



Variability in magnesium, carbon and oxygen isotope compositions of brachiopod shells: Implications for paleoceanographic studies



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ABSTRACT

This study presents the carbon, oxygen, and magnesium isotope compositions of two modern brachiopods, *Terebratalia transversa* and *Frieleia halli*, and one fossil specimen (2.3 Ma), *Terebratula scillae*. The aim of this study is to investigate the variability of these isotopic compositions and to evaluate the potential of brachiopods as a proxy of past seawater $\delta^{26}\text{Mg}$ values. The two investigated brachiopod shells present the same range of $\delta^{26}\text{Mg}$ variation (up to 2‰). This variation cannot be ascribed to changes in environmental parameters (temperature or pH). As has been previously observed, the primary layer of calcite shows the largest degree of oxygen and carbon isotope disequilibrium relative to seawater. In contrast, the $\delta^{26}\text{Mg}$ value of the primary layer is comparable to that of the secondary calcite layer value. In both *T. scillae* and *T. transversa*, negative trends are observable between magnesium isotopic compositions and oxygen and carbon isotopic compositions. These trends can be explained by kinetic effects linked to changes in growth rate during the brachiopod life. The innermost calcite layer of *T. transversa* is in isotopic equilibrium for both oxygen and magnesium and could therefore be the best target for reconstructing past $\delta^{26}\text{Mg}$ values of seawater.

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1. Introduction

Magnesium is one of the most abundant elements (≈ 1290 ppm) in the ocean and is involved in the carbon cycle through the dissolution and precipitation of carbonates, especially dolomites. Changes in Mg cycle, notably variations in the Mg/Ca ratio of seawater (Sandberg, 1983; Wilkinson and Algeo, 1989; Hardie, 1996; Horita et al., 1996; Stanley and Hardie, 1998; Zimmermann et al., 2000; Lowenstein et al., 2001; Dickson, 2002; Coggon et al., 2010; Hasiuk and Lohmann, 2010; Broecker and Yu, 2011), could be constrained using the magnesium isotope composition ($\delta^{26}\text{Mg}$) of carbonates. However, no consensus yet exists on the evolution of the ocean $\delta^{26}\text{Mg}$ value for the Cenozoic (Pogge von Strandmann et al., 2014; Higgins and Schrag, 2012). One of the causes may reside in our lack of understanding of vital effects affecting Mg isotope fractionation during biogenic carbonate formation (Saulnier et al., 2012; Saenger and Wang, 2014). Indeed, elemental and isotope proxies in biogenic calcite are often subject to vital effects (Urey et al., 1951), which can be due to kinetic, metabolic, or

physiological effects (for a review, Weiner and Dove, 2003). The Mg isotopic composition of the oceans is relatively constant ($\delta^{26}\text{Mg}_{\text{sw}} = -0.82 \pm 0.01\text{‰}$ (2σ , $n = 26$), Foster et al., 2010), in agreement with its long residence time in the ocean (≈ 10 Myr, Berner and Berner, 1987; 14–16 Myr calculated from Lécuyer et al., 1990). The main input of Mg to the ocean is the weathering of the continental crust (Berner et al., 1983), and its transport to the oceans by rivers and groundwaters (Berner and Berner, 1996; Burnett et al., 2001; Holland, 2003). The main sinks are the alteration of the oceanic crust that takes place during hydrothermal activity (e.g. Michard and Albarède, 1986; Elderfield and Schulz, 1996), precipitation of marine carbonates, notably with dolomitisation (e.g. Ronov, 1956; Given and Wilkinson, 1987; Wilkinson and Algeo, 1989) and the formation of clays (Holland, 2005). The balance between input and output fluxes of Mg in the ocean having distinct isotopic compositions is recorded in the $\delta^{26}\text{Mg}$ value of seawater, which could allow to decipher the causes of its temporal variations.

Calcium carbonate precipitation experiments that were performed under controlled conditions help to decode the influence of parameters such as pH, temperature, the Mg/Ca ratio of the fluid and the growth rate (Immenhauser et al., 2010; Li et al., 2012; Saulnier et al., 2012; Wang et al., 2013; Mavromatis et al., 2013). Li et al. (2012) precipitated calcite over a large range of temperatures that match the main part of

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those prevailing on Earth surface, from 4 to 45 °C, and a weak gradient was observed between $\Delta^{26}\text{Mg}_{\text{cal-sol}}$ (Mg isotope fractionation factor between calcite and solution) and temperature ($0.011 \pm 0.002\text{‰}/^\circ\text{C}$). This result was consistent with the gradient obtained by Galy et al. (2002) on speleothems. No relationship between $\Delta^{26}\text{Mg}_{\text{cal-sol}}$ and pH or Mg/Ca of the solution was observed (see Saenger and Wang, 2014, for a review). A growth-rate dependency of $\Delta^{26}\text{Mg}_{\text{cal-sol}}$, characterised by a decrease in the magnesium isotope fractionation factor with an increase in the growth rate, was reported by Immenhauser et al. (2010), Saulnier et al. (2012) and Mavromatis et al. (2013).

Due to their low magnesium content (between ≈ 0.5 and 7 mol wt.% according to Lowenstam, 1961), brachiopod calcite (low magnesium calcite = LMC) is relatively resistant to diagenesis compared to aragonite or high magnesium calcite (HMC) (e.g. Brand and Veizer, 1980; Al-Aasm and Veizer, 1982). Brachiopod shells are often used for reconstructing the oxygen, carbon and strontium isotope evolution of seawater, as well as past environmental conditions such as marine productivity, salinity or temperature of seawater (e.g. Grossman et al., 1996; Veizer et al., 1999; Curry and Fallick, 2002; Brand et al., 2003; Korte et al., 2003, 2005, 2006; Farkas et al., 2012). Brachiopods, as marine environmental proxies, have also the advantage to occur worldwide in a depth range from intertidal to abyssal, and have been found in the geological record since the Cambrian (Rudwick, 1970). Only three studies reported $\delta^{26}\text{Mg}$ values of brachiopod shells (Hippler et al., 2009; Wombacher et al., 2011; Farkas et al., 2012), but no detailed information about vital effects, or processes responsible of them are available yet.

Here we report $\delta^{26}\text{Mg}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ values along with trace element contents of two modern brachiopod specimens (*Terebratalia transversa* and *Frieleia halli*) and one fossil specimen (*Terebratulina scillae*, 2.3 Ma). By combining $\delta^{26}\text{Mg}$ determinations with oxygen and carbon isotope compositions and trace element contents, we aim to look for possible shell geochemical heterogeneities in order to investigate the processes that control the Mg isotope composition of brachiopod shells. The results should provide new insights into the possible use of the magnesium isotope compositions of brachiopod shells as proxies of seawater $\delta^{26}\text{Mg}$.

2. Samples

The two modern brachiopods and the fossil one are all articulated types of brachiopod and their shells are made of calcite. *T. transversa* (Sowerby, 1846), Lamshell brachiopod, was collected alive, in October 2007, at La Jolla, California (32.8591 N, 117.2586 W), at a depth of 20 m. This species is mainly found in benthic environments along American coastlines. Most of the specimens from this species are between 4 and 6 cm length and the shell studied here was ≈ 4.6 cm long. At the time of collection, the temperature was around 14.5 °C and the salinity was about 33.5. The annual temperature range is between 11.5 and 16 °C, with a mean value of 15.2 °C based on the World Ocean Atlas 2013 (Locarnini et al., 2013). A live specimen of *F. halli* (Dall, 1895), a deep-sea brachiopod, was collected in March 2011, at San Diego Trough (32.60333 N, 117.54183 W) at a depth of 1210 m. The shell was about 1.5 cm long. The temperature at the time of collection was 3.5 °C and the salinity was 34.5. Over a one-year period, there is almost no temperature variation at this sampling location. For the two modern samples, hydrographic data are available at www.calcofi.org. A $\delta^{18}\text{O}_{\text{sw}}$ value of $\approx -0.2\text{‰}$ (V-SMOW), based on The Global Seawater Oxygen-18 Database, can be assumed at the sample sites (Epstein and Mayeda, 1953). The $\delta^{13}\text{C}$ value of DIC is assumed between 0.5 and 2‰, as measured by Santos et al. (2011) in Southern California during the period of the brachiopod growth.

The fossil brachiopod sample, *T. scillae* (Seguenza, 1871) was collected from Plio-quaternary sediments in Galina Calabre, Italy. The specimen was 2.5 cm long. A model age of 2.3 ± 0.3 Ma was determined by Sr isotope measurements ($^{87}\text{Sr}/^{86}\text{Sr} = 0.709092 \pm 0.000018, 2\sigma$).

3. Methods

3.1. Sampling strategy

In this study, we have chosen to measure on the same sample the isotopic compositions of oxygen, carbon and magnesium and the trace and major element compositions to get more insights on the mechanisms of precipitation of the brachiopod calcite. This strategy precludes the possibility to sample the brachiopod along the growth axis as in, e.g., Auclair et al. (2003) and von Allmen et al. (2010). Indeed, 5 to 10 mg of powders are needed for the oxygen and carbon isotopic analyses, and 15 mg for the measurements of magnesium isotopic compositions. For these measurements, this amount is necessary due to the low content of magnesium in brachiopod calcite and also to the high blank level. The analyses of trace and major elements were performed at Service d'Analyse des Roches et des Minéraux (SARM) national facility (Nancy, France). They normally needed about 1 g of material to perform this type of analyses. In this study, they decreased this amount down to ≈ 200 mg per sample. The sampling strategy of this study is thus a compromise between a rational sampling of the brachiopod shell and the quantity of material needed to perform the entire set of analyses.

3.2. Sample preparation

Brachiopod shells were first ultrasonicated in distilled water and a Dremel® smoother was used to remove the remaining dirt (mostly sediments). The primary layer (hereafter referred to as TP) of *T. transversa* (Fig. 1) was sampled for further analyses by grinding the outermost surface with a drill bit. The innermost layer of *T. transversa* (hereafter referred to as TI) was also sampled using the same method. The primary layer of the *T. scillae* sample was also removed using the same technique, but was not analysed.

The dorsal valve of *T. transversa* and the two valves of *T. scillae* were divided into several pieces using a cut-off wheel (Fig. 2). The entire shell of the *F. halli* specimen was sampled due to its small size. Samples were then ground in an agate mortar and separated into three different aliquots for analysing of their magnesium, oxygen and carbon isotope compositions and major and trace elements. This sampling procedure was specifically designed to investigate the spatial geochemical variations within a brachiopod shell.

3.3. Analytical techniques

Magnesium was separated from the carbonate matrix before the isotope measurements according to the procedure detailed in Bolou-Bi et al. (2009). Samples containing 50 μg of magnesium were passed once through anion exchange resin (AGMP-1M) and then three times through the cation exchange resin (Bio-Rad AG 50W-X12) (Bolou-Bi et al., 2009, 2010; Saulnier et al., 2012). This procedure was validated by passing in-house standard solution (MCS) with a Mg/Ca ratio of 0.01 mol/mol (Saulnier et al., 2012). The pure magnesium fraction obtained after chemical separation was first dissolved in concentrated nitric acid and then diluted to 0.05 M HNO_3 and 150–250 ppb Mg. Magnesium isotopes were measured using a Neptune Plus MC-ICP-MS (at CRPG, Nancy, France). The $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values were estimated using the standard-sample bracketing technique with the NIST-SRM980_{CRPG} standard solution in order to correct for instrumental mass bias. All results were then normalised to the international solution standard (DSM3) (Galy et al., 2003). Each acquisition consisted of one block of 35 measurements. The blank was not negligible (~ 30 mV on the ^{24}Mg) and was systematically subtracted. The $\delta^{26}\text{Mg}$ value of the MCS was $-1.67 \pm 0.07\text{‰}$ ($2\sigma_n$, $n = 7$) close to the value of the pure magnesium solution (PMS) used to make this standard ($-1.76 \pm 0.04\text{‰}$, $2\sigma_n$, $n = 8$). The accuracy and the reproducibility of the isotope measurements were assessed by repeated measurement of DSM3 and a pure solution of magnesium (MBO) (Saulnier et al., 2012). The $\delta^{26}\text{Mg}$

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