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# 1 Introduction

Magnesium (Mg) is the fourth most abundant species in seawater [1], and the eighth most abundant element in the continental crust [2]; it is a major constituent of both silicate and carbonate minerals. Its transfer from rocks to the hydrosphere via chemical weathering on the continents and its return to rocks via (1) exchange with hydrothermal fluids at mid-ocean ridges [3, 4], (2) through carbonate sedimentation [5] and (3) through the formation of clays in the ocean (sometimes referred to as reverse weathering) [6] constitutes one of the major planetary global biogeochemical cycles. Secular variations in the Mg concentration of seawater over geological time, inferred from either fluid inclusions or the Mg/Ca ratio of marine carbonates, likely record changes in the balance between the inputs and outputs of Mg, providing an archive of this major geochemical cycle through Earth history. These records of oceanic Mg/Ca through time have been significantly refined in the last decade [7–15]. This is of fundamental significance to planetary history. For example, the rate of mid-ocean ridge spreading determines the rate of removal of Mg from seawater via modern hydrothermal circulation, one of the key mechanisms for cooling the oceanic crust [16]. The Mg/Ca ratio of seawater has a key role in regulating the main carbonate mineralogy from the ocean, aragonite, calcite or dolomite [5, 17], and as such it exerts a major influence on the biosphere. The chemical weathering of Mg-bearing silicates on the continents and the removal of Mg from seawater via low-temperature hydrothermal circulation may play a fundamental role in regulating planetary temperatures [18, 19], providing a negative temperature-dependent climate feedback.

Despite the fundamental role of oceanic Mg in planetary evolutionary history, the relative importance of the main inputs and outputs of Mg from the oceans remains debated, controversial and difficult to precisely constrain. For example, the hydrothermal sink of Mg has been estimated to range from 40 to 100 per cent of the total flux of Mg from the oceans relative to the dolomite sink that could vary from 0 to 60 per cent [17, 20, 21].

A potentially transformative tool to resolve the oceanic budget of Mg, both today and through planetary history, is the measurement of Mg stable isotope ratios. Mg has three stable isotopes, $^{24}$Mg, $^{25}$Mg and $^{26}$Mg, in the relative abundances of 78.99, 10 and 11.01 per cent respectively [22]. Although first measured in the 1960s [23], routine, reliable and precise measurements only became common in the year 2000 with the development of new multi-collector, inductively coupled plasma mass spectrometers (MC-ICP-MS) [24]. The use of Mg isotopes to constrain the oceanic budget of Mg was first attempted in 2006, presenting initial data of the inputs and outputs and summarising the

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problem [25]. Since that time, thousands of new measurements have been published, including records through time of marine carbonates thought to trace past seawater, with the potential to unlock the decades-old controversy of the global biochemical cycle of Mg. However, the records are still discrepant, and the extent to which diagenesis could influence some records remains underexplored [26]. The purpose of this Element is to provide a progress update on the oceanic budget of Mg, both in the present day and through the Cenozoic era, from a Mg isotope perspective. The pitfalls in the data and analysis are discussed, but the potential of Mg isotopes, a proxy still in its infancy, as a tracer to decipher seawater history and as one of the most important global biogeochemical cycles through time is emphasised.

### BOX 1 MG ISOTOPE NOTATION

Deviations in the $^{26}$Mg/$^{24}$Mg and $^{25}$Mg/$^{24}$Mg ratios are expressed in per mil (parts per thousand) notation as:

$$\delta^{X}Mg = 1000 \cdot \left\{ \frac{\left(\frac{^{X}Mg}{^{24}Mg}\right)_{sample}}{\left(\frac{^{X}Mg}{^{24}Mg}\right)_{standard}} - 1 \right\}, \tag{1}$$

where X refers to to either $^{25}$Mg or $^{26}$Mg, and the standard used in almost all publications is the Dead Sea Mg (DSM3) standard.

A prerequisite of analysis is that only solutions of pure Mg can be introduced into the mass spectrometer (< 5% other contaminant ions). Pure solutions are typically obtained by ion chromatography through many different methods. One difficulty is that Mg isotope ratios are fractionated by the chromatographic procedure, and that no Mg can be lost. It is therefore essential to continually process standards through the entire chromatographic process [27, 28]. Many studies collect a pre- and post-cut on either side of the Mg elution from column chemistry to verify that no Mg is lost. The majority of studies report the results of such standards with a similar matrix (chemical composition) to the samples. Unlike many other stable isotope isotope systems, the vast majority of analyses have not used a double-spike method (though it is technically possible) [29] because there are only three isotopes available. This makes 100% recovery even more important.

## 2 What Do Mg Isotopes Promise?

The key promise of Mg isotopes stems from the total terrestrial range in excess of 7‰ (Fig. 1) in the $^{26}$Mg/$^{24}$Mg ratio, meaning that on the one hand $\delta^{26}$Mg values are a valuable tracer of different sources of Mg but on the other hand a tracer of the processes that give rise to the 7‰ terrestrial variation. The average terrestrial silicate composition at the Earth's surface is well represented by the mean value of measurements of silicate rocks at −0.32‰ with well over 1,000 measurements [30] (standard deviation provided in Table 3). The rest of the terrestrial variability has likely developed because of mass-dependent fractionation (Box 2) induced by chemical and/or mineralogical reactions.

### Box 2 Mass-Dependent Fractionation

Mass-dependent fractionation is either an equilibrium (quantum mechanical) or a kinetic (classical mechanics) phenomenon that induces preferential transport or incorporation of one isotope relative to another during a chemical or mineralogical reaction. All substances are stabilised by the incorporation of the colloquially named 'heavy isotope', [31] $^{26}$Mg in the case of Mg, which lowers the energy of a phase in proportion to the inverse square root of the mass. Some phases, however, can minimise their energy more relative to others because of their bonding environment. A fractionation factor between two phases A and B is defined as the isotopic ratio in phase A divided by the isotopic ratio of phase B when these phases are in chemical equilibrium. This ratio is commonly denoted by the Greek letter $\alpha$, and the difference in delta notation is approximately equal to:

$$\delta^{26}Mg_A - \delta^{26}Mg_B = 1000 \cdot \ln(\alpha) = 1000 \cdot \ln\left\{\frac{\left(\frac{^{26}Mg}{^{24}Mg}\right)_A}{\left(\frac{^{26}Mg}{^{24}Mg}\right)_B}\right\}. \tag{2}$$

Any fractionation of the $^{25}$Mg/$^{24}$Mg ratio is related to the $^{26}$Mg/$^{24}$Mg ratio but is scaled by 0.520 (in the case of equilibrium fractionation) and known as mass-dependent fractionation [32]. There have been major advances in (1) the quantum mechanical calculation of equilibrium fractionation factors in the past two decades [33, 34] (known as density functional theory) and (2) experimental studies that determine fractionation factors [35, 36]. Key findings are that all carbonate minerals and some clays have an affinity for $^{24}$Mg [34, 36], meaning that carbonate minerals have a lower $\delta^{26}$Mg than the aqueous solution they precipitated from. This observation is qualitatively consistent with the distinct Mg bonding environment in the carbonate mineral compared to the fluid phase, as reflected by the average Mg-O distance, with the fluid having shorter (higher vibrational frequency) Mg-O bond lengths that can be stabilised to a greater extent by incorporation of

$^{26}$Mg. For example, the enrichment of brucite, magnesite and dolomite in $^{24}$Mg is consistent with the longer average Mg-O distance in these minerals compared to aqueous $Mg^{2+}$ [37].

Carbonate minerals show the greatest difference or degree of fractionation from silicate rocks. Modern marine carbonates show a very wide range of 6‰ for $\delta^{26}$Mg values, depending on mineralogy, such as dolomite (−1.9‰), high-Mg calcite (−2.6‰), low-Mg calcite (−3.7‰) and aragonite (−1.9‰). These contemporary marine carbonate phases have formed from modern seawater which has a very tightly defined value of −0.82‰, demonstrating the affinity of $^{24}$Mg for all carbonate minerals (see Box 2 for an explanation and Box 3 for a more detailed summary). The differences in the $\delta^{26}$Mg of carbonate minerals almost certainly arise from (1) differences in the bonding environments of Mg within the different carbonate minerals, (2) the mechanism of incorporation of Mg into the carbonate mineral (biomineralisation). For example, the calcitic microorganisms foraminifera and coccoliths both construct their tests from low-Mg calcite, but their $\delta^{26}$Mg typically differs by $> 2$‰ (Box 3) [38]. This difference is likely caused by biological processes during bio-crystallisation and illustrates the potential of Mg isotopes to trace and understand those processes. Thirdly, crystallisation rate (kinetics) has been shown to exert a major influence on the $\delta^{26}$Mg of inorganic calcite [35]. A higher precipitation rate reduces the difference between $\delta^{26}$Mg in the carbonate mineral and the fluid. This is thought to be because the limiting step for carbonate precipitation is the dehydration kinetics of the Ca and Mg ions. These dehydration kinetics are thought to be five orders of magnitude slower for Mg than for Ca, meaning that very slow precipitation rates are required to reach isotopic equilibrium in principle [35]. It is hoped that Mg isotopes will provide a window into these precipitation mechanisms.

The terrestrial hydrosphere (defined here as river waters, groundwaters, soil pore waters and cave drip waters) also shows a wide range in $\delta^{26}$Mg values from approximately 0 to −3‰ with a mean $\delta^{26}$Mg value of −1.08‰ (Fig. 1, Box 3) [25]. This composition of terrestrial waters is intermediate between carbonate and silicate minerals (the principal sources of aqueous Mg through mineral dissolution) and highlights one of the key potential applications of Mg isotopes: quantifying the proportion of carbonate and silicate Mg released to the hydrosphere. This variability in sources is present only because of mass-dependent fractionation in the first place, but this fractionation is also a challenge for partitioning sources. In addition to the source effect arising from carbonate and silicate rocks, $\delta^{26}$Mg values are subject to mass-dependent fractionation. For example, both the uptake of Mg in the biosphere by plants [39] and the formation of secondary mineral phases on the continents during chemical weathering fractionate Mg isotopes, meaning that Mg isotopes might make a useful tracer of these processes. Many aspects of geochemistry are challenged by the source-versus-process issue, and the Mg isotope budget of the modern ocean is an ideal illustration of this problem.

### BOX 3 SUMMARY OF THE $\delta^{26}$MG VALUES OF THE MAIN TERRESTRIAL RESERVOIRS

| Type | Mineralogy | median | mean | Standard deviation | Max | Min | n |
|---|---|---|---|---|---|---|---|
| Marine Carbonate | | −3 | −3.3 | 1.2 | −1 | −5.6 | 551 |
| Sponge | Aragonite | −2.6 | −2.4 | 0.7 | −3.2 | −1.5 | 13 |
| Coral | Aragonite | −1.8 | −1.8 | 0.1 | −2.2 | −1.5 | 80 |
| Coral | HMC | −3.5 | −3.5 | 0.1 | −3.5 | −3.4 | 2 |
| Foraminifera | HMC | −3.3 | −3.1 | 0.4 | −3.7 | −2.5 | 9 |
| Sponge | HMC | −3.2 | −3.2 | 0.1 | −3.4 | −3.2 | 6 |
| Coralline algae | HMC | −3.2 | −3.2 | 0.1 | −3.2 | −3 | 9 |
| Echinoderm | HMC | −2.2 | −2.1 | 0.6 | −2.8 | −1.3 | 30 |
| Foraminifera | LMC | −4.7 | −4.7 | 0.4 | −5.6 | −4 | 83 |
| Mollusc | LMC | −4.6 | −4.4 | 0.5 | −5.1 | −3.4 | 15 |
| Echinoderm | LMC | −3 | −3.2 | 1 | −5.5 | −1.3 | 55 |
| Brachiopod | LMC | −2.3 | −2.3 | 0.5 | −4 | −1.4 | 57 |
| Coccolithophore | LMC | −1.9 | −1.9 | 0.9 | −3.1 | −1 | 8 |
| Dolomite | | −2 | −1.9 | 0.6 | 0.4 | −3.8 | 412 |
| Terrestrial Water | | −1 | −1.1 | 0.5 | 0.6 | −3.9 | 831 |
| Seawater | | −0.8 | −0.8 | < 0.1 | −0.6 | −0.9 | 71 |
| Silicate Rock | | −0.3 | −0.3 | 0.4 | 1 | −3.1 | 1206 |
| Soil | | −0.2 | −0.1 | 0.5 | 1.8 | −1.3 | 252 |

Note: LMC refers to low-Mg calcite, and HMC refers to high-Mg calcite.

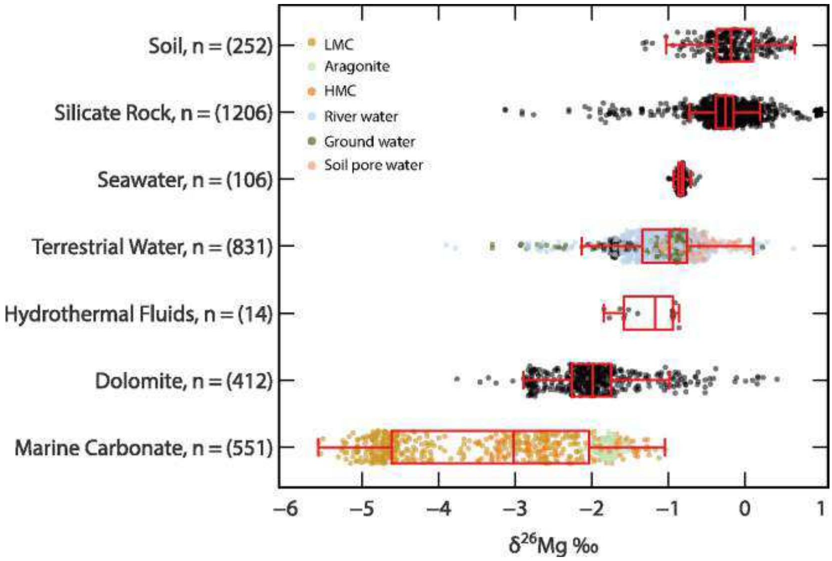

**Figure 1** Summary of $\delta^{26}$Mg values in the main terrestrial reservoirs of Mg.

### Box 4 Fractionation Associated with Clay Minerals (Phyllosilicates)

The direction and magnitude of magnesium (Mg) isotope fractionation associated with the formation of clay minerals is fundamental to the use of Mg isotopes to decipher the biogeochemical cycling of Mg both in the critical zone and for the oceanic Mg budget. Clay minerals, which form in both the continental and marine realms, contain appreciable amounts of Mg, and several recent studies have highlighted the formation of marine clays as being key regulators of both the global cycle of Mg and the carbon cycle through reverse weathering processes [6, 40]. Some of the first studies on riverine Mg noted that river waters draining first-order catchments with only silicate rocks are nearly always enriched in $^{24}$Mg relative to silicate rocks [41, 42]. This was interpreted to result from the formation of clay minerals preferentially incorporating $^{26}$Mg. This is consistent with soil showing a subtle enrichment in $^{26}$Mg in soils at a global scale (Fig. 1) [39, 43, 44]. However, in contrast, at a local scale some field studies have inferred that clays are enriched in $^{24}$Mg [45–47].

There are at least two potential mineralogical sites for Mg in a clay mineral: (1) structurally bound Mg in octahedrally coordinated lattice sites and (2) loosely bound adsorbed or exchangeable Mg sites associated with surface or interlayer negative charges. Each of these sites may have its

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More Information

own fractionation factor. Some field studies have endeavoured to distinguish fractionation factors associated with each mineralogical site [48, 49]. Experimental work has also tried to determine the fractionation factors associated with clays and to distinguish between different lattice sites. In addition, phyllosilicate minerals kerolite and lizardite are enriched in $^{26}$Mg [50] whereas hectorite, chrysotile and brucite (with one exception) [51] are enriched in $^{24}$Mg [36, 37].

These contrasting enrichments in $^{24}$Mg or $^{26}$Mg are predicted from the relative bond lengths of these minerals.

## 3 The Modern Oceanic Budget System

There is a large oceanic reservoir of Mg with a concentration of 53 mmol/l. This means that the residence time (defined as the ratio of the reservoir size to the output flux) is long (> 10 Ma) and much greater than the mixing time of the oceans (∼1,000 yrs), meaning that both the concentration and the isotopic composition of the ocean are uniform. The isotopic composition of seawater is perhaps the most homogenous reservoir of Mg on the planet with a $\delta^{26}$Mg of −0.82‰. This concentration and isotopic composition is maintained by inputs (rivers and groundwaters) and outputs (hydrothermal circulation and carbonate formation) as summarised in Fig. 2.

### 3.1 Inputs to the Modern Ocean

Mg is continually supplied to the oceans by rivers [25] and groundwaters [52], with average $\delta^{26}$Mg of −1.08‰. This is very similar to the flux weighted mean of large rivers where ∼50 per cent of the flux was sampled [25]. This agreement between the flux weighted mean and the overall average of terrestrial fresh waters is encouraging, suggesting that the input flux to the oceans is well constrained in the modern system. However, the wide range of terrestrial waters (Fig. 1) means that there is scope for the terrestrial $\delta^{26}$Mg to have changed in the past. It is noteworthy, for example, that rivers draining basalt have $\delta^{26}$Mg values that are higher than the terrestrial mean value [45], giving rise to the possibility that during the emplacement and weathering of large continental flood basalt provinces the $\delta^{26}$Mg of the continental input to seawater may adjust to higher values. Alternatively, during periods of orogenesis, when continental margin sedimentary sequences tend to be exhumed and weathered, a shift to a greater amount of carbonate weathering would lower the $\delta^{26}$Mg of the continental output.

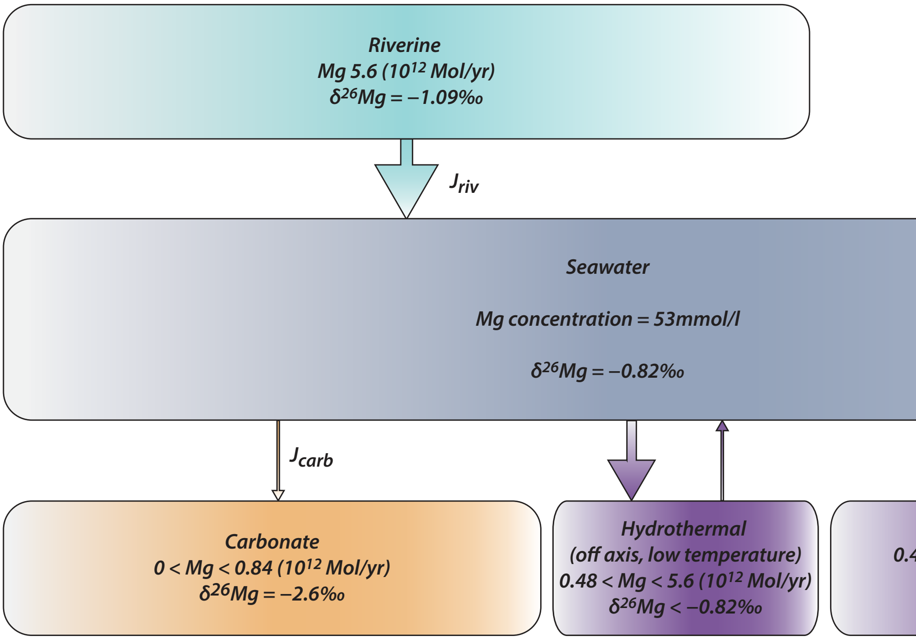

**Figure 2** Summary of the modern oceanic budget of Mg showing the main fluxes to and fron
magnitude in Tmol/yr and isotopic composition in per mil.

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Excerpt
More Information

In the modern system, the $\delta^{26}$Mg value of the continental input to seawater is lower than seawater $\delta^{26}$Mg values by $< 0.3‰$. This relatively small difference can only be explained by one or a combination of three mechanisms:

1. There is an additional supply of Mg enriched in $^{26}$Mg.
2. The processes which remove Mg from the ocean fractionate Mg isotope ratios.
3. The current system is not in steady state.

These mechanisms are explored below.

## 3.2 Outputs

Mg is continually removed from seawater by (1) hydrothermal circulation and (2) carbonate formation (Fig. 2). Hydrothermal circulation can be distinguished into two forms: high-temperature hydrothermal flow close to the ridge axis, and low-temperature, off-axis hydrothermal flow (Fig. 2) [17]. The removal of Mg from seawater via high-temperature hydrothermal circulation is thought to be quantitative because hydrothermal fluids collected from black smokers are highly depleted in Mg (< 5 per cent of the seawater value) [53]. Because this removal of Mg from seawater is quantitative, it is not accompanied by an isotopic fractionation because there is no return flux to seawater. Therefore, Mg removed via high-temperature hydrothermal circulation is removed with the $\delta^{26}$Mg value of seawater itself. The relatively small difference in the $\delta^{26}$Mg values of the inputs to seawater and seawater itself of $< 0.3‰$ is consistent with high-temperature hydrothermal circulation being the dominant sink of Mg, with no isotopic fractionation [17].

Low-temperature, off-axis circulation is, on the other hand, not quantitative. Measurements of $\delta^{26}$Mg in low-temperature hydrothermal fluids from the Juan de Fuca and Cocos plates yield $\delta^{26}$Mg values that are strongly offset to values lower than that of seawater (Fig. 1) [17]. Because of the difficulty in sampling hydrothermal fluids, it was previously hypothesised that the Mg in off-axis hydrothermal fluid samples could have resulted from seawater contamination. However, the significant offset in $\delta^{26}$Mg values between low-temperature hydrothermal fluids and seawater implies that even if there is seawater contamination during sampling, there must be a process that fractionates Mg isotope ratios during low-temperature hydrothermal circulation. Continental hydrothermal fluids flowing through Icelandic basalts are affected by a similar process [54].

This process is likely the formation of low-temperature secondary minerals, in particular smectites (clays), within the oceanic crust. The enrichment of low-temperature hydrothermal fluids in $^{24}$Mg is consistent with measurements of altered oceanic crust from the Troodos ophiolite and altered pacific MORB [55], which are enriched in $^{26}$Mg. The samples from the Troodos contain up to 66 per cent smectite, perhaps indicating an unusually high degree of alteration from MORB. Some of this chemical/mineralogical alteration could have occurred during post-tectonic exhumation. Nevertheless, this pairing of $^{24}$Mg-enriched fluids with $^{26}$Mg-enriched altered oceanic crust suggests that in the field, the smectites associated with hydrothermal circulation have an affinity for $^{26}$Mg (see Box 4 for further discussion about the Mg isotope fractionation factors into phyllosillicates). The net result of hydrothermal circulation is therefore that the inputs to seawater are more enriched in $^{24}$Mg than seawater itself. This fractionated removal of $^{26}$Mg to the oceanic crust effectively means that there is a return flux of Mg to seawater that is enriched in $^{24}$Mg. This would drive the difference between the $\delta^{26}$Mg values of the inputs to seawater and seawater itself to > 0.3‰.

Carbonate formation provides an additional sink of Mg from seawater (Fig. 1). It is likely that the vast majority of Mg removal via carbonate is via dolomite because of the high Mg/Ca ratio, close to 1 in stoichiometric dolomite. In the modern system, dolomite formation would qualitatively account for the offset in $\delta^{26}$Mg between the riverine input and seawater of < 0.3‰ (greater if the return flux from low-temperature hydrothermal circulation is accounted for). Since the riverine input has a lower $\delta^{26}$Mg value than seawater, dolomite, enriched in $^{24}$Mg on average by > 1‰ relative to seawater, could be enough to account for the higher $\delta^{26}$Mg value of seawater compared to rivers. Tipper et al [25] estimated that the minimum dolomite flux from modern seawater was 8 per cent and as high as 40 per cent. More recently, Shalev et al [17]. argued for an even greater removal of Mg (40–60 per cent) via dolomite after accounting for the low-temperature hydrothermal removal of $^{26}$Mg.

In the modern system, dolomite formation has been a long-standing conundrum since the kinetics of dolomite precipitation are slow, and there is a high energy of nucleation [5]. Prior to the mass balance constraint from Mg isotopes, some authors argued that the total proportion of dolomite removal of Mg in the modern system was < 10 per cent. The fraction of Mg removed from the oceans via dolomite relative to hydrothermal circulation has been contentious with regard to the modern ocean, but is thought to be one of the key drivers in changes in the Mg content of the ocean over geological history [5]. It is therefore possible that the reason for the offset in $\delta^{26}$Mg between the inputs and outputs is because the oceans are not at steady state.