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Impact of diagenetic alteration on brachiopod shell magnesium isotope ($\delta^{26}Mg$) signatures: Experimental versus field data

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ABSTRACT

Due to their thermodynamically stable low-Mg calcite mineralogy, the shells of brachiopods are often counted among the most reliable archives of the physicochemical conditions that occurred during the Phanerozoic in marine waters. Consequently, traditional and non-traditional isotope and elemental proxy data from brachiopod valves have been analyzed in numerous studies and results obtained have been placed in context with ancient seawater properties. This paper tests the sensitivity of brachiopod shell magnesium isotope ($\delta^{26}Mg$) data to diagenetic alteration. We apply a dual approach by: (i) performing hydrothermal alteration experiments using meteoric, marine, and burial reactive fluids; and (ii) comparing these data to naturally altered, ancient brachiopod shells. The degree of alteration of individual shells is assessed by a combination of fluorescence and cathodoluminescence microscopy. The absence of luminescence might indicate both well-preserved shell material, but also the secondary enrichment of quenching elements such as iron along diagenetic pathways. Complementary oxygen isotope data provide insight into the question of open versus closed system behavior of brachiopod shells. Brachiopod shell magnesium isotope values respond to differential fluid temperature, chemistry, and experiment durations. The patterns observed are complicated by the interplay of kinetic and thermodynamic patterns and the presence of variable amounts of water soluble and water insoluble organic matter within these biominerals. Generally, the range in bulk $\delta^{26}Mg$ from experimentally altered (1.52‰) and that of bulk samples from ancient, diagenetically altered brachiopod valves (1.53‰) exceed the geochemical variability of $\delta^{26}Mg_{brachiopod}$ bulk values of most recent specimens (1.26‰) in the lower and upper range. More ^{26}Mg enriched (0.8‰) and more ^{26}Mg depleted (0.7‰) values, respectively, are found in altered shells in comparison to unaltered ones. The data shown here are considered significant for those aiming to reconstruct palaeoenvironmental parameters based on brachiopod archives. Consequently, we propose tentative guidelines for magnesium isotope research applied to ancient carbonates.

1. Introduction

Marine carbonates, i.e. abiogenic, biogenic, and organomineralic aragonites and calcites arguably represent the most important archives of Phanerozoic climate dynamics known to science (Veizer et al., 1999; Immenhauser et al., 2016). This is because these minerals, sediments, and sedimentary rocks record mineralogical, petrographic, ultrastructural, and geochemical patterns that bear evidence of the physicochemical parameters of their ambient marine environment at deposition or secretion (Steuber, 1996; Allison et al., 2010; Wierzbowski and Rogov, 2011). Conventionally, research has focused on traditional isotope systems such as those of carbon ($\delta^{13}C$), oxygen ($\delta^{18}O$), strontium ($^{87}Sr/^{86}Sr$), or on main and trace elemental patterns and ratios (e.g., Ca, Mg, Sr, Mn, Fe etc.; Lowenstam, 1961; Jones et al., 1994; van Geldern et al., 2006; Yan et al., 2013). More recently, the advent of MC-ICP-MS has triggered intense research of what is referred to as "non-traditional isotope systems" (e.g., $\delta^{26}Mg$, $\delta^{44/40}Ca$, $\delta^{56}Fe$, $\delta^{88/86}Sr$, etc.) as proxies in palaeoenvironmental research (Zhu and Macdougall, 1998; Beard et al., 2003; Böhm et al., 2006; Hippler et al., 2009; Foster et al., 2010; Conway and John, 2014; Noireaux et al., 2015; Mavromatis et al., 2015, 2016; Fruchter et al., 2016).

Next to calcium, magnesium is the major cation most involved in the carbon cycle and the reaction of atmospheric CO_2 with Ca and Mg from silicate minerals is a dominant component of the global climate system. In seawater, Mg is mainly present as free Mg aquo ion ($(Mg(OH_2)_6^{2+}$; Shirokova et al., 2013; Li et al., 2014). Dehydration of the free Mg aquo ions during the incorporation into the carbonate crystal lattice is

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arguably one of the most important parameters controlling the distribution of Mg isotopes between carbonate precipitates and fluids $\Delta^{26}Mg_{carb\text{-}fluid}$ (Mavromatis et al., 2013; Li et al., 2014; Gautier et al., 2014). Generally, $\Delta^{26}Mg_{carb\text{-}fluid}$ values are based on complex reactions and probably depend on amorphous calcium carbonate (ACC) precursors, ion attachment/detachment kinetics, surface entrapment, growth rates of the crystal, aqueous Mg speciation, carbonate mineralogy and temperature (Rustad et al., 2010; Immenhauser et al., 2010; Schauble, 2011; Saulnier et al., 2012; Walter et al., 2015; Purgstaller et al., 2016; Schott et al., 2016). In most cases, Mg substitutes for Ca in the carbonate calcite crystal lattice, whilst it forms Mg^{2+} cation layers alternating with Ca^{2+} layers in dolomites.

The magnesium isotope signature of recent marine biogenic carbonates (e.g., foraminifera, echinoderms, bivalves, brachiopods etc.) is now increasingly exploited and tested as a new proxy in (palaeo)environmental research (e.g., Hippler et al., 2009; Wombacher et al., 2011; Rollion-Bard et al., 2016). With reference to ancient organic (biominerals), inorganic (carbonate cements) and sedimentary carbonate archives (limestones, dolostones), however, the reported data is still scarce (see discussion in Geske et al., 2015a). A main obstacle to the interpretation and application of magnesium isotope signatures of ancient carbonates is the poorly known sensitivity of this proxy to early and later diagenetic resetting in the meteoric, marine, and burial diagenetic realm (Swart, 2015). So far, only a limited number of studies deal with the impact of diagenetic alteration on $\delta^{26}Mg$ of carbonate rocks (e.g., Higgins and Schrag, 2010, 2012; Geske et al., 2012, 2015a, 2015b; Fantle and Higgins, 2014; Mavromatis et al., 2014). Moreover, to the knowledge of the authors, so far only one paper has dealt with magnesium isotopes in biogenic carbonates from the viewpoint of diagenesis research (foraminifera; Higgins and Schrag, 2012).

In order to obtain quantitative data on the sensitivity of magnesium isotopes in biogenic carbonates, we performed hydrothermal alteration experiments using the shells of recent brachiopods. The outcome of experimental work was compared with data from altered brachiopod shells from the geological rock record. Alteration experiments on brachiopod shells were performed using solutions representing meteoric, marine, and burial aqueous fluids as well as two temperature sets (100 °C and 175 °C). The aims of this study are threefold: (i) to determine the impact of different solutions and temperature conditions on the Mg isotopic composition of brachiopod shells; (ii) to compare the findings of these experiments with $\delta^{26}Mg$ data of fossil shell material. This was performed with the intention to test the applicability of experimental data to proxy data from geologically altered carbonate archives and (iii) based on these data to compile tentative guidelines for magnesium isotope research applied to ancient carbonates.

2. Materials and methods

The following terminology is applied: data described below include that from geochemical and optical-microscopic tools. The materials analyzed include brachiopod shells, and various aqueous fluids. We distinguish: (i) initial experimental aqueous fluids referring to the geochemistry of fluids at the onset of the experiment (meteoric, marine, or burial type) and (ii) reactive fluids, referring to the initial aqueous fluids having undergone increasing chemical or physical alteration during the experiment.

2.1. Study material

The shells of recent brachiopods (each comprising two corresponding valves) represent the experimental test materials used for this study. Living specimens of the species *Terebratalia transversa* were collected in Friday Harbor, Washington, USA (48°31.51′11″N; 122°59.59′ 87″W). Given that brachiopod shells consist of low Mg-calcite (LMC), they are significantly less sensitive to post-mortem dissolution-reprecipitation processes compared to for example aragonitic shells (e.g., Brand and Veizer, 1980). The limited diagenetic reactivity poses a potential obstacle for those aiming to assess patterns of diagenetic overprint in brachiopods under experimental conditions. This is because long-term alteration experiments are needed to significantly affect the dense brachiopod shell ultrastructure. In order to enhance the reactivity of brachiopod LMC, punctate brachiopods (punctuation = open channels in the shell wall known from different taxa of articulate brachiopods; e.g. Oleneva, 2014) were chosen. These shells offer a larger reactive surface area compared to the dense, impunctate brachiopods forming the main archive organisms in palaeoceanography. The soft tissue was removed using a scalpel and a pair of tweezers. The ventral valve was archived, whilst the dorsal one (Fig. 1a) was exposed to hydrothermal alteration experiments. Experimental data were compared with data from four ancient brachiopod shells: *Rhynchonella* sp. (Cretaceous, Morocco), *Cyrtospirifer grabauti* (Devonian, France), *Platyotrophia laticostata* (Ordovician, USA), and *Gibbirhynchia auviceps* (Jurassic, Germany).

2.2. Experimental setup

The alteration experiments were performed at the Graz University of Technology (Austria). A total of 48 brachiopod valves were altered using different solutions, temperatures, and experimental durations. Three different solutions were used reflecting meteoric, marine, and burial aqueous fluids. The meteoric fluid contained 10 mM NaCl, whilst the fluid representing the burial regime contained 100 mM NaCl and 10 mM $MgCl_2$. Seawater from the North Sea was treated with $BaCl_2$ to reduce SO_4^{2-} concentrations and subsequently was used as the marine

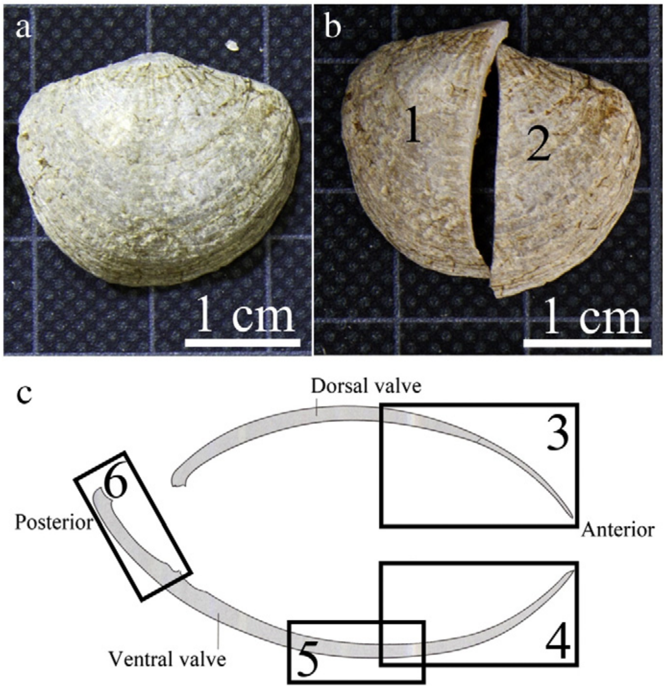

Fig. 1. a) Dorsal valve of *Terebratalia transversa* prior to hydrothermal alteration experiment. b) Dorsal valve of *Terebratalia transversa* after hydrothermal alteration experiment. The valve was sawn along the growth axis. The half marked with number 1 was used for thin sections and the one marked with number 2 was used for geochemical analyses. c) Schematics of the sampling strategy for geochemical analyses: Rectangle numbered 3 displays the part of the dorsal valve that was used for geochemical analyses of all experimentally altered brachiopods and one ancient brachiopod specimen (CHA-B-037). Rectangle numbered 4 displays the part of the ventral valve used for the unaltered brachiopods, whilst the ones numbered 5 and 6 display the sampling areas used for the ancient brachiopod CHA-B-001 and CHA-B-038/CHA-B-039, respectively.