TECHNICAL NOTE

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A fast double-stack chromatographic separation of germanium from silicate material for isotope analysis with MC–ICP-MS

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Germanium (Ge) isotope measurements ($\delta^{74/70}$Ge relative to NIST3120a) have attracted increasing attention in geochemistry and cosmochemistry; however, analyses of silicate material with low Ge contents remain difficult due to complex sample preparation and purification procedures. Here, we present a novel double-stack chromatographic procedure that purifies Ge from silicate digests. This protocol reduces evaporation steps and overall processing time, allowing higher sample throughput while preserving quantitative Ge recovery (~100%) and low procedural blanks (<0.1 ng Ge), together with effective matrix removal. Because Ge yields are quantitative under the conditions tested, this method is suitable for measuring Ge isotope signatures without the need for a double spike. This fast, user-friendly chemistry should broaden routine use of Ge isotopes in isotope geo- and cosmochemistry.

1. Introduction

Understanding germanium (Ge) isotope fractionation during Earth's formation requires accurate knowledge of Ge isotope compositions ($\delta^{74/70}$Ge relative to NIST3120a) in silicate reservoirs. Germanium isotopes are conventionally measured with MC-ICP-MS,[1–12] allowing the detection of sub-per-mille variations in natural samples from aqueous geochemistry,[13–18] igneous and metamorphic geochemistry,[4,19] to cosmochemistry.[3–5,20–23] Earlier studies on iron meteorites to constrain planetary differentiation processes benefitted from a straight-forward single step cation-exchange chemistry to purify Ge out of metal;[4–6] however, there are still relatively few data on silicate materials in isotope geochemistry. In particular, there are almost no data on mid-ocean ridge basalts (MORBs) or ocean island basalts (OIBs) beyond rock reference materials. This is partly due to complex and intensive laboratory sample preparation required to purify Ge in silicate matrices, which typically involves several chromatographic steps. There are also no unified protocols for digesting and separating Ge from silicate material, nor for measuring the Ge isotopic composition. Most of the approaches apply a solid-phase extraction (SPE) technique after acid digestion with a mixture of HF + HNO$_3$ through either a two-step ion-exchange chromatography utilizing anion- and cation-exchange resins[1,4,9,11] or only the first anion-exchange resin.[13–15,17] The latter method is only feasible when a hydride generator is used for sample introduction to the MC-ICP-MS, because the remaining matrix can be separated from the Ge during hydride generation.[24,25] However, any

remaining matrix might also cause a bias during the measurement with the hydride generator, as, *e.g.*, remaining transition metals in the matrix can inhibit the formation and/or cause the *in situ* decomposition of generated hydrides of Ge.[26,27] These processes can induce uncorrectable isotope fractionation of Ge within the hydride generator, as observed in doping experiments.[24,28,29] In particular, Meng *et al.* (2015)[29] showed that additions of Zn, although Zn itself does not form hydrides, markedly decrease Ge hydride yield and lead to isotopic offsets between reference solutions and samples. Similarly, Karasiński *et al.* (2021)[28] demonstrated that adding mixtures of transition metals (Cr, Fe, Ni, Cu, and Zn) to NIST Ge standards results in lower hydride yields and systematic shifts towards higher measured $\delta^{74/70}$Ge values.

The use of a double spike might correct to a certain degree for these effects during hydride generation, as supported by the overall accuracy for single step chromatographic protocols.[1,13–15,17] To the best of our knowledge, there are no published data on Ge isotopes measured through hydride generation MC-ICP-MS using only a single stage anion chemistry performed without a double spike. For solution-mode MC-ICP-MS without hydride generation, both chromatographic steps (anion- and cation-exchange) are likewise required to reduce Zn and other matrix elements such as Fe and Ti that cause non-spectral matrix effects in the plasma.[4,11] For these reasons, cleaner separation using a combined anion + cation configuration is beneficial, and in practice, necessary for both applications using hydride generation and conventional solution MC-ICP-MS. Other than SPE, there was also a liquid–liquid extraction method proposed for Ge isotope analysis of silicate materials.[28] An exception is the study of high-temperature geothermal fluids by Siebert *et al.* (2006),[18] who used a double

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spike with hydride generation but no prior SPE. However, this approach targets fluid matrices and is not directly transferable to silicate rock digests, where chromatographic purification remains essential to minimize transition metal-related matrix effects.

Better constraining the processes that influence the $\delta^{74/70}$Ge of mantle-derived melts, such as MORBs and OIBs, particularly given the relatively small isotope fractionations expected at high temperature equilibrium processes,[30] requires the measurement of a large and diverse sample suite of these rocks. To optimize the overall sample throughput for the Ge isotope analysis and keeping the matrix fraction low, we have opted here for a double-stack SPE technique that combines the previously established two-step chromatographic separation[4] into a single stage chemistry, making the technique also viable for non-hydride generation introduction systems. Because this method elutes minor Ti along with Ge, we determined the yield of low- and high-TiO$_2$ basalts BIR-1 and BHVO-1, respectively. Both reference materials approximately match the major element and Ge contents of typical MORB and OIB samples, respectively, verifying our method.

2. Methods

2.1 Sample digestion

Germanium purification was conducted in ISO6 class clean laboratory facilities equipped with ISO5 class laminar flow hoods with total extraction at CRPG Nancy. All concentrated acids used in this study are high-purity acids purchased from Seastar, and lower molarity acids were diluted from these by adding ultrapure 18.2 MΩ cm water and titrating with 0.1 M NaOH. During each evaporation step, we avoided any hotplate where HCl was evaporated to prevent volatilization and loss of Ge, and generally did not use any HCl where the sample handling was performed (except during the resin-cleaning procedure, where HCl is completely washed out with ultrapure water until neutral conditions are reached prior to sample conditioning). We digested the reference materials according to previous published methods established at CRPG.[4,5,21,22] In brief, reference materials were digested by weighing 200 mg of BHVO-1 rock powder in 15 mL Teflon vials and 4 g of BIR-1 in a 60 mL Teflon vial, followed by the addition of 4 mL and 54 mL of an HF–HNO$_3$ mixture (3 : 1 concentrated ratio), respectively. The samples were kept at room temperature overnight to allow the "cold reaction" to proceed, and were then placed for at least 3 days on a hotplate with closed lids at 65 °C. During this time, closed beakers were shaken and subsequently ultrasonicated each day for 30 min and returned to the hotplate. Any Ge that was potentially retained in and between the newly formed fluorides during the digestion process was then quantitatively recovered by leaching the residual fluorides with concentrated HF under ultrasonication and collecting the supernatant in a separate beaker. During this process, major elements such as Si, Mg, Mn, Ca, or Al are retained to significant and variable degrees in the fluorides, according to the element and the sample composition, avoiding over-saturation during ion chromatography.[4] Along with a quantitative recovery of P, there

is 70 to 100% of Ti recovered in the supernatant depending on the sample matrix, which might affect MC-ICP-MS measurements if not sufficiently separated in subsequent ion-exchange chromatography.[4] After repeating the leaching–centrifugation step three times, concentrated HNO$_3$ is added to the collected supernatant to ensure a 3 : 1 ratio of the HF–HNO$_3$ mixture before evaporating the samples at 65 °C. The evaporation step is stopped shortly before dryness to obtain a "gel", which is easily re-dissolved in concentrated HNO$_3$ and dried down again at 65 °C. The samples were then re-dissolved in 1 M HF ("loading acid") and ultrasonicated until the solution was clear, before being centrifuged using a filter cone to obtain the loading solution, where 1 mL corresponds to ca. 80–100 mg of the original sample powder.

For the chromatographic tests, the large amount of BIR-1 reference material was digested to create a homogeneous in-house "silicate stock solution" that was repeatedly processed using both the conventional two-step protocol and the new double-stack configuration to test inter- and intra-session variability for silicate material for both chromatographic separations. In addition, we chose BHVO-1 rather than BHVO-2, because the latter has been shown to be contaminated by metallic components during preparation, as indicated by Mo elemental and isotopic systematics.[31] BHVO-1 differs from BIR-1 in key matrix elements (e.g. higher Ti contents and different degrees of enrichment in incompatible elements), providing a complementary basaltic composition to test the method.

We emphasize that this digestion protocol follows the procedure of Luais (2012), who demonstrated quantitative Ge recovery for a range of silicate rock reference materials, including ultramafic rocks, basalts, granites, and sedimentary iron formations (see also ref. 19–21). Experimental studies have shown that, in HF media, Ge forms volatile fluorides and can be lost at the several-percent level during closed-system evaporation even at temperatures of 100 °C,[32] which in turn risks inducing Ge isotope fractionation.[5,9,25,28] These studies indicate that digestion and evaporation at ~65 °C in screw-top Teflon beakers, avoiding prolonged closed-system drying, prevent measurable Ge isotope fractionation, whereas higher temperatures increase the risk of fractionation if vapor loss occurs. For samples containing refractory minerals such as zircon, rutile or spinel, we recommend high-pressure, high-temperature closed-vessel bomb digestion (e.g., ~150 °C, ~25 bar; high-pressure PTFE/TFM Teflon BOLA bombs, Bohlender®).[33] These bombs achieve complete dissolution while avoiding vapor loss, therefore yielding quantitative Ge recovery. Importantly, basalts show the same quantitative yield and isotope composition, consistent with the results obtained for lower temperature protocols.[20]

2.2 Conventional 2-step purification of Ge

We have first performed a chromatographic separation of the digested BIR-1 solution by taking 10 aliquots (1 mL sample loading solution each) and processed them with the conventional two-stage SPE previously established at CRPG-Nancy.[4] The aim was to assess the within session error for $\delta^{74/70}$Ge
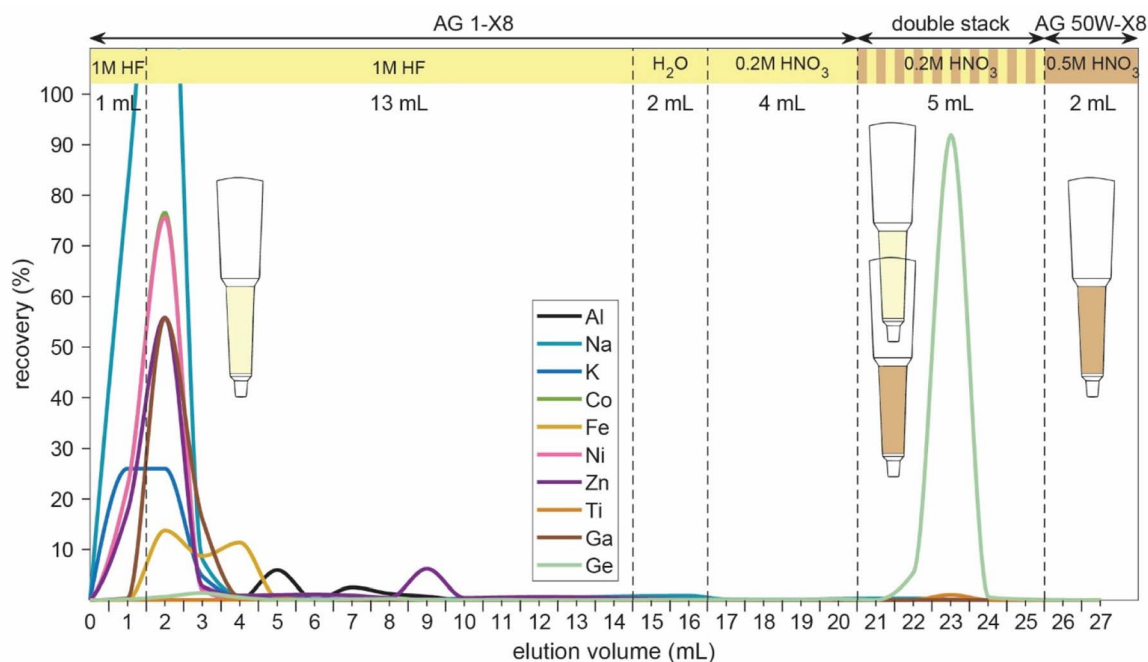
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Fig. 1 Germanium and other matrix element elution curves for the high-Ti rock reference material BHVO-1 during the double-stack chemistry, with 20 mL elution during the first AG1-X8 anion resin column (1 mL 1 M HF sample loading + 13 mL 1 M HF matrix washout + 2 mL H_2O preparing for acid change + 4 mL 0.2 M HNO_3), AG 50W-X8 cation resin (last 2 mL 0.5 M HNO_3), and both of the resins combined as a double-stack column (in between, 5 mL 0.2 M HNO_3). Data from the first 16 mL are taken from a previous column calibration on the same BHVO-1 rock reference material.[4]

measured for the same sample solution and to estimate the intra-session variability at this sample concentration. All ion-exchange resins were pre-cleaned and any remaining HCl from the cleaning procedure was washed off with H_2O before cleaning with 0.5 M HNO_3 and resin conditioning. The H_2O step was repeated multiple times until acid neutrality in the elution drops was confirmed using pH-indicator paper. The first column step involves 2 mL of AG 1-X8 anion resin (200–400 mesh, chloride form) in Bio-Rad columns, which is pre-cleaned and then conditioned with 1 M HF before loading 1 mL of sample solution. During this step, most matrix elements were directly washed off with an additional 13 mL of 1 M HF, whereas Ge together and Ti remained on the column (Fig. 1). After adding 2 mL of ultrapure water and 4 mL of 0.2 M HNO_3, Ge is eluted with 4 mL of additional 0.2 M HNO_3 with first traces of Ti elution and remaining traces of Fe and Zn. After evaporation and re-dissolution in 0.5 mL of 0.5 M HNO_3, the sample is loaded into Bio-Rad columns filled with 2 mL of pre-cleaned and conditioned Bio-Rad AG 50W-X8 cation-exchange resin (200–400 mesh, hydrogen form), and Ge is quantitatively recovered *via* adding 2 mL of 0.5 M HNO_3.

2.3 Double-stack (1 stage) purification of Ge

For the optimized double-stack chemistry, we have digested and leached BHVO-1 individually for each chromatographic separation, while aliquots were taken for BIR-1 from the already digested and leached stock solution. The double-stack chemistry was performed four times in a timeframe of four months and verified in individual analytical sessions to confirm the

long-term reproducibility of this method. The double-stack chemistry combines the above-mentioned established two-step purification scheme[4] into a single stage chemistry. Here, we repeat the rinsing of the matrix at the beginning on the anion resin column until an elution volume of 20 mL is reached (1 mL 1 M HF sample loading + 13 mL 1 M HF + 2 mL H_2O + 4 mL 0.2 M HNO_3) just before Ge is eluted (Fig. 1). Then, Bio-Rad columns filled with 2 mL of pre-cleaned and conditioned Bio-Rad AG 50W-X8 cation-exchange resin (200–400 mesh, hydrogen form) are inserted below the anion resin column (Fig. 1). Then, Ge was eluted and collected with 5 mL of 0.2 M HNO_3 through both ion-exchange resins to directly remove any remaining Zn, Fe, and other transition metals that could potentially interfere during hydride generation from the clean Ge cut. After that, the anion column is removed and 2 mL of 0.5 M HNO_3 are added only into the cation-exchange resin to further collect any traces of Ge, while avoiding additional Ti being eluted from the anion-exchange resin. To construct an elution curve for Ge and other matrix elements and to ensure a clean Ge cut during the double-stack purification, column cuts for BHVO-1 for each mL after switching to 0.2 M HNO_3 were obtained and measured using a *ThermoFischer Scientific X-Series* ICP-MS at CRPG-Nancy. After the chromatographic separation, BIR-1 and BHVO-1 Ge fractions were evaporated and subsequently dissolved and evaporated multiple times with 50 μl of concentrated HNO_3 to destroy any remaining organic material from the ion-exchange resins. The samples were then re-dissolved in 2 mL of 0.5 M HNO_3 and re-diluted to obtain a 10 ng mL^{-1} solution for the isotopic measurement.
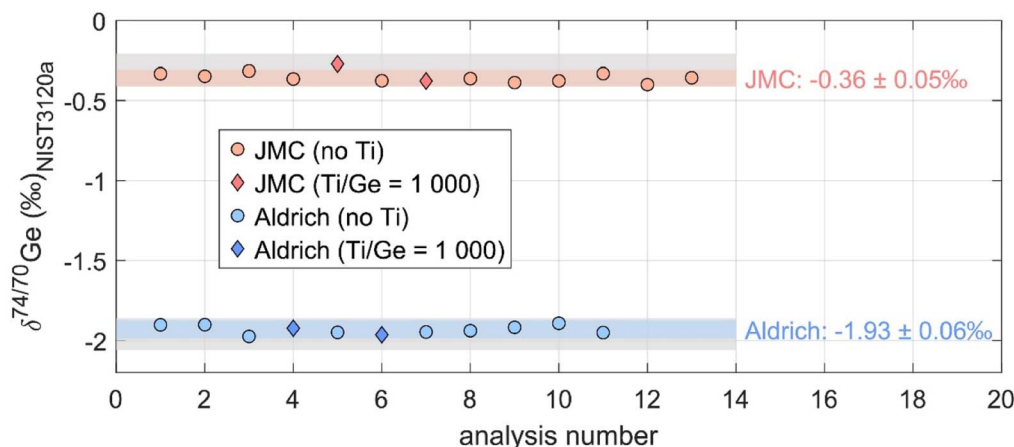
Fig. 2 Germanium isotope compositions of in-house standards measured with Ti doping (diamonds) and without Ti doping (circles). Each individual sample was measured at 10 ng mL^{-1} Ge, while the Ti-doped experiments contained 10 000 ng mL^{-1} Ti along with 10 ng mL^{-1} Ge. The colored shaded area shows the in-session variability of the in-house standards during the course of this study, and the grey shaded area shows the overall long-term reproducibility of JMC and Aldrich (average ± 2σ SD) with −0.31 ± 0.10‰ ($n = 68$) and −1.96 ± 0.10‰ ($n = 70$), respectively.[20]

2.4 Ge isotope measurements

Measurements of stable Ge isotopes were carried out at CRPG Nancy with a *ThermoFischer Scientific Neptune Plus* MC-ICP-MS coupled with a Cetac HGX-200 hydride generator with an uptake rate of *ca.* 200 μl min^{-1}. Five Ge isotopes (^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge) were measured simultaneously, as well as ^{77}Se and ^{78}Se. All isotopes were measured on Faraday cups equipped with 10^{11} Ω amplifiers in low resolution. During sample analysis, a combination of a standard Ni sampler cone and a 'H' Ni skimmer cone was used, which provided a signal intensity of ~0.1–0.2 V ppb^{-1} on ^{74}Ge. The sample and

Table 1 Individual and average Ge isotope compositions of BIR-1 and BHVO-1 reference materials and in-house standards Ge JMC and Aldrich with and without Ti doping analyzed in this study[a]

Sample	δ$^{72/70}$Ge (‰)	2σ SD	δ$^{73/70}$Ge (‰)	2σ SD	δ$^{74/70}$Ge (‰)	2σ SD	n
BIR-1 CC#12	0.29	0.03	0.40	0.09	0.55	0.07	3
BIR-1 CC#13	0.34	0.04	0.44	0.05	0.65	0.06	2
BIR-1 CC#14	0.31	0.06	0.40	0.09	0.61	0.07	3
BIR-1 CC#15	0.29	0.05	0.40	0.04	0.55	0.09	3
BIR-1 CC#16	0.33	0.12	0.46	0.22	0.61	0.31	2
BIR-1 CC#17	0.28	0.16	0.43	0.17	0.57	0.35	2
BIR-1 CC#18	0.28	0.02	0.41	0.02	0.56	0.03	3
BIR-1 CC#19	0.32	0.04	0.45	0.11	0.63	0.07	2
BIR-1 CC#20	0.25	0.03	0.33	0.00	0.49	0.11	2
BIR-1 CC#21	0.27	0.02	0.37	0.01	0.54	0.12	2
Average BIR-1, conventional	**0.30**	**0.06**	**0.41**	**0.08**	**0.58**	**0.10**	**24(10)**[b]
BIR-1 DS#1	0.33	n.d.	0.46	n.d.	0.65	n.d.	1
BIR-1 DS#2	0.33	0.01	0.42	0.11	0.61	0.08	3
BIR-1 DS#3	0.28	0.04	0.41	0.07	0.54	0.09	6
BIR-1 DS#4	0.36	0.10	0.50	0.11	0.65	0.13	5
Average BIR-1, double-stack	**0.32**	**0.07**	**0.45**	**0.08**	**0.61**	**0.10**	**15(4)**[b]
BHVO-1 DS#1	0.30	0.06	0.44	0.13	0.61	0.14	3
BHVO-1 DS#2	0.26	0.02	0.37	0.07	0.52	0.02	3
BHVO-1 DS#3	0.28	0.10	0.41	0.09	0.54	0.12	4
BHVO-1 DS#4	0.33	0.03	0.40	0.02	0.60	0.03	2
Average BHVO-1, double-stack	**0.29**	**0.05**	**0.40**	**0.05**	**0.57**	**0.08**	**12(4)**[b]
Average JMC	−0.16	0.03	−0.22	0.08	−0.36	0.05	11
Average JMC + Ti	−0.17	0.08	−0.23	0.04	−0.32	0.15	2
Average Aldrich	**−1.00**	**0.04**	**−1.50**	**0.09**	**−1.93**	**0.06**	**9**
Average Aldrich + Ti	**−1.01**	**0.03**	**−1.48**	**0.00**	**−1.94**	**0.06**	**2**

[a] CC = conventional chemistry; DS = double-stack. [b] Numbers in brackets denote amount of individually processed sample solutions through column chromatography

additional gas fluxes were set on each analytical session for optimum sensitivity and stability with both fluxes combined being mostly below 1.1 L min^{-1}, and the RF power set to ~1300 W. Other gas flows such as auxiliary gas were set to default values, and the extraction voltage was set to 2000 V. Analyses consisted of 40 cycles with a signal integration time of 8.4 s for each cycle. We prepared for every sample session a new reagent (8 g of NaBH$_4$ powder and 4 g of NaOH pellets per 1 L reductant). Sample solutions and solution standards were

measured at a Ge concentration of 10 ng mL^{-1}, with the NIST SRM 3120a Ge standard solution (Lot no. 080429) being used as a bracketing standard between every sample. We applied an online 2σ SD filter for the isotope ratios measured within the cycles. Along with the rock reference materials, the in-house standards JMC Ge (1000 ppm ICP standard solution, lot # 301230S, Johnson Matthey, Germany) and Aldrich Ge (10 200 ppm ICP standard solution, lot # 01704KZ, Aldrich Chemical Co., USA) were measured (Fig. 2). Bulk Ge procedural blanks were below <0.1 ng, and therefore no blank correction was applied. Validity of the data was confirmed by checking if samples/standards lie on the mass fractionation line by comparing $\delta^{74/70}$Ge with $\delta^{74/72}$Ge, $\delta^{72/70}$Ge and $\delta^{73/70}$Ge (Table 1 and Fig. 3), suggesting that no bias is induced by isobaric interferences from Zn, Se, or Ge-hydrides.[34]

3. Results and discussion

The first 20 mL eluted in the double-stack chromatographic separation presented here are adapted from the previous column calibration performed by Luais (2012),[4] while the elution of the Ge cut is directly performed with the additional cation-exchange resin (double-stack; Fig. 1). This allows that matrix elements such as Zn are removed in a similar degree as in the conventional 2-stage chemistry,[4] while Ti is slightly enriched compared to the previous method due to the additional 1 mL of 0.2 M HNO$_3$, which was added to ensure quantitative recovery of Ge. No other element is eluted with additional 2 mL of 0.5 M HNO$_3$ (25–27 mL in Fig. 1) in the cation-exchange resin, suggesting that the 5 mL of 0.2 M HNO$_3$ used during the double-stack step already yields 100% Ge. Approximately 1% of the original Ti was eluted, decreasing the Ti/Ge ratio of the original BHVO-1 powder from ~10 400 to ~110. This is the same range as the previous calibration of the two-stage chemistry, with Ti/Ge ratios of ~30 to 140 for other rock reference materials and ~80 for BHVO-1.[4] Within this range of Ti/Ge, no non-spectral matrix effects are expected during the measurement without a hydride generator.[4] We performed tests at even higher Ti/Ge ratios (e.g., 1000) using Ti-doped in-house Ge standards Aldrich and JMC, and observed no systematic offset in $\delta^{74/70}$Ge with hydride generation (Fig. 2). This is in line with a previous study showing that doping with high-field-strength elements (HFSE) such as Ti does not cause any detectable isotope fractionation during hydride generation without a double spike.[35] The detailed elution behavior for the individual anion- and cation-exchange steps is documented in Luais (2012)[4] and is not repeated here.

As discussed above, transition metals are effectively removed during double-stack chromatographic separation, and we did not observe any detectable Se hydride signal under our conditions. Previous work has shown that during the first chromatographic step (13 mL of 1 M HF on AG1-X8, 200–400 mesh), Se is largely removed while Ge is retained on the resin.[36] Any remaining Se in the final sample solution would be present predominantly as Se(vi) and must be reduced to Se(iv) (e.g., by heating in HCl) in order to form hydrides.[37,38] In our set-up, however, we use 0.5 M HNO$_3$ as the sample carrier solution,
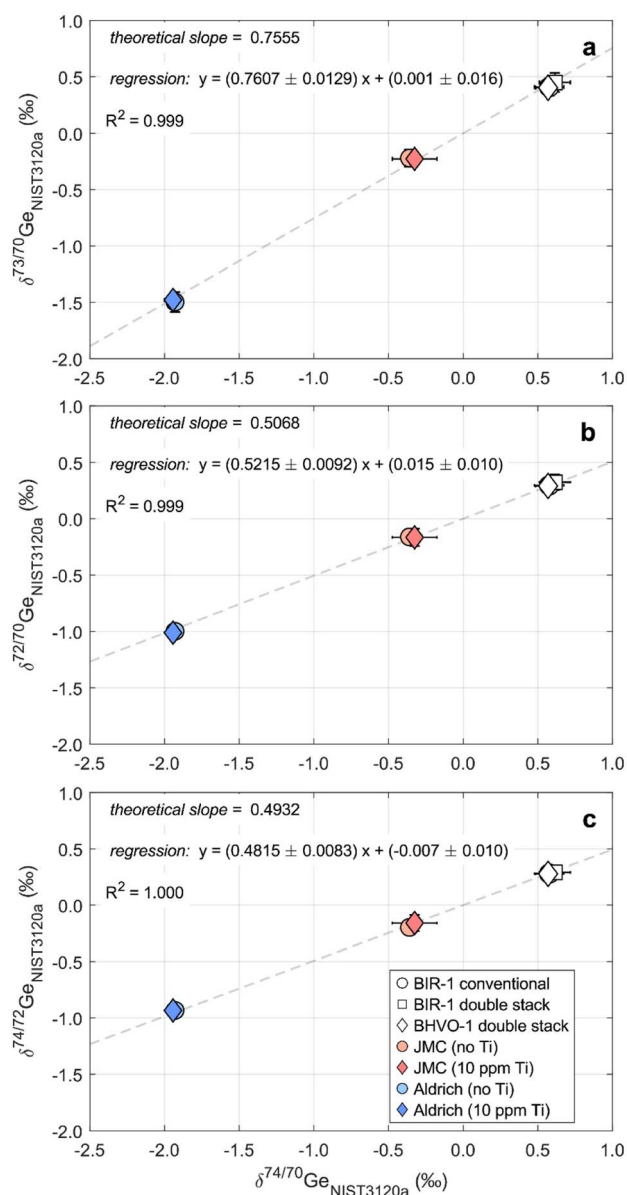

Fig. 3 Multiple three Ge isotope ratio plot of measured JMC and Aldrich in-house standards and BIR-1 and BHVO-1 reference materials processed *via* conventional and double-stack chromatographic separation. The samples are grouped, and error bars are individual 2σ standard errors, with the error-weighted regression computed with a "Yorkfit".[39,40] Because all isotope ratios follow the theoretical mass fractionation line (a–c), we do not expect any interference contribution such as ^{74}Se (a and b) or ^{70}Zn (c) on ^{74}Ge and ^{70}Ge, respectively (see the main text).

which inhibits Se reduction. This is supported by the simultaneously measured ^{77}Se and ^{78}Se intensities in purified rock solutions, solution standards, and bracketing background blanks that are indistinguishable, indicating that Se is effectively removed and does not contribute any detectable hydride signal under our HG conditions. Zinc is also not a hydride-forming element; however, it can still affect Ge hydride yield and bias Ge isotope ratios, as shown by Meng *et al.* (2015),[29] who reported biased $\delta^{74/70}$Ge during Zn doping, while the Zn monitor on ^{68}Zn remained unchanged. Overall, this ensures that Ge isotope measurements remain unaffected by Se and Zn interferences, as demonstrated in Fig. 3.

We have assessed the intra-session reproducibility of $\delta^{74/70}$Ge *via* analyzing the digested and leached BIR-1 stock solution by processing individual aliquots through 10 different columns (Table 1) through the conventional SPE.[4] By measuring $\sim$30 to 50 ng Ge for duplicate or triplicate analyses, respectively, we obtained an intra-session 2σ SD-reproducibility of 0.10‰ in line with the long-term variation of in-house standards JMC and Aldrich (Fig. 2) and with an average of 0.58‰, which is in agreement with previous studies.[1,4,20]

In four subsequent individual double-stack chromatographic separations and analytical sessions, we have processed and measured BHVO-1 (individually digested and leached) and BIR-1 (aliquot taken from the same digested and leached stock solution) to confirm accuracy and long-term 2σ SD reproducibility (Table 1). With the optimized chromatographic separation, BIR-1 and BHVO-1 yielded $\delta^{74/70}$Ge of 0.61 $\pm$ 0.10‰ and 0.58 $\pm$ 0.08‰, respectively, in line with previous studies.[1,4] Furthermore, the obtained long-term external 2σ SD reproducibility of $\leq$0.10‰ is similar to the intra-session 2σ SD-reproducibility of BIR-1 ($n = 10$) and that of the in-house standards JMC and Aldrich (Fig. 2), as well as to the external 2σ SD of previous methods, independent of whether a double spike was utilized or a different sample introduction system was used.[1,4,11,15]

4. Conclusion

We present a double-stack chromatographic protocol that combines the previously established anion- and cation-exchange steps into a single, streamlined separation for purifying germanium (Ge) from silicate material prior to high-precision MC-ICP-MS isotope analysis. Compared to the conventional two-step approach, the double-stack set-up reduces handling, evaporation steps, and the number of clean Teflon beakers required, thereby lowering potential contamination risks and enabling higher sample throughput while maintaining effectively quantitative Ge recovery ($\sim$100%) and low procedural blanks ($\ll$0.1 ng Ge).

Method performance was validated on basalt reference materials spanning low and high Ti contents (BIR-1 and BHVO-1). The protocol achieves efficient matrix removal (including transition metals relevant for hydride-generation biases) while keeping residual Ti sufficiently low. Replicate measurements of purified rock solutions yield a long-term external reproducibility of $\leq$0.10‰ (2σ SD) for $\delta^{74/70}$Ge at $\sim$50 ng Ge consumed

for triplicate analyses, comparable to the long-term reproducibility of our in-house standards. This new protocol is well suited for routine Ge isotope analysis without requiring a double spike and should facilitate larger silicate sample throughput in the field of isotope geochemistry and cosmochemistry.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting the findings of this study can be found in the main text.

Acknowledgements

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