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TECHNICAL NOTE

Controlling the mass bias introduced by anionic and organic matrices in silicon isotopic measurements by MC-ICP-MS

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One of the most widely used sample preparation methods for Si isotopic analyses (δ^{30}Si and δ^{29}Si) is based on cationic chromatography, which does not remove anions from samples. Although it was first thought that the presence of anions in natural concentrations does not distort the isotopic analyses, it has recently been shown that the presence of sulfate can induce a significant shift in isotopic ratio measurements above SO_4^{2-}/Si ratios (wt) of 0.02. Here, we show that dissolved organic matter can also induce a major Si isotopic bias when analysing river waters. To overcome these non-spectral matrix effects we propose fast and reliable ways, tested on natural freshwater and rock digestion solutions. The sulfate matrix effect is solved by adding to both sample and bracketing standard sulfuric acid in large excess compared to the naturally occurring SO_4^{2-}. The organic matrix is mineralized by the combined action of UV-C and ozone. We also provide the first δ^{30}Si signature measurements of two common geostandards: SGR-1 (δ^{30}Si = +0.03‰) and FeR-1 (δ^{30}Si = −0.20‰).

1. Introduction

The thorough monitoring and correction of analytical mass bias is a key to accurate isotopic ratio analyses with Multi-Collector Inductively Coupled Plasma Mass Spectrometery (MC-ICP-MS). Different matrices affect plasma geometry and ionisation efficiency and may consequently modify the instrumental mass bias. This prevents the standard-sample bracketing technique to accurately measure relative Si isotopic variations as required by the standardized δ-notation. Therefore, a similar matrix between samples and standards is needed to cancel out matrix effects. This could be achieved either by: (i) Analysing pure solutions where only the analyte is present (apart from the solvent). This imposes the need of a high degree of purification, which is sometimes difficult to achieve in natural samples. (ii) The addition of a known strong artificial matrix to both sample and standard solutions so that the natural concentration of the contaminant is overwhelmed and any effect that would be induced by the initial sample matrix is equal in both. Such a doping approach was proposed by Barling and Weis[1] for Pb isotopic ratio measurements by MC-ICP-MS where a strong Mg matrix was added in order to mask the cations remaining after purification. Such a method has not been tested for Si isotopes so far, despite the fact that difficulties in purifying samples have been recently reported (van den Boorn *et al.*, 2009).

A sample purification technique using a cation exchange resin has been described by Georg *et al.*[2] As dissolved silicon is either neutral or negatively charged (H_4SiO_4 or $H_3SiO_4^-$ for pH > 8), a cation-specific resin can be used to separate silicon from positively charged ions (*e.g.*, BioRad's DOWEX 50W-X12 200–400 mesh in H^+ form). This method has been applied on different kinds of natural samples such as river water or rocks.[2,3] It offers the advantages of being fast and allows the processing of very small quantities of sample (*i.e.*, just the required amount for one isotopic analysis) with an excellent silicon recovery, without requiring HF. However, this method removes neither anionic species nor any other species that are not positively charged. Although it was first thought that the presence of sulfate in samples does not influence isotopic analyses,[2] it has recently been reported by van den Boorn *et al.*[3] that the presence of sulfate in samples can induce an offset in silicon isotopic measurements that becomes significant above SO_4^{2-}/Si weight ratios of *ca.* 0.02. Such ratios are easily reached in sulfur-rich rocks or in river waters. To eliminate the interference caused by the presence of SO_4^{2-}, van den Boorn *et al.*[3] proposed an additional purification step to remove sulfur by ignition under a constant stream of oxygen. Though quite effective, this method is valid solely for rock samples and requires specific equipment. We propose a simple methodology that extends the one described by Georg

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et al.[2] to be valid for sulfate rich rocks and all river water samples. It is a combination of cationic purification, with anionic matrix additions and organic matter mineralization. Indeed, it is shown here that the presence of dissolved organic matter—referred below as dissolved organic carbon (DOC)—also causes non-isobaric matrix effects.

2. Material and methods

2.1. Instrumentation

Si isotopes were measured using a Nu Plasma MC-ICP-MS (ULB, Brussels) in dry plasma mode with a Cetac Aridus II desolvating sample introduction system equipped with a PFA nebulizer and a spraychamber. The mass bias and instrumental drift were corrected using a combined external Mg doping and standard-sample bracketing approach.[5] All measurements were done in 2 mg L^{-1} Si and the Mg concentration was adjusted on a daily basis to get a signal intensity similar to that of the Si. Silicon isotopic ratios were measured relative to NBS28 silica sand standard (or in house standard: pro analysi Quartz from Merck). Data acquisition was done in medium resolution mode as in Abraham *et al.*[6] The $^{14}N^{16}O$ interference on the ^{30}Si peak was resolved by measuring at the low-mass side of the ^{30}Si peak, which is not affected by the interference ("pseudo high resolution"). Data were acquired from numerous sessions spread over several months.

2.2. Material and sample preparation

Two silicon isotopic references (BHVO-1 and Diatomite) and five natural samples with contrasted matrix (2 rock standards and 3 river waters) have been used to test the new procedure. Rock samples include a shale (SGR-1 standard from the U.S. Geological Survey) and an iron formation (FeR-1 standard from the Geological Survey of Canada). This standard was also chosen owing to the growing interest in Si isotopes for banded iron formations.[7,8] Diatomite (opal standard) and BHVO-1 (basalt)—two reference materials of known Si isotopic values[6,9] with low sulfate content—were analysed to check the accuracy. The three river samples were selected from various environments owing to their contrasted SO_4^{2-}/Si ratios and DOC concentrations (Table 1): Tana in Kenya (TN21), the Congo River (CNG 4/07), and Vuilbeek 10/08 (a small stream running in a forested region in Belgium). River samples were filtered through 0.2 μm or 0.45 μm filters immediately after sampling. The Si content and SO_4^{2-}/Si ratios of the samples are provided in Table 1. SO_4^{2-}/Si ratios (wt) in the selected samples vary up to 0.65, far above the 0.02 threshold reported by van den Boorn *et al.*[3] for the appearance of an offset in Si isotopic values. Anions and DOC contents were measured respectively by ionic chromatography and by a total organic carbon analyzer on a highly modified Thermo HiPerTOC coupled to IRMS.[10]

Bracketing quartz standards and Diatomite were prepared following a digestion technique adapted from Georg *et al.*[2] About 5 mg of powdered rocks were melted with a sodium hydroxide flux at 730 °C for 10 minutes in silver crucibles (Silver Boats from Elemental Microanalysis, Ref. D5035), then immerged overnight in 50 mL of unacidified MilliQ water. Na^+ was then removed by using a cation exchange resin as described by Georg *et al.*[2] Proceeding so allowed us to produce matrix-free standards and references. For rock samples (SGR-1, BHVO-1 and FeR-1), the same digestion technique was used, but the recovery of the digestion was achieved in 30 mL of water and acidified with HCl, following the recommendation of Fitoussi *et al.*[11] to adjust the pH of the solution between 2 and 2.4 prior loading on cationic resin, thereby preventing precipitation of other cations such as iron for FeR-1. As first underlined by Fitoussi *et al.*,[11] it is recommended to use a ratio of 1–5 mg sample for ~200 mg of solid NaOH pellet during the fusion process for Fe-rich rocks like FeR-1 to reach complete rock dissolution. Indeed, a lower flux-to-sample ratio was not always sufficient to dissolve such particularly resistant rock types, as part of Fe-oxides remained undissolved. While using the flux-to-sample ratio from Fitoussi *et al.*,[11] the recovery of the digestion was 97 ± 7% for all samples and 99 ± 3% for FeR-1. After NaOH fusion, the solution was diluted to decrease the Na^+ concentration at about 1.5 g L^{-1} before loading it on the cationic resin as incomplete cation removal was sometimes observed at higher concentrations. Here the cation concentration is probably too high for the adsorption kinetics of the resin.

Samples with no previously published $\delta^{30}Si$ value (rivers, FeR-1 and SGR-1) have also been prepared by triethylamine–molybdate (TEA–Moly) co-precipitation, which removes all elements but Si and O,[12] and redissolved in dilute HF–HCl.[5] Isotopic ratios measured after TEA–Moly purifications were used as reference values and compared with the values obtained with our new method.

2.3. Matrix effect counter measures

After cationic exchange chromatography following Georg *et al.*[2] and prior to MC-ICP-MS analyses, sulfuric acid (H_2SO_4, Merck Suprapur) is added to both the standard and the samples in order

Table 1 Natural ratios between sulfates, nitrate, chloride, and dissolved organic carbon (DOC) and Si—n.a. means not applicable

		Si concentration	Natural SO_4^{2-}/Si ratio (by weight)	Natural NO_3^-/Si ratio (by weight)	Natural Cl^-/Si ratio (by weight)	Natural DOC/Si ratio (by weight)
		Si % (weight)				
Rocks	Diatomite	46.7	0	0	0	0
	BHVO-1	23.3	<0.01	n.a.	<0.01	n.a.
	SGR-1	13.2	0.35	n.a.	<0.01	n.a.
	FeR-1	7.9	0.10	n.a.	<0.01	n.a.
		mg L^{-1} Si				
River waters	TN21	8.3	0.65	0.13	1.01	0.14
	CNG 4/07	5.5	0.16	<0.02	0.14	1.75
	Vuilbeek 10/08	12.1	0.26	n.a.	0.54	0.69

to reach the same SO_4^{2-}/Si ratio, *e.g.* 20 mg L^{-1} or 100 mg L^{-1} SO_4^{2-} for 2 mg L^{-1} Si (*i.e.* 10/1 and 50/1 SO_4^{2-}/Si mass ratios). Added sulfuric acid is thereby in large excess in comparison with the naturally occurring SO_4^{2-} in the sample (*i.e.*, at least *ca.* ten times the natural concentration). This imposes similar SO_4^{2-}/Si ratios in the sample and the standard solutions. Although the natural NO_3^- levels in river water samples are low (Table 1), NO_3^- has been added in a similar way up to 100 mg L^{-1} with bidistilled nitric acid in addition to the SO_4^{2-} doping. Exceptionally, the Vuilbeek 10/08 sample had been acidified with HNO_3 during sampling and was therefore doped with up to 1500 mg L^{-1} HNO_3 for analyses, as well as its bracketing standards (Table 2). Note that a strong HNO_3 matrix had already been used by van den Boorn *et al.*[4] without any noticeable increase in the $^{14}N^{16}O$ interference. Similarly, the presence of Cl^- in rivers is resolved by the use of hydrochloric acid as a solvent in the solution (Merck Suprapur, HCl 2000 mg L^{-1}, equivalent to 0.6% HCl by volume). SGR-1 has also been analysed after cationic purification without SO_4^{2-} doping in order to test the importance of the offset on uncorrected samples in our analytical configuration.

A possible analytical bias induced by dissolved organic matter cannot be resolved by balancing the contaminant in both the sample and the standard, as a doping solution reproducing the organic matrix would be too complex to create. Moreover, adding an important organic matrix in the solutions is not recommended, as it may clog the membrane of the desolvating unit, perturb analyses, and cause soot deposit in the mass spectrometer. It is therefore necessary to decompose the organic matter prior to the analyses. Various methods exist to mineralize the organic matrix (see lit. 13 for an overview), we opted here for photo-ozonolysis. Dissolved oxygen is transformed into ozone under the action of the UV-C and both ozone and UV-C will act to decompose DOC in CO_2 that will not affect the analyses. For that purpose, 7.5 mL of the river sample is transferred to a 15 mL Savillex® PFA vial and submitted to UV-C radiations (254 nm and 185 nm, low pressure mercury lamp from Heraeus Noblelight, reference GPH287T8VH/4) under constant oxygen bubbling during 0.5 to 3 hours. The UV lamp was placed as close as possible to the surface of the sample (~2 cm). PFA vials were chosen owing to their resistance to UV. The mineralization of the organic matter is carried out prior to the cationic purification to avoid contamination of the resin. Hydrogen peroxide (H_2O_2), often used for DOC destruction, was avoided as it was feared that this strong oxidizing agent would damage the resin. After the oxidation treatment, the river samples were processed as the previous ones, *i.e.* purified with the cationic resin and doped with SO_4^{2-} and NO_3^- before analysis. The heat of the UV lamp produces a slight evaporation of the sample of about 100 μL h^{-1}. Since Si is not a volatile element, no isotopic fractionation due to this evaporation was expected. However, this has been checked through an evaporation test carried out on the Diatomite Si isotopic reference:[9] 5 mL of a solution of 5 mg L^{-1} Si has been evaporated down to 2.5 mL by warming on a hot-plate at 60 °C. The volume was readjusted to 5 mL with MilliQ water. This evaporation step was repeated 3 times. The standard was then purified for isotopic analyses following the same procedure as the other samples.

Table 2 Anion concentrations in samples after acid doping

	NO_3^-/mg L^{-1}	Cl^-/mg L^{-1}	SO_4^{2-}/mg L^{-1}
Diatomite	100	2000	20 or 100
BHVO-1	—	2000	20 or 100
SGR-1	—	2000	20 or 100
FeR-1	—	2000	20 or 100
TN21	100	2000	100
CNG 4/07	100	2000	100
Vuilbeek 10/08	1500	2000	100
Evaporated Diatomite	100	2000	100

3. Results and discussion

Isotopic results are presented in Table 3. For rock samples with no previously published δ^{30}Si value, the δ^{30}Si signatures were measured after TEA–Moly purification. SGR-1 exhibits a δ^{30}Si signature of +0.03 ± 0.06‰ (±1σ), within the range of crystal derived components.[14] For the FeR-1, the δ^{30}Si signature is −0.17 ± 0.09‰, within the heaviest range of values published so far for banded iron formations.[7,8] Among the river samples, the CNG 4/07 has a δ^{30}Si signature of +0.90‰, which is consistent with the previously published values for the Congo River.[15] Vuilbeek 10/08 and TN21 present higher δ^{30}Si signatures of +2.03‰ and +1.79‰, respectively.

If we now compare the results for SGR-1 with both the TEA–Moly method and the cationic purification method as described by Georg *et al.*[2] (*i.e.*, not corrected for the presence of SO_4^{2-}), an offset of δ^{30}Si of +0.28‰ is observed for a SO_4^{2-}/Si ratio of 0.35. Although this offset is significant, it is much smaller than the large offsets observed by van den Boorn *et al.*[3] at similar SO_4^{2-}/Si ratio (more than +1‰ for δ^{30}Si). Several factors could explain this difference. It is possible that the Nu Plasma MC-ICP-MS used here and by Georg *et al.*[2] is less sensitive to a sulfate matrix effect than the ThermoFinnigan Neptune MC-ICP-MS used by van den Boorn *et al.*[3] Another possibility is that the acid matrix has an impact on the induced bias. Indeed, these samples were analysed in a 0.6% HCl matrix while van den Boorn *et al.*[3] used a 1% HNO_3 matrix. In the two following sections, results show that the δ^{30}Si offsets observed are indeed due to the presence of SO_4^{2-} and/or DOC and that our proposed doping method is able to reconcile TEA–Moly *vs.* cationic purifications. Note that we also tested the possibility of removing anionic species from the solution by means of a weak anion-exchange resin in Cl^- form (BioRad's AG4-X4), but we could not achieve complete SO_4^{2-} removal (SO_4^{2-}/Si > 0.02) despite the complete Si recovery (data not presented).

3.1. Doped samples

For the two SO_4^{2-}-free reference materials (Diatomite and BHVO-1), we observe that the doping in SO_4^{2-} does not induce any bias in comparison with the well constrained published values, since the difference in the mean δ^{30}Si is less than 0.01‰, much smaller than the standard deviation (1σ = 0.07‰). This result confirms that if SO_4^{2-} is present in a similar quantity in both the sample and the bracketing standards, its effects are nil. Similarly, the good result for the Diatomite confirms that the addition of NO_3^- does not cause a problematic increase in the

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Table 3 Measured δ^{30}Si and δ^{29}Si values for the different purification techniques: the TEA–Moly removes all elements but Si and O and is used as a reference to compare with the other values. The cationic resin columns list results obtained by purification of the samples on the cationic resin only, and with the addition of the additional steps resolving the matrix effects of anionic species (SO_4^{2-} doping for rocks and SO_4^{2-} and NO_3^- dopings for rivers) and organic matter (mineralization). Note that the doped Diatomite was analysed either with sulfate doping or with sulfate and nitrate doping. Published values (italic) for standards Diatomite and BHVO standards are from the literature.[6,9] The standard error is given as one standard deviation (SD) on the *n* measurements

	TEA–Moly or published value					Cationic resin					Cationic res. + doping					Cationic res. + dop. + mineralization				
	δ^{30}Si		δ^{29}Si			δ^{30}Si		δ^{29}Si			δ^{30}Si		δ^{29}Si			δ^{30}Si		δ^{29}Si		
	‰	SD	‰	SD	*n*	‰	SD	‰	SD	*n*	‰	SD	‰	SD	*n*	‰	SD	‰	SD	*n*
Diatomite	***1.25***	−0.10	0.65	0.07	Lit. 9						**1.26**	0.07	**0.67**	0.04	11					
BHVO-1	***−0.33***	0.05	**−0.17**	0.03	Lit. 6						**−0.32**	0.05	**−0.16**	0.03	8					
SGR-1	**0.03**	0.06	**0.01**	0.07	5	**0.31**	0.13	**0.15**	0.07	5	**0.03**	0.09	**0.02**	0.03	6					
FeR-1	**−0.17**	0.09	**−0.09**	0.05	9						**−0.24**	0.09	**−0.09**	0.06	5					
TN21	**1.79**	0.09	**0.92**	0.05	5						**1.80**	0.05	**0.93**	0.05	5					
CNG 4/07	**0.90**	0.05	**0.47**	0.03	5						**1.50**	0.12	**0.82**	0.06	4	**0.85**	0.09	**0.43**	0.04	4
Vuilbeek 10/08	**2.03**	0.06	**1.05**	0.06	4						**2.23**	0.15	**1.15**	0.11	10	**1.94**	0.08	**1.01**	0.07	6
Evaporated Diatomite											**1.24**	0.08	**0.60**	0.06	7					

$^{14}N^{16}O$ interference on the ^{30}Si peak when using a desolvating introduction system and measuring at the low-mass side of the ^{30}Si peak. For the other rock samples and the TN21 river water (low DOC/Si ratio) the comparison between values obtained after TEA–Moly purification with the values measured on the sample purified with cationic resin and with SO_4^{2-} doping shows no significant difference. The isotopic ratios being identical within error confirm that the doping of SO_4^{2-} efficiently corrects the offset induced by the natural presence of SO_4^{2-}. The combined mean δ^{30}Si values from TEA–Moly and doped resin-purified samples for SGR-1 are +0.03 ± 0.08‰ ($n = 11$) and for FeR-1 −0.20 ± 0.10‰ ($n = 14$). Similarly, the doping with NO_3^- in the TN21 river water also corrects for the natural nitrate-induced mass bias. However, δ^{30}Si ratios measured on river water samples with high DOC/Si ratios (Vuilbeek 10/08 and CNG 4/07) remain far too high in comparison with the isotopic signatures measured after TEA–Moly purification (shift of δ^{30}Si signatures of +0.29‰ and +0.65‰, respectively) probably as a result of their high DOC. Counteracting the effect of high DOC concentrations on the mass bias was investigated further in the following section.

3.2. UV treated samples

The test of DOC mineralization was carried out on the river samples CNG 4/07 and Vuilbeek 10/08 with initial DOC concentrations of 9.64 mg L^{-1} C and 8.37 mg L^{-1} C (±0.13), respectively. Results show that most of the DOC had disappeared after only 0.5 hours of exposure to UV-C and O_3 (Fig. 1), and reached a stable low concentration after one hour. The DOC/Si ratios are then below 0.05. Since DOC can exhibit various complex forms it is recommended however to expose samples for two hours at least, which should be enough for most river samples, including black rivers (*e.g.*, the Rio Negro is mostly below 26.6 mg L^{-1} C[16]). The method for DOC mineralization presented here is only one oxidation process among many others.[13] It has been chosen because it does not require the addition of any contaminating reactant. However, despite good results for river samples, this oxidation process is rather mild and is inappropriate to mineralize very high charges of organic matter such as those of soil solutions, where the amount of humic acid can be high and very resistant to oxidation. Indeed, this oxidation step was tested on soil solutions and in some samples, DOC contents were still above 100 mg L^{-1} after 2 hours exposure time (data not shown).

After the mineralization step, δ^{30}Si results (Table 3) are in agreement with those obtained after TEA–Moly purification, confirming that the DOC was responsible for the bias reported in the results from Section 3.1. Furthermore, such bias can be avoided by mineralizing most of the DOC initially present using UV-C and ozone. With a lower DOC/Si ratio of 0.14, the δ^{30}Si signature measured in the untreated TN21 river sample was not affected by the presence of DOC. However, it seems difficult to predict the influence of each specific organic matrix and it is recommended to treat every sample containing significant amounts of DOC relative to Si systematically with this method. Average precisions on long term isotopic measurements expressed as $\pm 1\sigma$ standard deviation are ±0.07‰ and ±0.04‰ (Diatomite, $n = 11$) for δ^{30}Si and δ^{29}Si respectively. No clear difference was observed in average precision between the samples purified by the TEA–Moly method and samples purified by the resin and treated against the DOC.

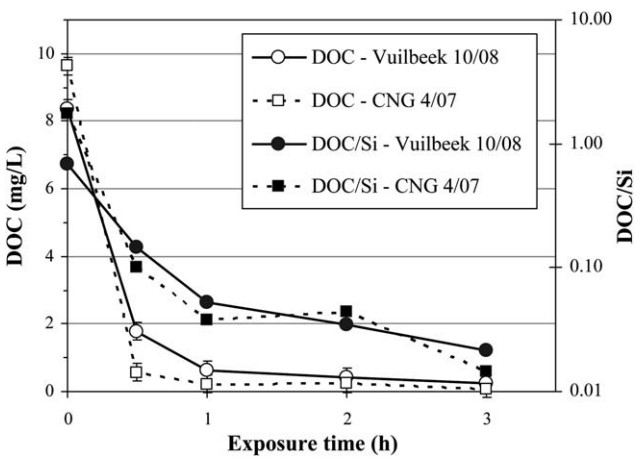

Fig. 1 DOC concentration and DOC/Si ratio in the Vuilbeek and the Congo water samples after exposure to UV-C and ozone treatment.

After the evaporation test on the Diatomite, a δ^{30}Si composition of +1.24 ± 0.08‰ ($n = 7$) was measured, which is similar to the recommended value of the Diatomite (+1.25‰). This shows that the three evaporation steps have no effect on the isotopic ratio of the Diatomite, thus evaporation induced by the heat of the UV lamp is not an issue for δ^{30}Si measurements. Moreover, this implies that evaporation can be used to concentrate samples in which the Si concentration is too low for an accurate isotopic measurement.

4. Conclusion

Results confirm that sulfate matrix effects may bias silicon isotopic measurements when only using cationic chromatography purification. This is also the first time that published results show a matrix effect due to the presence of dissolved organic matter, a common component of waters, particularly in tropical rivers and rivers under high anthropogenic pressure. These results provide a strong evidence that the purification step in the Si isotopic analyses is of extreme importance and also that the purification does not need to be fully complete as long as the level of contaminant is known and can be balanced both in the sample and the bracketing standard. This can be easily solved for sulfate by adding sulfuric acid. Similarly, the presence of NO_3^- in the river samples seems to be efficiently corrected by adding nitric acid, with this method likely being used for other contaminating anions. Results also show that the important mass offset induced by dissolved organic matter in river samples can be remedied by decomposing with UV-C and oxygen bubbling. Nevertheless, our results confirm that the extent of matrix effect cannot be directly transferable from one laboratory to another, probably because of a combination of different instrument and sample types, analytical settings, and/or purification processing (*e.g.*, lit. 2 *vs.* lit. 3 *vs.* this study). Therefore we recommend that each lab test the doping ratios we used to their specific routine procedure. Finally, the first δ^{30}Si values of two contrasted geostandards are given, making them potential rock reference materials once values have been confirmed by further independent laboratories: SGR-1 (shale) with a δ^{30}Si ratio of +0.03 ± 0.08‰ and FeR-1 (Banded Iron Formation) with a δ^{30}Si ratio of −0.20 ± 0.10‰.

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