Mg Isotopes in Phanerozoic Brachiopods

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Abstract

This literature review summarizes information on Mg isotopes as a paleoenvironmental tool, together with applied methodologies, advanced analytics, as well as current state of research. Furthermore, the focus and the sample materials of the main research are described. The priorities are to generate a Phanerozoic Mg isotope record based on the analyses of Brachiopod shells. This will make it possible to draw conclusions on the oceanic Mg cycle, hydrothermal fluxes, and dolomitization events in oder to contribute valuable knowledge to research in this field.

1. INTRODUCTION

Magnesium is an alkaline earth element that is lithophile, mobile, soluble, and occurs as conservative ion in water, i.e. its concentration varies only in proportion to salinity [1]. The global (bio-)geochemical cycles of Mg and Ca are closely linked together and contribute significantly to the consumption of atmospheric CO_2. Climate change is coupled with the oceanic Mg/Ca ratio, e.g. cooling over the Cenozoic was accompanied by an enrichment of Mg over Ca [2]. Mg isotopic ratios in the ocean, which in turn vary by the underlying processes of the relative Mg excess, such as continental weathering and carbonate precipitation, represent an ideal tracer for the relative contribution from sources of input fluxes. However, the linkage of climate and seawater chemistry is not well understood, even though it has been clearly proven. The interest is therefore intense to gain further knowledge.

The Mg isotope system is among the unconventional ones and investigations on Mg isotope variability are made possible recently only with the advent of Multicollector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS). Early investigations on Mg isotope variations using Thermal Ionisation Mass Spectrometry (TIMS) were limited to 1 to 2 ‰ uncertainty. Galy et al. [3, 4] applied new techniques and demonstrated an improvement about one order of magnitude for the discrimination of Mg isotope ratios. Recently, the long-term reproducibility, based on 4-year analyses of olivine and seawater samples, of ≤0.05 and ≤0.07 ‰ for $\delta^{25}Mg$ and $\delta^{26}Mg$ (2σ) was achieved [5]. Thus, the approximate overall natural $\delta^{26}Mg$ range of 5 ‰ in terrestrial materials [2, 6, 7] (see fig. 1) varies outside current uncertainty.
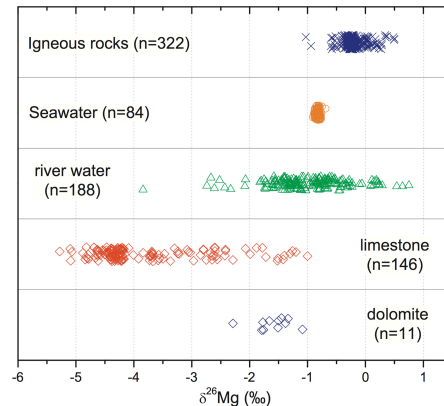

**Figure 1:** *Natural variation of $\delta^{26}Mg$ values of important geological reservoirs after [8].*

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For the current research, Mg isotope ratios from calcitic shells of Brachiopods will be studied. Brachiopod shells are biomineralised calcitic skeletons synthesised by long-lived, long ranging, extant marine organisms [9]. The prevailing (physico-)chemical information of the adjacent marine environment is built into the valves and can be preserved [10]. Brachiopods can precipitate low-Mg calcite (LMC)[1] shell layers [9], that are relatively diagenetically stable and retain their primary marine isotopic signal. Thus, shells could be used to study elemental or isotopic ratios in the ocean for the time they were built. For example, the utilisation of Mg as a proxy for marine temperatures as mentioned above, i.e. as a paleothermometer or palaeoseasonality proxy in the carbonate skeleton shells of brachiopods have been reported in the light of the ratio of Mg/Ca by measuring intra-shell variations by LA-ICP-MS [9]. Moreover, Brachiopod shells can be a useful proxy for Mg isotope composition of seawater, which reflects e.g. continental weathering, dolomitization and hydrothermal activity [11] cf. section 2.2. However, vital effects and analytical uncertainties will limit the use as e.g. paleothermometer. In order to gain more knowledge, the tools being used include modern and fossil calcitic shells from Brachiopods, as well as brood experiments for proxy calibration. The acquired δ^{26}Mg data from both modern and fossil samples, and the generated marine δ^{26}Mg trends (i.e., time-series), will be used to model the oceanic Mg cycle during the Phanerozoic.

2. THEORY

2.1. Biogeochemical cycle of Mg

The biogeochemical cycling of Mg is intimately linked to the global C cycle. The generalized *Urey reaction* eq. (1) represents the weathering of both Mg and Ca silicates with the associated simultaneous consumption of atmospheric CO_2.

$$CO_2 + CaSiO_3 \longrightarrow CaCO_3 + SiO_2 \qquad (1)$$
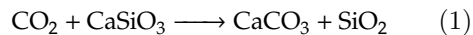
[1]<4 mol % $MgCO_3$

Equation (1) can be extended with Mg being involved, that can be coprecipitated with Calcium (Ca) to form dolomite (eq. (2)).

$$CO_2 + (Ca, Mg)SiO_3 \longrightarrow (Ca, Mg)CO_3 + SiO_2 \quad (2)$$
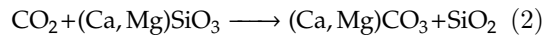
The weathering products (Ca^{2+}, Mg^{2+} and HCO_3^-) are transported to the ocean by rivers and precipitated on site as Ca and Mg carbonates in the sediments [12]. The overall reaction for marine precipitation or dissolution of calcium carbonate is often referred to as wet dissolution-reprecipitation reaction and can be written as eqs. (3) and (4).

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2 \qquad (3)$$

$$Mg(HCO_3)_2 \longrightarrow MgCO_3 + H_2O + CO_2 \qquad (4)$$

2.2. Mg isotopes

MC-ICP-MS techniques enabled to measure Mg isotope ratios driven by chemical fractionations with sufficient precision. Magnesium isotope ratios as a paleoenvironmental tracer are particularly well suited for surface processes, such as continental weathering [6, 8, 13]. A short non-exhaustive overview about relevant examples based on chemical fractionation of Mg isotopes follows. Huang et al. [14] reported on the enrichment of residues during dissolution at weathering of basalts, whereas Ryu et al. [15] observed only little fractionation in granites. Magnesium-clays are modestly enriched in δ^{26}Mg, Mg carbonates are depleted by 1 to 4 ‰ relative to the precipitation solution [4, 6, 13, 16–18]. Further studies on carbonates such as dolomites e.g. [7, 19, 20], (a-)biotic calcite [8, 13, 21–24], as well as cave carbonates [4, 25, 26] have been examined. Investigations on Mg fractionation in biogenic carbonates were carried out but show a low fractionation between carbonate mineral and solution for the LMC of Brachiopods [11]. Magnesium isotopic studies on pore waters of marine sediments [16], as well as on riverine fluxes into the ocean were published. Tipper et al. [6] analysed Mg isotopes in 45 rivers covering 30 % of the global Mg riverine

flux to the ocean (see fig. 2) and found a range of riverine δ^{26}Mg of 2.5 ‰, half the varation in terrestrial rock.
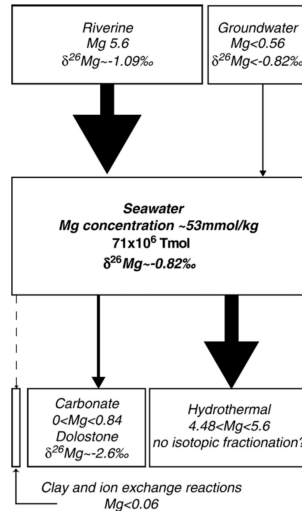

Figure 2: *Schematic overview on the main Mg cycle, with estimates of fluxes in* Tmol yr^{-1} *after [6]*

The global runoff δ^{26}Mg has been estimated at −1.09 ‰ distinct from seawtater at −0.82 ‰ relative to DSM-3 (see section 2.3). This implies that the the ocean is either not in steady state with respect to Mg isotope ratios, or Mg isotope ratios must be fractionated [6]. However, the variation of Mg isotopic rations can reflect the relative contributions of changes in silicate or carbonate input to the global Mg budget. Tipper et al. [6] postulated that the difference of global runoff and seawater is consistent with fractionation by carbonate precipitation.

2.3. Reference materials

In order to correct the Mg instrumental mass bias, reference materials are required. The initially widespread NIST-SRM 980, a purified Mg metal standard, was proven to be heterogeneous. Today, Mg isotope data is usually reported relative to DSM-3 by Galy et al. [27]. This reference material consists of 10 g Mg metal extracted from the Dead Sea. It is already in solution, and therefore immune to heterogeneity [27]. The $\delta^{26}Mg_{SRM980}$ data

can be approximately converted using $\delta^{26}Mg = \delta^{26}Mg_{SRM980} + 3.405$ [28]. Although DSM-3 has been frequently applied, it is not a standard certified or issued by a reference material institute [29] and generally, there is still no interlaboratory consensus on one suitable Mg reference material. Teng and Yang [30] published Mg isotope compositions for 24 reference materials, the long-term reproducibility for δ^{25}Mg was 0.05 ‰ and for δ^{26}Mg 0.07 ‰.

3. METHODOLOGY

3.1. Notation

With ^{26}Mg, ^{25}Mg, and ^{24}Mg the Mg isotope system has three stable isotopes with relative abundances of 11.01 %, 10.00 %, and 78.99 % [1]. Mg isotopic studies are reported using the standard per mil (‰) notation relative to those of the reference standard.

$$\delta^{25,26}\text{Mg} = \left[\frac{(^{25,26}\text{Mg}/^{24}\text{Mg})_{\text{sample}}}{(^{25,26}\text{Mg}/^{24}\text{Mg})_{\text{standard}}} - 1 \right] \times 10^3 \quad (5)$$

Initially the δ notation was applied for the decay of δ^{26}Al to radiogenic δ^{26}Mg but to be consistent with other stable isotope systems it was adapted to mass fractionation effects. The δ^{25}Mg is reserved for mass independent fractionation analogous to, e.g. Δ^{33}S, and δ^{26}Mg* to radiogenic variations in δ^{26}Mg.

3.2. Analytical considerations

Magnesium isotope studies based on mass fractionation were only made possible by the advancement in mass spectrometry, i.e. the advent of MC-ICP-MS. The Faradey cup collectors of MC-ICP-MS are used to simultaneously measure all three Mg isotopes, thus instrumental bias can be monitored precisely. For the Mg isotope system the standard-sample bracketing method [3] is used to correct the internal mass bias. Magnesium isotope ratios can be, in contrast to earlier studies, resolved more precise about an order in magnitude.

However, proxy analyses on skeletal carbonates can be problematic because 1) proxies re-

spond to more than one environmental parameter and 2) due to "vital effects" during biomineralisation [21]. Furthermore, it needs to be taken into account that shell structures of different brachiopod species vary and the primary layers of the shells need to be extracted exclusively prior to separation, in order to produce satisfactory analytes. These aspects will be carefully considered during this project.

3.3. Mg chromatographic separation

The validity of isotope ratio values measured by MC-ICP-MS largely depends on the quality Mg purification, i.e. the separation of matrices. Purification is accomplished by eluting samples through columns with cation resins, commonly Bio-Rad AG® 50W-X12 [31–34] and Bio-Rad AG® A550W-X8 [35–37]. In the case of calcitic shells Na, Sr, Fe and especially Ca, which in doubly charged state interferes with $\delta^{24}Mg$, can disturb Mg isotope mass signals. Most Mg purification methods are based on chromatographic column separation through volumetric elution in various samples [21, 28, 34, 36, 38–42]. Reports on methods using a single step strategy [6, 13, 21, 26, 37, 43, 44], as well as two-stepped approaches, e.g. [8, 34, 42, 45] exist. However, there is no standard procedure and the calibration of columns should be considered.

4. Summary (research aims)

The current research will address the following aspects:

- Improve the efficiency of already established Mg purification protocols.
- Generate Mg isotope data from modern and selected Phanerozoic fossil Brachiopods.
- Test selected samples of laboratory-grown specimens (proxy calibration).
- Model the oceanic Mg cycle over geologic timescales.
- Draw implications on changing rates of hydrothermal activity vs. dolomite formation.

- Investigations on the coupled approach $\delta^{26}Mg$ and δ^7Li to shed light on the possible role of marine clay formation (i.e. reverse weathering and on the long-term evolution of marine Mg/Ca ratios).

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