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Enrichment of ^{88}Sr in continental waters due to calcium carbonate precipitation

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ABSTRACT

$\delta^{88/86}$Sr data published over the last few years suggest that continental waters are enriched with ^{88}Sr as compared to the rocks in their drainage basins. In an attempt to understand this phenomenon, this study established the fractionation in the ^{88}Sr/^{86}Sr ratio during precipitation of continental carbonates (i.e., carbonates precipitated on land from surface, pedogenic, or ground waters), and evaluated the contribution of this process to the ^{88}Sr-enrichment in rivers. For this, stable and radiogenic Sr isotopes (^{88}Sr, ^{87}Sr and ^{86}Sr) were measured in calcite samples and their precipitating waters collected in various continental environments, such as soil, cave, streams and groundwater.

The results indicate that continental carbonates are ^{88}Sr-depleted relative to their precipitating waters, placing them as one of the most ^{88}Sr-depleted reservoirs on earth. The average difference in $\delta^{88/86}$Sr values between waters and solid CaCO$_3$ (tufas or speleothems) that they precipitate is $\Delta_{\text{carb-water}} = -0.218 \pm 0.014‰$ (1SD). An even larger fractionation ($\varepsilon_{\text{carb-water}} = -0.285 \pm 0.02‰$) was measured in groundwater with particularly high carbonate-alkalinity and high carbonate precipitation rate that depleted ~65% of the Sr in the groundwater, resulting in substantial ^{88}Sr-enrichment in the residual dissolved Sr ($\delta^{88/86}\text{Sr} = 0.656‰$). Results also suggest that pedogenic carbonate precipitation in soil profile removes 50–85% of the Sr from the recharging soil–water, thereby increasing the $\delta^{88/86}$Sr value of the soil-water from ~ 0.18‰ to 0.3‰–0.6‰. Similar ^{88}Sr-enrichment was observed in drip water from a karst cave.

A maximum removal flux of Sr into continental carbonates of about 20 Gmol$_{(\text{Sr})}\cdot\text{y}^{-1}$ is required to yield the reported ^{88}Sr-enrichment in global rivers ($\delta^{88/86}\text{Sr} = 0.32‰$) relative to their rock sources when using the fractionation factor derived in this study, $\Delta_{\text{carb-water}} = -0.218‰$, and the published $\delta^{88/86}$Sr composition of marine carbonates of 0.16‰. This surprisingly large flux requires that ~40% of the originally weathered Sr should co-precipitate with continental carbonates. This calculation may suggest that CaCO$_3$ precipitation is a significant mechanism in the continental Sr cycle. It is possible however that other mechanisms such as Sr uptake by plants or incongruent weathering of silicates, could also contribute to the riverine ^{88}Sr-enrichment. Alternatively, the average $\delta^{88/86}$Sr value of marine carbonate rock sections undergoing weathering is higher than suggested in current literature. It is concluded that additional $\delta^{88/86}$Sr data on marine carbonate rock sections should be collected to resolve the enigma of the high value of riverine $\delta^{88/86}$Sr.

1. Introduction

The continental strontium cycle and its effect on the strontium content and isotope composition of the oceans have traditionally been evaluated through the ^{87}Sr/^{86}Sr isotope ratio of the major rivers that drain the exposed continental terrains (e.g. Faure, 1986; Veizer, 1989). Recently, with the advances in mass spectromet-

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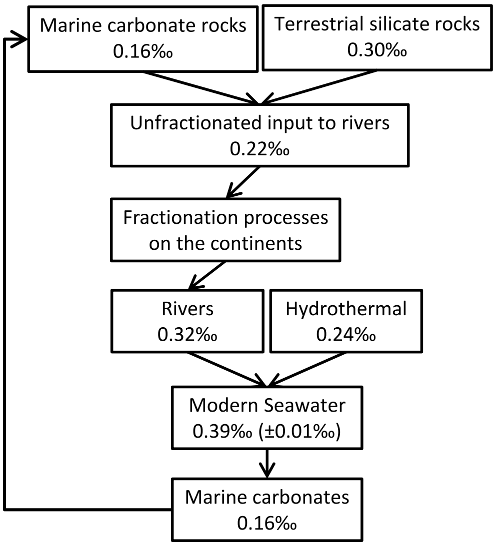

Fig. 1. Major Sr fluxes and their published mean $\delta^{88/86}$Sr values (After: Krabbenhöft et al., 2010; Moynier et al., 2010; Charlier et al., 2012; Vollstaedt et al., 2014; Pearce et al., 2015).

ric analysis of the stable isotopes of strontium ($\delta^{88/86}$Sr), the Sr continental–ocean budget was re-evaluated (e.g., Halicz et al., 2008; Krabbenhöft et al., 2010; Wei et al., 2013; Chao et al., 2015; Pearce et al., 2015). It was suggested that processes occurring on land are accompanied by Sr isotope fractionation that affect the $\delta^{88/86}$Sr of rivers and, in turn, that of the ocean (e.g., Chao et al., 2015; Pearce et al., 2015). The modern ocean has a $\delta^{88/86}$Sr value of 0.39‰ (e.g., Fietzke and Eisenhauer, 2006; Ohno and Hirata, 2007; Halicz et al., 2008), which is higher than the modern riverine discharge (0.32‰; Fig. 1; Krabbenhöft et al., 2010; Pearce et al., 2015). However, the rivers are ^{88}Sr-enriched relative to both carbonate and silicate rock sources. While the $\delta^{88/86}$Sr value of terrestrial silicate rocks is estimated at 0.30‰ (Moynier et al., 2010; Charlier et al., 2012), the mean $\delta^{88/86}$Sr value of carbonate rocks exposed on the continents is largely uncertain. The flux-weighted average $\delta^{88/86}$Sr value of modern biogenic marine carbonates and the Phanerozoic mean marine carbonates, based on brachiopods and belemnites record, are 0.21‰ and 0.16‰, respectively, significantly lower than that of modern seawater (Halicz et al., 2008; Krabbenhöft et al., 2010; Vollstaedt et al., 2014).

Based on riverine ^{87}Sr/^{86}Sr, the proportion of Sr derived from weathering of carbonate and silicate rocks is estimated to be about 60:40, respectively (Pearce et al., 2015 and references therein). Given this ratio and the $\delta^{88/86}$Sr compositions of carbonate and silicate rocks quoted above (16‰ and 0.30‰, respectively; Moynier et al., 2010; Charlier et al., 2012; Vollstaedt et al., 2014), the $\delta^{88/86}$Sr of the global rivers should have been ∼ 0.22‰. However, this value is considerably lower than the measured riverine $\delta^{88/86}$Sr composition of 0.32‰ (Krabbenhöft et al., 2010; Pearce et al., 2015), reinforcing the suggestion that weathering-related processes fractionate Sr isotopes on the continents (Fig. 1).

Several mechanisms were proposed for the ^{88}Sr-enrichment of continental waters (summarized in Chao et al., 2015): 1) Preferential adsorption of the lighter isotopes onto particles; 2) Biological fractionation during uptake of Sr (De Souza et al., 2010; Andrews et al., 2016; Bullen and Chadwick, 2016); 3) Incongruent weathering of silicate minerals, during which the heavy ^{88}Sr isotope is preferentially released into solution (Halicz et al., 2008; Wei et al., 2013; Chao et al., 2015; Stevenson et al., 2016); and 4) Precipitation of ^{88}Sr-depleted continental carbonates, which enriches the residual solution with ^{88}Sr (Chao et al., 2013, 2015).

Continental carbonates precipitate on land from surface, pedogenic, or ground waters (Deocampo, 2010) in a range of environments, including rivers (tufa), lakes, soil (pedogenic carbonates), veins, caves and through local re-crystallization of marine carbonates by freshwater. The total amount of these carbonates is not known, but elevated Sr/Ca ratios in Himalayan water were explained by the precipitation of an unexpectedly large amount of continental carbonate in the catchment area: 50–80% of the originally weathered Ca (Galy et al., 1999; Jacobson et al., 2002; Bickle et al., 2015). If this estimate is representative of other environments in which continental carbonates precipitate, then carbonate sink is huge, and may also be a sink for Sr. However, measurements of $\delta^{88/86}$Sr values of such carbonates and their associated waters are rare and inconclusive (Chao et al., 2013; Shalev et al., 2013; Chao et al., 2015; Pearce et al., 2015).

The present study aims at providing new data on the impact of precipitation of continental carbonates on the $\delta^{88/86}$Sr value of continental waters. The stable and radiogenic Sr isotopic compositions of different types of continental carbonates and associated waters in several environments, including streams, groundwaters and soils, were investigated. The dual isotopic system of $\delta^{88/86}$Sr and ^{87}Sr/^{86}Sr was used to determine the sources and evolution of continental Sr for each environment, and to quantify the Sr isotope fractionation. Finally, the implications of the new results for the global continental Sr budget are addressed.

2. Materials and methods

2.1. Materials

Several continental carbonates and their precipitating waters from Israel, and one such pair from France, were selected to represent a range of continental carbonate types and environments, including groundwater-tufa, streams-tufa, desert springs-tufa, speleothems and pedogenic carbonates. Sampling details are presented in Table A.1 (Appendix A).

2.1.1. Stream waters and tufas

Several streams, draining mainly Mesozoic carbonate rocks, were sampled (Fig. 2): the Banias and Dan streams are fed by the Jurassic limestone aquifer of Mt. Hermon in northern Israel, which is characterized by its highly developed karst system. Tufa was sampled within the Banias stream in the form of a thin coating on bedload boulders, and within the Dan stream in the form of a coating on a submerged metal pipe. The base flow at the David stream, located in the Judean Desert, eastern Israel, is derived from springs issuing from an Upper Cretaceous carbonate aquifer. Tufa, up to few tens of centimeters thick, covers the rocks wherever the water forms small waterfalls. A sample was collected from the uppermost ∼2 cm tufa closest to the water stream. In addition, the Huveaune River, Provence, France, draining the Jurassic karstic limestones of the Sainte Baume Massif was sampled. $CaCO_3$ precipitation, enhanced by the presence of Cyanobacteria, forms terraces and local ponds along the river. Soft carbonate deposits that cover the river bed were sampled, along with river water.

2.1.2. Drip water and speleothems

Drip water and its associated carbonates (stalagmites) were sampled in the well-studied Soreq cave, central Israel (e.g. Bar-Matthews et al., 1991; Fig. 2). The stalagmites were sampled from their surface (∼2 mm), representing recent precipitation. The 10–40 m thick caprock above the cave consists of Cenomanian dolostone, locally covered by ∼30 cm thick terra rossa soil, which evolved mostly from settled dust (Yaalon, 1997). Soreq caprock and Jerusalem dust were sampled as well.

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