

# The magnesium isotope budget of the modern ocean: Constraints from riverine magnesium isotope ratios

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## Abstract

We have measured the magnesium (Mg) isotope ratios in 45 rivers including 16 of the largest rivers in the world, covering a range of geologic, tectonic and climatic drainage basin environments. The range in riverine  $\delta^{26}\text{Mg}$  is 2.5‰, half the variation in terrestrial rock. Although the Mg isotopic composition of the source rock is important for small rivers, at a global scale lithology is of limited significance for Mg isotope ratios in rivers. Part of the variability at a global scale may be attributed to fractionation in the weathering environment. The rivers analysed constitute 30% of the global Mg riverine flux to the oceans and a flux weighted Mg isotope composition of global runoff has been estimated at  $-1.09\text{‰}$ . Even taking into account uncertainty, this is distinct from seawater at  $-0.82\text{‰}$ . This difference arises either from the fractionation of Mg isotope ratios in the ocean and/or a Mg budget which is not at steady state. The difference is consistent with fractionation by carbonate precipitation. In the simplest steady state scenario, where the oceanic mass balance is maintained by riverine input and hydrothermal and dolomite output, Mg isotope ratios imply a minimum dolomite Mg flux of 9% of the total output Mg flux. The implications of the distinct isotopic composition of the riverine flux from modern seawater, is that the Mg isotope ratio of seawater has probably varied outside of current analytical uncertainty. Mg isotope ratios may therefore provide a valuable new tracer in palaeo-oceanography.

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## 1. Introduction

Magnesium (Mg) is the 8th most abundant element in the continental crust [1] and the 4th most abundant species in seawater [2,3]. Its transfer from the continents to the oceans via rivers, and its return to the solid Earth via hydrothermal exchange at mid-ocean ridges [4] constitutes

one of the major chemical exchanges between the mantle and the hydrosphere [5–7]. Mg in rivers is derived from the weathering of both carbonate and silicate minerals of the continental crust [8]. Mg weathered from silicates, exchanged for calcium (Ca) at mid-ocean ridges and stored as carbonate in marine sediments, impacts on the long term atmospheric carbon budget. Secular variation in the Mg concentration of seawater through geological time has been invoked as a controlling factor on the dominant carbonate mineralogy of the ocean [7,9,10]. Previous investigations have led to an understanding of the key

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processes affecting Mg in the modern ocean [4,7,9,11–18]. Both the modern Mg concentration and the isotopic composition are uniform at 53 mmol/l [19] and  $-0.82\%$  [20–22] as anticipated from the long residence time [23], although some small concentration anomalies have been reported [24]. The main source of Mg to the oceans is from continental waters. Most of this Mg flux is from river waters. Groundwater however, may contribute up to 10% of the riverine discharge [25,26] and may have a concentrated dissolved load [27]. The main sinks of Mg are exchange with the oceanic crust during hydrothermal circulation at mid-ocean ridges, the precipitation of dolomite, and ion-exchange reactions with clays [12]. However the modern Mg budget remains difficult to quantify with ranges in the hydrothermal sink from 61 to 100% of the total flux [18,14].

The advent of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has enabled the analysis of Mg isotope ratios to a sufficient precision to resolve differences in the Mg isotope composition of terrestrial reservoirs of Mg, and the processes which induce mass dependent fractionations of Mg isotope ratios [28,29]. The few studies of Mg isotope ratios on terrestrial material [22,29–33] have revealed that Mg isotope ratios are fractionated by carbonate precipitation, one of the main processes affecting Mg in the oceanic cycle. There is also evidence that Mg isotope ratios are fractionated during silicate weathering with heavy Mg retained in the soil [32].

In this study, we present analyses of Mg isotope ratios for 45 rivers. Sixteen of the largest rivers in the world have been analysed, including two separate samples of the Amazon, Ganges, Brahmaputra, Mekong and Chang Jiang (Yangtze). The rivers analysed cover a range of geologic, tectonic and climatic settings permitting an assessment of the global controls on the Mg isotope ratios of rivers. In addition, Mg isotope ratios have been measured on a series of small rivers draining specific lithology, which has enabled a first order assessment of the lithological control on dissolved Mg isotope ratios. The data demonstrate that, although the Mg isotopic composition of the source rock is important for small rivers, at a global scale lithology is of limited significance. Mg isotope ratios in rivers at a global scale may not be adequately modelled as a simple mixture between two end member lithologies such as dolomite and Mg bearing silicate minerals. These rivers contribute ca. 30% of the riverine flux of Mg to the oceans and provide a representative sample set for determining the mean Mg isotope composition of global runoff. The flux weighted Mg isotope ratio of the riverine flux is compared to the modern seawater Mg isotope composition.

## 2. Materials and methods

The samples analysed were either collected from archives of river water collections or were sampled specifically for the purposes of this study. All samples collected for this study were filtered on collection through  $<0.45\ \mu\text{m}$  filters for cool storage. Two types of river have been selected; small rivers draining monolithological catchments such as silicate (basaltic and granitic) and carbonate (dolostone and limestone), and large rivers which integrate continental outputs.

Large rivers such as the Lena and Mackenzie are from arctic environments and in contrast the Congo and Orinoco are from the tropics. The rivers with their headwaters in the Himalaya–Tibetan-Plateau (HTP) region are weathering limited while the Congo and Orinoco are transport limited following the terminology of [34].

Where possible samples have been collected from the mouth, at the high water stage to provide the most representative samples of global runoff, as most of the Mg flux occurs at maximum discharge. For the Chiang Jiang, sample ace160 is from the headwaters in Tibet and the second sample is from the mouth. For the Mekong and Salween samples ace158 and ace156 are from the Tibetan headwaters. All other rivers (apart from tributaries and the small rivers draining specific lithologies) are from the mouth with the exception of the Columbia and the Nile. The Nile was sampled at Luxor (Egypt) 830 km upstream of the mouth, and the Columbia was sampled at Trojan, Oregon, 120 km upstream of the mouth.

### 2.1. Analytical procedure

Mg isotope ratios were measured by MC-ICP-MS following a chemical purification of Mg from all other elements which can introduce matrix effects or isobaric interferences in the mass spectrometer [28]. Mg was purified by ion chromatography using Biorad AG50 X12 cation exchange resin. This resin fractionates Mg isotope ratios [29,30] and therefore 100% recovery from the column is imperative. Typically 20  $\mu\text{g}$  of Mg was processed through chemistry except for dilute rivers where as little as 5  $\mu\text{g}$  of Mg was processed. Following chemistry, all samples were dissolved in 0.3 N  $\text{HNO}_3$  and centrifuged before introduction into the mass spectrometer. The total procedural blank is estimated as 2 ng,  $<10^{-3}$  of the smallest sample processed.

Mg isotope ratios have been analysed using the sample–standard bracketing method of [28] and reported as  $\delta^{26}\text{Mg}$  on the DSM3 scale [35]. The samples are diluted to the same concentration as the standard ( $\pm 10\%$ ), typically 0.5–1.5 ppm. Samples are introduced into the

*Nu* Instruments MC-ICPMS via an ARIDUS desolvating nebuliser. Prior to analysis, levels of aluminum, iron, manganese, potassium, sodium, silicon (Si) and Ca are monitored to verify chemical purification. The  $^{25}\text{Mg}/^{24}\text{Mg}$  ratio is always analysed to ensure mass dependent behaviour. All samples have had at least duplicate analyses of a single column processed sample. The long term reproducibility of Mg isotope ratios is evaluated by repeat analysis of mono-elemental standards, Cambridge1 and DSM3. The long term error (2 standard deviations) is 0.14‰,  $N=339$ , during the two year period of analysis of the samples presented in this study. The integrity of the total analytical procedure was verified by chemical separation and analysis of a multi-elemental standard of known Mg isotopic composition [32]. A synthetic multi-elemental standard was purified through chemistry 16 times in total and underwent duplicate analysis each time, yielding an average  $\delta^{26}\text{Mg}$  offset by only 0.06‰ compared to the mono-elemental standards [32]. In addition two total procedural replicates of natural samples are presented in Table 1. A conservative estimate of the uncertainty is from these total procedural replicates.

Mg, Ca and Si concentrations on samples collected for this study have been measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) against synthetic standards and cross calibrated against natural water standards ION 20 and SPSSW2 following [36]. Repeat analysis of these standards demonstrates a reproducibility within 3%. Strontium (Sr) isotope analyses on samples has been achieved following a chemical separation using Eichrom Sr spec SPS 50–100  $\mu$  mesh resin and analysis by MC-ICP-MS. Analysis of NBS987 gave 0.710244 ( $2\sigma_{\text{ext}}=0.000035$ ,  $N=199$ ) during the period of analysis.

### 3. Results

Mg isotope ratios are presented as  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  (Table 1). The regression of  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  yields a slope<sup>1</sup> of  $0.519\pm 0.009$  compared to the theoretical equilibrium fractionation slope of 0.521 [37]. Deviation from the equilibrium fractionation line is expressed as  $\Delta^{25}\text{Mg}'$  [37] (Table 1). All samples in this study have a  $\Delta^{25}\text{Mg}'$  within error of equilibrium behaviour. Major element concentrations and Sr isotope ratios are either from this study or compiled from several sources referenced in the caption of Table 1.

There is a large range in Mg concentration in rivers around the world. The most dilute river studied here is

the Amazon. However, the Amazon has the largest discharge in the world [38] making the Amazon the second largest river to supply Mg to the oceans after the Chiang Jiang (Yangtze) at 8%<sup>2</sup> of the total riverine flux. The Huanghe (Yellow river) is the most concentrated large river in this study, at 800  $\mu\text{mol/l}$  but because of the small discharge contributes only 1.4% of the riverine Mg flux. Some rivers have been analysed more than once and there is considerable variability between Mg concentrations.

#### 3.1. Mg isotope ratios in rivers

This study finds a range of 2.5‰ in  $\delta^{26}\text{Mg}$  for the 45 rivers analysed. This is approximately half the total terrestrial range reported for  $\delta^{26}\text{Mg}$  so far [20]. The heaviest water measured is Volvic mineral water at  $-0.3\text{‰}$  draining volcanic rocks as a spring. The lightest Mg isotope ratios in the present study are small rivers draining limestone at ca.  $-2.5\text{‰}$ .

To assess the variability between samples, more than one sample has been analysed where possible. The difference of 0.5‰ for the Chiang Jiang (Yangtze) is probably related to the different localities of the samples (Tibetan headwaters and mouth). Repeats on the Ganges and Amazon from different years give good agreement within  $2\sigma_{\text{ext}}$  (Table 1). However, Tipper et al [32] have observed an annual variation of 0.4‰ in a small limestone dominated river and seasonal variations in  $\delta^{26}\text{Mg}$  are clearly possible in large rivers.

#### 3.2. Small rivers draining silicate rock

The range in  $\delta^{26}\text{Mg}$  for seven rivers draining silicate rock is only 0.6‰. The rivers draining basalt and arc complexes average  $-0.6\pm 0.2\text{‰}$  ( $2\sigma_{\text{mean}}$ ,  $N=5$ ). Although there are significant differences in major element chemistry between rivers draining basic igneous rock and granite [39,40], the rivers in this study draining granite and gneiss have a similar  $\delta^{26}\text{Mg}$  to the rivers draining basic igneous rock. The Arran sample represents the average of two small rivers draining the Arran granite of the British Tertiary Igneous Province in Scotland [41]. The small tributary of the Marsyandi (M0316) is from Formation 1 of the High Himalayan Crystalline series (Nepal Himalaya) draining dominantly biotite gneiss [42]. These rivers draining acidic crystalline rock have a  $\delta^{26}\text{Mg}$  of  $-0.8\text{‰}$ . However, some of these small rivers are dilute in Mg concentrations and

<sup>1</sup> The gradient is calculated by regressing  $\delta^{26}\text{Mg}'$  and  $\delta^{25}\text{Mg}'$  following Young and Galy [20].

<sup>2</sup> Out of the 60 largest rivers in the world.



Table 1 (continued)

River	Sample	Date	Stage	Mg conc ( $\mu\text{mol/l}$ )	Discharge ( $\text{km}^3/\text{yr}$ )	Mg flux $10^{10}$ (mol/yr)	$\delta^{26}\text{Mg} \pm$ $2\sigma_m$	$\delta^{25}\text{Mg} \pm$ $2\sigma_m$	$\Delta^{25}$ Mg'	$N$	$^{87}\text{Sr}/^{86}\text{Sr}$	Si(OH) <sub>4</sub> / Ca molar ratio
<i>Dolostone</i>												
Andhi Khola <sup>(b,c)</sup>	Nh7	Mar-95	L	811	na	na	$-1.35 \pm 0.08$	$-0.69 \pm 0.06$	0.01	3	0.7846	0.11
Marsyandi LHSS trib	ett153	Sep-02	H	841	na	na	$-1.39 \pm 0.08$	$-0.73 \pm 0.04$	0.00	3	0.8441	0.29
<i>Limestone</i>												
Jura mean			na	185	na	na	$-2.52 \pm 0.11$	$-1.31 \pm 0.06$	0.01	9	0.7076	0.02
Soaso	K154	Aug-04	L	171	na	na	$-2.43 \pm 0.04$	$-1.24 \pm 0.03$	0.03	2	na	0.02

$N$  represents the number of analyses by MC-ICP-MS of a single column processed sample except for the limestone rivers of the Jura and the rivers from Arran where the data represent the average of  $N$  separate samples. For Volvic mineral water  $N$  is the number of total procedural replicates. na is not available, rep = total procedural replicate. Discharge data is from Gaillardet et al. (1999) [54]. Chemical data sources are: <sup>(a)</sup> = Gaillardet et al. (1999) [54], <sup>(b)</sup> = major element data from Galy and France-Lanord, (1999) [65] <sup>(c)</sup> = Sr isotope data from Galy et al. (1999) [66], <sup>(d)</sup> = major element data from Hu et al. (1982) [67], <sup>(e)</sup> = Sr isotope data from Palmer and Edmond, (1992) [46], <sup>(f)</sup> = major element and Sr isotope data from Millot et al. (2003) [53], <sup>(g)</sup> = major element data from Edmond et al, (1996)[48], <sup>(h)</sup> = major element and Sr isotope data from Stallard and Edmond, (1883) [34], <sup>(i)</sup> = major element and Sr isotope data from Gaillardet et al, (1997) [68], <sup>(j)</sup> = major element and Sr isotope data from Huh et al. (1997) [69], <sup>(k)</sup> = S. Rad (Personal communication), <sup>(l)</sup> = major element and Sr isotope data from Gaillardet et al. (2003) [70], <sup>(m)</sup> = major element and Sr isotope data from Louvat and Allégre, (1997) [71].

cyclic input may contribute to the Mg budget in these rivers. At present there are no analyses of Mg isotope ratios in rainwater and it is not possible to correct  $\delta^{26}\text{Mg}$  for cyclic input. The small difference in  $\delta^{26}\text{Mg}$  between rivers draining basic igneous rock and acid igneous rock is within uncertainty and is therefore difficult to interpret at present.

### 3.3. Rivers draining dolostone

Two representative small rivers draining the dolomitic formations of the Lesser Himalayan Sedimentary Series of Nepal were analysed. Both of these tributaries are very concentrated in Mg at  $>800 \mu\text{mol/l}$ . The Mg/Ca molar ratio of both samples is 0.93 close to the stoichiometry of 1 as anticipated by the weathering of dolostone. The  $\delta^{26}\text{Mg}$  of both these tributaries is very similar at  $-1.37 \pm 0.06\text{‰}$ . This is  $0.7\text{‰}$  lower than rivers draining silicate rock.

### 3.4. Rivers draining limestone

Nine samples from the Jura mountains in Eastern France were selected because they drain only limestone. The  $\delta^{26}\text{Mg}$  presented in Table 1 represents the average of these rivers. The Soaso is a small river from the Spanish Pyrénées and drains only limestone. For these rivers the Si(OH)<sub>4</sub>/Ca molar ratio  $<0.02$  and the low dissolved Na (63 and  $9 \mu\text{mol/l}$  for the Jura mean and Soaso, respectively) can be accounted for by cyclic input leading to Na/Ca molar ratios of ca. zero. The Mg budget in rivers

draining limestone can be strongly influenced by small amounts of silicate material or dolomite because Mg is commonly a major constituent of silicate minerals and dolomite but only a trace component of calcite. In spite of this, the  $\delta^{26}\text{Mg}$  of these 10 limestone rivers are the lightest that have been analysed in the present study averaging  $-2.5\text{‰}$ , nearly  $2\text{‰}$  lower than that of silicates and defining a very narrow range.

### 3.5. Large rivers

There is a range of  $1.2\text{‰}$  in the  $\delta^{26}\text{Mg}$  of the large rivers analysed in this study. All the rivers have a  $\delta^{26}\text{Mg}$  between the extremes defined by limestone and silicate. The heaviest river is the Nile at  $-0.5\text{‰}$  and the lightest is the Mackenzie at  $-1.7\text{‰}$ .

There are small differences between the Asian rivers, many of which have their headwaters in the Himalayan–Tibetan-Plateau (HTP) region. The Ganges has an average value of  $-1.3\text{‰}$  similar to its large tributaries which average  $-1.4\text{‰}$ . The large Himalayan rivers which drain the Eastern HTP have slightly heavier Mg isotope ratios. The average of the Brahmaputra, Yarlung Tsangpo, Irrawaddy, Salween and Mekong is  $-0.9 \pm 0.2\text{‰}$ . The Meghna (mixture of the Brahmaputra and Ganges) is intermediate between the Brahmaputra and Ganges at  $-1.1\text{‰}$ . The Chiang Jiang has the lightest  $\delta^{26}\text{Mg}$  of the Asian rivers at  $-1.45\text{‰}$  at the mouth. This is significant as it is the largest river in terms of Mg flux to the oceans.

The second largest river (in terms of Mg flux), the Amazon, has an average  $\delta^{26}\text{Mg}$  of  $-0.95\text{‰}$ . Of the



remaining large rivers, there is a range in  $\delta^{26}\text{Mg}$ , with the Orinoco, Congo, Nile, Narmada and Columbia similar to small rivers which drain silicate rock with heavy  $\delta^{26}\text{Mg}$ .

#### 4. Controls on the Mg isotope ratios of rivers

The controls on the isotopic composition of rivers waters are two fold. The composition of bedrock often dominates the chemistry of rivers [38]. For stable isotopes however, fractionation in the weathering environment may be important during soil reactions or biomass uptake [32,43,44]. Calcite precipitation is known to fractionate Mg isotope ratios [29] and the preferential retention of heavy Mg in soil during weathering of silicate minerals also induces the formation of isotopically light Mg in the dissolved load [32]. Deconvolving a fractionation control from a lithological control is difficult for Mg isotope ratios, because the range in rocks is about twice the range observed in most rivers for  $\delta^{26}\text{Mg}$ . The approach in this study has been to analyse mono-lithological small catchments to understand the lithological control.

##### 4.1. Small rivers

The small rivers draining silicate, dolostone and limestone have distinct Mg isotope ratios which are similar to the rock values (Fig. 1). The small rivers draining silicate lithologies have a slightly lighter  $\delta^{26}\text{Mg}$  than the bedrock (by 0.4‰ on average). This is consistent with a retention of heavy Mg in soil reported by [32].

The small Himalayan rivers draining dolomite have a  $\delta^{26}\text{Mg}$  indistinguishable from the  $\delta^{26}\text{Mg}$  of the dolomite rocks from the area at  $-1.46 \pm 0.20\text{‰}$  ( $2\sigma_{\text{mean}}$ ,  $N=3$  [29]). A similar result has been found for speleothem drip waters draining dolostone [29]. The data therefore imply that Mg isotope ratios are not fractionated during dolomite dissolution. It is noted, however, that there is a large range in reported  $\delta^{26}\text{Mg}$  of dolomite from different sample sites across the globe [29,45].

The small rivers draining limestone fall within the range of  $\delta^{26}\text{Mg}$  defined by limestone bedrock (Fig. 1) but are 0.8‰ heavier than the global average of limestone reported so far [29,32]. A similar result has been found in the Tethyan Himalaya [32] where limestone dominated rivers are heavier than bedrock limestone. This is also found in speleothem drip waters [29] and may result from contamination by silicate material, or in the case of the Jura and Soaso, may result from cyclic contributions as these rivers are dilute.

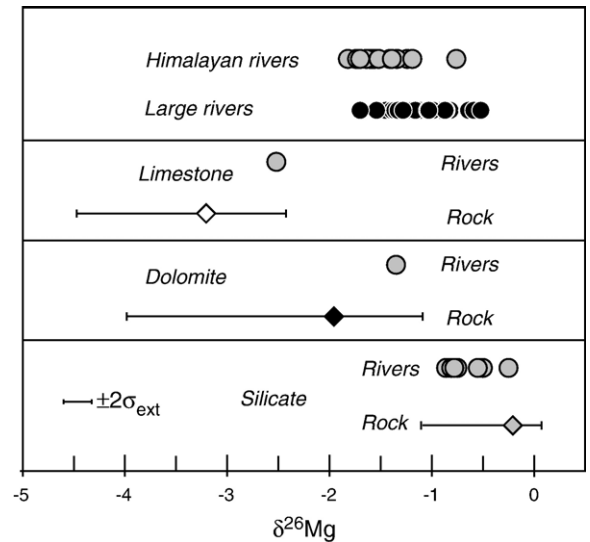


Fig. 1. Range in  $\delta^{26}\text{Mg}$  for both rock and water. The limestone is an average of values from [29,32] ( $N=8$ ). Dolostone is from [29,45] ( $N=6$ ). Silicate is an average of continental crust, basalt and mineral separates from [20,32,33,63,64] ( $N=41$ ). The uncertainty of the small limestone and dolomite draining rivers is smaller than the size of the symbol. The error bars denote the range in rock values. The Himalayan rivers are limestone dominated from [32]. Average  $\pm 2\sigma$  error bar is shown.

##### 4.2. Large rivers

At a global scale, the riverine Mg budget is derived mainly from silicate and dolostone dissolution with Mg-poor limestone contributing negligible amounts of Mg [23]. On average, dolostone is 1.5‰ lighter than silicate rock (Fig. 1). Based on our limited data, the incongruent dissolution of silicate rocks induces an enrichment in light isotopes of less than 0.4‰ in small catchments (see previous section). The expected lithological control on the isotopic composition of dissolved Mg at a global scale is weak as evidenced by the lack of correlation with parameters distinguishing dolostone from silicate rocks (such as dissolved  $\text{Si}(\text{OH})_4/\text{Ca}$  or  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, Fig. 2a and b). Sr isotope ratios have been previously used as a tracer of carbonate to silicate source lithologies [46]. However, Himalayan rivers are distinct from global trends [47] and rivers draining mantle derived igneous rocks have distinct  $^{87}\text{Sr}/^{86}\text{Sr}$  from continental derived silicates. Even if these rivers are excluded from the global data set there is no discernable trend between  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{26}\text{Mg}$ , which combined with the lack of trend with  $\text{Si}(\text{OH})_4/\text{Ca}$  suggests that lithology is not the first order control of riverine Mg isotope ratios.

There may be several reasons why Mg isotope ratios in rivers at a global scale cannot be described as a simple two component mixture between dolostone and silicate.

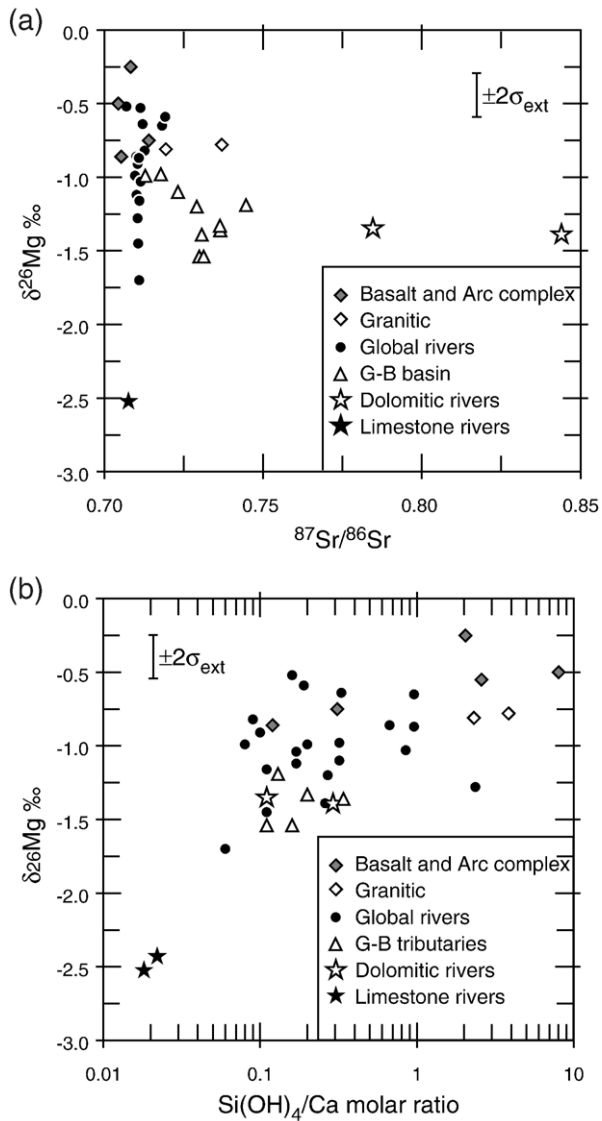


Fig. 2. (a) Cross plot of  $\delta^{26}\text{Mg}$  vs  $^{87}\text{Sr}/^{86}\text{Sr}$ . (b) Cross plot of  $\delta^{26}\text{Mg}$  vs Si(OH)<sub>4</sub>/Ca molar ratio. Sr isotope and Si(OH)<sub>4</sub>/Ca data is either from this study or from references in the caption of Table 1.

Firstly, despite the limited number of analysis, there is already a range of 3‰ in the  $\delta^{26}\text{Mg}$  of dolomite (Fig. 1), which could lead to scatter. Secondly, there is evidence that Mg isotope ratios are fractionated during silicate weathering [32]. The retention of heavy Mg in soil enriches rivers in the light isotopes of Mg compared to silicate rock. Part of the global variation in  $\delta^{26}\text{Mg}$  in rivers may be attributed to fractionation in the weathering environment.

There may be a distinction between transport and weathering limited rivers. The Orinoco and Congo rivers drain shield terrains and are transport limited [48–

50]. In these rivers erosion is at steady state and 90% of the Mg flux is transported in the dissolved load [51]. The dissolved  $\delta^{26}\text{Mg}$  is within uncertainty of silicate rock at  $-0.65$  and  $-0.59$ ‰, respectively. However, slightly lighter Mg in the dissolved load would be consistent with the enrichment in heavy isotopes in soil [32]. Assuming that the maximum difference between unweathered rock and the dissolved  $\delta^{26}\text{Mg}$  of the Congo is the analytical uncertainty of 0.14‰, the Mg enrichment factor associated with silicate weathering would be 10 times this difference (i.e.  $-1.4$ ‰), by mass balance. Altogether, the heavier Mg in soil compared to silicate rock (0.5‰ [32]), the offset by 0.4‰ towards lighter Mg in the dissolved in small rivers draining silicates, and the mass balance of Mg in transport limited rivers strongly suggest a Mg enrichment factor in the order of  $-1.5$  to  $-0.5$ ‰ associated with silicate weathering.

The Columbia, Nile and Narmada also have similar  $\delta^{26}\text{Mg}$  to the rivers which drain silicate rocks but are not transport limited. These rivers drain dominantly basalt [46,52] (The Columbia flood basalt, Ethiopian traps and Deccan traps) consistent with the low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. Similar values for the  $\delta^{26}\text{Mg}$  of the dissolved load and fresh rock in these rivers could either reflect a smaller fractionation factor during the weathering of basaltic lithologies, or the chemical weathering of soil in a non-steady state scenario. In contrast, rivers which are weathering limited have lighter Mg isotope ratios than silicate bedrock. The Himalayan rivers and Arctic rivers have  $\delta^{26}\text{Mg} < -0.9$ ‰. Assessing the extent to which this reflects a fractionation or a mixture with a carbonate source is not straightforward. The Mackenzie river, with the lightest  $\delta^{26}\text{Mg}$  of the large rivers in this study, is known to have Mg-rich limestone and also black shale in the catchment [53]. Despite the large climatic differences between the rivers, such as the Mackenzie and Lena from arctic environments and the Congo or Amazon from tropical environments, there is little systematic variation in  $\delta^{26}\text{Mg}$  suggesting that at a global scale, climate is not a first order control.

## 5. The oceanic mass balance of Mg

The rivers analysed in this study constitute approximately 30% of the riverine flux of Mg to the oceans and it is therefore possible to estimate the  $\delta^{26}\text{Mg}$  of global runoff. The two most influential rivers for the oceanic Mg budget are the Chiang Jiang and the Amazon (8 and 7% of the total riverine flux respectively<sup>3</sup>) because of their very high discharge (Table 1). A flux weighted

<sup>3</sup> Out of the 60 largest rivers in the world [54].

mean  $\delta^{26}\text{Mg}$  of the riverine input to the ocean has been estimated as

$$\overline{\delta^{26}\text{Mg}} = \frac{\sum_{i=1}^n F_i C_i \delta^{26}\text{Mg}_i}{\sum_{i=1}^n F_i C_i} \quad (1)$$

where  $F_i$  is the discharge in an individual river and  $C_i$  is the concentration in an individual river. The Salween data used in this average was collected in Tibet ca. 1000 km from the mouth and has a similar  $\delta^{26}\text{Mg}$  to the Mekong and the Irrawaddy. Therefore it is probably representative of the  $\delta^{26}\text{Mg}$  close to the mouth. The best estimate from the data presented in the present study is  $\delta^{26}\text{Mg} = -1.09\text{‰}$ .

The uncertainty in the estimate of the mean riverine  $\delta^{26}\text{Mg}$  arises from both scatter in the set of rivers analysed but is dominated by the 70% of the Mg flux which has not been analysed, notably the Mississippi and Danube accounting for 6 and 7% of the riverine Mg flux respectively. The uncertainty in  $\delta^{26}\text{Mg}$  needs to take account of the rivers that have not been analysed. This is estimated as the standard deviation of the flux weighted  $\delta^{26}\text{Mg}$  of the rivers which have been analysed for  $\delta^{26}\text{Mg}$ :

$$\text{SD} = \sqrt{\frac{\sum_{i=1}^n \{F_i C_i (\delta^{26}\text{Mg}_i - \overline{\delta^{26}\text{Mg}})^2\}}{(n-1) \sum_{i=1}^n F_i C_i}} \quad (2)$$

following [55]. The uncertainty,  $\sigma_{\delta^{26}\text{Mg}}$ , of the riverine  $\delta^{26}\text{Mg}$  is then estimated as:

$$\sigma_{\delta^{26}\text{Mg}} = \sqrt{\frac{\text{SD}^2 F_u C_u^2 + \sum_{i=1}^n \{\sigma_i F_i C_i\}^2}{\left(F_u C_u + \sum_{i=1}^n F_i C_i\right)^2}} \quad (3)$$

following [55], where  $F_u C_u$  is the riverine flux of Mg which has not been measured for  $\delta^{26}\text{Mg}$ , and  $\sigma_i$  is the analytical uncertainty on  $\delta^{26}\text{Mg}$  for each river analysed. The uncertainty on  $\delta^{26}\text{Mg}$  ( $\sigma_{\delta^{26}\text{Mg}}$ ) is estimated as 0.05‰, smaller than the analytical uncertainty on each measurement. This uncertainty assumes that the distribution of unsampled rivers is similar to the sampled

rivers and does not take into account uncertainty in discharge and concentration but given that the estimate is based on 16 samples, the associated uncertainty is likely smaller than the analytical uncertainty of Mg isotope measurements.  $\delta^{26}\text{Mg}$  is therefore distinct from seawater  $\delta^{26}\text{Mg}$  at  $-0.82 \pm 0.1\text{‰}$  by almost 0.3‰. Although some large rivers such as the Danube have not been analysed, this river has a Mg/Ca ratio of 0.76 [38], suggestive of dolomite weathering and it is probable that its  $\delta^{26}\text{Mg}$  is lighter than seawater.

Groundwater could modify the isotopic composition of the continental flux to the oceans as it could comprise as much as 10% of the riverine discharge to the oceans [25,26]. At present there are only two measurements of groundwater for  $\delta^{26}\text{Mg}$  [29,32] and both are isotopically lighter than both seawater and  $\delta^{26}\text{Mg}$ . Tipper et al [32] have suggested Himalayan groundwaters are fractionated to isotopically lighter values than silicate rock. It is therefore assumed that groundwater is distinct from seawater and probably isotopically lighter than  $\delta^{26}\text{Mg}$ .

### 5.1. Constraining the oceanic cycle of Mg

The measurement of the Mg isotope composition of the riverine input of Mg to the oceans allows a first order assessment of the marine Mg budget. To sustain a difference between the riverine  $\delta^{26}\text{Mg}$  and the  $\delta^{26}\text{Mg}$  of seawater requires either:

- (1) The modern ocean is not at steady state with respect to Mg isotope ratios, or
- (2) Mg isotope ratios must be fractionated in the ocean.

Both of these possibilities have been investigated and they are not mutually exclusive. In a simplified oceanic system, Mg is delivered to the oceans via the riverine flux (Fig. 3). The oceanic sinks of Mg are two fold. Analysis of hydrothermal fluids has revealed that they are depleted in Mg relative to seawater [4,56–58] and it has been assumed that the removal of Mg by hydrothermal circulation at mid-ocean ridges is quantitative. This is a reasonable assumption in high temperature hydrothermal fluids where >80% of the Mg present is removed from solution [58]. However, estimates vary as to the relative importance between high temperature axial circulation and low temperature off axis hydrothermal circulation where only a small amount of Mg (<10%) is removed from solution [58,59]. This return flux of Mg is potentially associated with an isotopic fractionation. There are presently no measurements of Mg isotope ratios in hydrothermal fluids, but given that



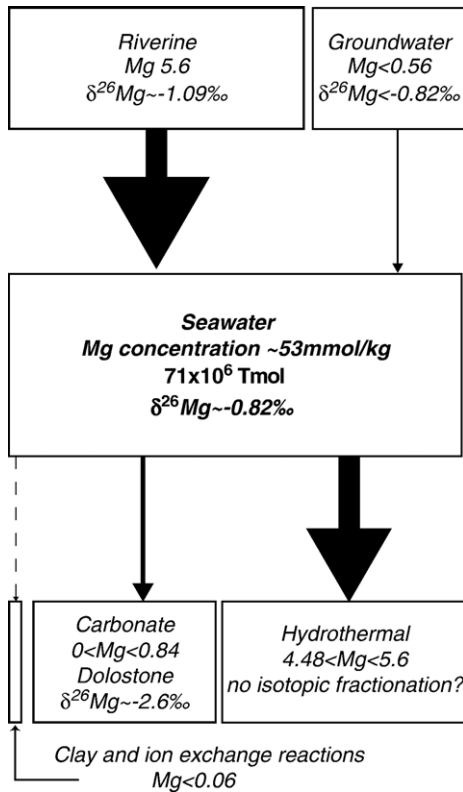


Fig. 3. Schematic of the global Mg cycle, with estimates of fluxes in Tmol/yr from [7].

small rivers draining silicate rock are enriched in the light isotopes of Mg (Fig. 1), it is probable that any fractionation during hydrothermal alteration will enhance the isotopic difference between seawater and the source of Mg.

Estimates of the hydrothermal sink of Mg vary from 54 to 100% [18,14] and a recent review proposed that 80–87% of the input flux of Mg is removed by hydrothermal circulation at mid-ocean ridges [12]. The remaining Mg is removed by a combination of marine carbonate (biogenic calcite and dolomite), ion exchange reactions between Ca and Mg in clays and the precipitation of authigenic minerals [11,12]. Therefore, solving the isotopic mass balance for the modern ocean should place new constraints on the importance of the hydrothermal sink of Mg.

The governing equation for the budget of an isotopic ratio such as  $^{26}\text{Mg}/^{24}\text{Mg}$  in seawater may be derived from the conservation equations for individual isotopes of Mg [60] and the rate of change of  $\delta^{26}\text{Mg}$  in the oceans ( $\delta_{\text{sw}}$ ) is given by

$$\frac{dN_{\text{Mg}}\delta_{\text{sw}}}{dt} = \delta_{\text{riv}}J_{\text{riv}} - \delta_{\text{hyd}}J_{\text{hyd}} - \delta_{\text{other}}J_{\text{other}} \quad (4)$$

where  $\delta_{\text{sw}}$  is the  $\delta^{26}\text{Mg}$  of seawater,  $\delta_{\text{riv}}$  is the  $\delta^{26}\text{Mg}$  of the riverine input,  $\delta_{\text{hyd}}$  is the  $\delta^{26}\text{Mg}$  of the hydrothermal output and  $\delta_{\text{other}}$  is the  $\delta^{26}\text{Mg}$  of the remaining output flux of Mg considered in the following as carbonate with the other sinks such as ion exchange reactions and clays assumed to be negligible in this first order assessment.  $N_{\text{Mg}}$  is the total number of moles of Mg in the ocean.  $J$  represents the fluxes for each of the inputs and outputs.

## 5.2. Steady state scenario

Assuming the ocean is at steady state with respect to isotopic composition, Eq. (4) simplifies to:

$$\delta_{\text{riv}}J_{\text{riv}} = \delta_{\text{hyd}}J_{\text{hyd}} + \delta_{\text{other}}J_{\text{other}} \quad (5)$$

As a consequence of steady state with respect to concentration, the input flux of Mg must equal the output:

$$J_{\text{other}} = J_{\text{riv}} - J_{\text{hyd}} \quad (6)$$

hence

$$\delta_{\text{other}} = \frac{\delta_{\text{riv}}J_{\text{riv}} - \delta_{\text{hyd}}J_{\text{hyd}}}{J_{\text{riv}} - J_{\text{hyd}}} \equiv \frac{\delta_{\text{riv}}\frac{J_{\text{riv}}}{J_{\text{hyd}}} - \delta_{\text{hyd}}}{\frac{J_{\text{riv}}}{J_{\text{hyd}}} - 1} \quad (7)$$

Assuming that no Mg is returned to the ocean from hydrothermal circulation [4], implies that  $\delta_{\text{hyd}} = \delta_{\text{sw}}$ . Assuming that ion exchange reactions and clays are a negligible sink of Mg (they represent between 0 to 16% of the total Mg sink [18,7]), the  $\delta_{\text{other}}$  in Eq. (7) corresponds to the  $\delta^{26}\text{Mg}$  of bulk carbonate. To satisfy the oceanic mass balance of Ca this carbonate must be mainly dolomite and not calcite [7] because of the lower Mg/Ca ratio of calcite would require 100–1000 times more Ca to be precipitated than Mg. Therefore, a first order assessment of a steady state scenario for the modern ocean predicts that the  $\delta^{26}\text{Mg}$  of modern dolomite is only a function of the isotopic composition of the riverine input and the relative importance of the hydrothermal output and the dolomite output (Fig. 4a).

For the  $\delta^{26}\text{Mg}$  estimated from the global rivers the  $\delta_{\text{other}}$  falls within the range  $-3.2$  to  $-2\text{‰}$  using the 80–87% range in  $J_{\text{hyd}}/(J_{\text{hyd}} + J_{\text{other}})$  as estimated by [12] (Fig. 4). This is consistent with the literature range of  $\delta^{26}\text{Mg}$  for marine carbonates [29,32,45]. The inferred  $\delta_{\text{other}}$  of  $-3.2$  to  $-2\text{‰}$  is on average slightly lighter than the current best estimate for dolomite at  $-2\text{‰}$  but unsurprisingly given the biomineralisation of dolomite

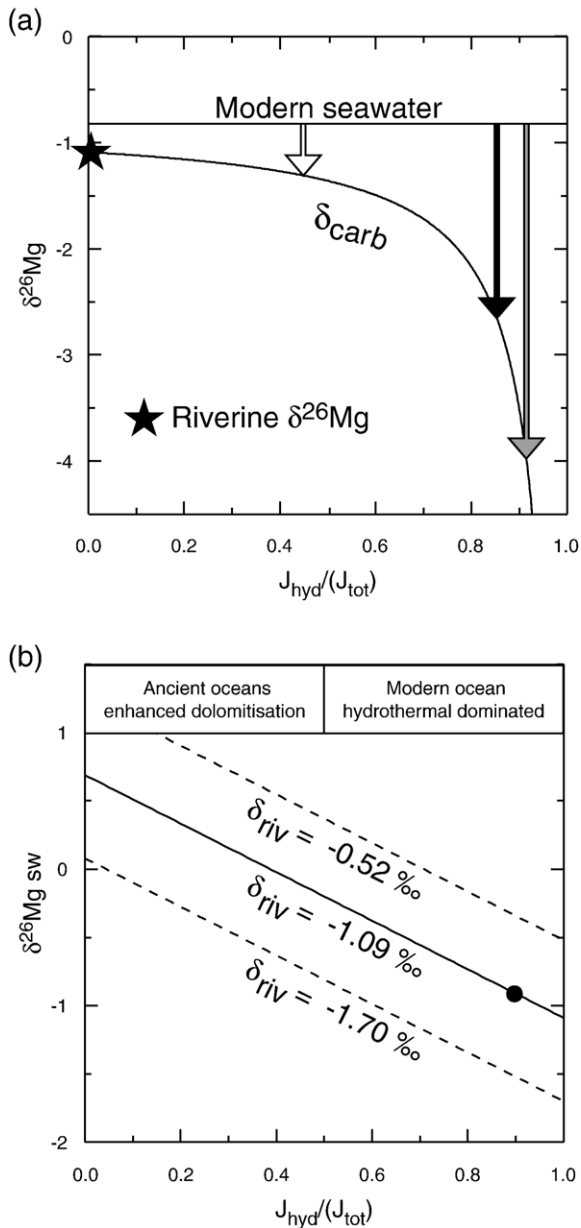


Fig. 4. (a)  $\delta_{\text{carb}}$  plotted as a function of the proportion of hydrothermal to total Mg sink for a steady state modern ocean. The black arrow shows the current best estimate for the difference in  $\delta^{26}\text{Mg}$  between modern seawater and modern dolomite. The grey arrow shows the maximum estimate for the difference in  $\delta^{26}\text{Mg}$  between modern seawater and modern dolomite and the white arrow the minimum estimate. (b) Schematic showing the likely response of  $\delta^{26}\text{Mg}$  in seawater by changing the proportion of the Mg sink between hydrothermal circulation and carbonate. The solid line is calculated for the estimated  $\delta^{26}\text{Mg}$  of runoff for the present day and the dotted lines are calculated for the  $\delta^{26}\text{Mg}$  of the heaviest and lightest large rivers presented in this study. With a greater carbonate sink of Mg (as may have been the case in the geological past) the ocean is likely to evolve to a heavier  $\delta^{26}\text{Mg}$  (see Section 5.4 for further discussion). The dot shows modern seawater.

leads to variable fractionation factors between seawater and dolomite [45].

A lower Mg removal by dolomite of 0.1 Tmol/yr based on an estimate of  $J_{\text{hyd}}/(J_{\text{hyd}}+J_{\text{carb}})$  of 0.98 [5,7] would require a very negative composition of the carbonate sink with an unrealistic  $\delta_{\text{carb}}$  of  $-14\text{‰}$ . The most negative dolomite composition measured so far may be used to place a minimum dolomite flux from the ocean using Eq. (7). A dolomite  $\delta^{26}\text{Mg}$  of  $-4\text{‰}$  [45] would require that 9% of the sink of Mg from the oceans is via dolomite and only 91% via hydrothermal circulation. Whilst this is greater than some estimates of the dolomitic sink of Mg, it is consistent with that of Holland, (2005) [18] and Elderfield and Schultz, (1996) [12]. It is possible that the dolomitic sink is smaller, but the other sinks such as ion-exchange reactions, reverse weathering or hydrothermal circulation must preferentially scavenge light isotopes in order to fulfill the steady state scenario. This is unlikely given that the Mg enrichment factor (see Section 5) associated with continental silicate weathering and soil formation is (1) small, and (2) in the wrong direction to reconcile the difference between modern seawater and the riverine  $\delta^{26}\text{Mg}$ .

### 5.3. Non steady state scenario

Alternatively, it is possible to reconcile the difference between the riverine input to the ocean and the Mg isotope composition of the ocean by a system which is not at steady state as has recently been proposed for Mg concentrations [18]. It is possible that the ocean is not at steady state for Mg concentration but maintained at steady state for Mg isotope ratios, given a restricted set of boundary conditions, for the Mg isotope composition of the riverine input, the importance of the dolomite sink and the fractionation associated to it. More likely, if the Mg concentration is not at steady state, then the Mg isotope composition is not at steady state and will have changed through time.

### 5.4. Potential changes in Mg isotope ratios in seawater through time

Over geological time scales there is strong evidence that the ocean has not been at steady state for Mg concentrations. Several studies have modelled the evolution of seawater over geological time [7,9,13,17,18] or have estimated changes in seawater composition from fluid inclusions [15,16,61]. Whilst there is discordance over the changes in seawater composition, there is an agreement that both the Mg concentration in seawater and the amount of dolomite accumulation during the

Phanerozoic has been variable. It is therefore anticipated that the Mg isotope composition of seawater may also have been variable over geological timescales. It is not possible to accurately predict how oceanic  $\delta^{26}\text{Mg}$  may have varied in the past, but the magnitude of potential changes in oceanic  $\delta^{26}\text{Mg}$  can be predicted by considering models of oceanic Mg cycling.

One of the major factors which may impact marine  $\delta^{26}\text{Mg}$  is a shift in the relative proportion of marine Mg lost to hydrothermal circulation and dolomite precipitation. Wilkinson and Algeo, (1989) [7] suggested that as much as 90% of Mg is lost to a carbonate sink during enhanced periods of dolomitisation. Such a change could induce a shift in the  $\delta^{26}\text{Mg}$  of seawater by up to 1.5‰ towards isotopically heavier values (Fig. 4b). Maintaining the Mg isotope composition of seawater constant with a greater dolomitic sink of Mg would require a significantly lighter input of Mg compared to the modern riverine input (Fig. 4b). A lighter riverine input could be achieved by enhanced dolomite weathering or enhanced silicate weathering in a weathering limited regime similar to the modern Amazon or HTP rivers. Periods of enhanced dolomitisation are thought to occur during extended periods of high sea level and atmospheric  $\text{CO}_2$  [62] which are probably less favorable for weathering limited conditions, compared to the modern day.

The implications from these simple simulations (Fig. 4a and b) are that the  $\delta^{26}\text{Mg}$  of seawater may be variable in geological time outside of analytical uncertainty. Small imbalances between the isotopic composition of the input and output fluxes will create differences in the  $\delta^{26}\text{Mg}$  of seawater. This is, in part a consequence of Mg isotope fractionation during the weathering of silicate rock and in part because of the fractionation induced by the precipitation of marine carbonate. Further imbalances in the Mg isotope budget of the ocean through time derive from shifting the proportion of the output flux to more dolomite and less hydrothermal circulation.

## 6. Conclusions

We have measured the Mg isotope ratios in 45 rivers including 16 of the largest rivers in the world from a range of lithotectonic and climatic settings. There is a 2.5‰ range in the rivers analysed reflecting Mg isotope heterogeneity in source rock and fractionation during weathering. There are no correlations between  $\delta^{26}\text{Mg}$  and proxies for lithology such as  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\text{Si}(\text{OH})_4/\text{Ca}$  and Mg isotope ratios in rivers at a global scale cannot be adequately represented by a two component mixture. The rivers analysed constitute 30% of the global riverine

flux of Mg to the oceans. A flux weighted average of the Mg isotope composition of global runoff has been calculated as  $-1.09 \pm 0.05\text{‰}$ . This is distinct from the  $\delta^{26}\text{Mg}$  of seawater at  $-0.82\text{‰}$ , even if  $2\sigma$  uncertainty is considered. An important implication from this is that either Mg isotope ratios must be fractionated in seawater by carbonate precipitation, or, the modern ocean is not at steady state with respect to Mg. To a first order, the marine mass balance of Mg isotopic ratios can be approximated by a riverine input and output via hydrothermal circulation at mid-ocean ridges and via Mg carbonate. The mass balance of Mg isotope ratios of the modern ocean implies that at least 9% of the Mg flux from the oceans must be removed by deposition of dolomite, assuming that the modern ocean is in steady state. This is greater than some estimates of the dolomite flux and will need to be accounted for in future models of oceanic Mg. The implications for seawater over geological time are the Mg isotope ratios may have varied outside of current analytical uncertainty. Mg isotope ratios may therefore provide a valuable new tracer in palaeo-oceanography.

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