Constraining the marine strontium budget with natural strontium isotope fractionations ($^{87}\text{Sr}/^{86}\text{Sr}^\ast$, $\delta^{88/86}\text{Sr}$) of carbonates, hydrothermal solutions and river waters

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Received 4 August 2009; accepted in revised form 5 April 2010; available online 24 April 2010

Abstract

We present strontium (Sr) isotope ratios that, unlike traditional $^{87}\text{Sr}/^{86}\text{Sr}$ data, are not normalized to a fixed $^{88}\text{Sr}/^{86}\text{Sr}$ ratio of 8.375209 (defined as $\delta^{83/86}\text{Sr} = 0$ relative to NIST SRM 987). Instead, we correct for isotope fractionation during mass spectrometry with a $^{87}\text{Sr}-^{84}\text{Sr}$ double spike. This technique yields two independent ratios for $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{88}\text{Sr}/^{86}\text{Sr}$ that are reported as ($^{87}\text{Sr}/^{86}\text{Sr})^\ast$ and ($\delta^{88/86}\text{Sr}$), respectively. The difference between the traditional radiogenic ($^{87}\text{Sr}/^{86}\text{Sr}$ normalized to $^{88}\text{Sr}/^{86}\text{Sr} = 8.375209$) and the new $^{87}\text{Sr}/^{86}\text{Sr}^\ast$ values reflect natural mass-dependent isotope fractionation. In order to constrain glacial/interglacial changes in the marine Sr budget we compare the isotope composition of modern seawater (($^{87}\text{Sr}/^{86}\text{Sr})^\ast$, $\delta^{88/86}\text{Sr})_{\text{Seawater}}$) and modern marine biogenic carbonates (($^{87}\text{Sr}/^{86}\text{Sr}^\ast$, $\delta^{88/86}\text{Sr})_{\text{Carbonates}}$) with the corresponding values of river waters (($^{87}\text{Sr}/^{86}\text{Sr}^\ast$, $\delta^{88/86}\text{Sr})_{\text{River}}$) and hydrothermal solutions (($^{87}\text{Sr}/^{86}\text{Sr}^\ast$, $\delta^{88/86}\text{Sr})_{\text{HydEnd}}$) in a triple isotope plot. The measured ($^{87}\text{Sr}/^{86}\text{Sr}^\ast$, $\delta^{88/86}\text{Sr})_{\text{River}}$ values of selected rivers that together account for ~18% of the global Sr discharge yield a Sr flux-weighted mean of ($0.7114(8)$, $0.315(8)$). The average ($^{87}\text{Sr}/^{86}\text{Sr}^\ast$, $\delta^{88/86}\text{Sr})_{\text{HydEnd}}$ values for hydrothermal solutions from the Atlantic Ocean are ($0.7045(5)$, $0.27(3)$). In contrast, the ($^{87}\text{Sr}/^{86}\text{Sr}^\ast$, $\delta^{88/86}\text{Sr})_{\text{Carbonates}}$ values representing the marine Sr output are ($0.70926(2)$, $0.21(2)$). We estimate the modern Sr isotope composition at ($0.7106(8)$, $0.310(8)$). The difference between the estimated ($^{87}\text{Sr}/^{86}\text{Sr}^\ast$, $\delta^{88/86}\text{Sr})_{\text{Input}}$ and ($^{87}\text{Sr}/^{86}\text{Sr}^\ast$, $\delta^{88/86}\text{Sr})_{\text{Output}}$ values reflects isotope disequilibrium with respect to Sr inputs and outputs. In contrast to the modern ocean, isotope equilibrium between inputs and outputs during the last glacial maximum (10–30 ka before present) can be explained by invoking three times higher Sr inputs from a uniquely “glacial” source: weathering of shelf carbonates exposed at low sea levels. Our data are also consistent with the “weathering peak” hypothesis that invokes enhanced Sr inputs resulting from weathering of post-glacial exposure of abundant fine-grained material.

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1. INTRODUCTION

The residence time of Sr in seawater of 2.4 Myr is long compared to the mixing time of the oceans of ~1.5 kyr. The radiogenic Sr isotope composition ($^{87}\text{Sr}/^{86}\text{Sr} = 0.709175$; Veizer, 1989) is therefore homogeneous in

0016-7037/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.gca.2010.04.009
seawater and in modern marine carbonates (Faure and Fel-der, 1981; McArthur, 1994; McArthur et al., 2001). The modern \( ^{87}\text{Sr}/^{86}\text{Sr} \) value of seawater is determined by mixing of two isotopically distinct sources: (1) \( {\text{Sr}} \) from the weathering of old, rubidium (Rb)-rich continental silicate rocks that have been enriched in \( ^{87}\text{Sr} \) by the decay of \( ^{87}\text{Rb} \); (2) \( {\text{Sr}} \) with low \( ^{87}\text{Sr}/^{86}\text{Sr} \) values derived from the Earth’s mantle that enters the ocean at mid-ocean ridges and ridge flanks, and from weathering of mantle-derived rocks exposed on the continents (Palmer and Edmond, 1992; Godderis and Veizer, 2000). A minor \( {\text{Sr}} \) influx from diagenetic alteration and dissolution of sediments on the seafloor has a \( ^{87}\text{Sr}/^{86}\text{Sr} \) value only slightly lower than modern seawater (Elderfield and Gieskes, 1982). While average riverine \( ^{87}\text{Sr}/^{86}\text{Sr} \) values are distinctly different from seawater, the large difference in \( {\text{Sr}} \) concentration \( \langle {\text{Sr}} \rangle_\text{Rivers} \sim 1.0 \mu \text{M} \) ensures that even in marginal seas with high riverine input seawater \( ^{87}\text{Sr}/^{86}\text{Sr} \) values are close to the global seawater value \( \langle ^{87}\text{Sr}/^{86}\text{Sr} \rangle_\text{Seawater} = 0.709175 \). Exceptions are brackish seas such as the Baltic Sea with salinities below 15 psu (Andersson et al., 1992). The average \( {\text{Sr}} \) concentration of river waters that are dominated by silicate weathering input is \( \sim 0.2 \mu \text{M} \). The average \( ^{87}\text{Sr}/^{86}\text{Sr} \) value of young volcanic provinces is \( \sim 0.705 \), but is \( \sim 0.735 \) for old crustal terrains (Palmer and Edmond, 1992). Rivers draining carbonate rocks, in contrast, have much higher \( {\text{Sr}} \) concentrations of \( \sim 4 \mu \text{M} \) with typical \( ^{87}\text{Sr}/^{86}\text{Sr} \) values ranging from 0.707 to 0.709 (Gaillardet et al., 1999). On average, global river water is characterized by \( {\text{Sr}} \) concentration of \( \sim 1 \mu \text{M} \) and a \( ^{87}\text{Sr}/^{86}\text{Sr} \) value of \( \sim 0.7111 \) (Peucker-Ehrenbrink et al., 2010). About one-third of this riverine \( {\text{Sr}} \) is derived from silicate weathering and about two-thirds from weathering of carbonate rocks exposed on the continents (Gaillardet et al., 1999; Palmer and Edmond, 1989).

Although the principles of marine \( {\text{Sr}} \) geochemistry are well understood, there is an ongoing discussion about the effects of glacial/interglacial changes in continental weathering on the marine \( {\text{Sr}} \) budget. Recent findings indicate that \( \sim 70\% \) of the silicate weathering flux is affected by non-steady-state processes, possibly creating a \( \sim 100 \) kyr periodicity and an imbalance between input and output fluxes during the Quaternary (Vance et al., 2009). However, the \( {\text{Sr}} \) imbalance created by the non-steady-state conditions cannot be quantified by radiogenic \( {\text{Sr}} \) ratios alone. Marine \( {\text{Sr}} \) budgets that are solely based on radiogenic \( {\text{Sr}} \) focus on the input fluxes, because marine calcium carbonate (CaCO\(_3\)) and seawater have identical radiogenic \( {\text{Sr}} \) isotope values. This approach is a direct consequence of the normalization of measured \( ^{87}\text{Sr}/^{86}\text{Sr} \) values to a fixed \( ^{87}\text{Sr}/^{86}\text{Sr} \) ratio of 0.710250 (Nier, 1938) to correct for mass-dependent \( {\text{Sr}} \) isotope fractionation in nature and during mass spectrometry, thereby allowing the ability to extract information about natural isotope fractionation.

In order to overcome this obstacle and investigate combined radiogenic and stable \( {\text{Sr}} \) isotope compositions, we determine natural \( {\text{Sr}} \) isotope fractionation with a TIMS double spike method (Krabbenhöft et al., 2009). First results showed that the \( ^{87}\text{Sr}/^{86}\text{Sr} \) \( \delta^{87}\text{Sr} = 0.020 \) in seawater is homogeneous (0.709312(9), 0.386(7)\( _{\text{1σ}} \)), Liebetrau et al., 2009; see Appendix A for definitions and notations. We also demonstrated that the stable \( {\text{Sr}} \) isotope composition of marine carbonates and corals \( (^{88}\text{Sr}/^{86}\text{Sr})_{\text{Carbonates}} \) is \( \sim 0.2\% \) lighter than seawater. This is caused by the preferential uptake of lighter isotopes during carbonate precipitation (Fietzke and Eisenhauer, 2006; Halicz et al., 2008; Ohno et al., 2008). The still limited data base of stable \( {\text{Sr}} \) isotope ratios indicates that marine basalts have \( \delta^{88}\text{Sr}/^{86}\text{Sr} \) values of \( \sim 0.25\% \) (Halicz et al., 2008; Ohno et al., 2008), significantly different from continental igneous rocks and soils that show lighter values in the range of \( \sim 0.2/0.02 \).

When natural \( {\text{Sr}} \) isotope fractionation is taken into account the \( {\text{Sr}} \) isotope composition of marine carbonates and seawater differ. This allows for the simultaneous calculation of input and output fluxes using complete \( {\text{Sr}} \) budget equations. This new approach extends the well-established radiogenic \( {\text{Sr}} \) isotope systematic to an additional dimension and allows for simultaneous determination of paired \( ^{87}\text{Sr}/^{86}\text{Sr}, \delta^{88}/^{86}\text{Sr} \) ratios. Here, we present the first results of paired \( ^{87}\text{Sr}/^{86}\text{Sr}, \delta^{88}/^{86}\text{Sr} \) values for rivers, hydrothermal fluids, marine carbonates and seawater to constrain the contemporary marine \( {\text{Sr}} \) budget.

2. MATERIALS AND METHODS

2.1. River waters

In order to reevaluate the \( {\text{Sr}} \) isotope supply via river discharge to the ocean and to constrain the riverine \( {\text{Sr}} \) budget for paired \( ^{87}\text{Sr}/^{86}\text{Sr}, \delta^{88}/^{86}\text{Sr} \) ratios, we analyzed a suite of rivers representing \( \sim 18\% \) of the global annual riverine \( {\text{Sr}} \) flux to the ocean. The \( {\text{Sr}} \) isotope values are presented together with complementary information about water discharge, sampling locations and the riverine \( {\text{Sr}} \) fluxes (Table 1 and Fig. 1). The analyzed rivers drain various proportions of 9 of the 16 large-scale exorheic drainage regions on Earth (Graham et al., 1999; Peucker-Ehrenbrink and Miller, 2007; Peucker-Ehrenbrink, 2009). We assume that river water samples investigated here are reasonably representative of the nine large-scale draining regions, because both the average bedrock age (399 Ma) and the relative abundances of sedimentary (70%), volcanic (9%) and intrusive/metamorphic (21%) bedrock are similar to global exorheic bedrock weighted according to water discharge (405 Ma, 73%, 9%, 18%, respectively). The set of rivers investigated here thus does not appear to be significantly biased with respect to the lithological setting and bedrock ages (Peucker-Ehrenbrink and Miller, 2007).

2.2. Hydrothermal solutions

Seven hydrothermal vent-fluid samples from the active area at 4°54′/S on the Mid-Atlantic Ridge (MAR) have been analyzed for this study (Table 2). The 4°54′/S hydrothermal system is located on-axis at a water depth of \( \sim 3000 \) m. It is dominated by fresh to slightly altered lava flows and pillows (Haase et al., 2007). On this plateau at least three high-temperature vent fields (Turtle Pits [TP], Comfortless Cove [CC] and Red Lion [RL]) are located on a flat, 2 km wide, volcanically and tectonically active area (Haase et al., 2007). The samples analyzed in this study were taken from
these high-temperature vent fields using an ROV equipped with a “Multiport Valve-based all-Teflon Fluid Sampling System, (KIPS)” during the RV l’Atalante cruise MAR-SUED IV in 2007. Comfortless Cove as well as TP are characterized by high fluid temperatures >407 °C and water depth, close to the critical point of seawater, and show indications of phase separation (Haase et al., 2007). The RL vent field emits ~370 °C fluids that show no indications of phase separation.

The measured Mg and Sr concentrations of the fluids are positively correlated suggesting that $[\text{Sr}]_{\text{HydEnd}}$ of the phase-separated Sr sources is lower than seawater. Extrapolating Mg/Sr ratios of the TP and CC fluid samples to a Mg/Sr ratio of zero yields a $[\text{Sr}]_{\text{HydEnd}}$ of 34(5) µM. Likewise, the $[\text{Sr}]_{\text{HydEnd}}$ of RL was estimated at ~56(5) µM. Strontium isotope compositions measured in this study are presented in Table 2 and in Fig. 2a and b.

### 2.3. Marine carbonates

The major sink of Sr in the ocean is the formation of aragonitic and calcitic CaCO$_3$ (Milliman and Droxler, 1996) where calcium (Ca) is substituted by Sr. In order to quantify the Sr burial flux and its isotope composition we performed Sr isotope measurements on important calcifying marine organisms (Table 3). CaCO$_3$ deposition rates are primarily (~39%) controlled by species living on the shelves and slopes (e.g. mussels, star fish, sea urchins, benthic foraminifera, bryozoans, calcareous algae). Most of the remainder is determined in almost equal proportions by reef corals (20%), coccoliths (16%) and planktic foraminifera (20%). The higher Sr concentrations in aragonite cause larger Sr/Ca ratios than observed in calcite (see Table 3). Sr/Ca ratios are well constrained for reef corals, Halimeda, planktic foraminifera and also for many shelf and slope species (e.g. mussels: 1.5 mM, star fish: 2.5 mM, aragonitic algae: 11 mM). However, the average value for shelf and slope species cannot be constrained well because the relative proportions of calcite and aragonite are not well-known.

We therefore arbitrarily assume that shelf species are composed of two-thirds aragonite (Sr/Ca: 1.8 mM), yielding an average shelf $[\text{Sr}]_{\text{HydEnd}}$ of 39% controlled by species living on the shelves and slopes (e.g. mussels, star fish, sea urchins, benthic foraminifera, bryozoans, calcareous algae). Most of the remainder is determined in almost equal proportions by reef corals (20%), coccoliths (16%) and planktic foraminifera (20%). The higher Sr concentrations in aragonite cause larger Sr/Ca ratios than observed in calcite (see Table 3). Sr/Ca ratios are well constrained for reef corals, Halimeda, planktic foraminifera and also for many shelf and slope species (e.g. mussels: 1.5 mM, star fish: 2.5 mM, aragonitic algae: 11 mM). However, the average value for shelf and slope species cannot be constrained well because the relative proportions of calcite and aragonite are not well-known.

We therefore arbitrarily assume that shelf species are composed of two-thirds aragonite (Sr/Ca: ~9 mM) and one-third calcite (Sr/Ca: ~1.8 mM) yielding an average shelf carbonate Sr/Ca of ~6.6 mM.

### 2.4. Sample preparation

All solid carbonate samples were weighed in Teflon beakers together with 2 ml H$_2$O (18.2 MΩ Milli-Q water).
Samples were dissolved in 500 l 4.5 N HNO₃, heated for at least 5 h and then dried at ~90 °C. In order to remove organic matter 50 l H₂O₂ and 200 l 2 N HNO₃ were added and samples were heated to ~80 °C for at least 5 h in closed beakers. Subsequently, samples were dried again at ~80 °C, dissolved in 2 ml 8 N HNO₃ and split into two fractions that each contained 1000–1500 ng Sr, corresponding to a carbonate sample weight of 1–2 mg. The Sr double spike was added to one fraction and both fractions were then dried at ~90 °C. Chromatographic column separation was performed using 650 l BIO-RAD columns filled to one-third with Eichrom Sr-SPS resin (grain size 50–100 μm). The resin was washed three times with 4.5 ml H₂O and 4.5 ml 8 N HNO₃. The resin was then conditioned three times with 1 ml 8 N HNO₃ before the sample – dissolved in 1 ml 8 N HNO₃ – was loaded onto the column. In order to remove the sample matrix the resin was washed six times with 1 ml 8 N HNO₃. The Sr-fraction was eluted into a Teflon beaker in three steps with 1 ml H₂O each. Any resin residue was removed by drying down and then heating samples to 80 °C in 50 μl H₂O₂ and 200 μl 2 N HNO₃ for at least 5 h in closed beakers. Finally, samples were dried at ~80 °C. About 500 ng Sr was loaded together with 2 l H₃PO₄ onto a single Re filament after addition of 1.5 l of Ta₂O₅-activator to stabilize signal intensity. The sample was then heated on the filament at 0.6 A to near dryness before being dried at 1 A and slowly heated to 1.8 A within 2 min. Then, the sample was heated to a dark red glow. After keeping the filament glowing for about 30 s the current was turned down and the filament was mounted onto the sample wheel. With the exception of the dissolution step, hydrothermal- and river water samples were treated as described above.

![Graph](image)

Fig. 1. Individual (²⁷Sr/²⁶Sr*, δ²⁸/²⁶Sr)river values corresponding to ~18% of the global Sr discharge to the ocean are plotted in a triple isotope plot. There is a considerable scatter in both the ²⁷Sr/²⁶Sr* and the δ²⁸/²⁶Sr values. The Sr flux-weighted global mean of all rivers is marked by a square.

<table>
<thead>
<tr>
<th>Label</th>
<th>Location</th>
<th>Depth (m)</th>
<th>Fluid (%)</th>
<th>T (°C)</th>
<th>Mg/Sr (mol/mol)</th>
<th>²⁷Sr/²⁶Sr*</th>
<th>δ²⁸/²⁶Sr (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42ROV-3</td>
<td>4°48'S, CC</td>
<td>2990</td>
<td>72</td>
<td>&gt;400</td>
<td>303</td>
<td>0.707488(4)</td>
<td>0.361(6)</td>
</tr>
<tr>
<td>42ROV-4</td>
<td>4°48'S, CC</td>
<td>2990</td>
<td>80</td>
<td>&gt;400</td>
<td>236</td>
<td>0.706643(3)</td>
<td>0.346(5)</td>
</tr>
<tr>
<td>42ROV-7</td>
<td>4°48'S, CC</td>
<td>2995</td>
<td>88</td>
<td>&gt;400</td>
<td>144</td>
<td>0.706276(2)</td>
<td>0.324(5)</td>
</tr>
<tr>
<td>35ROV-8</td>
<td>4°48'S, TP</td>
<td>2990</td>
<td>100</td>
<td>450</td>
<td>3</td>
<td>0.705066(3)</td>
<td>0.26(2)</td>
</tr>
<tr>
<td>67ROV-4</td>
<td>4°48'S, RL</td>
<td>3045</td>
<td>80</td>
<td>366</td>
<td>177</td>
<td>0.705808(3)</td>
<td>0.29(1)</td>
</tr>
<tr>
<td>67ROV-5</td>
<td>4°48'S, RL</td>
<td>3045</td>
<td>98</td>
<td>366</td>
<td>23</td>
<td>0.703857(1)</td>
<td>0.253(1)</td>
</tr>
<tr>
<td>67ROV-6</td>
<td>4°48'S, RL</td>
<td>3045</td>
<td>81</td>
<td>366</td>
<td>164</td>
<td>0.705179(1)</td>
<td>0.294(3)</td>
</tr>
</tbody>
</table>

Note: TP, Turtle Pits; CC, Comfortless Cove; RL, Red Lion. The errors are 2 standard error of the mean (2σmean).
Fig. 2. ($^{87}$Sr/$^{86}$Sr*, $\delta^{88/86}$Sr) values of hydrothermal fluid samples. Assuming that pure hydrothermal solutions are free of Mg (Mg/Sr = 0), hydrothermal $\delta^{88/86}$Sr (a) and $^{87}$Sr/$^{86}$Sr* (b) end-members can be extrapolated (dotted line) from our data. Circles refer to Comfortless Cove (CC) and Turtle Pits (TP), whereas triangles refer to the Red Lion (RL) hydrothermal field at the mid-Atlantic Ridge. Broken lines mark the uncertainties associated with the extrapolated values in (a) and (b).
Table 3: Sr burial fluxes and isotopic composition.

<table>
<thead>
<tr>
<th>Carbonate sediment type</th>
<th>CaCO₃ deposition (10¹² mol/yr)</th>
<th>CaCO₃ polymorph</th>
<th>Mean Sr/Ca (mmol/mol)</th>
<th>Sr Burial Flux (10⁹ mol/yr)</th>
<th>⁸⁷Sr/⁸⁶Sr*</th>
<th>³⁸⁸⁶Sr (%_orm) (SRM987)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reef corals (JCp-1 coral standard)</td>
<td>~6.0 (20%)</td>
<td>Aragonite</td>
<td>~9.0</td>
<td>~54 (31%)</td>
<td>0.70923 (1)</td>
<td>0.19 (1)</td>
</tr>
<tr>
<td>Halimeda</td>
<td>~1.5 (5%)</td>
<td>Aragonite</td>
<td>~11</td>
<td>~16 (9%)</td>
<td>0.70926 (3)</td>
<td>0.27 (3)</td>
</tr>
<tr>
<td>Coccoliths</td>
<td>~5.0 (16%)</td>
<td>Calcite</td>
<td>2.2</td>
<td>~11 (6%)</td>
<td>0.70926 (3)</td>
<td>0.26 (7)</td>
</tr>
<tr>
<td>Planctonic foraminifera</td>
<td>~6.0 (20%)</td>
<td>Calcite</td>
<td>1.4</td>
<td>~8 (5%)</td>
<td>0.70920 (2)</td>
<td>0.14 (1)</td>
</tr>
<tr>
<td>Continental shelf and slope taxa (mussels, starfish, etc.)</td>
<td>~13.0 (33%)</td>
<td>Aragonite and calcite</td>
<td>~6.6</td>
<td>~8.5 (49%)</td>
<td>0.70924 (1)</td>
<td>0.22 (3)</td>
</tr>
<tr>
<td>Total carbonates</td>
<td>~32.0 (100%)</td>
<td>–</td>
<td>n.a.</td>
<td>~174 (100%)</td>
<td>0.70924 (2)</td>
<td>0.22 (2)</td>
</tr>
</tbody>
</table>

Column 1: Reef corals: The deposition rate of reefs has been estimated at 7.0 × 10¹² mol/yr (Milliman and Droxler, 1996). Note that the deposition rates in column 1 are afflicted with large statistical uncertainties: reef corals, coccoliths and planktonic foraminifera have uncertainties on the order of ±50%, and continental shelf and slope taxa have uncertainties of 50% and >100%, respectively. The CaCO₃-burial rate related to reef coral formation is estimated at ~6.0 × 10¹² mol/yr based on estimates that ~85% of reef CaCO₃ is derived solely from corals (Hubbard et al., 1990). Mean Sr/Ca values are compiled from published data on Acropora, Diploria, Montastrea, Montipora, Pocillopora and Pocillopora (Cohen and Thorrold, 2007; Gallup et al., 2006; Sun et al., 2005). The average ⁸⁷Sr/⁸⁶Sr*, ³⁸⁸⁶Sr values are adopted from the long-term average value of the JCp-1 coral standard.

Halimeda: Halimeda Sr/Ca ratio is from (Delaney et al., 1996). ⁸⁷Sr/⁸⁶Sr, ³⁸⁸⁶Sr values are measured on Halimeda specimens from Tahiti and the Mediterranean Sea.

Coccoliths: CaCO₃-burial rate is from (Schiebel, 2002) and (Broecker and Clark, 2009). Mean Sr/Ca ratios are from (Stoll and Schrag, 2000). The ³⁸⁸⁶Sr value is the average of various measurements on laboratory-cultured Emiliania huxleyi and Coccolithus pelagicus.

Planktic foraminifera: The CaCO₃-burial rate is from (Schiebel, 2002). Mean Sr/Ca ratios are from (Kisakurek et al., 2008). The ⁸⁷Sr/⁸⁶Sr*, ³⁸⁸⁶Sr values were determined on G. ruber and G. sacculifer, separated from core SO 164-03-4 from the central Caribbean Sea (16°32’37”N, 72°12’11”W, 2744 m).

Continental shelf and slope taxa: CaCO₃ sediments on the continental shelves and slopes are produced by a variety of taxa, including species mentioned above. For further discussion we assume shelf species to be two-thirds aragonitic (Sr/Ca/CaCO₃ = 1.4) and one-third calcitic (Sr/Ca/CaCO₃ = 1.2 mmol/mol), yielding a Sr/Ca ratio of ~6.6 mmol/mol. Note, that despite their importance to the total Sr burial flux, the contribution of the shelf taxa is afflicted with a large uncertainty (50%–100%).

Column 4 is calculated from the values in columns 1 and 3. The values in brackets in columns 5 and 6 correspond to 2σ mean that reflect only Sr isotope error propagation. Burial rate uncertainties are not included in the uncertainties in columns 5 and 6.

2.5. TIMS measurements

The use of a ⁸⁷Sr–⁸⁴Sr double spike enables us to determine natural Sr isotope fractionation after correction for mass-dependent fractionation during TIMS measurements. The details of the ⁸⁷Sr–⁸⁴Sr double spike production, measurement procedure and data reduction are discussed by (Krabbenhöft et al., 2009).

The Sr isotope measurements were carried out at the IFM-GEOMAR mass spectrometer facility in Kiel and at the “Geowissenschaftliches Zentrum der Universität Göttingen”, Germany, using TRITON mass spectrometers (ThermoFisher, Bremen, Germany). The TRITONs were operated in positive ionization mode with a 10 kV acceleration voltage. The instruments are equipped with nine moveable Faraday cups with 10¹¹ Ω resistors that allow for simultaneous detection of all Sr masses.

Mass 85 was measured in order to monitor and correct for interfering ⁸⁴Rb assuming an ⁸⁵Rb/⁸⁴Rb ratio of 2.59. Data were acquired at a typical signal intensity of 10 V for mass 88 at an average filament temperature of ~1450 °C. For each sample 9 blocks with 14 cycles corresponding to 126 single scans were measured. Before each block the baseline was recorded and the amplifier rotation was performed.

The ⁸⁷Sr/⁸⁴Sr double spike technique required two separate analyses of each sample: one ic-analysis (ie, isotope composition; unspiked) and one id-analysis (id, isotope dilution; spiked) with well-known ⁸⁶Sr/⁸⁴Sr*, ⁸⁷Sr/⁸⁴Sr* and ⁸⁸Sr/⁸⁴Sr ratios of the double spike. The ⁸⁷Sr/⁸⁴Sr* and the ⁸⁸Sr/⁸⁴Sr ratios are normalized to the mean of the first block of the ⁸⁸Sr/⁸⁴Sr isotope ratio using an exponential fractionation law in an off-line data processing routine. Following this procedure the average internal precision of single ⁸⁶Sr/⁸⁴Sr ratio measurements is ~7 ppm (RSD), and ~9 ppm for single ⁸⁷Sr/⁸⁴Sr ratio determinations in the ic-analyses. We measured ~11 ppm (RSD) for the ⁸⁶Sr/⁸⁴Sr ratio and ~21 ppm for the ⁸⁷Sr/⁸⁴Sr ratio in the id-analyses. Variations in ⁸⁸Sr/⁸⁴Sr are reported in the usual δ notation: ³⁸⁸Sr ≡ [⁸⁸Sr/⁸⁴Sr]sample – ⁸⁸Sr/⁸⁴Sr}_{SRM987} / ⁸⁸Sr/⁸⁴Sr}_{SRM987} × 1000. We use the SRM987 standard with an internationally accepted ⁸⁸Sr/⁸⁴Sr value of 8.375209 (Nier, 1938) for normalization. Notations (e.g. ⁸⁷Sr/⁸⁴SrNorm and ⁸⁷Sr/⁸⁴Sr*) and additional information about mass-dependent fractionation are summarized in Appendix A.

3. RESULTS

3.1. Sr isotope composition of the marine input

3.1.1. Sr composition of the riverine discharge to the ocean

The ⁸⁷Sr/⁸⁴SrNorm and ⁸⁷Sr/⁸⁴Sr* values of rivers presented in Table 1 and Fig. 1 show variations from...
Our total flux estimate is in good agreement with the global uncertainties that reflect the assumptions that are deduced by riverine discharge to the ocean and to a lesser extent by groundwater (Palmer and Edmond, 1989). The good agreement between our more restricted dataset (18% of the river water flux) and earlier comprehensive analyses (47% of the river water flux) of exorheic rivers (e.g. Palmer and Edmond, 1989) clearly indicates that our sample set is representative of global river runoff.

The $\delta^{88/86}\text{Sr}$ values vary between 0.243(6) for the Lena river and 0.42(2)$\%_{\text{r}}$ for the Maipo river. The Sr flux-weighted mean ($^{87}\text{Sr}/^{86}\text{Sr}^\ast, \delta^{88/86}\text{Sr}_{\text{HydEnd}}$ values at (0.7045(5), 0.27(3)$\%_{\text{r}}$) extrapolated by the measured values to a Mg/Sr ratio of zero (Table 2, Fig. 2a and b). The $\delta^{88/86}\text{Sr}_{\text{HydEnd}}$ values are isotopically lighter than seawater. This is in good agreement with the reported radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88/86}\text{Sr}$ values of basalt of 0.70412(4) and 0.26(3)$\%_{\text{r}}$, respectively (Ohno et al., 2008). The latter observation indicates that the isotopic composition of hydrothermal fluids simply reflect the isotopic composition of ocean crust.

3.1.2. Sr isotope composition of the hydrothermal discharge to the ocean

Following the procedure of Amini et al. (2008) and assuming that pure hydrothermal solutions are free of Mg, we estimated the ($^{87}\text{Sr}/^{86}\text{Sr}^\ast, \delta^{88/86}\text{Sr}_{\text{HydEnd}}$ values at (0.7045(5), 0.27(3)$\%_{\text{r}}$) extrapolated by the measured values to a Mg/Sr ratio of zero (Table 2, Fig. 2a and b). The $\delta^{88/86}\text{Sr}_{\text{HydEnd}}$ values are isotopically lighter than seawater. This is in good agreement with the reported radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88/86}\text{Sr}$ values of basalt of 0.70412(4) and 0.26(3)$\%_{\text{r}}$, respectively (Ohno et al., 2008). The latter observation indicates that the isotopic composition of hydrothermal fluids simply reflect the isotopic composition of ocean crust.

3.1.3. Sr composition of the combined riverine and hydrothermal input to the ocean

The mean ocean input flux and its corresponding isotope compositions can be estimated from the measured and compiled values of the riverine discharge and of the hydrothermal input (Table 4; $^{87}\text{Sr}/^{86}\text{Sr}^\ast, \delta^{88/86}\text{Sr}_{\text{HydInput}}$; $\sim$0.7106(8), $\sim$0.310(8)$\%_{\text{r}}$). These composite values are affected by larger uncertainties that reflect the assumptions that are described in detail in Table 4. The compilation of flux data in Table 4 show that the present-day Sr supply of $\sim$56 x 10$^9$ mol/yr is mainly ($\sim$60%) controlled by Sr delivered by riverine discharge to the ocean and to a lesser extent by groundwater ($\sim$29%) and hydrothermal ($\sim$4%) inputs. Our total flux estimate is in good agreement with the global Sr flux of $\sim$50 x 10$^9$ mol/yr that Basu et al. (2001) estimated based on riverine and groundwater inputs alone. They did not include Sr from low temperature alteration of oceanic crust and diagenetic mobilization of Sr from marine sediments. Our estimate is higher than that of Stoll and Schrag (1998) and Stoll et al. (1999) of $\sim$40 x 10$^9$ mol/yr, because these authors did not take groundwater inputs into account. Addition of our estimate of the groundwater Sr flux (16.5 x 10$^9$ mol/yr) brings both estimates in close agreement.

3.2. Isotope composition of the marine Sr output

The primary sink for marine Sr is marine CaCO$_3$ precipitation. The most simplistic approach to estimate mean global ocean ($^{87}\text{Sr}/^{86}\text{Sr}^\ast, \delta^{88/86}\text{Sr}_{\text{Carbonate}}$ values is to average ($^{87}\text{Sr}/^{86}\text{Sr}^\ast, \delta^{88/86}\text{Sr}$) values of the major calcifying species such as tropical corals, green algae (Halimeda), foraminifera and coccoliths (Table 3). This approach yields mean global ($^{87}\text{Sr}/^{86}\text{Sr}^\ast, \delta^{88/86}\text{Sr}_{\text{Carbonate}}$ values of (0.70924(3), 0.22(1)$\%_{\text{r}}$) (Table 3).

A more refined approach for determining mean global ocean ($^{87}\text{Sr}/^{86}\text{Sr}^\ast, \delta^{88/86}\text{Sr}_{\text{Carbonate}}$ values is to also consider the individual Sr burial fluxes. These burial fluxes can be estimated from the species-dependent CaCO$_3$-burial rates (Table 3) and the respective species-dependent Sr/Ca ratios. The mean global ($^{87}\text{Sr}/^{86}\text{Sr}^\ast, \delta^{88/86}\text{Sr}_{\text{Carbonate}}$ values are determined by the Sr burial flux-weighted means of the major calcifying species and their respective ($^{87}\text{Sr}/^{86}\text{Sr}^\ast, \delta^{88/86}\text{Sr}$) values. The main disadvantage of this approach is related to the fact that CaCO$_3$-burial rates are uncertain by at least 50% (Milliman and Droxler, 1996).

For corals we adopt the ($^{87}\text{Sr}/^{86}\text{Sr}^\ast, \delta^{88/86}\text{Sr}$) values of the JCP-1 coral standard (0.70923(1), 0.19(1)$\%_{\text{r}}$). Aragonitic zooxanthellate coldwater corals of the species Lophelia pertusa that grow between 6 and 10 °C show slightly lower $\delta^{88/86}\text{Sr}$ values of 0.06–0.18$\%_{\text{r}}$ (Rüggeberg et al., 2008). However, coldwater corals contribute only ~1% to the global carbonate sediment budget (Lindberg and Mienert, 2005) and are therefore not included in the Sr isotope budget. In contrast, tropical coral reefs contribute ~31% to the ocean’s Sr burial flux (Table 3). For tropical corals we did not take into account any temperature sensitivity of the paired ($^{87}\text{Sr}/^{86}\text{Sr}^\ast, \delta^{88/86}\text{Sr}$) values, as the new double spike technique did not confirm the previously predicted temperature sensitivity of Sr isotope fractionation (Fietzke and Eisenhauer, 2006).

For this study paired ($^{87}\text{Sr}/^{86}\text{Sr}^\ast, \delta^{88/86}\text{Sr}$) values of aragonitic Halimeda specimen from Tahiti and the Mediterranean Sea yielded average values of 0.70926(3), 0.27(3)$\%_{\text{r}}$ (Table 3). Halimeda mounds contribute ~9% to the ocean’s Sr burial flux.

Despite being calcitic, the ($^{87}\text{Sr}/^{86}\text{Sr}^\ast, \delta^{88/86}\text{Sr}$) values of ~0.70926(3), 0.26(7)$\%_{\text{r}}$ from cultured coccoliths are similar to those of the aragonitic species (Table 3). Coccoliths contribute ~6% to the global Sr burial flux.

The two species Globigerinoides ruber and Globigerinoides sacculifer are taken to be representative of the Sr isotope composition of calcitic planktic foraminifera. They show identical ($^{87}\text{Sr}/^{86}\text{Sr}^\ast, \delta^{88/86}\text{Sr}$) values of (0.70920(2), 0.14(1)$\%_{\text{r}}$). Note that the paired ($^{87}\text{Sr}/^{86}\text{Sr}^\ast, \delta^{88/86}\text{Sr}$) values of these foraminifera are considerably lower than those of other species, pointing to a strong physiological control of the trace metal uptake by planktic foraminifera. Planktic foraminifera, like coccoliths, contribute ~5% to the ocean’s Sr burial flux.

A significant part of the Sr flux is contributed by non-reef carbonate production on the continental shelf and slope (Milliman and Droxler, 1996). However, shelf carbonate contributions are rather uncertain due to the unknown partitioning between calcite and aragonitic species.
Table 4
Sources of Sr to the ocean.

<table>
<thead>
<tr>
<th>Sr sources</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}_{\text{norm}}$</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}^*$</th>
<th>$^{88}\text{Sr}/^{86}\text{Sr}$</th>
<th>Flux (10$^9$ mol/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River discharge</td>
<td>J$_{\text{River}}$</td>
<td>0.7119(9)$^{13}$</td>
<td>0.7113(4)</td>
<td>0.7114(8)</td>
<td>~33.3 ± 10$^4$</td>
</tr>
<tr>
<td>Groundwater discharge</td>
<td>J$_{\text{GW}}$</td>
<td>0.7110$^{12}$</td>
<td>n.a.</td>
<td>n.a.</td>
<td>~16.5 ± 8$^2$</td>
</tr>
<tr>
<td>Oceanic crust-seawater interaction at mid-ocean ridges</td>
<td>J$_{\text{OCC}}$</td>
<td>0.7025$^{13}$</td>
<td>0.7043(3)</td>
<td>0.7045(5)</td>
<td>~2.33 ± 1.2$^2$</td>
</tr>
<tr>
<td>Low-temperature interaction on ridge flanks and within the cold oceanic crust</td>
<td>J$_{\text{HydEnd}}$</td>
<td>0.7025$^{13}$</td>
<td>n.a.</td>
<td>n.a.</td>
<td>~0.8 ± 0.4$^2$</td>
</tr>
<tr>
<td>Diagenetic flux from marine sediments</td>
<td>J$_{\text{DIA}}$</td>
<td>0.7084$^{1}$</td>
<td>n.a.</td>
<td>n.a.</td>
<td>~3.4 ± 1.7$^1$</td>
</tr>
<tr>
<td>Sr Flux-weighted average</td>
<td>J$_{\text{input}}$</td>
<td>~0.7109$^{14}$</td>
<td>n.a.</td>
<td>~0.7106(8)</td>
<td>~0.310(8)</td>
</tr>
</tbody>
</table>

Note: All ($^{87}\text{Sr}/^{86}\text{Sr}$, $^{88}\text{Sr}/^{86}\text{Sr}$) values are from this study, (1) (Palmer and Edmond, 1989), (2) (Basu et al., 2001), 50% uncertainty is arbitrarily assigned to this value, (3) (Davis et al., 2003), 50% uncertainty is arbitrarily assigned to this value. The major Sr inputs to the ocean are river discharge (J$_{\text{Riv}}$), groundwater discharge (J$_{\text{GW}}$) and oceanic crust-seawater interaction (J$_{\text{HydEnd}}$) at mid-ocean ridges. All other Sr fluxes generated by low temperatures interactions on ridge flanks, (J$_{\text{OCC}}$), Sr inputs from sedimentary pore waters and from recrystallizing sediments (J$_{\text{DIA}}$) are arbitrarily assigned uncertainties of 50%. “n.a.” not available. The Sr isotope composition of the input is calculated from the values above. For simplicity and due to the lack of data we assume that the ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$) values of J$_{\text{GW}}$ are equal to J$_{\text{Riv}}$, and that the ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$) values of J$_{\text{OCC}}$ and of J$_{\text{DIA}}$ are equal to J$_{\text{HydEnd}}$. #: the statistical uncertainty was estimated from the half difference between the minimum estimate of the global mean value of 0.7101 (Goldstein and Jacobsen (1987) and the maximum estimate by Palmer and Edmond (1989)). * Estimates of the hydrothermal input range from minimum values of ~1.9 × 10$^9$ mol/yr (Goldstein and Jacobsen (1987) to 15 × 10$^9$ mol/yr (Palmer and Edmond, 1989). However, the maximum value is based estimated on the assumption of Sr equilibrium, whereas the lower values are based on different independent approaches. Hence, for our discussion we adopted the most recent estimate of (Davis et al., 2003) as the best approximation of the global hydrothermal Sr flux. The Sr flux-weighted global mean ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$)$_{\text{input}}$ values of (0.7106(8)$^{15}_{\text{mean}}$, 0.310(8)$^{16}_{\text{mean}}$) were calculated with Eq. (A6) (Appendix).

and the lack of knowledge on CaCO$_3$ production rates of different contributing taxa (Table 3). Based on the data compiled in Table 3 we approximate the mean ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$) ratios of shelf carbonates at ~0.70924(1), 0.22(3)$^{17}_{\text{mean}}$). We assume that shelf and slope carbonates are two-thirds aragonitic with mean ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$) values of reef corals and Halimeda (0.70925, 0.23$^{18}_{\text{mean}}$), and one-third calcitic with mean ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$) values of coccoliths and planktonic foraminifera (0.70923, 0.20$^{19}_{\text{mean}}$).

Based on data summarized in Table 3 we estimate the Sr burial flux-weighted ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$) ratios of the total marine carbonate production at ~0.70926(2), ~0.21(2)$^{20}_{\text{mean}}$). The mean global ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$)$_{\text{Carbonate}}$ values are therefore similar to the values of continental shelf and slope taxa. Furthermore, the flux-weighted average values are within statistical uncertainty identical to those estimated by just averaging the ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$) values of the main calcifying species (0.70924(2), 0.22(2)$^{21}_{\text{mean}}$). Table 3). The close agreement between the two approaches may indicate that the relative contributions of the various burial fluxes are well constrained despite considerable uncertainties in the absolute burial fluxes. Hence, we consider both approaches to be reasonable approximations of the true mean global ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$)$_{\text{Carbonate}}$ values.

4. DISCUSSION

Compilations of the modern input and output data (Tables 3 and 4) indicate that the Sr outputs (~174 × 10$^9$ mol/yr) are larger than Sr inputs (~56 × 10$^9$ mol/yr), and that the Sr isotope compositions of input and output fluxes are considerably different. Although the estimated difference between input and output values seems to be large, we cannot assign statistical significance because all estimates are afflicted with considerable uncertainties. In order to further examine and better constrain the observed trends, we compare the Sr isotope balance of Sr inputs, outputs and of [Sr]$_{\text{seawater}}$ in a triple isotope plot. This new approach in Sr isotope geochemistry critically depends on taking Sr isotope fractionation into account.

4.1. Sr budget of the global ocean

In Fig. 3 the global means of the ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$)$_{\text{River}}$ and ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$)$_{\text{HydEnd}}$ values define the two end-members of a binary mixing line between the two major sources of Sr in the modern ocean. The calculated combined ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$)$_{\text{input}}$ values fall on this binary mixing line and plot relatively close to the Sr isotope composition of average river water, indicating that riverine input is the major Sr source to the present-day ocean (~60%). In contrast, the modern Sr isotope values of ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$)$_{\text{seawater}}$ and ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$)$_{\text{Carbonates}}$ form a mass-dependent isotope fractionation line. Carbonates are isotopically lighter because they preferentially incorporate the lighter isotopes and leave seawater enriched in the heavy ones.

The intercept of the binary mixing line and the fractionation line ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$)$_{\text{Intercept}}$ (~0.70927, ~0.30$^{23}_{\text{mean}}$) defines the isotope composition of the combined Sr input into the ocean (Fig. 3). These values are significantly different (~0.0011(8), ~0.01(2)$^{24}_{\text{mean}}$) from the calculated ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$)$_{\text{input}}$ values, and this difference reflects isotope disequilibrium. There is also a significant difference between the Sr isotopic composition of the ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$)$_{\text{input}}$ and the Sr output values represented by ($^{87}\text{Sr}/^{86}\text{Sr}$*, $^{88}\text{Sr}/^{86}\text{Sr}$)$_{\text{Carbonates}}$ of (~0.0011(8), ~0.10(2)$^{25}_{\text{mean}}$). This also indi-
cates disequilibrium between inputs and outputs, because at isotope equilibrium ($^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{88/86}\text{Sr}$)input and ($^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{88/86}\text{Sr}$)output should be identical (see Appendix).

In a first approach taking only $^{87}\text{Sr}/^{86}\text{Sr}$ values into account and leaving $J_{\text{HydEnd}}, J_{\text{OCC}}$ and $J_{\text{Dia}}$ (Table 4) unchanged we can calculate from our isotope data that the combined $J_{\text{River}}$ and $J_{\text{GW}}$ input ($\sim 49 \times 10^6$ mol/a) is about a factor of three too high to be in agreement with the $^{87}\text{Sr}/^{86}\text{Sr}$ output values. This observation is in general accord with earlier statements using traditional $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that the estimated modern riverine flux is relatively accurate within ~30% but is probably not representative of the past, particularly not for elements with residence times in excess of 10$^5$ years. In this regard, our observation that the modern ($^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{88/86}\text{Sr}$)input value is higher than the ($^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{88/86}\text{Sr}$)intercept value is compatible with earlier statements based on traditional $^{87}\text{Sr}/^{86}\text{Sr}$ values that modern continental weathering rates are 2–3 times higher than the long-term mean (Vance et al., 2009). This post-glacial “weathering peak” (Fig. 3) is likely caused by weathering of fine-grained material left exposed by the retreating continental ice masses (c.f. Blum and Erel, 1995, see discussion in Section 6).

At equilibrium the complete marine Sr budget requires agreement in the $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88/86}\text{Sr}$ values of input and output fluxes. Interestingly, this cannot simply be achieved by reducing individual input fluxes because – within statistical uncertainties – there is no Sr source with a corresponding $\delta^{88/86}\text{Sr}$ value equal to or even lower than the modern $\delta^{88/86}\text{Sr}$ value (see Table 4). This major discrepancy indicates that the marine Sr budget cannot be at equilibrium given the known Sr sources. At least one additional Sr source of sufficient size and with a $\delta^{88/86}\text{Sr}$ value lower than the mean $\delta^{88/86}\text{Sr}$ value is required to achieve equilibrium. The nature of this isotopically light, missing Sr source is discussed below.

Isotope equilibrium can be disturbed by sufficiently large addition or removal of Sr relative to the size of the marine Sr reservoir, provided the isotope composition is significantly different from that of seawater (Stoll and Schrag, 1998). The duration of such a perturbation is a function of the residence time, ~2.4 Myr in the case of Sr. On time scales much longer than the Sr residence time slight imbalances between input and output fluxes can occur in quasi isotope equilibrium. It is thus very unlikely that the Sr fluxes and isotope compositions of hydrothermal sources are subject to a rapid change, as submarine hydrothermal circulation is controlled by processes in the Earth’s mantle characteristic time scales of 10$^6$–10$^8$ yrs, far in excess of the residence time of Sr in seawater.

A change of the preferred carbonate polymorphism may also lead to changes in Sr concentration of seawater, be-
cause Sr/Ca ratios of aragonite are about an order of magnitude higher than those of calcite. Strontium isotope measurements of calcitic foraminifera (Table 3) confirm earlier conclusions based on Ca isotopes (Farkas et al., 2007) that fractionation factors for aragonite and calcite differ. A change of the preferred carbonate polymorphism could therefore lead to changes in the isotopic composition of seawater. However, global changes of the preferred marine carbonate polymorphisms occur on time scales much longer than the residence time of Sr in seawater (Stanley and Hardie, 1998), leaving the system in quasi steady-state.

In contrast, continental weathering and related riverine inputs into the ocean may be subject of relatively rapid changes (10–100 kyr) when compared to the Sr residence time (~2.4 Myr). In addition, glacial/interglacial changes in sea level and the related dynamics of weathering of carbonates exposed on continental shelves may be responsible for substantial and short-term disequilibria between Sr inputs and outputs of the ocean, as proposed earlier by Stoll et al. (1999).

5. SR ISOTOPE EQUILIBRIUM IN THE OCEAN DURING THE LAST GLACIAL

A ~120 m drop in glacial sea level (c.f. Bard et al., 1996; Fairbanks, 1989) exposed continental shelves and provided an additional supply of elements from the continents to the ocean. In particular, alkaline earth elements such as Mg, Ca and Sr are mobilized from weathering of carbonate-dominated continental shelves in larger amounts during glacial periods (c.f. Stoll et al., 1999). Polymorphism exerts strong controls over Mg and Sr delivery, because calcite is Mg-rich compared to aragonite, whereas aragonite contains about 10 times more Sr than calcite (Table 3). During meteoric diagenesis aragonite will eventually recrystallize to calcite and release Sr to the sea. Stoll and Schrag (1998) and Stoll et al. (1999) hypothesize that this additional flux caused Sr/Ca of glacial seawater to increase. In contrast, sea level high-stand during interglacials flooded the shelves that then act as Sr sinks, causing seawater Sr/Ca values to decrease. These glacial/interglacial variations result in an oscillation of the marine Sr/Ca ratio of the order of ~±1% relative to the present-day value (Stoll and Schrag, 1998).

From the numerical integration of the Stoll and Schrag (1999) data we estimate, for the time interval from 10 to 20 ka, the average annual Sr flux of ~150 × 10^9 mol/yr, approximately three times larger than the modern global mean Sr input (~56 × 10^9 mol/yr, Table 4). The Sr input during the last glacial maximum (~206 × 10^9 mol/yr) was therefore dominated by carbonate weathering on the continental shelves rather than by weathering of the continental interiors. Taking shelf carbonate weathering and the above data into account, we estimate glacial (\(^{87}\)Sr/\(^{86}\)Sr\(^{\text{input}}\) = 1.011, \(^{87}\)Sr/\(^{86}\)Sr\(^{\text{output}}\) = 0.70918 (2σ)). These values differ significantly from the present-day (\(^{87}\)Sr/\(^{86}\)Sr\(^{\text{input}}\) = 0.7069, \(^{87}\)Sr/\(^{86}\)Sr\(^{\text{output}}\) = 0.70918 (2σ)). Most importantly, the estimated glacial (\(^{87}\)Sr/\(^{86}\)Sr\(^{\text{input}}\) = 0.7069, \(^{87}\)Sr/\(^{86}\)Sr\(^{\text{output}}\) = 0.70918 (2σ)) values are within uncertainty of the modern (\(^{87}\)Sr/\(^{86}\)Sr\(^{\text{input}}\) = 0.7071, \(^{87}\)Sr/\(^{86}\)Sr\(^{\text{output}}\) = 0.70927 (2σ)), indicating isotopic equilibrium rather than disequilibrium conditions during the last glacial maximum (Fig. 3).

6. CREATING SR BUDGET DISEQUILIBRIUM DURING GLACIAL/INTERGLACIAL TRANSITIONS

The predicted marine Sr equilibrium was probably terminated at the end of the glacial period by the rapid ~120 m sea level rise between the glacial low-stand at ~20 ka and the Holocene sea level maximum at ~6 ka. This rise eliminated shelf carbonate weathering as the major source of Sr, leaving riverine, groundwater and hydrothermal inputs as the major, though drastically reduced, Sr fluxes to the modern ocean. Without shelf carbonate weathering, the new post-glacial mean Sr input value is expected to approach the intercept value defined by the binary mixing line and the mass-dependent fractionation line (Fig. 3). However, the post-glacial (0.71068, 0.31080) input value is significantly more radiogenic in \(^{87}\)Sr/\(^{86}\)Sr and tend to be heavier in the \(^{88}\)Sr/\(^{86}\)Sr value than the intercept values (~0.70927, ~0.3080). This could indicate that riverine Sr inputs increased during glacial/interglacial transitions while continental shelf input decreased. Enhanced continental weathering may be caused by warmer post-glacial climate, higher atmospheric pCO₂ and enhanced precipitation. The retreating continental glaciers have also exposed finely ground material that provided an extra supply (“weathering peak”, Fig. 3) of isotopically more radiogenic Sr to the ocean (c.f. Blum and Erel, 1995; Vance et al., 2009). This “weathering peak” has not yet disappeared, and the Sr isotope compositions of modern input and output values have not yet reached a new post-glacial equilibrium.

7. CONCLUSION

During glacial periods weathering of continental shelf carbonates complemented inputs from rivers, groundwater and hydrothermal fluids as a fourth source of Sr to seawater. This fourth source dominated Sr fluxes to the ocean during glacial periods. The close agreement of the glacial Sr input values with modern carbonate output values is suggestive of isotope equilibrium during the last glacial maximum. A fundamental change in weathering regime during the glacial/interglacial transition perturbed the glacial Sr equilibrium towards the observed modern disequilibrium. The inferred change in weathering regime was facilitated by the rapid post-glacial sea level rise that flooded the continental shelves, terminated weathering fluxes from shelf carbonates and left riverine, groundwater and hydrothermal Sr fluxes as the major sources to the modern oceans. An additional shift towards heavier and more radiogenic Sr isotope composition may have occurred due to an additional flux of isotopically heavy and radiogenic Sr (“weathering peak”) from the fine-grained, highly reactive detritus that the retreating continental ice shields left behind.
Sr isotope fractionation constraining the marine Sr budget

ACKNOWLEDGMENTS

Financial support was provided by the “Deutsche Forschungsgemeinschaft, DFG, EI272/29-1 and EI272/30-1 (TRION)”. We thank A. Kolevica, T. Atwood and C. Miller for laboratory assistance and technical support. The comments and suggestions of two anonymous reviewers and the associate editor Prof. S. Krishnaswami helped to significantly improve this article.

APPENDIX A. NOTATION AND TERMINOLOGY

$^{87}\text{Sr} / ^{86}\text{Sr}$ This is the notation for the traditional radiogenic Sr isotope value. This ratio is measured by plasma or thermal ionization mass spectrometry and normalized to a $^{86}\text{Sr} / ^{86}\text{Sr}$ ratio of 8.735209

$^{87}\text{Sr} / ^{86}\text{Sr}$ This ratio refers to the $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio as measured and normalized to an $^{87}\text{Sr} / ^{86}\text{Sr}$ double spike (see Krabbenhöft et al., 2009). This ratio was not normalized to a $^{86}\text{Sr} / ^{86}\text{Sr}$ ratio of 8.735209

$\delta^{87/86}\text{Sr}$ This ratio refers to the $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio as measured and normalized to an $^{87}\text{Sr} / ^{86}\text{Sr}$ double spike (see Krabbenhöft et al., 2009). The measured $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio is presented in the usual δ notation in permil ($\delta^m$) deviation from the SRM987 standard. Note that a $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio of 8.735209 corresponds to a $\delta^{87/86}\text{Sr}$ value of zero

$^{87}\text{Sr} / ^{86}\text{Sr}_{\text{Norm}}$ This ratio refers to the $^{87}\text{Sr} / ^{86}\text{Sr}$* ratio which is renormalized to a $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio of 8.735209. The subscript “Norm” stands for normalization. The $^{87}\text{Sr} / ^{86}\text{Sr}_{\text{Norm}}$ is equivalent to the traditional radiogenic $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio. However, in order to provide comparability and to emphasize the double spike origin of the original value it is marked with the subscript “Norm”

APPENDIX B. SR MASS FRACTIONATION

$^{87}\text{Sr} / ^{86}\text{Sr}$ and $^{88}\text{Sr} / ^{86}\text{Sr}$ are determined from a double spike measurement following the procedures previously described by (Krabbenhöft et al., 2009). The relationship between the traditional radiogenic $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio, $^{87}\text{Sr} / ^{86}\text{Sr}_{\text{Norm}}$ and $^{87}\text{Sr} / ^{86}\text{Sr}$* is defined by Eq. (A1):

$$A1: \left( \frac{\delta^{87/86}\text{Sr}_{\text{Norm}}}{\delta^m} \right) = \left( \frac{\delta^{87/86}\text{Sr}_{\text{Nier}}}{\delta^m} \right) \left[ \frac{m_{86\text{Sr}}}{m_{86\text{Sr}}} \right] \left[ \frac{m_{87\text{Sr}}}{m_{87\text{Sr}}} \right] \left[ \frac{m_{88\text{Sr}}}{m_{88\text{Sr}}} \right]$$

The ($^{87}\text{Sr} / ^{86}\text{Sr})_{\text{Nier}}$ value has been defined as 8.375209 (Nier, 1938), and corresponds to a $\delta^{87/86}\text{Sr} = 0$ relative to NIST SRM 987. The masses of the various Sr isotopes are: $m_{86}\text{Sr} = 85.909273$ $m_{87}\text{Sr} = 86.908880$, and $m_{88}\text{Sr} = 87.905625$. For further details see (Krabbenhöft et al., 2009).

APPENDIX C. ERROR NOTATION AND PROPAGATION

All statistical uncertainties represent 2 standard errors of the mean (2σ$_{\text{mean}}$). We present the statistical uncertainties for $^{87}\text{Sr} / ^{86}\text{Sr}$ and $\delta^{87/86}\text{Sr}$ in brackets. The values in the brackets refer to the last digit of the measured values. For example $^{87}\text{Sr} / ^{86}\text{Sr} = 0.711111(1)$ correspond to 0.711111 ± 0.000001 and $\delta^{88/86}\text{Sr} = 0.386(1)_{\text{so}}$ correspond to 0.386 ± 0.001$_{\text{so}}$

APPENDIX D. CALCULATION OF FLUX-WEIGHTED MEAN GLOBAL RIVER DISCHARGE TO THE OCEAN

$$\left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{River}} = \frac{\sum_i \left( \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{River}} \right) \cdot \text{Discharge river } i}{\sum \text{Discharge river } i} \quad (A2)$$

$$\delta^{88/86}\text{Sr}_{\text{River}} = \frac{\sum_i \left( \delta^{88/86}\text{Sr} \right)_{\text{River}} \cdot \text{Discharge river } i}{\sum \text{Discharge river } i} \quad (A3)$$

APPENDIX E. CALCULATION OF FLUX-WEIGHTED MEAN GLOBAL INPUT TO THE OCEAN

$$\left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{input}} = \frac{\sum_i \left( \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{input}} \right) \cdot \text{input } i}{\sum \text{input } i} \quad (A4)$$

$$\delta^{88/86}\text{Sr}_{\text{input}} = \frac{\sum_i \left( \delta^{88/86}\text{Sr} \right)_{\text{input}} \cdot \text{input } i}{\sum \text{input } i} \quad (A5)$$

APPENDIX F. ISOTOPE EQUILIBRIUM

Following the approach of (De La Rocha and DePaolo, 2000) the condition of isotope equilibrium with respect to element input and output fluxes to the ocean can be mathematically described for the Sr isotope systems as follows. Note that the equations are given for $\delta^{88/86}\text{Sr}$, but are analogous for $^{87}\text{Sr} / ^{86}\text{Sr}$:

$$N_{\text{Sr}} \cdot \frac{\partial \delta^{88/86}\text{Sr}_{\text{Seawater}}}{\partial t} = J_{\text{input}} \cdot (\delta^{88/86}\text{Sr}_{\text{input}} - \delta^{88/86}\text{Sr}_{\text{Seawater}}) - J_{\text{output}} \cdot \Delta_{\text{output}} \quad (A6)$$

In a steady-state ocean where Sr input and output fluxes are equal ($J_{\text{input}} = J_{\text{output}}$) both the Sr isotope composition of seawater and the amount of Sr present in seawater are invariant ($\text{d}[\text{Sr}]_{\text{Seawater}}/\text{dt} = \text{d}(\delta^{88/86}\text{Sr}(t))/\text{dt} = 0$). Eqs. (A2) and (A3) are reduced to (A4):

$$\Delta_{\text{output}} = \delta^{88/86}\text{Sr}_{\text{Carbonates}} - \delta^{88/86}\text{Sr}_{\text{Seawater}} \quad (A7)$$

REFERENCES


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