Testing miniaturized extraction chromatography protocols for combined $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88/86}\text{Sr}$ analyses of pore water by MC-ICP-MS

Claudio Argentino $^1$, Federico Lugli$^{2,3}$, Anna Cipriani $^{3,4}$, Giuliana Panieri$^1$

$^1$CAGE - Centre for Arctic Gas Hydrate, Environment and Climate, Department of Geosciences, UiT The Arctic University of Norway, Tromsø, Norway
$^2$Department of Cultural Heritage, University of Bologna, Ravenna, Italy
$^3$Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, Modena, Italy
$^4$Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York

Abstract

We tested two miniaturized extraction chromatography protocols for strontium isolation based on 300 μL (Protocol 1) and 30 μL (Protocol 2) column volumes of Sr-Spec resin, for the simultaneous determination of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88/86}\text{Sr}$ by MC-ICP-MS. The accuracy and precision of the Sr isotope ratios have been evaluated by analyzing JCt-1 and SRM 1640a reference materials, resulting in a reproducibility of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88/86}\text{Sr}$ values of 0.000026 and 0.04‰ (Protocol 1) (2SD, $n = 3$), and of 0.000074 and 0.13‰ (Protocol 2) (2SD, $n = 4$), respectively. The Sr isotopic composition of SRM 1640a, presented here for the first time, is $^{87}\text{Sr}/^{86}\text{Sr} = 0.708790 \pm 0.000062$ and $\delta^{88/86}\text{Sr} = 0.07 \pm 0.10$‰ (2SD, $n = 6$). Protocols 1 and 2 were successfully applied to pore waters extracted from marine sediment cores from the northern Barents Sea. Our results demonstrate that both protocols attain accurate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and allow the detection of natural variations in $\delta^{88/86}\text{Sr}$ in marine pore waters. Compared to previous Sr/matrix separation methods, Protocol 2 is significantly less costly, making it particularly suitable for large-scale oceanological and limnological studies.

The geochemistry of radiogenic strontium isotopes is a well-established and powerful tool in ocean sciences, with a wide range of applications. The ratio between the $^{87}\text{Sr}$ isotope, generated from the decay of $^{87}\text{Rb}$, and the stable $^{86}\text{Sr}$ has been measured in rocks, sediments, and water samples and used as a “geological tracer” for fluid/rock interaction and mixing processes for a long time (Faure and Powell 1972). In the last decades, however, analytical and instrumental advancements (Fietzke and Eisenhauer 2006; Krabbenhöft et al. 2009) have enabled the detection of mass-dependent fractionation in the stable $^{86}\text{Sr}/^{86}\text{Sr}$ isotope ratio, previously considered to be constant (Steiger and Jäger 1977). This finding opened a new research field in non-traditional stable isotope geochemistry, and stimulated further research leading to the discovery of sub-permil $\delta^{88/86}\text{Sr}$ variations in aqueous and solid natural matrices (Halicz et al. 2008; Chao et al. 2013; Shalev et al. 2013a; Neymark et al. 2014; Kim et al. 2016; Andrews and Jacobson 2017; Hajj et al. 2017). Studies of the former matrices have been mainly conducted on seawater and riverine water to model the global marine Sr budget and its variation during Phanerozoic (Fietzke and Eisenhauer 2006; Krabbenhöft et al. 2010; Vollstaedt et al. 2014; Paytan et al. 2021). Previous work has also found that modern seawater has an homogeneous $\delta^{88/86}\text{Sr}$ of 0.39‰ (Fietzke and Eisenhauer 2006; Krabbenhöft et al. 2009, 2010; Voigt et al. 2015), whereas the few studies performed on sediment pore waters have shown a wide compositional range (0.17–0.82‰), reflecting a direct influence of diagenetic processes, that is, carbonate dissolution and secondary precipitation, on the pore water Sr stable isotope composition (Chao et al. 2013; Voigt et al. 2015).

Strontium isotope data have been collected from different materials and for many purposes leading to a variety of analytical approaches and protocols for the chemical processing of the samples. High analytical accuracy can be obtained with the use of double-spike thermal ionization mass spectrometry (DS-TIMS) (Krabbenhöft et al. 2009), but also by multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) (Fietzke and Eisenhauer 2006). These two techniques are both suitable to the simultaneous determination of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88/86}\text{Sr}$; however, they present some differences that make the choice of the proper technique dependent on the specific research target. DS-TIMS shows better accuracy and precision than MC-ICP-MS, but it requires the preparation and measurement of at least two aliquots of each sample, one unspiked.
and one with double spike added (Krabbenhöft et al. 2009), which increases the time required for analysis. MC-ICP-MS has higher sample throughput compared to DS-TIMS and can be employed for the analysis of a wide range of elements due to its high ionization efficiency (Walczyk 2004). It is worth mentioning that the use of double-spike in MC-ICP-MS can improve precision, and all three methods (DS-TIMS, DS-MC-ICP-MS, and MC-ICP-MS) have been proven to yield distinguishable δ²⁸/²⁶Sr values in the range of natural samples (Shalev et al. 2013b).

The first crucial step in the preparation of samples for isotope analyses through DS-TIMS and MC-ICP-MS is the separation of the analyte (e.g., Sr) from the matrix to minimize mass interferences during analysis, which would affect the overall precision and accuracy (Ohno and Hirata 2007). Generally, isolation of strontium from potential interfering elements in solution (e.g., Ca, Rb, and REE) is done by extraction chromatography as it is less susceptible to isotopic fractionation compared to cation-exchange chromatography (Ohno and Hirata 2007). The Sr/matrix separation step may result in a time-consuming and expensive procedure that represents a bottle neck of the applicability of Sr/Sr separation methods. It is worth mentioning that the separation of Sr-Spec resin employed for ⁸⁷Sr/⁸⁶Sr analysis in geological and environmental studies has been successfully applied to a case study represented by sediment pore water samples from the northern Barents Sea, enabling the detection of natural variations both in ⁸⁷Sr/⁸⁶Sr ratio and δ²⁸/²⁶Sr.

### Materials and methods

#### Pore water sampling

Pore waters were sampled from gravity cores GC782 (77°16′S1.0°N; 27°56′12.2°E) and from multicores MC785 (77°15′41.4°N; 27°55′45.3°E) and MC786 (77°16′14.8°N; 27°59′0.6°E) collected during the CAGE 19-2 cruise with R/V Helmer Hanssen to the northern Barents Sea. After core retrieval, we inserted the rhizone solution samplers with 10 mL syringes attached into predrilled holes, and then we used spacecrs to create a vacuum inside the syringes. A total of 47 pore water samples were collected and immediately transferred to 5 mL Eppendorf Tubes®, to which we added 10 μL of Suprapur® grade 65% nitric acid to lower the pH to <2. Pore water samples were then stored at 4°C.

### Reference materials

Sample preparation has been carried out in the class 1000 clean laboratory of the Department of Chemical and Geological Sciences of the University of Modena and Reggio Emilia (Italy). Chemical extraction chromatography was conducted under a class-10 laminar flow hood. Reference isotopic standards JCT-1 and SRM 1640a were also prepared, run through column chemistry and measured as unknowns to assess the accuracy and precision of the proposed protocols. All our data and literature ⁸⁷Sr/⁸⁶Sr values reported in the present study are reported to the internationally accepted ratio of 0.710248 for SRM 987 (Thirlwall 1991; McArthur et al. 2012; Weber et al. 2018), allowing direct comparison of previous studies with our results. In addition, it is worth mentioning that the ⁸⁷Sr/⁸⁶Sr values reported in the international GeoReM database (http://georem.mpch-mainz.gwdg.de/sample_query.asp) vary from 0.701243 to 710,250 (n = 2174) and the long term variability of our laboratory is 0.71025 ± 0.00002 (n = 343; unpublished data), which falls well within the GeoReM range.

JCT-1 reference material consists of biogenic carbonate (Giant Clam Tridacna) with Sr concentration of 1400 μg/g (GeoReM database). Its ⁸⁷Sr/⁸⁶Sr composition is 0.709169 ± 0.000009 (Weber et al. 2018) and its stable Sr isotopic composition is δ²⁸/²⁶Sr = 2.08 ± 0.08‰ (Ohno and Hirata 2007). SRM 1640a reference standard consists of acidified spring water with certified mass fraction and concentration for 29 elements. It is widely used in geochemical studies.
of natural water, but its Sr isotopic composition has not yet been published. Therefore, we decided to include SRM 1640a in our study in order to provide its first \(^{87}\text{Sr}/^{86}\text{Sr}\) and \(^{88}\text{Sr}/^{86}\text{Sr}\) values. A total of six SRM 1640a samples were prepared by adding 1 mL of 3 N HNO\(_3\) to 2 mL stock solution to obtain a final Sr concentration of ~85 \(\mu\)g/kg. For JCT-1, 1.1 mg were dissolved in 6 mL 3 N HNO\(_3\) to obtain a final concentration of ~260 \(\mu\)g/kg.

**Extraction chromatography**

For the isolation of Sr ions from solutions, we applied two protocols (Protocol 1 and Protocol 2), which differ from each other in the volume of adsorbent resin and in the elution steps. Columns with two different sizes were prepared for Protocol 1 (~3 mL reservoir) and Protocol 2 (~0.5 mL reservoir). The 3 mL columns were made in-house using polypropylene Pasteur pipette (manufactured by LP ITALIANA SPA and sold by VWR – lot # W0909A). The 0.5 mL columns were made in-house using shrinkable PTFE tubes (manufactured by ZEUS Industrial Products). Column frits were made from POREX PTFE sheets (POREX\(^{\text{cs}}\)). The technical specifics of the two chromatography protocols are summarized in Fig. 1.

Protocol 1 was utilized for the preparation of 3 JCT-1 standards, 2 SRM 1640a standards, and 9 pore water samples collected from gravity core GC782. We used 3 mL polypropylene columns packed with 300 \(\mu\)L Eichrom Sr-Spec resin (100–150 \(\mu\)m bead size) (Eichrom Technologies, LLC). Detailed characteristics of the resin are reported in Philip Horwitz et al. (1992). Resin is pipetted into the column and allowed to settle to avoid the formation of bubbles or gaps that would reduce Sr retention. The resin is precleaned by rinsing three times with MilliQ\(^{\text{®}}\) water (full column reservoir) and then conditioned with 1 mL 3 N HNO\(_3\). Three milliliters of sample solution are then loaded into the column. Matrix elements are subsequently removed by addition of 3 mL 3 N HNO\(_3\) in three steps (1 mL each). The bulk solution passed so far in the column is discarded. Strontium is finally recovered by addition of 3 mL MilliQ\(^{\text{®}}\) water in three separate steps (0.25, 1.25, and 1.5 mL) and collected directly in a clean 15 mL Falcon\(^{\text{®}}\) tube. In order to evaluate if the volume of MilliQ\(^{\text{®}}\) and number of steps in the elution phase may influence the final Sr result, one SRM 1640a sample and one JCT-1 sample were treated with a modified elution procedure after Deniel and Pin (2001) (Weber et al. 2018), hereafter defined Protocol 1b. In Protocol 1b, 2.5 mL MilliQ\(^{\text{®}}\) are added in five steps (0.5 mL each). All final solutions containing Sr are adjusted to 4% HNO\(_3\) for MC-ICP-MS analysis.

Protocol 2 was tested on four SRM 1640a standards and applied to the processing of 38 pore water samples from MC785 and MC786. In this procedure, we employed 0.5 mL micro-columns packed with 30 \(\mu\)L of resin. To the best of our knowledge, this is the first attempt to use less than 50 \(\mu\)L resin for simultaneous \(^{87}\text{Sr}/^{86}\text{Sr}\) and \(^{88}\text{Sr}/^{86}\text{Sr}\) analysis. Columns are conditioned with 0.3 mL 3 N HNO\(_3\) and samples are loaded with 1 mL of 3 N HNO\(_3\). Matrix elements are removed by addition of 0.9 mL 3 N HNO\(_3\) in three steps (0.3 mL each). Strontium ions are then eluted from the resin using 2.1 mL MilliQ\(^{\text{®}}\) water added in three separate steps (0.70 mL each).

Before analysis, all sample solutions were spiked with zirconium standard solution (Alfa Aesar\(^{\text{™}}\) Zirconium). Ten microliters of standard solution (1000 \(\mu\)g/g) were diluted in 3 N HNO\(_3\) to obtain 1 \(\mu\)g/g Zr solution and added to each sample after Sr/matrix separation, in order to obtain a final Zr concentration of ~200 \(\mu\)g/kg.

**Mass spectrometry**

Isotope data were collected at Centro Interdipartimentale Grandi Strumenti (C.I.G.S.) of the University of Modena e Reggio Emilia (Italy) using a MC-ICP-MS Thermo Scientific\(^{\text{™}}\) Neptune. \(^{82}\text{Kr}, {84}\text{Kr}, {84}\text{Sr}, {85}\text{Rb}, {86}\text{Sr}, {87}\text{Sr}, {88}\text{Sr}, {90}\text{Zr},\) and \(^{91}\text{Zr}\) ion-beams were measured in sample, standard, and blank solutions during two separate sessions. In Session 1, we examined sample solutions treated with chromatography protocols 1 and 1b and adopted a bracketing sequence for instrumental drift correction in which two samples are measured consecutively with no standards or blanks in between (standard/blank/sample/blank/standard/blank) to reduce the bracketing timing and to avoid inaccuracies due to mass-bias fluctuations. Each measurement consisted of a single block of 100 cycles with an integration time of 8.389 s per cycle. The internal reproducibility for each measurement is given as two standard errors (2SE; \(SE = s/\sqrt{n}\) where \(s\) is the sample standard deviation, \(n = 100\)). In Session 1, one SRM 1640a and one JCT-1 standards prepared with modified elution steps (Protocol 1b) were also included. In Session 2, we examined sample solutions treated with protocol 2, following the conventional bracketing sequence (blank/standard/blank/sample/blank) (Fietzke and Eisenhauer 2006). In Session 2, solutions were measured in a single block of 60 cycles with an integration time of 8.389 s per cycle. This setup improved significantly the analytical precision. Standard solutions of SRM 987 (10 \(\mu\)g/g) were diluted to 250 \(\mu\)g/kg and used for instrumental bias correction, with a reference \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio of 0.710248 (Thirlwall 1991). SRM 1640a and JCT-1 standards were analyzed as unknowns to evaluate the reliability of the two Sr/matrix separation protocols. During the two analytical sessions, repeated measurements of the SRM 987 standard yielded a mean \(^{87}\text{Sr}/^{86}\text{Sr}\) value of 0.710211 ± 0.000022 (2SD, \(n = 9\); Session 1) and 0.710240 ± 0.000023 (2SD, \(n = 43\); Session 2; Fig. 2a). Isobaric interferences of \(^{86}\text{Kr}\) and \(^{87}\text{Rb}\) on \(^{86}\text{Sr}\) and \(^{88}\text{Sr}\) species, respectively, were corrected. The mass bias effect (mass fractionation during analysis) on the \(^{87}\text{Sr}/^{86}\text{Sr}\) data was corrected assuming a constant \(^{88}\text{Sr}/^{86}\text{Sr}\) = 8.375209 as normalizing ratio and an exponential law (Steiger and Jäger 1977) in order to obtain a traditional radiogenic ratio that can be compared with the existing and large body of literature data. In fact, a constant \(^{88}\text{Sr}/^{86}\text{Sr}\) ratio is widely

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employed in oceanography (Mokadem et al. 2015; Struve et al. 2020) and fluid/rock interaction studies on both the marine and continental environments (Joseph et al. 2012; Kim et al. 2016; Hong et al. 2018; Blank et al. 2018; Torres et al. 2020; Moffat et al. 2020), and it is a strict requirement for all Sr isotope analyses of carbonates used for Strontium Isotope Stratigraphy (McArthur et al. 2001, 2012; Petersen et al. 2016; Korte and Ullmann 2018). Although, recent technical studies have started addressing and discussing the assumed invariant nature of the $^{88}\text{Sr} / ^{86}\text{Sr}$ ratio (Horsky et al. 2016), we stress that our choice of using $^{88}\text{Sr} / ^{86}\text{Sr} = 8.375209$ is based on the comparability to the vast majority of published data in the oceanographic (and geological) fields of research. Finally, the mass bias correction of the $^{87}\text{Sr} / ^{86}\text{Sr}$ data was performed using the $^{91}\text{Zr} / ^{90}\text{Zr}$ ratio and exponential law (Ohno and Hirata 2007), consequently, any variability related to natural fractionation processes can be detected.

In the present study, the mass-dependent fractionation of Sr stable isotopes is manifested as variations in the ratio $^{88}\text{Sr} / ^{86}\text{Sr}$ and expressed in standard delta notation $\delta^{88/86}\text{Sr}$ calculated as follows:

$$\delta^{88/86}\text{Sr} = \frac{2 \left( ^{88}\text{Sr} / ^{86}\text{Sr} \right)_{\text{sample}} - 1}{\left( ^{88}\text{Sr} / ^{86}\text{Sr} \right)_{\text{SRMb}} + \left( ^{88}\text{Sr} / ^{86}\text{Sr} \right)_{\text{SRMa}}}$$

where $\left( ^{88}\text{Sr} / ^{86}\text{Sr} \right)_{\text{sample}}$ is the ratio measured in the sample and $\left( ^{88}\text{Sr} / ^{86}\text{Sr} \right)_{\text{SRMb}}$ and $\left( ^{88}\text{Sr} / ^{86}\text{Sr} \right)_{\text{SRMa}}$ are the ratios measured in the SRM 987 standard before and after the sample in the analytical sequence. Each $^{88}\text{Sr} / ^{86}\text{Sr}$ measurement is associated with a double standard error (2SE) representing the internal analytical precision. The mean drift-corrected $\delta^{88/86}\text{Sr}$ value of SRM987 standards for the whole Session 1 is $\delta^{88/86}\text{Sr} = -0.02\%_{\text{o}} \pm 0.25\%_{\text{o}}$ (2SD; $n = 9$). The overall analytical uncertainty reflects time-dependent fluctuations at the beginning of the session, also due to the limited number of measured standards. Analytical stability drastically improved after 3 h 15', resulting in a mean $\delta^{88/86}\text{Sr} = 0.00\%_{\text{o}} \pm 0.06\%_{\text{o}}$ for the remaining SRM987

**Fig. 1.** Schematic representation of the basic Sr isolation steps in the different extraction chromatography protocols proposed in this study. (a) In Protocol 1, 300 μL of resin are conditioned using 1 mL 3N HNO₃ prior to sample loading. The matrix is separated using 3 mL HNO₃ added in three separate steps (1 mL each) and Sr is removed by addition of 3 mL MilliQ® water (0.25, 1.25, and 1.5 mL). Protocol 1b differs from Protocol 1 in the Sr elution step. (b) Protocol 2 is based on the use of 30 μL of resin and smaller volumes of solutions during conditioning, matrix separation, and Sr elution.
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JCT-1 samples processed with Protocol 1 and 1b show $\delta^{88/86}$Sr = 0.21‰ ± 0.02‰ (2SD, n = 2) and 0.25‰, respectively, with a mean $\delta^{88/86}$Sr = 0.22‰ ± 0.04‰ (2SD, n = 3) (Table 1). SRM 1640a samples treated following Protocols 1, 1b, and 2 provided $\delta^{88/86}$Sr of 0.05‰, 0.06‰, and 0.07‰ ± 0.13‰ (2SD, n = 4). Mean $\delta^{88/86}$Sr of all examined SRM 1640a samples is 0.07‰ ± 0.10‰ (2SD, n = 6) (Table 1). In pore water samples from MC786, $\delta^{88/86}$Sr falls between 0.22‰ and 0.38‰ (Fig. 3a). In MC785, $\delta^{88/86}$Sr values range between 0.23‰ and 0.35‰ (Fig. 3b). In GC782, $\delta^{88/86}$Sr values vary between 0.29‰ and 0.41‰ (Fig. 3b).

**Assessment of the methodologies and discussion**

**Protocols 1 and 1b**

During analytical Session 1, standard solutions of SRM 1640a and JCT-1 prepared following two extraction chromatography protocols (Protocol 1, 1b) were run along with nine pore water samples previously processed with Protocol 1. Those standard solutions were measured as unknowns in order to check the quality of the two Sr isolation methodologies and the reproducibility of the isotopic data. Available published Sr data for JCT-1 measured by MC-ICP-MS report a $\delta^{87/86}$Sr ratio of 0.70915 ± 0.00005 and a $\delta^{88/86}$Sr of 0.23‰ ± 0.08‰ (Ohno and Hirata 2007). Weber et al. (2018) obtained a $\delta^{87/86}$Sr ratio of 0.709169 ± 0.000009 (n = 3). Our results, obtained from JCT-1 samples prepared following Protocols 1 and 1b (modified elution steps) (Table 1), agree with the published values. The JCT-1 reproducibility (2SD; n = 2) of $\delta^{87}$Sr/86Sr and of $\delta^{88/86}$Sr prepared with Protocol 1 was 0.000032 and 0.02‰, respectively (Table 1). There is also good consistency between the Sr data ($\delta^{87}$Sr/86Sr and $\delta^{88/86}$Sr) obtained from SRM 1640a samples prepared following the two different protocols (Table 1). Shalev et al. (2013b) conducted repeated measurements of IAPSO seawater standard using DS-MC-ICP-MS and SSBB-MC-ICP-MS (sample-standard bracketing), obtaining a reproducibility 1SD of $\delta^{88/86}$Sr of 0.018 (n = 14) and 0.07 (n = 6). Although they do not mention the amount of Sr-Spec resin and the volumes of solutions used in each chromatographic step, we can use their values to assess the overall quality of our protocols in terms of reproducibility. By simple comparison, the results obtained by our Protocol 1 are similar to those obtained by Shalev et al. (2013b) using DS-MC-ICP-MS and one order of magnitude better than SSBB-MC-ICP-MS. It is worth mentioning that isotopic fractionation of Sr may occur during extraction chromatography, when the ion recovery from the resin is lower than 95% (Kramchaninov et al. 2012; Wakaki et al. 2017). These authors report that during the elution step, the composition of the extracted Sr progressively changes from an initial $88$Sr-enriched value to lighter $\delta^{88/86}$Sr values in the late fractions. This process mostly influences the $\delta^{88/86}$Sr ratio of the eluted solution and may lead to inaccurate $\delta^{88/86}$Sr values. We do not have elution curves for our samples; however, we argue that the level of isotopic fractionation during sample preparation is

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**Results**

**Sr isotope data**

The radiogenic Sr isotope composition of JCT-1 solutions treated with Protocol 1 and 1b are 0.709160 ± 0.000032 (2SD, n = 2) and 0.709149 ± 0.000018 (2SE), respectively (Table 1). The mean $\delta^{87}$Sr/86Sr ratio of all JCT-1 values is 0.709156 ± 0.000026 (2SD, n = 2). SRM 1640a samples processed with Protocol 1 and 1b yielded $\delta^{87}$Sr/86Sr ratios of 0.708800 ± 0.000017 (2SE) and 0.708766 ± 0.000020 (2SE) (Table 1). SRM 1640a standard solutions subjected to Protocol 2 yielded a mean $\delta^{87}$Sr/86Sr = 0.708794 ± 0.000074 (2SD, n = 4). The mean $\delta^{87}$Sr/86Sr of all SRM 1640a values is 0.708790 ± 0.000062 (2SD, n = 6) (Table 1).

The $\delta^{87}$Sr/86Sr values of pore waters of sediment cores MC786 and MC787 show a seawater signature in the upper 25 and 13 cm, respectively, with values around 0.7092 (Mokadem et al. 2015), and then progressively increase toward more radiogenic values (Fig. 3a,b). In MC786, $\delta^{87}$Sr/86Sr values range between 0.709168 and 0.709373 (Fig. 3a) while in MC785 from 0.709186 to 0.710117 (Fig. 3b). The $\delta^{87}$Sr/86Sr composition in GC782 varies from 0.709289 to 0.709560 and shows a linear pore water profile (Fig. 3c).

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**Fig. 2.** (a) $\delta^{87}$Sr/86Sr values for SRM 987 standard measured during analytical Session 2 and corrected for Sr-Rb isobaric interference. The solid red line represents the mean $\delta^{87}$Sr/86Sr = 0.710240, associated with an external reproducibility of 0.000023 (2SD; n = 43). (b) Drift-corrected $\delta^{88/86}$Sr values for SRM 987 standard measured during Session 2. The long-term mean $\delta^{88/86}$Sr value is 0.00‰ ± 0.07‰ (2SD; n = 43).
negligible if compared to the analytical uncertainty associated with the measured values. Moreover, a tentative estimation of JCt-1 Sr concentration from SRM987 signals suggests a recovery higher than 95%. Therefore, based on our measured data, we demonstrated that the total volume of MilliQ® water and the number of elution steps used to extract Sr from the resin did not influence the final δ88/86Sr value and both methodologies are adequate to provide accurate δ88/86Sr determinations.

**Protocol 2**

During analytical Session 2, we analyzed four standard solutions of SRM 1640a and a total of 38 pore water samples processed with Protocol 2. The mean 87Sr/86Sr and δ88Sr values obtained from SRM 1640a in Session 2 agree with the values from Session 1 within analytical uncertainty (Table 1), indicating good accuracy. Reproducibility (2SD; n = 4) of 87Sr/86Sr and of δ88Sr were 0.000069 and 0.13‰, respectively. Protocol 2 yielded larger uncertainties compared to Protocol 1, but they are similar to those obtained by Shalev et al. (2013b) using SSB-MC-ICP-MS. The range of δ88Sr measured in natural Sr-bearing solids and waters is ~2.4‰ (Neymark et al. 2014), with riverine water values from 0.24‰ to 0.50‰ (Krabbenhöft et al. 2010; Andrews and Jacobson 2017) and groundwater from 0.17‰ to 0.82‰ (Krabbenhöft et al. 2010; Chao et al. 2013; Voigt et al. 2015; Andrews and Jacobson 2017). These ranges of values are analytically resolvable using all protocols discussed in this work. The main advantage of Protocol 2 compared to Protocol 1 is the 90% decrease in resin consumption, which reduces the cost associated with each sample preparation and analysis and encourages the use of fresh resin for each sample, with the added benefit of minimizing contamination. The estimated cost related to resin consumption is ~ 6 USD/sample for Protocol 1 and ~ 0.6 USD/sample for Protocol 2 (based on the price of the Sr-Spec resin available to the Italian market; dry resin consumption of 15 mg for 30 μL volume columns and 150 mg for 300 μL volume columns). It follows that laboratories conducting Sr/matrix separation using Eichrom Sr-Spec resin would save, for example, ~ 5400 USD every 1000 samples when adopting Protocol 2. The cost reduction is highly

**Table 1.** Strontium isotopic composition of standard samples JCt-1 and SRM 1640a processed following the different extraction chromatography protocols presented in this study. All uncertainties on single measurements are given as two standard errors (2SE); average values of replicate measurements are associated with two standard deviations (2SD) and marked with an asterisk *.

| Material   | Protocol | n   | 87Sr/86Sr | δ88Sr (%) |
|------------|----------|-----|----------|----------|
| JCt-1      | 1        | 2   | 0.709160 ± 0.000032* | 0.21 ± 0.02* |
| JCt-1      | 1b       | 1   | 0.709149 ± 0.000018 | 0.25 ± 0.04 |
| SRM 1640a  | 1        | 1   | 0.708800 ± 0.000017 | 0.05 ± 0.03 |
| SRM 1640a  | 1b       | 1   | 0.708766 ± 0.000020 | 0.06 ± 0.03 |
| SRM 1640a  | 2        | 4   | 0.708794 ± 0.000074* | 0.07 ± 0.13* |
| JCt-1      | All      | 3   | 0.709156 ± 0.000026* | 0.22 ± 0.04* |
| SRM 1640a  | All      | 6   | 0.708790 ± 0.000062* | 0.07 ± 0.10* |

**Fig. 3.** Strontium isotope results (87Sr/86Sr, δ88Sr) from multicores MC786 (a), MC785 (b), and gravity core GC782 (c). The vertical dashed lines in 87Sr/86Sr and δ88Sr plots indicate the seawater composition of ~ 0.7092 (Mokadem et al. 2015) and 0.39‰ (Krabbenhöft et al. 2010), respectively. Error bars in the δ88Sr plot correspond to the double standard error (2SE). Note that the depth scales are different for the three cores.
variable when comparing protocols of different authors/research groups and can be up to ~39 USD/sample (if using 2 mL of resin). The raw cost of analysis via MC-ICP-MS for internal users at our laboratory is ~12 USD/h (8 €/h), and the time required for the analysis of one sample is ~42 min (including the sample-standard bracketing sequence). Therefore, a rough estimation of the average cost per sample is 8.4 USD/sample. It is clear that the use of a cost-efficient Sr/matrix separation protocol would have a remarkable impact in the overall cost of sample preparation + Sr isotope analysis. Finally, we recommend the use of Protocol 2 to researchers and professionals working with routine analysis of water samples for $^{87}$Sr/$^{86}$Sr and $\delta^{88/86}$Sr investigations. Further applications to more complex environmental matrices such as carbonates, silicates, and soils are fundamental in order to expand the range of applicability of the proposed protocol.

Application of Protocols 1 and 2 to pore water samples from the Barents Sea

The pore water samples collected from the northern Barents Sea were subjected to the Sr/matrix separation Protocols 1 (GC782) and 2 (MC786 and MC785). Their radiogenic Sr isotope composition ranges widely from 0.709163 to 0.709373 in MC786 (Fig. 3a), from 0.709186 to 0.710117 in MC785 (Fig. 3b), and from 0.709289 to 0.709560 in GC782 (Fig. 3c). Protocols 1 and 2 gave a reproducibility 2SD of 0.000026 ($n = 3$) and 0.000074 ($n = 4$), respectively, and they are both adequate to resolve the observed variability. Samples from the upper sediment (down to 23 cm in core MC786, down to 13 cm in core MC785) show seawater values ($^{87}$Sr/$^{86}$Sr $\approx$ 0.7092; Mokadem et al. 2015; Paytan et al. 2021) and pass to $^{87}$Sr-enriched compositions at the bottom of the cores. Radiogenic $^{87}$Sr/$^{86}$Sr values have been previously reported from areas characterized by ongoing silicate weathering in the sediments (Hong et al. 2018). The lowering of pH related to CO$_2$ production during methanogenesis has been found to induce extensive weathering of detrital silicates with consequent release in pore water of cations (K$^+$, Mg$^{2+}$, Ca$^{2+}$, and Sr$^{2+}$) and silicic acid (H$_4$SiO$_4$) (Wallmann et al. 2008; Kim et al. 2016). Strontium released by this process is expected to have a $^{87}$Sr/$^{86}$Sr composition similar to continental detritus ($^{87}$Sr/$^{86}$Sr $\approx$ 0.7119-0.7133) (Elderfield 1986), but the final isotopic value of the pore water Sr pool is generally lower due to mixing with Sr from seawater. In our study, the highest $^{87}$Sr/$^{86}$Sr in the three cores (~0.7094 in MC786, ~0.7101 in MC785, and ~0.7096 in GC782) are similar to values reported in previous studies showing pore water $^{87}$Sr/$^{86}$Sr ratios as high as 0.7099 (Hong et al. 2018) and 0.7104 (Kim et al. 2016; Torres et al. 2020). We suggest that the radiogenic Sr isotope composition in our study is the result of low-temperature silicate weathering in the microbial methanogenic zone. In addition, the three cores show similar narrow $\delta^{88/86}$Sr ranges (from 0.22‰ to 0.38‰ in MC786, from 0.23‰ to 0.35‰ in MC785, and from 0.29‰ to 0.41‰ in GC782; Fig. 3), which fall within the variability range of $\delta^{88/86}$Sr in pore water reported in the literature (0.17–0.82‰; Chao et al. 2013; Voigt et al. 2015). Protocols 1 and 2 displayed a reproducibility 2SD of 0.04 ($n = 3$) and 0.13 ($n = 4$), respectively. Therefore, both Protocols 1 and 2 can successfully resolve the variability encountered in natural pore water samples. All the pore water samples showed $\delta^{88/86}$Sr values lower to or equal to the mean seawater value of 0.39‰ (Krabbenhøft et al. 2010; Vollstaedt et al. 2014; Paytan et al. 2021) within analytical errors, suggesting isotope fractionation related to in situ natural processes, whose interpretation is not the aim of the present study.

The two extraction chromatography protocols reported in our study enabled the accurate determination of $^{87}$Sr/$^{86}$Sr and $\delta^{88/86}$Sr in pore waters by MC-ICP-MS and encourage further research to explore the silicate weathering process and the natural fractionation of stable Sr isotopes in marine sediments. These off-line manual methods can be easily implemented in all laboratories and are suitable to oceanological and limnological Sr isotope studies. In particular, the drastic reduction in resin consumption associated with the application of Protocol 2 compared to previous methods makes this protocol suitable to large-scale hydrological studies.

Comments and recommendations

We tested two extraction chromatography protocols based on miniature columns packed with 300 μL (Protocol 1) and 30 μL (Protocol 2) volumes of Sr-Spec resin, for Sr isotope analysis by MC-ICP-MS. The JCT-1 and SRM 1640a standards were subjected to the two chromatography protocols and measured as unknowns to check the quality of the proposed methodologies. Reproducibility of $^{87}$Sr/$^{86}$Sr and $\delta^{88/86}$Sr values are 0.000026 and 0.04‰ for Protocol 1 (2SD, $n = 3$, JCT-1), and 0.000074 and 0.13‰ for Protocol 2 (2SD, $n = 4$, SRM 1640a).

Finally, we tested Protocols 1 and 2 on sediment pore waters from the northern Barents Sea, demonstrating that both methods allow the accurate determination of $^{87}$Sr/$^{86}$Sr and $\delta^{88/86}$Sr in marine pore waters, and can resolve the range of $\delta^{88/86}$Sr values reported so far for natural waters as well as terrestrial materials. The use of Protocol 2 dramatically reduces the cost of sample analysis when compared to previous protocols, making it particularly suitable to large-scale hydrological studies.

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Conflict of Interest
None declared.