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Assessing the role of submarine groundwater discharge as a source of Sr to the Mediterranean Sea

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Abstract

Submarine groundwater discharge (SGD) has been identified as an important source of Sr to the ocean and the SGD-driven Sr flux to the global ocean has been recently re-evaluated (Beck et al., 2013). However, the uncertainty of this value is still high because of the uncertainties related to the determination of SGD flow rates and the paucity of ^{87}Sr/^{86}Sr data in SGD end-members. As carbonates have high Sr concentrations and are subjected to intense heightened weathering, they might significantly influence the SGD input of Sr to the ocean. Here we present data on Sr concentrations and ^{87}Sr/^{86}Sr ratios in three carbonate dominated sites of the western area of the Mediterranean Sea, a semi-enclosed basin characterized by abundant coastal carbonates. The ^{87}Sr/^{86}Sr ratios in groundwater were lower compared to modern seawater (~0.70916), as expected for areas dominated by carbonate lithologies. Concentrations of Sr and ^{87}Sr/^{86}Sr ratios in groundwater showed conservative mixing in the studied subterranean estuaries. By using SGD flow rates reported in the literature for the study areas, a flow-weighted fresh SGD end-member characterized by a Sr concentration of 27–30 μM and a ^{87}Sr/^{86}Sr ratio of 0.707834–0.708020 was calculated for the eastern coast of the Iberian Peninsula.

Integrating these Sr data with literature data (i.e. values of Sr concentration and ^{87}Sr/^{86}Sr ratio from other lithologies as well as SGD flow rates), we also calculated the fresh SGD-driven Sr flux to the entire Mediterranean Sea, obtaining a value of $(0.34–0.83)\cdot 10^9$ mol y^{-1}, with a ^{87}Sr/^{86}Sr of 0.7081–0.7086. Thus, for the entire Mediterranean basin, SGD is globally a source of Sr less radiogenic compared to seawater. The SGD Sr flux to the Mediterranean Sea represents 5–6% of the SGD Sr flux to the global ocean and the Mediterranean SGD end-member has higher Sr concentration (5–12 μM) than the global SGD end-member (2.9 μM). This confirms the significant role of carbonate lithologies on SGD-driven Sr fluxes to seawater.

The fresh SGD-driven Sr flux to the Mediterranean Sea is about 20–50% of the riverine Sr input and significantly higher than the input through atmospheric dust deposition. Therefore SGD should be considered as an important continental source of Sr to the basin.

Keywords: Strontium; Submarine groundwater discharge; Carbonates; Conservative mixing; Mediterranean Sea

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1. INTRODUCTION

The $^{87}Sr/^{86}Sr$ ratio in marine carbonates reflects the composition of seawater at the time of the carbonate deposition and thus can be used as a tool for studies on paleoclimatic reconstructions and stratigraphic correlations (Burke et al., 1982). The residence time of Sr in seawater (>2.5 My) is much longer than the time of ocean mixing (~1500 y), so that the $^{87}Sr/^{86}Sr$ ratio is homogeneous in seawater with a salinity of about 35, with a current value of ~0.70916 (Broecker and Peng, 1982; Beck et al., 2013), but with large variation over geological time scale (Burke et al., 1982). However, the $^{87}Sr/^{86}Sr$ ratio can be different in seawater with lower salinity in marginal seas and coastal areas (Andersson et al., 1992; Huang et al., 2011).

The $^{87}Sr/^{86}Sr$ ratio of seawater is related to the isotope composition of the Sr inputs, including mainly rivers, hydrothermal systems, seafloor sediments and submarine groundwater discharge (SGD) (e.g. Albarède et al., 1981; Palmer and Edmond, 1989; Davis et al., 2003; Martin and Moore, 2008; Allègre et al., 2010; Beck et al., 2013). The different Sr isotope compositions of these sources of Sr reflect the Rb/Sr ratio of the minerals of the rocks interacting with the water. Generally, rocks composed of K-rich minerals (intrusive, metamorphic and siliciclastic sedimentary rocks) have higher $^{87}Sr/^{86}Sr$, as ^{87}Sr is produced from the decay of ^{87}Rb ($T_{1/2} = 4.9 \cdot 10^{10}$ y), which can substitute K in minerals. In contrast, rocks largely composed of Ca-rich minerals (carbonates, evaporites and volcanic rocks) have lower $^{87}Sr/^{86}Sr$, primarily due to a lower Rb/Sr ratio; these rocks are enriched in Sr, as Sr can substitute Ca in minerals (McNutt, 2000).

Early calculations of the marine Sr isotope budget considering only rivers, hydrothermal systems and diagenesis of seafloor sediments, yield a significant imbalance, mainly because the worldwide fluvial transport of more radiogenic Sr exceeded the contribution of less radiogenic Sr from the other sources (Albarède et al., 1981; Palmer and Edmond, 1989; Davis et al., 2003). The significance of SGD inputs of Sr has been evaluated only in recent years (Basu et al., 2001; Allègre et al., 2010; Rahaman and Singh, 2012; Beck et al., 2013). SGD is the combination of meteoric groundwater and recirculated seawater, discharging into the coastal sea through coastal aquifers (Moore, 1996; Burnett et al., 2003). This process is a significant source of chemical compounds (e.g., macronutrients, trace metals, carbon, REEs) to the coastal ocean (e.g. Cai et al., 2003; Slomp and Van Cappellen, 2004; Windom et al., 2006; Johannesson et al., 2011). Beck et al. (2013) conducted the first calculation of the SGD contribution on the marine Sr isotope budget, concluding that SGD (fresh and brackish components) accounts for 13–31% of this budget and represents generally a source of Sr less radiogenic than modern seawater. This reduces the imbalance of the marine Sr isotope budget in the ocean.

Despite the significant improvements in estimating the marine Sr isotope budget, the uncertainty of the SGD-driven Sr flux is still large. This is primarily due to the uncertainties associated with the volumetric discharge of groundwater and the paucity of $^{87}Sr/^{86}Sr$ data in SGD. In particular, new data on carbonate SGD end-members may be essential to refine the global SGD estimation, as carbonates have major effects on SGD fluxes, being characterized by a high Sr concentration and alteration grade (Beck et al., 2013).

The Mediterranean Sea is an interesting site for the study of SGD-driven Sr fluxes primarily due to: i) the wide areas of carbonate bedrock in the drainage basin (Amiotte Suchet et al., 2003; Dürr et al., 2005); ii) the magnitude of SGD flow rates (Rodellas et al., 2015); iii) the significance of SGD as source of chemical compounds to this basin (e.g. Tovar-Sánchez et al., 2014; Rodellas et al., 2015; Trezzi et al., 2016a,b).

In this work, we investigate the SGD-driven Sr fluxes in three different carbonate-dominant coastal areas in the Western Mediterranean Sea: the Irta Range, the Peníscola wetland and the Ebro Delta. The focus is primarily on the eastern coast of the Iberian Peninsula, where SGD fluxes have been quantified recently (Garcia-Solsona et al., 2010; Mejías et al., 2012; Rodellas et al., 2012, 2017) and the hydrogeological sites are well-known and the role of SGD are well-known (Garcia-Orellana et al., 2013; Zarroca et al., 2014). We also attempt to estimate the SGD-driven Sr flux to the entire Mediterranean Sea and to compare it to the other sources of Sr to the basin.

2. METHODOLOGY

2.1. Area of study

The Mediterranean Sea is a semi-enclosed marginal basin that covers a surface of about $2.5 \cdot 10^6$ km^2. It is connected to the Atlantic Ocean through the Strait of Gibraltar, with a width of 14 km at its narrowest point and a minimum depth of 290 m (Soto-Navarro et al., 2010). The inflow of Atlantic water into the Mediterranean Sea through the Strait of Gibraltar is around $26 \cdot 10^{12}$ m^3 y^{-1} and exceeds the outflow of Mediterranean waters, which is around $25 \cdot 10^{12}$ m^3 y^{-1} (Soto-Navarro et al., 2010). Evaporation in the Mediterranean Sea is higher than freshwater inputs and this difference exceeds the net inflow of oceanic waters, so that the salinity of the Mediterranean Sea is higher than the salinity of the global oceans (Flecker et al., 2002).

The Mediterranean Sea is characterized by a drainage basin with predominant sedimentary bedrock (Peucker-Ehrenbrink et al., 2010). Carbonate rocks occupy up to 20% of the drainage basin, dominating in particular the northern catchment (Mesozoic carbonates) (Dürr et al., 2005; Topper et al., 2011). In relative terms, the area covered by carbonates is about two times larger than the area occupied by carbonates in the global ocean drainage basin. Riverine discharge to the basin is currently around $0.3 \cdot 10^{12}$ m^3 y^{-1} (Ludwig et al., 2009). The total SGD flow rate to the Mediterranean Sea ranges from $0.3 \cdot 10^{12}$ to $4.8 \cdot 10^{12}$ m^3 y^{-1} (Rodellas et al., 2015), while the flow rate of fresh groundwater is about $0.07 \cdot 10^{12}$ m^3 y^{-1} (Zektser et al., 2007).

The eastern coast of the Iberian Peninsula is located in the Western Mediterranean Sea and is characterized by out-