were determined by Ge standard addition to the fused solution before purification (Ge addition from 10 ng l<sup>-1</sup> to 100 ng l<sup>-1</sup>; Fig. 1). The recovery yields for BHVO-2 (99±2%; n=4) indicated a complete recovery for Ge. In the case of GBW 07401 (Ge addition from 10 ng l<sup>-1</sup> to 1000 ng l<sup>-1</sup>; Fig. 1), recoveries of approximately 118±5% (n=6) were found when compared to the certified value (Wang et al., 2013). Considering the

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

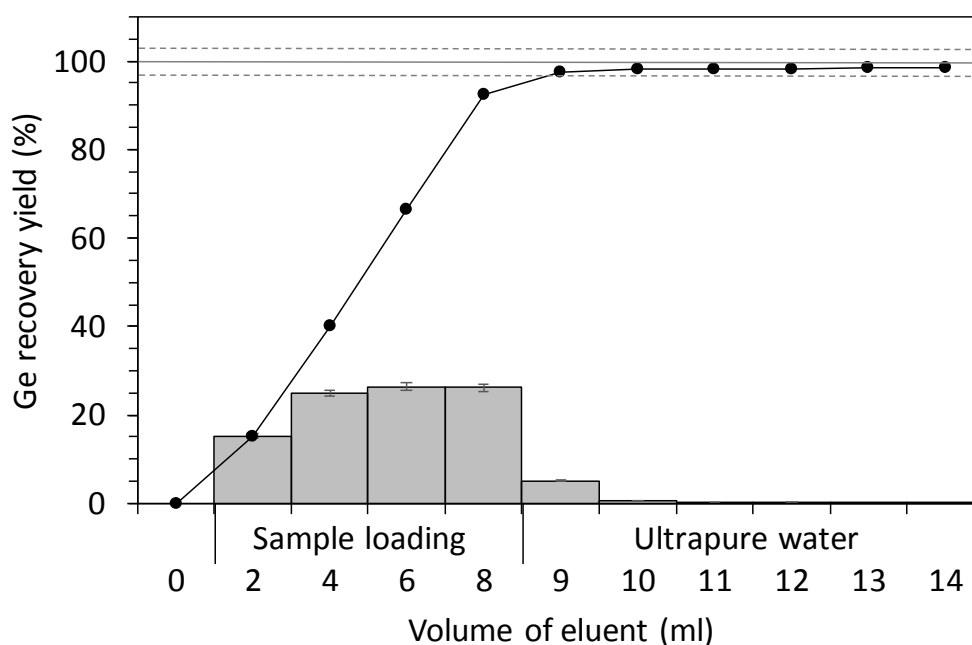
Ge concentrations of Liu et al., (2014), who suggested that the Ge concentration of this standard should be revised, our recovery yield was  $109\pm2\%$  (Fig. 1). As the procedural blanks displayed very low levels of Ge ( $3\pm2\text{ ng l}^{-1}$ ;  $n=11$ ) and the given large error range associated with the certified value of this standard (Table 1), we assume our recovery for this standard to be complete. A better agreement would require refining the reference value for the GBW 07401 standard (see section 3.2). Based on single element Ge standard solution and BHVO-2, we assume that Ge recovery is complete during cationic purification. The standard addition of BHVO-2 and GBW 07401 show that Si and other neutral, as well as anionic species do not create any matrix effect.



**Fig. 1** Comparison of the Ge concentrations obtained by ICP-MS after cationic purification and expected values for single element Ge standard solution at various Ge concentrations (gray circles) and reference materials (BHVO-2, black squares; GBW 07401, open diamonds) with Ge standard addition (Ge addition from  $10\text{ ng l}^{-1}$  to  $1000\text{ ng l}^{-1}$ ). The dashed gray line represents a recovery yield of 100%. Expected values for reference materials are calculated

considering Ge data from the literature (Escoube et al., 2012; Scribner et al., 2006 and Liu et al., 2014, see section 3.2). Error bars represent the analytical repeatability (3%).

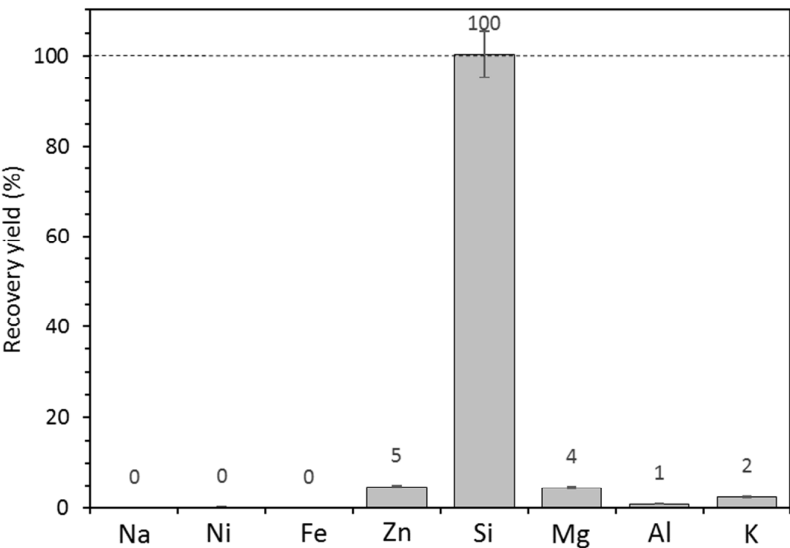
The separation efficiency is demonstrated by the elution curves of two samples (a single element Ge standard solution and a fused BHVO-2) that were loaded onto the pre-cleaned cation exchange resins (Fig. 2). Ge is not retained by the resin and migrates straight through the column and nearly 90% of the loaded Ge is already recovered while the sample load is still infiltrating the resin bed. The last 10% is recovered with 2 ml of ultrapure water (Fig. 2).



**Fig. 2** Elution of germanium during chemical purification of BHVO-2 on AG50W-X8 resin.

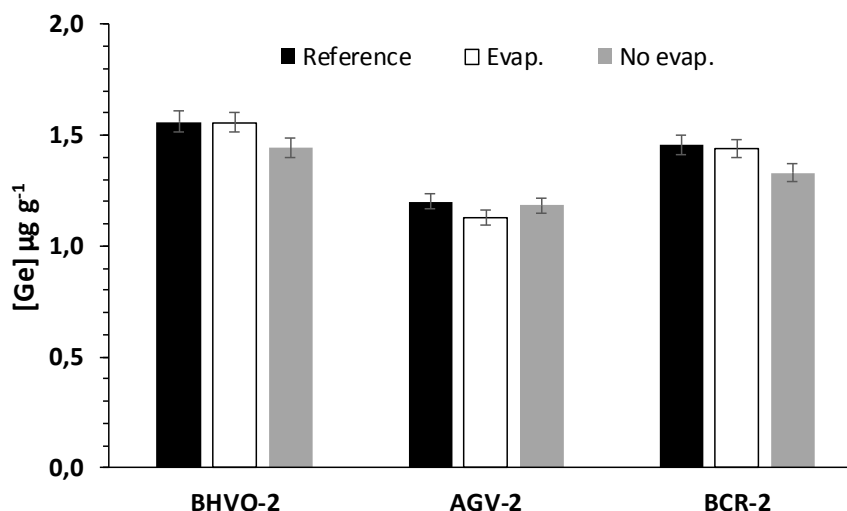
The black circles corresponds to the cumulated Ge recovered whereas grey bars represent Ge recovered in each volume loaded. Error bars represent the analytical repeatability.

Furthermore, ICP-MS screening of the purified solution confirms the absence of major cations and interfering cations after purification (Fig. 3). As demonstrated for Si by Georg et al., (2006), this shows a complete separation of Ge from the ambient cation matrix. Matrix effects and interferences are then negligible and should not be corrected for, minimizing the errors in Ge contents. In addition, Ar-based molecular interferences are not detectable in the blanks.



**Fig. 3.** Recovery yields of the main matrix elements and interfering elements of NaOH fused BHVO-2 after purification with AG50W-X8 resin.

Besides overcoming matrix effects and interferences, cationic purification has the advantage to minimize the dilution for analysis, as samples are salt-free. Indeed, the above described sample purification resulted in a dilution of the sample by a factor of 1.2. This is far less than the dilution necessary to reduce total dissolved salt to the maximum of 0.1% accepted for ICP-MS analysis (a dilution by a factor 2 being the minimum). However, some samples with low Ge content might still be close to the detection limit. To overcome this issue, a preconcentration step is helpful. A preconcentration step through low temperature evaporation was feasible, as solutions were free of major elements, limiting the risk of precipitation. For samples that might be close to detection limits, typically plants, an evaporation step at 60°C on a hotplate was performed to increase Ge concentrations. In this study, a maximal preconcentration factor of 2 was achieved without any modification of Ge recoveries. Indeed, aliquots of purified solutions of geostandards BHVO-2, AGV-2 and BCR-2, with or without evaporation, displayed similar Ge contents (Fig. 4).



**Fig. 4** Ge contents in reference materials (black; Escoube et al., 2012; Scribner et al., 2006; Jochum et al., 2016) compared to ICP-MS Ge contents obtained using our preparation protocol, with (white) or without a final evaporation step (gray). Error bars on our results represent an uncertainty of 3%, the ICP-MS analytical repeatability.

### 3.2. Detection limits, repeatability and accuracy

The contribution of Ge from the whole procedural chemistry blank was measured on 11 procedural blanks and has been found to be  $3 \pm 2$  ng l<sup>-1</sup> and indistinguishable from the instrumental blank. According to the IUPAC definition (IUPAC, 1997), method detection limits were calculated as the mean concentration of 11 procedural blanks plus three standard deviations of these 11 procedural blanks (Table 4). The lowest detection limit was obtained for <sup>74</sup>Ge (6 ng l<sup>-1</sup>), the most abundant Ge isotope. For comparison, the detection limit for <sup>72</sup>Ge is 5 times higher, approximately 30 ng l<sup>-1</sup> most likely due to the ArO<sub>2</sub> interference. Considering that 20 mg of powdered sample was dissolved in 100 ml, this corresponds to a detection limit of approximately 0.03 μg g<sup>-1</sup> in the solid sample (Table 4). For the plant standard (200-600 mg dissolved in 100 ml), the detection limit is approximately 0.001 μg g<sup>-1</sup> in the solid sample. Additionally, the linearity limit was demonstrated over the entire



1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

calibration range. The linearity limit was above 1000 ng l<sup>-1</sup>, the highest standard in the calibration curve, as the coefficient correlation of the calibration curve is above 0.995.

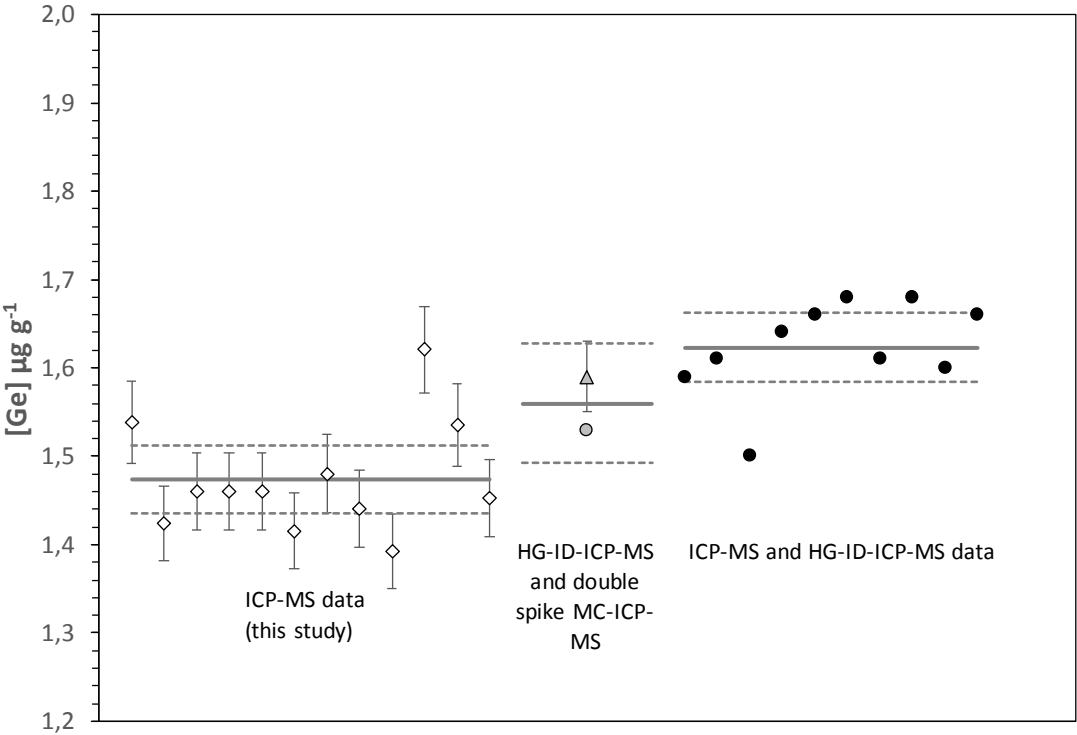
Method	Dissolution	Preliminary steps	DL in solution	DL in solid samples	Reproducibility	Difference with previously published values	Samples	References
ID-HG-ICP-MS	acid	ID	0.5 ng l <sup>-1a</sup>	-	<3%	n.s.	natural waters	Evans and Derry, 2002
HR-ICP-MS	fusion	-	10 ng l <sup>-1</sup>	n.s.	4%	n.s.	plants and soils	Delvigne et al., 2009
ICP-MS	fusion	-	2 ng l <sup>-1</sup>	0.05 µg g <sup>-1</sup>	15%	n.s.	plants and soils	Cornelis et al., 2010
LA-ICP-MS	-	-	-	< 1 µg g <sup>-1</sup>	8% <sup>b</sup>	n.s.	rocks	Belissont et al., 2011; Shen et al., 2011
X-ray fluorescence	-	-	-	1.5 µg g <sup>-1c</sup>	1%	15%	rocks	Frei and Polat, 2007
Spectrophotometry	acid	Polysulfone membrane filter	2 ng l <sup>-1</sup>	n.s.	5%	n.s.	waters and soils	Soylak and Yigit, 2015
ICP-MS	fusion	Cationic purification	6 ng l <sup>-1</sup>	0.03 µg g <sup>-1</sup>	3%	6%	plants, soils, rocks	This study

<sup>a</sup> blank level  
<sup>b</sup> valid for Ge/Si ratio as detailed in Shen et al., 2011  
<sup>c</sup> minimum Ge concentration analyzed (no limit of detection provided)

**Table 4.** Comparison of metrological characteristics of different techniques used for Ge determination. n.s. = not specified. DL = detection limit.

The relative repeatability of ICP-MS analysis based on a Ge single element standard solution (400 ng l<sup>-1</sup>) and analyzed six times on a single day is 3% (n=6, confidence level 95%). Similarly, four aliquots of one fused solution (BHVO-2) passed through four different columns and analyzed twice on the same day gives a relative repeatability of 2%. Reference materials of different composition (BHVO-2; AGV-2; BCR-2; GBW 07401; GBW 07404; GBW 07407) were analyzed to evaluate the accuracy of results (Supplementary Table 1). However, the absence of properly certified Ge values complicated the exercise. As shown in Fig. 5, our BHVO-2 data agree within 10% with the published value from the compilation of Jochum et al. (2016) (Table 5). However, a careful sorting of compiled data reveals that most of the dissolution protocols are not adapted to Ge, except for that of Scribner et al. (2006). Indeed, all but one of the studies employed acid attacks using HCl, HClO<sub>4</sub> or HF (at temperature above 60°C) or a combination of these, which induce loss of Ge (Luais et al., 2012). Tests performed by Luais (2012) demonstrated that Ge loss is at 85% when HClO<sub>4</sub> is employed in the acid dissolution mixture. In addition, it is unclear if ICP-MS analysis were corrected for spectroscopic interferences and selected Ge isotopes were not specified. Thus,

Ge might be underestimated due to potential Ge volatilization during dissolution, while uncorrected interferences would overestimate Ge content. In the literature, Ge contents estimated using specific techniques devoted to Ge analysis (ID-HG-ICP-MS or double-spike MC-ICP-MS) appear to be systematically lower than Ge contents estimated with ICP-MS techniques. In the case of BHVO-2, ID-HG-ICP-MS and double spike MC-ICP-MS techniques provided a compiled value of  $1.56 \pm 0.07 \mu\text{g g}^{-1}$  (Table 5; Scribner et al., 2006; Escoube et al., 2012), while ICP-MS techniques (acid attacks and interferences corrections not specified) averaged approximately  $1.62 \pm 0.04 \mu\text{g g}^{-1}$  (Table 5; Jochum et al., 2016). Similarly, BHVO-1 data show a comparable shift between the two techniques ( $1.46 \pm 0.12 \mu\text{g g}^{-1}$ ,  $n=2$  for ID-HG-ICP-MS and double spike MC-ICP-MS;  $1.64 \pm 0.06 \mu\text{g g}^{-1}$ ,  $n=3$  for ICP-MS; Jochum et al., 2016). An intermediate Ge content ( $1.58 \mu\text{g g}^{-1}$ ) is obtained by Luais (2012) using dedicated acid attack removing 80% of matrix analyzed by ICP-MS suggesting that discrepancy between techniques is likely induced by matrix and interferences. Despite being more limited in number, data acquired using isotope dilution techniques are the most robust (Escoube et al., 2012; Scribner et al., 2006). Considering the compiled values from these two studies, our BHVO-2 results agree within 6% (Fig. 5, Table 5).



**Fig. 5** Ge content in BHVO-2 from our study (open diamonds), high quality data (gray symbols) from Escoube et al. (2012) (gray circle; double spike MC-ICP-MS), and Scribner et al. 2006 (gray triangle; ID-HG-ICP-MS), compiled data from Jochum et al. 2016 (filled circles; ICP-MS and one ID-HG-ICP-MS from Scribner et al., 2006). Bold and dashed lines represent the mean and uncertainties (95% confidence level) of each subgroup, respectively. Errors bars represent the analytical precision when provided (*i.e.*, the 3% repeatability in this study).

Regarding the other rock standards (AGV-2 and BCR-2), there is a better agreement between our data and the compiled data from Jochum et al., (2016) (Table 5). Considering these three rock standards, our data agree within ~5% with published values.

Regarding soil standards (GBW 07401, 07404, 07407), our results are systematically 20 to 30% higher than certified values provided in Wang et al. (2013). However, a better agreement is noted when compared to data from Liu et al. (2014), suggesting that certified values should

be revised. The use of  $\text{HClO}_4$  in the sample decomposition procedure calls into question the accuracy of these data and may explain our systematically higher Ge contents.

Sample type	Ge value (this study)	n	Difference with published values	Published values	n	Technique	References
BHVO-2	basalt	1.47±0.04 $\mu\text{g g}^{-1}$	11	9%	10	ICP-MS but one	Jochum et al., 2016
				8%	3	ID-HG-ICP-MS and double spike MC-ICP-MS	Scribner et al., 2006 and Escoube et al., 2012
AGV-2	andesite	1.14±0.08 $\mu\text{g g}^{-1}$	6	5%	6	ICP-MS	Jochum et al., 2016
BCR-2	basalt	1.43±0.14 $\mu\text{g g}^{-1}$	5	2%	6	ICP-MS but one	Jochum et al., 2016
GBW 07401	soil	1.67±0.09 $\mu\text{g g}^{-1}$	11	11%	6	ICP-MS	Liu et al., 2014
				25%	at least 8	n.s.	Wang et al., 2013
GBW 07404	soil	2.41±0.18 $\mu\text{g g}^{-1}$	4	15%	6	ICP-MS	Liu et al., 2014
				27%	at least 8	n.s.	Wang et al., 2013
GBW 07407	soil	1.89±0.10 $\mu\text{g g}^{-1}$	3	18%	at least 8	n.s.	Wang et al., 2013
ERM-CD281	plant	70±3 $\text{ng g}^{-1}$	9			ICP-MS	This study

<sup>a</sup> Compiled value of average values of each study and uncertainty values (95% confidence limit)

**Table 5.** Comparison of Ge contents in different reference materials between this study and data from the literature. n.s. = not specified. Uncertainties are provided with 95% confidence level.

To provide the first Ge data on a plant standard, the standard ERM-CD281 was analyzed. Its Ge content is estimated to be approximately  $70\pm 3 \text{ ng g}^{-1}$  ( $n=9$ ; Supplementary Table 1).

### 3.3. Perspectives

This method provides a convenient procedure for determining accurate and precise Ge concentrations in rocks, soils and plants. Additionally, the combination of Ge concentrations with  $\delta^{30}\text{Si}$  analyses is the great advantage of this method, as both Si cycle tracers can be analyzed from a single procedure allowing a better understanding of the continental Si cycle. As emphasized in Cornelis et al. (2011), the combination of Ge/Si ratios and silicon isotopes turned out to be a great asset for tracing the sources and fate of Si in the critical zone, where numerous co-occurring processes are difficult to decipher.

The method can likely be expanded to water samples under the condition of respecting the detection limits. The purification step of this procedure would then be suitable for hydrothermal fluids ( $12\pm 13 \mu\text{g l}^{-1}$  up to  $50 \mu\text{g l}^{-1}$ ; Evans and Derry, 2002) and soil solutions

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

( $7.1 \pm 1.4 \mu\text{g l}^{-1}$ ; Cornelis et al., 2010). However, the analysis of silicon isotopes on the same chemical preparation may not be straightforward because of DOC and anions responsible for isotopic bias (Hughes et al., 2011). Water samples with lower Ge contents, such as freshwater and seawater, might be pre-concentrated using Mg-coprecipitation (Escoubé, 2008). As many other elements are scavenged by this method, the Mg-coprecipitation should be followed by the cationic purification step. As both Ge and Si recoveries are complete during Mg-coprecipitation (Escoubé, 2008; Cardinal et al., 2005), the analysis of silicon isotopes and Ge concentrations could again be performed on the same preparation. However, as anionic species will not be removed completely, care should be taken to control the bias induced by anionic species on  $\delta^{30}\text{Si}$  analysis (Hughes et al., 2011).

In addition to silicon isotopes analysis, this method paves the way towards a new approach to perform Ge isotopes in soils and plants, which has never been done before. Combining silicon isotopes, germanium isotopes and Ge/Si ratios would be a powerful multi-proxy approach to tackle continental Si biogeochemical cycle.

4. Conclusions

The fusion and purification technique based on the Si isotopes preparation protocol (Georg et al., 2006) allows precise determination of Ge concentrations in environmental samples down to a detection limit of approximately  $6 \text{ ng l}^{-1}$ . Analyses performed on  $^{74}\text{Ge}$ , the most abundant isotope, show the best precision of approximately 3%. Accuracy, difficult to assess given the scarcity of reliable data available for comparison, was assessed with an error of approximately 5%. This method provides data with equivalent or better metrological characteristics than other published procedures and analytical techniques except for ID-HG-ICP-MS, which shows the best precision and lowest detection limit (Table 4) but is much more time consuming. In addition to the reliability of generated data, this technique has two major

advantages: (1) it does not require peculiar instruments such a hydride generation system, not found in most laboratories unless specific needs, and (2) Ge concentrations and Si isotopic analysis can be performed on the same solution. This last point represents a precious gain of time in terms of sample preparation as one procedure serves to perform both analyses. A systematic coupling of Ge/Si ratios and  $\delta^{30}\text{Si}$  compositions is a great asset in the interpretation of the Si cycle, as both tracers are very complementary.

#### Acknowledgments

This study has been funded by the ANR project BIOSiSOL (ANR-14-CE01-002). The French Agence Nationale de la Recherche supported the study through the Project EQUIPEX ASTER-CEREGE. Authors thank Hélène Mariot for her management of the clean laboratory.

#### References

- Blecker S.W., King S. L., Derry L.A., Chadwick O.A., Ippolito J.A. and Kelly E.F. (2007) The ratio of germanium to silicon in plant phytoliths: quantification of biological discrimination under controlled experimental conditions. *Biogeochemistry*, 86,189-199.
- Belissont R., Boiron M.-C., Luais B. and Cathelineau M. (2014) LA-ICP-MS analyses of minor and trace elements and bulk Ge isotopes in zoned Ge-rich sphalerites from the Noailhac – Saint-Salvy deposit (France): Insights into incorporation mechanisms and ore deposition processes. *Geochimica et Cosmochimica Acta* 126, 518–540.
- Cardinal D., Alleman L. Y., Dehairs F. , Savoye N., Trull T.W., André L. (2005) Relevance of silicon isotopes to Si-nutrient utilization and Si-source assessment in Antarctic waters. *Global Biogeochemical cycles*, 19, GB2007, doi:10.1029/2004GB002364.

- 387 Cornelis J.-T., Delvaux B., Cardinal D., André L., Ranger J., Opfergelt S. (2010). Tracing  
388 mechanisms controlling the release of dissolved silicon in forest soil solutions using Si  
389 isotopes and Ge/Si ratios. *Geochimica et Cosmochimica Acta* 74 (2010) 3913–3924.
- 390 Cornelis J.-T., Delvaux B., Georg R. B., Lucas Y., Ranger J., Opfergelt S. (2011) Tracing the  
391 origin of dissolved silicon transferred from various soil-plant systems towards rivers: a  
392 review. *Biogeosciences*, 8, 89–112.
- 393 Delvigne C., Opfergelt S., Cardinal D., Delvaux B. and André L. (2009) Distinct silicon and  
394 germanium pathways in the soil-plant system: Evidence from banana and horsetail.  
395 *Journal of Geophysical Research*, 114, G02013, doi:10.1029/2008JG000899.
- 396 Delvigne, C., Cardinal, D., Hofmann, A., André, L., (2012) Stratigraphic changes of Ge/Si,  
397 REE+Y and silicon isotopes as insights into the deposition of a Mesoarchean banded  
398 iron formation. *Earth and Planetary Science Letters*, 355-356, 109–118.
- 399 Delvigne C., Opfergelt S., Cardinal D., Hofmann A. and André, L., (2016) Desilication in  
400 Archean weathering processes traced by silicon isotopes and Ge/Si ratios. *Chemical*  
401 *Geology*, 420, 139–147.
- 402 Derry L.A., Kurtz A. C., Ziegler K., and Chadwick O. A. (2005) Biological control of  
403 terrestrial silica cycling and export fluxes to watersheds. *Nature*, 433, 728-731.
- 404 Dong L., Shen B., Lee C.-T. A., Shu X.-J., Peng Y., Sun Y., Tang Z., Rong H., Lang X., Ma  
405 H., Yang F. and Guo W. (2015) Germanium/silicon of the Ediacaran-Cambrian Laobao  
406 cherts: Implications for the bedded chert formation and paleoenvironment interpretations.  
407 *Geochemistry, Geophysics, Geosystems*, 16, 751–763, doi:10.1002/2014GC005595.
- 408 Ellwood M.J., Kelly M., Maher W. A. and De Deckker P. (2006) Germanium incorporation  
409 into sponge spicules: Development of a proxy for reconstructing inorganic germanium

- 410 and silicon concentrations in seawater. *Earth and Planetary Science Letters*, 243, 749–  
411 759.
- 412 Ellwood M.J. and Maher W.A. (2003) Germanium cycling in the waters across a frontal zone:  
413 the Chatham Rise. *New Zealand, Marine Chemistry* 80, 145– 159.
- 414 Evans M. J. and Derry L.A. (2002) Quartz control of high germanium/silicon ratios in  
415 geothermal waters. *Geology*, 30, 1019-1022.
- 416 Escoubé R. (2008) Iron and germanium isotope geochemistry in river and hydrothermal  
417 systems. PhD Thesis, Université de Pau et des pays de l'Adour, 275 pages.
- 418 Escoubé R., Rouxel O. J., Luais B., Ponzevera E. and Donard O. F.X. (2012) An  
419 Intercomparison Study of the Germanium Isotope Composition of Geological Reference  
420 Materials. *Geostandards and Geoanalytical Research*, 36, 149-159.
- 421 Filippelli G.M., Carnahan J.W., Derry L.A., and Kurtz A. (2000) Terrestrial paleorecords of  
422 Ge/Si cycling derived from lake diatoms. *Chemical Geology*, 168, 9–26.
- 423 Frei R. and Polat A. (2007) Source heterogeneity for the major components of ~3.7 Ga  
424 Banded Iron Formations (Isua Greenstone Belt, Western Greenland): Tracing the nature  
425 of interacting water masses in BIF formation. *Earth and Planetary Science Letters*, 253,  
426 266–281.
- 427 Fitoussi C., Bourdon B., Kleine T., Oberli F. and Reynolds B. C. (2009) Si isotope  
428 systematics of meteorites and terrestrial peridotites: implications for Mg/Si fractionation  
429 in the solar nebula and for Si in the Earth's core. *Earth and Planetary Science Letters*,  
430 287, 77–85.



1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

431 Georg R.B., Reynolds B.C., Frank M. and Halliday A.N. (2006) New sample preparation  
432 techniques for the determination of Si isotopic compositions using MC-ICPMS. Chemical  
433 Geology, 235, 95–104.

434 Hamade T., Konhauser K., Raiswell R., Goldsmith S. and Morris R. (2003) Using Ge/Si  
435 ratios to decouple iron and silica fluxes in Precambrian banded iron formations. Geology,  
436 31, 35- 38.

437 Hammond D. E., McManus J. and Berelson W. M. (2004) Oceanic germanium/silicon ratios:  
438 Evaluation of the potential overprint of temperature on weathering signals.  
439 Paleoceanography, 19, doi/10.1029/2003PA000940.

440 Hughes H.H., Delvigne C., Korntheuer M., de Jong J., André L. and Cardinal D. (2011)  
441 Controlling the mass bias introduced by anionic and organic matrices in silicon isotopic  
442 measurements by MC-ICP-MS. Journal of Analytical Atomic Spectrometry, 26, 1892-  
443 1896.

444 Höll R., Kling M. and Schroll E. (2007) Metallogensis of germanium—A review. Ore  
445 Geology Reviews, 30, 145–180.

446 IUPAC (1997). Compendium of Chemical Terminology, 2nd ed. (the "Gold Book").  
447 Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications,  
448 Oxford.

449 Jochum K.P., Weis U., Schwager B., Stoll B., Wilson S.A., Haug G.H., Andreae M.O. and  
450 Enzweiler J. (2016) Reference Values Following ISO Guidelines for Frequently  
451 Requested Rock Reference Materials. Geostandards and Geoanalytical Research, 40,  
452 333-350.

- 1  
2  
3 453 Kurtz A.C., Lugolobi F., and Salvucci G. (2011) Germanium-silicon as a flow path tracer:  
4  
5 454 Application to the Rio Icacos watershed. *Water Resources Research*, 47, W06516,  
6  
7 455 doi:10.1029/2010WR009853, 2011  
8  
9  
10 456 Kurtz A. C., Derry L. A., and Chadwick O. A. (2002) Germanium-silicon fractionation in the  
11  
12 457 weathering environment. *Geochimica et Cosmochimica Acta*, 66,1525-1537.  
13  
14  
15 458 Kurtz A. C. and Derry L. A. (2004) Tracing silicate weathering and terrestrial silica cycling  
16  
17 459 with Ge/Si ratios. In Wanty, R. B. and Seal, R. R., editors, *Proc. 11th Int. Symp. on*  
18  
19 460 *Water Rock Interaction*, 833-836, The Netherlands.Balkema Pubs.  
20  
21  
22 461 Luais B. (2007) Isotopic fractionation of germanium in iron meteorites: Significance for  
23  
24 462 nebular condensation, core formation and impact processes. *Earth and Planetary Science*  
25  
26 463 *Letters*, 262, 21-36.  
27  
28  
29  
30 464 Luais B. (2012) Germanium chemistry and MC-ICPMS isotopic measurements of Fe–Ni, Zn  
31  
32 465 alloys and silicate matrices: Insights into deep Earth processes. *Chemical Geology*, 334,  
33  
34 466 295–311.  
35  
36  
37 467 Liu Y., Diwu C., Zhao Y., Liu X., Yuan H., and Wang J. (2014) Determination of trace and  
38  
39 468 rare-earth elements in Chinese soil and clay reference materials by ICP-MS. *Chinese*  
40  
41 469 *Journal of Geochemistry*,33, 095–102.  
42  
43  
44 470 Lugolobi F., Kurtz A.C. and Derry L.A. (2010) Germanium–silicon fractionation in a tropical,  
45  
46 471 granitic weathering environment. *Geochimica et Cosmochimica Acta*, 74, 1294–1308.  
47  
48  
49  
50 472 Makishima A. and Nakamura E. (2009) Determination of Ge, As, Se and Te in Silicate  
51  
52 473 Samples Using Isotope Dilution-Internal Standardisation Octopole Reaction Cell ICP-  
53  
54 474 QMS by Normal Sample Nebulisation. *Geostandards and Geoanalytical Research*, 33,  
55  
56 475 369-384.  
57  
58  
59  
60

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

476 Mc Mahon M., Regan F. and Hughes H. (2006) The determination of total germanium in real  
477 food samples including Chinese herbal remedies using graphite furnace atomic  
478 absorption spectroscopy. *Food Chemistry*, 97, 411-417.

479 Mortlock R.A. and Froelich P.N. (1996) Determination of germanium by isotope dilution-  
480 hydride generation inductively coupled plasma mass spectrometry. *Analytica Chimica*  
481 *Acta*, 332, 277-284.

482 Mortlock R. A., Froelich P. N., Feely R. A., Massoth G. J., Butterfield D. A., and Lupton J. E.  
483 (1993) Silica and germanium in Pacific-ocean hydrothermal vents and plumes. *Earth and*  
484 *Planetary Science Letters*, 119, 365-378.

485 Opfergelt S., Cardinal D., André L., Delvigne C., Bremond L. and Delvaux B. (2010)  
486 Variations of  $\delta^{30}\text{Si}$  and Ge/Si with weathering and biogenic input in tropical basaltic ash  
487 soils under monoculture. *Geochimica et Cosmochimica Acta*, 74, 225-240.

488 Pokrovski G.S., and Schott J. (1998) Thermodynamic properties of aqueous Ge (IV)  
489 hydroxide complexes from 25 to 350°C: Implications for the behavior of germanium and  
490 the Ge/Si ratio in hydrothermal fluids. *Geochimica et Cosmochimica Acta*, 62, 1631-  
491 1642.

492 Qi H.-W., Rouxel O., Hu R.-Z., Bi X.-W., Wen H.-J. (2011) Germanium isotopic systematics  
493 in Ge-rich coal from the Lincang Ge deposit, Yunnan, Southwestern China. *Chemical*  
494 *Geology*, 286, 252-265.

495 Rouxel O., and Luais B. (2017) Germanium isotope geochemistry. *Reviews in Mineralogy*  
496 *and Geochemistry*, 82, 601-656.

497 Rosenberg E. (2009) Germanium: environmental occurrence, importance and speciation.  
498 *Reviews in Environmental Science Bio/Technology*, 8, 29-57.

- 499 Scribner A. M., Kurtz A. C., and Chadwick O. A. (2006) Germanium sequestration by soil:  
500 Targeting the roles of secondary clays and Fe-oxyhydroxides. *Earth and Planetary*  
501 *Science Letters*, 243, 760-770.
- 502 Shen B., Lee C.-T. A., Xiao S. (2011) Germanium/silica ratios in diagenetic chert nodules  
503 from the Ediacaran Doushantuo Formation, South China. *Chemical Geology*, 280, 323-  
504 335.
- 505 Soylak M. and Yigit S. (2015) Preconcentration-separation of germanium at ultra trace levels  
506 on polysulfone membrane filter and its determination by spectrophotometry. *Journal of*  
507 *Industrial and Engineering Chemistry*, 24, 322-325.
- 508 Sutton J., Ellwood M.J., Maher W.A., and Croot P.L. (2010) Oceanic distribution of inorganic  
509 germanium relative to silicon: Germanium discrimination by diatoms. *Global*  
510 *Biogeochemical Cycles*, 24, GB2017, doi:10.1029/2009GB003689.
- 511 Tribouvillard N., Bout-Roumazelles V., Riboulleau A., Baudin F., Danelian T. and Riquier L.  
512 (2011) Transfer of germanium to marine sediments: Insights from its accumulation in  
513 radiolarites and authigenic capture under reducing conditions. Some examples through  
514 geological ages. *Chemical Geology*, 282, 120–130.
- 515 Wang Y., Gu T., Wang X., Gao Y.-S., Jochum K.P., Müller W.E.G. (2013) Practical  
516 handbook of reference materials for geoanalysis, second, Geological Publishing House,  
517 Beijing.
- 518 Wiche O., Zertani V., Hentschel W., Achtzige R. and Midula P. (2017) Germanium and rare  
519 earth elements in topsoil and soil-grown plants on different land use types in the mining  
520 area of Freiberg (Germany). *Journal Geochemical Exploration*, 175, 120-129.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

521 Wheat C.G. and McManus J. (2005) The potential role of ridge-flank hydrothermal systems  
522 on oceanic germanium and silicon balances. *Geochimica et Cosmochimica Acta*, 69,  
523 2021–2029.  
524

For Review Only