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High magnesium isotope ratios in subglacial icelandic waters: impacts of carbonate precipitation and implications for CO_2 sequestration☆

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ABSTRACT

Magnesium isotopes are increasingly used to trace silicate weathering, one of the key removal processes of atmospheric CO_2. Generally, silicate weathering processes are thought to drive Mg isotopes in river waters to isotopically lighter compositions than silicate rocks. An anomaly in this behaviour has been glacially-sourced rivers from Iceland, which are isotopically heavier. This study examines this phenomenon further, by analysing more high-pH glacial and groundwaters from Iceland, which tend to have high δ^{26}Mg values. Mineral Mg/Si stoichiometry shows that the cause of this isotopic change is unlikely to be associated with Mg-silicate secondary minerals, but rather with the sub-glacial and groundwater precipitation of calcite. The riverine δ^{26}Mg of specifically sub-glacial and groundwaters also co-vary with pH and the calcite saturation index. This likely dominance of the Mg isotope fractionation by a single phase allows the calculation of how much of that phase is forming, given "known" fractionation factors. This suggests that calcite formation fluxes are on average ~0.7 t/km^2/yr for the Langjökull glacier, and 25 t/km^2/yr for the considerably larger Vatnajökull icecap. Overall, this study apparently answers the enigma of isotopically heavy surface waters in Iceland, and also demonstrates the potential use of Mg isotopes in determining carbonate precipitation rates, and their effects on atmospheric pCO_2.

1. Introduction

The chemical weathering of silicate rocks drives a key CO_2 removal process in the long-term carbon cycle (Berner, 2003; Berner et al., 1983; Walker et al., 1981). The weathering of basaltic rocks, in particular, is thought to have a significantly greater influence on global atmospheric CO_2 concentrations than would be expected from their global extent. Estimates suggest they are about an order of magnitude more efficient at CO_2 drawdown than a comparable area of felsic continental crust (Dessert et al., 2003; Gaillardet et al., 1999; Meybeck, 1987; Wolff-Boenisch et al., 2006), and their emplacement and weathering likely strongly affected past climates (e.g. Allegre et al., 2010; Jones and Jenkyns, 2001; Pogge von Strandmann et al., 2013). Iceland, as an example of a basaltic terrain, has the advantage that it has relatively little anthropogenic influence (at least in the upper catchment areas), has a wide variety in weathering regime and rate (Gíslason et al., 1996; Louvat et al., 2008), and also has a combination of both volcanoes (providing fresh basalt) and glaciers.

Therefore, tracers that inform on weathering fluxes, rates or processes have been sought. Recently, attention has focussed on magnesium isotopes (e.g. Chen et al., 2023; Foster et al., 2010; Gou et al., 2023; Higgins and Schrag, 2010; Opfergelt et al., 2014; Teng et al., 2010; Tipper et al., 2006b; Tipper et al., 2012b), because Mg is one of the elements directly involved in CO_2 sequestration, via weathering of Mg-silicates, and the precipitation of dolomite or high-Mg calcite in the oceans, or the exchange of Mg for Ca at mid-ocean ridges, where that Ca then goes on to form carbonates. In principle, Mg isotope behaviour in the oceans is relatively simple, with continental weathering serving as

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the dominant Mg source, and hydrothermal removal, dolomite formation, and low-temperature clay formation all acting as sinks (Holland, 2005; Tipper et al., 2006b).

However, the study of global rivers has revealed a large range in dissolved Mg isotope ratios (e.g. Brenot et al., 2008; Chen et al., 2023; Gou et al., 2023; Huang et al., 2012; Liu et al., 2014; Pogge von Strandmann et al., 2008b; Pogge von Strandmann et al., 2012; Pogge von Strandmann et al., 2020; Tipper et al., 2006a; Tipper et al., 2008; Tipper et al., 2010; Tipper et al., 2012a; Tipper et al., 2012b; Wimpenny et al., 2011), and it has become clear that, like all major elements, Mg and its isotopes are affected by a wide range of processes, including carbonates vs. silicates in the catchment (Gou et al., 2023; Pogge von Strandmann et al., 2014; Tipper et al., 2008), carbonate mineralogy (Geske et al., 2012; Geske et al., 2015; Immenhauser et al., 2010; Saulnier et al., 2012; Wombacher et al., 2011), organic vs. inorganic carbonate precipitation (Chang et al., 2004; Pogge von Strandmann, 2008; Saenger and Wang, 2014; Wombacher et al., 2011), precipitation rate (Mavromatis et al., 2013), fractionation mechanism (Buhl et al., 2007), and potentially speciation (Schott et al., 2016), resulting in a wide range in isotope ratios. In addition, Mg isotopic fractionation occurs due to the silicate weathering process or intensity itself, owing to preferential incorporation and adsorption of Mg isotopes by silicate secondary minerals (Brewer et al., 2018; Huang et al., 2012; Liu et al., 2014; Opfergelt et al., 2011a; Opfergelt et al., 2010; Pogge von Strandmann et al., 2008b; Pogge von Strandmann et al., 2012; Tipper et al., 2012b), where uptake by the exchangeable fraction can also partly or wholly buffer the composition of solution Mg (Cai et al., 2022; Ma et al., 2024), and seasonal hydrological changes can change the balance of sources (Gou et al., 2023; Novak et al., 2021). Finally, the uptake of Mg by plants causes variable isotope fractionation (Black et al., 2006; Bolou-Bi et al., 2010; Bolou-Bi et al., 2012).

The fractionation mechanisms of Mg isotopes accompanying silicate weathering can be more simply studied in monolithologic basaltic terrains like Iceland, where primary carbonates are scarce. Many studies from areas outside Iceland have shown that river waters tend to be isotopically lighter than the bedrock silicate composition (e.g. Lee et al., 2014; Liu et al., 2014; Tipper et al., 2008; Tipper et al., 2006b; Wimpenny et al., 2011). This is consistent with silicate secondary minerals preferentially retaining isotopically heavy Mg (Hindshaw et al., 2020; Huang et al., 2012; Liu et al., 2014; Opfergelt et al., 2011a; Opfergelt et al., 2010; Pogge von Strandmann et al., 2012; Wimpenny et al., 2014; Wimpenny et al., 2010b). However, in a previous study of Iceland, Pogge von Strandmann et al. (2008a) reported riverine δ^{26}Mg values both higher and lower than those of pristine basalt (δ^{26}Mg = -0.96 to + 0.64 ‰, compared to basalt at −0.23 ‰), and this behaviour has remined an enigma in our understanding of Mg isotope behaviour. This was originally interpreted to be due to differential fractionation during Mg uptake onto secondary minerals such as smectites and allophane relative to chlorites or talc-silicates. In particular, the latter appeared to be forming only in high pH glacial rivers, which had higher δ^{26}Mg values than the direct-runoff rivers. Clay formation experiments have suggested that the direction of Mg isotope fractionation could be controlled by the clay mineral structure, but that study also notes that direct field evidence for this is largely lacking (Hindshaw et al., 2020). The same study also suggests that the formation of trace carbonates may have a bigger effect on the Mg isotope composition of rivers than previously thought, due to the faster reaction kinetics of carbonates compared to silicates.

These two possibilities mentioned by Hindshaw et al. (2020) effectively summarise the motivation for this study. If the isotopically heavy river waters were due to uptake by different secondary silicates than those causing isotopically light waters, it may be field evidence for a mineralogical control on fractionation direction, which would have significant consequences for the interpretation of riverine Mg isotope ratios. If, on the other hand, trace carbonate precipitation or dissolution can affect the δ^{26}Mg of waters even in silicate-dominated catchments, then this could also affect interpretations.

Resolving the processes that could drive dissolved Mg isotopically heavy has also gained greater importance with the increasing number of Mg isotope studies. Recent studies have reconstructed past seawater Mg isotope compositions from carbonate minerals (e.g. Dunlea et al., 2017; Gothmann et al., 2017; Higgins and Schrag, 2015; Kasemann et al., 2014; Pogge von Strandmann, 2008; Pogge von Strandmann et al., 2014), and therefore it has become important to understand and constrain the Mg isotope behaviour during weathering. This study revisits the subject of high riverine δ^{26}Mg values in Icelandic rivers, by combining the original dataset (Pogge von Strandmann et al., 2008b) with new river and groundwater samples from high-pH waters, in order to determine the origin of these unusual isotope signatures.

2. Samples and settings

The aim of this study is to examine the Mg isotope fractionation that may occur during high pH sub-glacial- or groundwater-basalt interactions. Therefore, the only samples from the Pogge von Strandmann et al. (2008a) study that are included here are those that comprise glacier-fed rivers or groundwaters, where the majority have a pH > 8.5. Further samples were collected in 2012, also from close to glaciers or from groundwaters. Both sample sets are shown in Fig. 1.

The basaltic terrains studied here have been described in detail elsewhere, and in general, the weathering environment of Iceland is well-characterised (Gíslason et al., 1996; Stefansson and Gislason, 2001; Stefansson et al., 2001). Briefly, the original 2008 study examined two catchment areas: one in the west, and the other in the south-east of the island. Given that this study focuses on glacier-fed rivers, we have retained samples from close to Vatnajökull ice-cap in the south-east, and Langjökull glacier in the west. These samples were collected in 2003 and 2005, and until now have been examined for the isotopes of Li, Mg, Ca, Mo, Sr, U and Th, as well as for trace elements (Hindshaw et al., 2013; Pearce et al., 2010; Pogge von Strandmann et al., 2008b; Pogge von Strandmann et al., 2006; Pogge von Strandmann et al., 2011a). More recently, in 2012, another sampling trip was undertaken, adding to high-pH glacier- and spring-fed samples in both field areas. In addition, a further sample was taken from a groundwater spring to the east of Reykjavik, north of Laugarvatn Lake (Fig. 1).

3. Methods

3.1. Sample collection

The collection and analytical methods of the 2003 and 2005 trips are detailed in Pogge von Strandmann et al. (2006, 2008b). The same methods were used in the 2012 trip. In brief, on the day of collection, samples were filtered through 0.2 μm cellulose acetate filters using a pressurised PFA filter unit, and stored in pre-cleaned HDPE bottles. At each site pH, temperature and total dissolved solids (conductivity) were measured. Alkalinity was determined by titration within a few hours of collection in 2003 and 2005, and immediately upon collection in 2012.

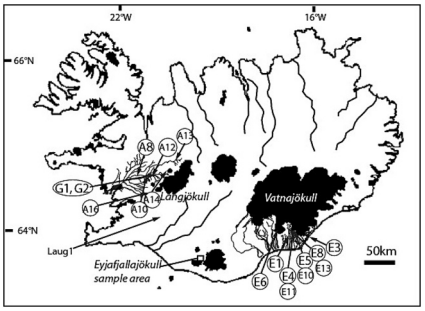

Fig. 1. Sample location map. The solid black areas are the ice caps.

3.2. Element concentrations

Major anions and cations from the 2012 samples were analysed using ion exchange chromatography (Dionex D-500X) at Durham University, and repeated using an Element 2 ICP-MS at Oxford University. Calibrations were performed using standards mixed from single-element standards, and the accuracy and precision were assessed by analyses of the international river water standards SLRS-5 and the estuary standard SLEW-3. Precision was within ± 4 % for the former, and ± 5 % for the latter.

3.3. Leaching

Several bedload samples were sequentially leached, in order to separate the exchangeable, carbonate, oxide and silicate fractions (Tessier et al., 1979). The exchangeable fraction was leached in 1 M Na acetate for 1 h at room temperature (Pogge von Strandmann et al., 2019b; Tessier et al., 1979). Subsequently, the carbonate fraction was then leached in 1 M Na acetate buffered to pH 5 with acetic acid for 5 h at room temperature (Liu et al., 2022). Following this, the oxide fraction was leached in 0.04 M hydroxylamine hydrochloride in 25 % v/v acetic acid at room temperature for 1 h (Liu et al., 2022). The residual fraction was then dissolved in standard steps of HNO_3-HF, followed by HNO_3 and then HCl.

The leachates were also analysed for their concentrations by ICP-MS at the LOGIC laboratories, UCL. The calibration occurred with matrix-matched standards – for example, when the sample contained Na acetate, the calibration standards were matrix-matched to the Na concentration.

3.4. Mg isotope ratios

In the 2008 study, Mg was purified using dilute HCl as an eluent through AG50W X-12 cation exchange columns, and analysed on a Nu Instruments multi-collector ICP-MS at the Open University (OU). As described in that study, samples were measured relative to the internal standard OU-Mg, and then renormalised relative to DSM-3 (Galy et al., 2003), which was measured as a secondary standard.

The 2012 samples were purified using dilute HNO_3 as an eluent, using the same resin. The two methods give identical results for rock standards (Pogge von Strandmann et al., 2011b) and seawater (Foster et al., 2010; Pogge von Strandmann et al., 2008a; Pogge von Strandmann et al., 2008b; Pogge von Strandmann et al., 2012). The new samples were then analysed on a Thermo Finnegan Neptune MC-ICP-MS at the Bristol Isotope Group (BIG) (Pogge von Strandmann et al., 2012; Pogge von Strandmann et al., 2011b). Here, samples were directly measured relative to the standard DSM-3.

Finally, the leachates were purified at the LOGIC laboratories, UCL, using the same column types, with the first column using dilute HNO_3 and the second column using dilute HCl, in order to completely separate both Fe and Ca. Analyses were conducted on a Nu Plasma 3 at LOGIC, also relative to DSM-3. The rock standards and seawater analyses from this method also give identical results to those above (Chen et al., 2023; Nielsen et al., 2024).

Accuracy and external reproducibility was assessed by repeated analyses of seawater, as well as USGS and GSJ international basaltic rock standards. Details are given in Pogge von Strandmann et al., 2008b and 2011, Foster et al., 2010 and Chen et al., 2023, but for seawater the reported $\delta^{26}Mg$ is −0.89 ± 0.18 ‰ (2sd; n = 20, chemistry = 18) at the OU, −0.82 ± 0.06 ‰ (2sd; n = 34, chemistry = 20) at BIG, and −0.82 ± 0.04 ‰ (2sd; n = 14, chemistry = 14) at LOGIC. The results of two inter-laboratory rock standard comparisons also show that both our silicate and river water $\delta^{26}Mg$ values are both accurate and precise (Shalev et al., 2018; Teng et al., 2015).

4. Results

4.1. River and groundwater samples

Glacial meltwater outwash in Iceland can vary dramatically depending on seasonality and climate. In other words, the source of the water varies between high pH water from the base of the glacier, and low pH surface water runoff. This is apparent especially between sampling in 2003 compared to 2012, where rivers in the former were more dominated by basal flow. For example, sample A8 had a pH ~ 1.5 units lower in 2012 than 2003. This also affects other chemical compositions, as discussed below.

The PHREEQC programme was used to calculate mineral saturation states (using a series of thermodynamic databases, including Phreeqc 3.0.6 and THERMODDEM)(Parkhurst and Appelo, 1999), using the measured physical parameters, major and trace element concentrations as inputs. These are reported as SI, the saturation index, where positive numbers indicate oversaturation, and negative numbers undersaturation. In general, like most Icelandic rivers, Mg-containing primary minerals such as forsterite, diopside and hydrated basaltic glass (Gislason and Oelkers, 2003; Oelkers and Gislason, 2001) are undersaturated, with increased undersaturation at lower pH (which ranges from 7.56 to 9.89). Secondary minerals such as gibbsite, smectite or kaolinite/allophane are most oversaturated at lower pH, and approach saturation at higher pH. In contrast, minerals such as talc and calcite favour oversaturation at higher pH.

Magnesium concentrations in the newly sampled rivers and springs ranges between 6 and 32 μmol/l, which is similar to the glacial rivers in Pogge von Strandmann et al. (2008b), and the Mg/Na mass ratios range between 0.03 and 0.27 (average 0.12). These ratios are considerably lower than those in pristine basalt or riverine bedloads (3.1–10.4), and reflect the preferential mobility of Na over Mg in basaltic rivers (Gíslason et al., 1996). The Ca/Sr ratios tend to scatter between values both lower and higher than basalt. While low Ca/Sr is thought to be indicative of carbonate precipitation, it has been shown that in Iceland considerable variation is caused both by back-reactions and zeolite formation (Fridriksson and Arnorsson, 2004; Hindshaw et al., 2013). In particular, the formation of heulandite is common in Iceland, and this mineral has strong affinities for Ca and Sr (Jacobson et al., 2015), but not for Mg.

The newly measured Mg isotope ratios ($\delta^{26}Mg$) in all river and groundwater samples vary between −0.74 and −0.10 ‰. Relevant samples (i.e. high-pH rivers) from Pogge von Strandmann et al. (2008b) have a $\delta^{26}Mg$ range of −0.39 to + 0.64 ‰; several samples of that study have been re-analysed using different methods, and found to have the same isotope ratio within analytical uncertainty (see Supplement). However, the samples were often taken at the outflow of glaciers, consequently a significant proportion of these samples is meltwater, ultimately derived from rainwater or snow. Groundwaters can be similarly affected, through infiltration of meteoric water. Therefore, it is necessary to perform a precipitation or meltwater correction to both the concentrations and isotope ratios of the samples, using standard mixing equations (e.g. Langmuir et al., 1978), assuming that the measured values are a mixture of weathering-derived Mg and precipitation-derived Mg:

$$[Mg]^{*} = [Mg]_{measured} - [Cl]_{measured} \times \left(\frac{[Mg]}{[Cl]}\right)_{seawater} \quad (1)$$

$$f_{Mg\ from\ precipitation} = 1 - \frac{[Mg]^{*}}{[Mg]_{measured}} \quad (2)$$

$$\delta^{26}Mg^{*} = \left(\delta^{26}Mg_{measured} - f \times \delta^{26}Mg_{seawater}\right)/(1-f) \quad (3)$$

where * denotes precipitation-corrected values. Both this and the previous study (Pogge von Strandmann et al., 2008b) have determined that

Icelandic glacial ice from different locations has a δ^{26}Mg value identical to seawater, which comprises the dominant source of dissolved constituents in Icelandic precipitation (elemental concentrations are given in the Supplement). Therefore, the composition of Icelandic ice, combined with the chloride concentration of the individual samples can be used to correct the analyses, which is also justified by the low Cl^- concentrations of Icelandic basalt (Gíslason et al., 1996; Pogge von Strandmann et al., 2008b; Pogge von Strandmann et al., 2012). Hence, the precipitation-corrected δ^{26}Mg* values from the 2008 study range between −0.27 and + 1.47 ‰, while in the new samples this range is −0.39 to + 3.99 ‰, compared to −0.23 ‰ in pristine basalt. The very high δ^{26}Mg* values in some samples are due to high proportions of rainwater Cl^-, with values up to 96 %.

4.2. Leachates

While sequential leaches are never completely efficient at recovering the phase of interest, the elemental ratios of our method indicate that the leaches have largely targeted the correct phases (Liu et al., 2022; Liu et al., 2023; Pogge von Strandmann et al., 2022). For example, the carbonate phases of the leached bedloads have high [Ca] compared to the other leached phases, and Mg/Ca ratios of ~ 8–16 mmol/mol, in keeping with values of inorganic calcite (e.g. Day et al., 2021; Gabitov et al., 2011), and low Al/Ca (1.6 ± 1 mmol/mol). The oxide leach contains high [Fe] and [Al], and higher [Li] than in the carbonate phase.

On average, ~0.47 % of "solid" Mg in the bedload is in the exchangeable fraction, ~0.21 % in the carbonate phase, ~0.66 % in the oxide phase and > 97 % in the residue. In terms of Mg isotope ratios, in each leached sample the carbonate phase is isotopically lightest (δ^{26}Mg = -1.98 to −0.72 ‰; Fig. 2), while the oxides (−0.44 to −0.32 ‰), and the exchangeable fraction (−0.46 to −0.30 ‰) are broadly similar to the residue (−0.55 to −0.39 ‰), which in turn is similar to unaltered Icelandic basalt (−0.31 to −0.23 ‰ (Opfergelt et al., 2014; Pogge von Strandmann et al., 2008b)).

In comparison, leaching of the USGS standard BCR-2 shows almost an order of magnitude less Mg or Ca in the nominal carbonate fraction, as well as a much higher Al/Ca ratio. Hence, in this basalt that has not been subjected to weathering, there is effectively no carbonate fraction, and other secondary minerals (oxides, clays) are also apparently significantly less abundant. This also demonstrates that the leaching apparently is attacking the correct phases in the weathered basalts.

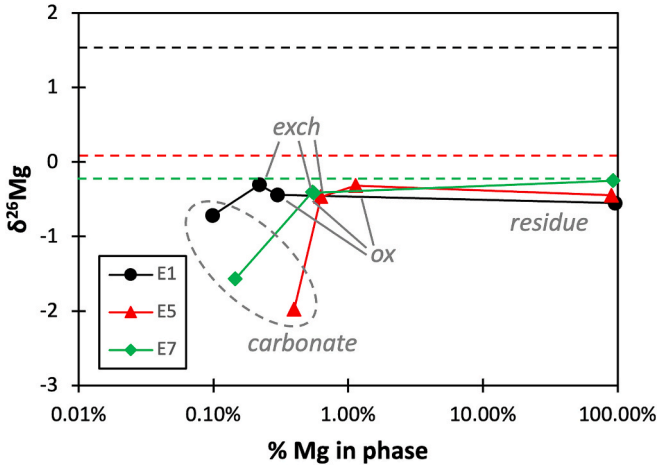

Fig. 2. The results from the sequential leaching (carbonate, exchangeable, oxide and residue) of three glacial river bedloads. The horizontal dashed lines represent the δ^{26}Mg* of the dissolved load of each sample.

5. Discussion

5.1. Secondary mineral formation during basaltic weathering

Given the focus of this study, a brief discussion of secondary mineral formation during basaltic weathering is relevant. Recent highly detailed examinations of basaltic weathering (Alfredsson et al., 2013; Aradottir et al., 2012; Gislason and Oelkers, 2014; Snæbjörnsdóttir et al., 2017) show that secondary minerals that form during water–rock interaction, and contain sufficient Mg to affect the isotopic mass balance, include Mg-rich smectites, mixed layer clays, chlorite, talc, chrysotile, sepiolite, and carbonates such as calcite and aragonite, as confirmed by microscope observation and XRD analyses (Alfredsson et al., 2013; Bishop et al., 2002; Gislason et al., 1993; Hannington et al., 2001; Kristmannsdottir, 1975; Le Gal et al., 1999; Leveille et al., 2007; Neuhoff et al., 1999; Wimpenny et al., 2010b). Siderite forms at the highest pCO_2, Mg-rich carbonates at intermediate pressure and calcite at the lowest pCO_2. Chlorite and talc have been shown more likely to form at hydrothermal temperatures (Hannington et al., 2001; Kristmannsdottir, 1975), which suggests that part of the interpretation in Pogge von Strandmann et al. (2008b) may have been incorrect. Pure water-basaltic glass and crystalline basalt experiments at the slightly lower temperatures of 45–70 °C (albeit still much higher than sub-glacial rivers) and lower-than-atmospheric pCO_2 resulted in the formation of Mg-secondary minerals such as chrysotile, kerolite, smectite, possibly talc (layer spacing was not obtained), and "calcite", where the latter can initially precipitate in forms such as ikaite (hydrated calcite) before reverting rapidly to true calcite (Gislason et al., 1993; Hu et al., 2014; Olsson et al., 2014). Magnesium-rich carbonates, such as dolomite or magnesite only start to form abiotically at temperatures > 50 °C, while calcite, and sometimes aragonite, are the only carbonate that generally forms during low-temperature and low-pCO_2 basalt-water interactions (Aradottir et al., 2012). In particular, calcites tend to form in waters that are isolated from atmospheric CO_2 and therefore have high pH values, such as groundwaters and sub-glacial waters (Alfredsson et al., 2013; Aradottir et al., 2012). Based on structural evidence, it is likely that at 0–4 °C, the initial carbonate that forms is ikaite, which then rapidly transforms to calcite (Olsson et al., 2014).

Generally, in sub-glacial settings, carbonate precipitation during weathering is well-documented (Hallet, 1976; Lacelle, 2007; Souchez and Lemmens, 1985; Thomazo et al., 2017). In most settings, this is caused by the dissolution of calcite from carbonate bedrock on the stress sides of obstacles, and re-precipitation on the lee side by freezing of the meltwater. The freezing of these solutions means that they become supersaturated with CO_2, thus precipitating $CaCO_3$ (Hallet, 1976). In basaltic settings, the processes are somewhat different, as it is the dissolution of the primary silicate minerals and/or glass that provides the Ca, and simultaneously consumes H^+, raising the pH of the interacting water (Gislason and Eugster, 1987). Carbonate precipitation then largely depends on water chemistry: pH is high due to isolation from the atmosphere and other external CO_2 sources, and the consumption of the protons during basalt dissolution; hence calcite becomes supersaturated and precipitates. The primary difference between basaltic groundwaters and sub-glacial waters in Iceland is that sub-glacial rock is often dominated by glassy hyaloclastite rather than crystalline basalt. During hyaloclastite alteration by weathering, the same Mg-rich secondary minerals tend to form: primarily clays (e.g. smectites), and, in particular, calcite (Alfredsson et al., 2013; Allen et al., 1982; Allen et al., 1981; Barry et al., 2014; Galeczka et al., 2014; Galeczka et al., 2015; Le Gal et al., 1999).

The formation and presence of these secondary minerals in subglacial environments was demonstrated during the 1996 jökullhlaup (glacial flood) from under the Vatnajökull icecap, subsequent to the Gjálp subglacial eruption. The suspended matter contained in this flood consisted of around 11 % secondary minerals such as zeolites and calcite (Stefansdottir and Gislason, 2005). Other glacial floods in Iceland have

demonstrated the same effect, including significant CO_2 drawdown by carbonate precipitation (Galeczka et al., 2014; Galeczka et al., 2015).

To summarise, during low-temperature groundwater and subglacial weathering, the main Mg-rich secondary minerals that form are clays such as Mg-smectites, and calcite, with the potential crystallisation of minor chrysotile and sepiolite. The precipitation of carbonates in groundwater has become particularly relevant recently, due to the negative emissions technology mineral carbonation (e.g. Gunnarsson et al., 2018), which seeks to sequester CO_2 in exactly these phases.

The mean global riverine δ^{26}Mg is ~ -1.09 ‰ (Tipper et al., 2006b), significantly lower than the composition of the mantle, and mantle-derived rocks, of −0.23 ‰ (Hin et al., 2017; Lai et al., 2015; Pogge von Strandmann et al., 2011b). A major part of the process that causes rivers to be isotopically light, relative to the mantle, is weathering of isotopically light carbonates, which have a range of δ^{26}Mg between −4.5 and −1‰ (Hippler et al., 2009; Li et al., 2012; Mavromatis et al., 2012; Pogge von Strandmann, 2008; Saenger and Wang, 2014; Saulnier et al., 2012; Tipper et al., 2006a; Wombacher et al., 2011). However, while mixing between the isotope ratios of silicate relative to carbonate rocks may be able to explain much of the difference in composition of large rivers (Chen et al., 2023; Gou et al., 2023; Tipper et al., 2008; Tipper et al., 2006b; Xu et al., 2022), additional Mg isotope fractionation during silicate weathering has also been observed, as silicate secondary minerals preferentially take up isotopically heavy Mg, driving river waters isotopically lighter (Huang et al., 2012; Lee et al., 2014; Liu et al., 2014; Opfergelt et al., 2012; Opfergelt et al., 2014; Pogge von Strandmann et al., 2008b; Pogge von Strandmann et al., 2012; Tipper et al., 2006a; Tipper et al., 2008; Tipper et al., 2010; Tipper et al., 2012a; Tipper et al., 2012b; Wimpenny et al., 2010a; Wimpenny et al., 2011).

Nevertheless, Pogge von Strandmann et al. (2008a) reported δ^{26}Mg values for river waters that were higher than those of any accompanying solid phases (pristine bedrock, bedload or suspended load) in basaltic terrains in Iceland. This relationship has not been observed in other volcanic terrains from around the globe. Basaltic soil pore waters have on occasion been reported to be isotopically heavier than corresponding soils (Pogge von Strandmann et al., 2012), but in this case the phenomenon is likely due to adsorption of Mg onto the surface of secondary minerals that do not include Mg as a constituent element (e.g. allophane or ferrihydrite), and likely have a limited influence on rivers (Huang et al., 2012; Opfergelt et al., 2014). Pogge von Strandmann et al. (2008a) suggested these heavy riverine values were due to precipitation of minerals such as chlorite or talc that are theoretically stable at high pH, although they tend only to form at temperatures > 180 °C (Hannington et al., 2001; Kristmannsdottir, 1975), although laboratory experiments have possibly observed them forming at 65 °C (Gislason et al., 1993). Metamorphic chlorite has been shown to have a range of δ^{26}Mg values, from similar to other silicates in the rock (Pogge von Strandmann et al., 2015) to values that are lighter (Ryu et al., 2011); however, neither of these cases was basaltic. It is also unknown whether they form in sufficient quantity in this environment to dominate the Mg budget. Hence, the phenomenon of isotopically heavy rivers is yet to be fully understood (Fig. 3).

To produce higher aqueous δ^{26}Mg values than the primary rock, isotopically light minerals must be precipitating, or isotopically heavy minerals must be dissolving. Mineral Mg/Si stoichiometry can assist in identifying the mineral(s) responsible, given that most relevant secondary minerals are Mg-silicates. As Fig. 4 shows, solution Mg/Si is only

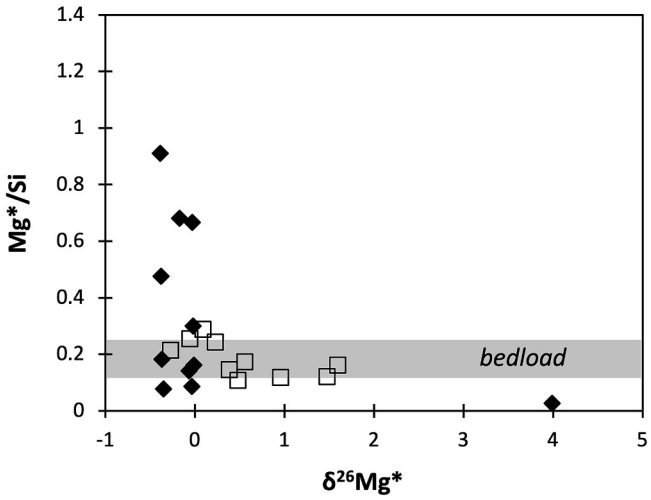

Fig. 4. Solution molar Mg*/Si ratios plotted as a function of δ^{26}Mg* values. Filled diamonds are samples from this study, while open squares are glacier-fed samples from Pogge von Strandmann et al. (2008a). The grey band is the range of average bedload samples from these rivers (Pogge von Strandmann et al., 2006). Mineral stoichiometry suggests that the high δ^{26}Mg values are not caused by minerals with Mg:Si ratios significantly different from bulk basalt, eliminating most silicate secondary minerals from controlling δ^{26}Mg.

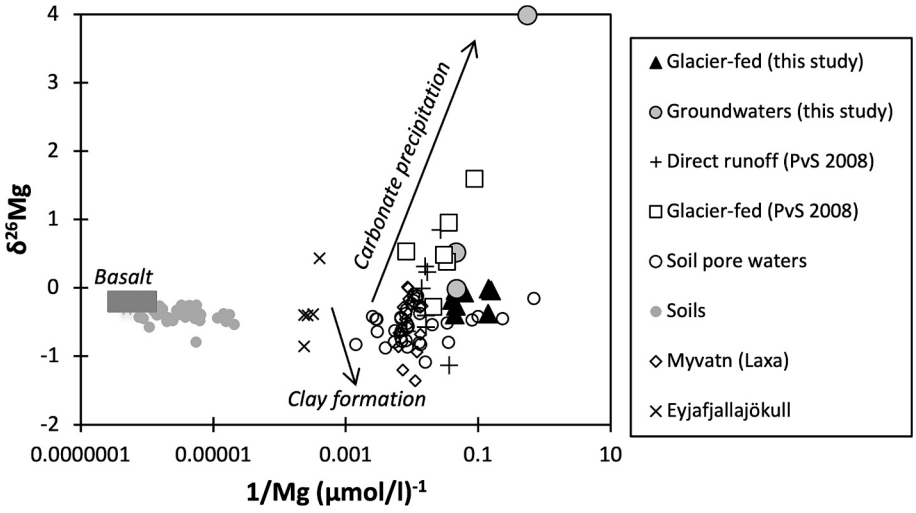

Fig. 3. Isotope vs. reciprocal concentration diagram for all measured and published Icelandic Mg isotope ratios (Opfergelt et al., 2014; Pogge von Strandmann et al., 2008b; Pogge von Strandmann et al., 2019a; Pogge von Strandmann et al., 2012; Pogge von Strandmann et al., 2020), showing the different fractionation directions due to carbonate and silicate secondary mineral formation. Diagram is adapted from Pogge von Strandmann et al., 2012. Solution data are δ^{26}Mg* where Cl^- data are available.

high (>0.3) when $\delta^{26}Mg^*$ <0. When $\delta^{26}Mg^*$ >0, the solutions' Mg/Si is generally similar to that of bulk basalt (average bedload Mg/Si = 0.193 ± 0.06; average Mg/Si of samples with $\delta^{26}Mg > 0$ is 0.189 ± 0.13). Therefore the cause of solutions with $\delta^{26}Mg > 0$ is unlikely to be re-dissolution of isotopically heavy secondary minerals, because most of the potential secondary minerals have stoichiometric Mg/Si ratios greater than basalt (talc ~ 0.75; chlorite ~ 1.67; chrysotile ~ 1.5; sepiolite ~ 0.67 (Deer et al., 1992)). Smectites have a lower Mg/Si (~0.125–0.5, depending on mineralogy (Aradottir et al., 2012; Deer et al., 1992)), and so their dissolution could in theory be controlling the Mg/Si of the waters. However, in the pH range 8–10, Icelandic Mg-smectites are generally oversaturated and stable (Gíslason et al., 1996; Stefansson and Gislason, 2001). There is also no relationship in this study between the saturation of different Mg-smectites (even when factoring in saturation uncertainty) and $\delta^{26}Mg^*$ (r^2 = 0.003–0.08; see Supplement). Undersaturated samples (SI = −4–0), where clays could be dissolving, show both heavy and light Mg isotope ratios (−0.38 to + 3.9 ‰), hence smectite dissolution is unlikely to be a controlling influence in these waters. The dissolution of isotopically heavy primary minerals is also unlikely to be the source of high dissolved $\delta^{26}Mg$ values, given that primary basaltic minerals (i.e. glass, olivine, plagioclase, pyroxene) have a very narrow range around the bulk basaltic value of −0.23 ‰ (Teng, 2017), in turn indistinguishable from that the mantle (e.g. Handler et al., 2009; Pogge von Strandmann et al., 2011b). Further, adsorption of Mg is also a candidate. However, adsorption is generally thought to drive solution $\delta^{26}Mg$ to lower values (e.g. Huang et al., 2012; Opfergelt et al., 2014; Pogge von Strandmann et al., 2012), and the remarkably similar mobility of Si and Mg during Icelandic weathering (Gíslason et al., 1996) also suggests that this process would not affect Mg/Si ratios.

Precipitation of secondary minerals would drive Mg/Si significantly lower than observed, and, in the case of those minerals that have been examined (e.g. smectites (Wimpenny et al., 2014)), would also drive solution Mg isotopes lighter. Two groundwater samples (Laug1, collected in 2012, and G1, from 2008) have Mg/Si ratios < 0.1. This may be because those waters have access to fresh, unweathered basaltic glass, which has a low Mg/Si ratio.

A possible alternative is that calcite precipitation is the overall fractionation mechanism in these high-pH samples. It is well established from experimental studies and work on oceanic carbonate-bearing sediments that calcite preferentially incorporates light Mg isotopes (Immenhauser et al., 2010; Saenger and Wang, 2014; Saulnier et al., 2012; Wombacher et al., 2011). Calcite stoichiometry can also explain the values observed in Fig. 4, assuming as discussed below, that only high-pH samples are precipitating calcite. If no Si and only 10 % of solution Mg were removed by calcite precipitation, then the Mg/Si stoichiometry would be changed by the degree observed, and the high Mg isotope fractionation factor of calcite would explain the observed isotopic ratios. It therefore seems possible that sub-glacial and groundwater calcite formation is driving some of the analysed waters to isotopically heavy compositions.

Several previous studies on Icelandic rivers have suggested that dissolved Mg isotopes are on occasion controlled by carbonate precipitation. Following the 2010 eruption of Eyjafjallajökull, travertine was observed precipitating in a stream emerging from under the resulting lava (Olsson et al., 2014). The stream $\delta^{26}Mg$ values increased with flow distance (from −2.37 to + 0.43 ‰), as more Mg was removed into the travertines (Pogge von Strandmann et al., 2019a).

Further, a time-series of the river draining Lake Myvatn, Iceland, which is one of the most productive lakes in the northern hemisphere, was analysed. Seasonally, the productivity changes considerably (Opfergelt et al., 2011b), and during the summer this causes the lake to be supersaturated with respect to calcite. This is mimicked by the solution Mg isotope ratios, which also increase during the summer, and correlate with the calcite saturation index (Pogge von Strandmann et al., 2020).

5.2. Sub-glacial calcite precipitation

In this study, there is an overall co-variation between precipitation-corrected Mg isotope ratios and pH, and the rivers with $\delta^{26}Mg^*$ values greater than that of basalt tend to be those with high pH (>8), and are largely associated with a glacial or groundwater source (Fig. 5b). As detailed above, stoichiometry suggests that these values are being driven high by precipitation of a mineral that contains Mg, but no Si, and preferentially takes up isotopically light Mg. Such a mineral is likely to be calcite, which is well-documented to precipitate as a secondary mineral during reactions isolated from the atmosphere (Section 1.1).

There is a co-variation between $\delta^{26}Mg$ and calcite SI (Fig. 5a; r^2 = 0.62; >99 % significant Spearman Rank correlation). Interestingly, riverine $\delta^{26}Mg$ values start to increase above basaltic values when calcite saturation indices are still just below saturation (i.e. < 0). There may be several reasons for this, including uncertainty in thermodynamic data (likely small in the case of calcite) and uncertainty from analyses of fluid composition (pH, concentration, etc.), which propagates to ~ ±0.5SI units (Stefansson and Gislason, 2001). Further, there is a difference between samples taken from the centre of a stream (such as our samples) compared to where precipitates tend to form, which is in the shallower edges of streams where water–air interactions control a greater proportion of the mass balance. Hence it is possible that the centre of a stream is slightly undersaturated, while stream edges are supersaturated and vice versa, depending on the initial partial pressure of CO_2 with respect to atmosphere. Some rivers were also sampled several km from the glacier snouts, giving time for invasion of CO_2 from the atmosphere into the waters, lowering pH and therefore the saturation index (SI) of the water with respect to calcite. The in situ partial pressures of CO_2 are plotted as a function of pH in Fig. 6, and are mostly below the present CO_2 atmospheric partial pressure (<400 ppmv at the time of sampling; log $pCO_2 = 10^{-3.40}$), therefore tending to absorb CO_2 from the atmosphere (Gíslason et al., 1996). The CO_2 invasion causes changes in saturation index calculations, but not in $\delta^{26}Mg$ since most of the calcite is left behind at the weathering site and therefore does not dissolve. Therefore, it is likely that PHREEQC-derived calcite saturation states in this case do not provide the same sensitivity as Mg isotopes. Such an effect has also been observed in Icelandic groundwaters, when comparing calcite saturation with Ca isotopes (Pogge von Strandmann et al., 2019c).

The existence of carbonates in riverine materials is further demonstrated by the sequential leaches that were performed on three of the glacial bedload samples. Even though these waters are both under- and supersaturated for calcite (SI = −0.29 to +0.22), their bedloads contain a carbonate portion that is isotopically light (Fig. 2). Notably, Fig. 2 also shows the corresponding dissolved $\delta^{26}Mg^*$ values, which for two of the samples are higher than their bedload residue, or any leached phase, which requires Mg being taken into an isotopically light reservoir. The Mg isotope fractionation between the carbonate fraction of the bedload and the coeval precipitation-corrected dissolved load ranges between $\Delta^{26}Mg_{carb\text{-}water}$ = -2.31 and −1.36 ‰. In comparison, the fractionation imposed by experimental inorganic calcite precipitation ranges between −3.3 to −1.3 ‰ (Mavromatis et al., 2013; Saulnier et al., 2012), with effects from the precipitation rate of the calcite. The similarity between these measured fractionations and those in laboratory experiments further suggests that calcite precipitation is a factor driving the dissolved $\delta^{26}Mg^*$ to high values.

5.3. Modelling carbonate precipitation

With the measured solution $\delta^{26}Mg^*$, [Mg*] and published partition coefficients, as well as either measured or published calcite fractionation factors, it is possible to calculate the amount of calcite that precipitates to cause the observed isotope ratio changes from a basaltic starting composition (Pogge von Strandmann et al., 2019a; Pogge von Strandmann et al., 2019c). This assumes that, at the point of sample collection,

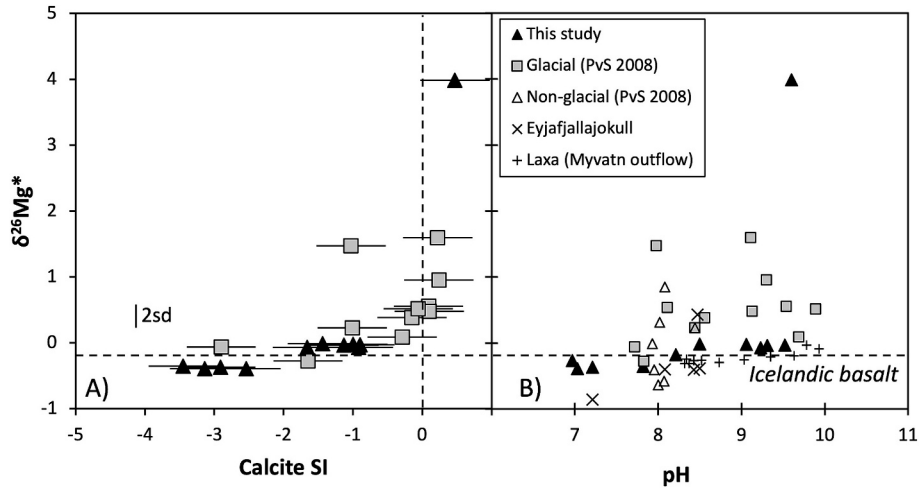

Fig. 5. A) precipitation-corrected dissolved Mg isotope ratios plotted again the calcite saturation index (the error bars represent the propagated uncertainty on snapshot PHREEQC calculations) and B) pH. The horizontal dotted line represents the δ^{26}Mg composition of primary basalt, and the vertical line calcite saturation.

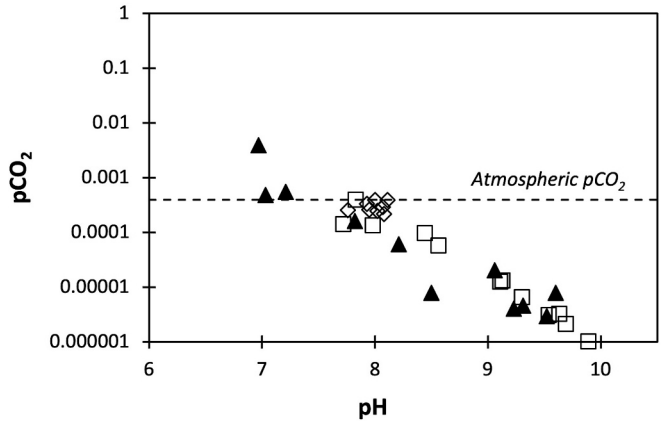

Fig. 6. Calculated CO_2 partial pressures for the Icelandic samples (figure symbols are the same as for Fig. 5). Most samples, except low-pH ones, are absorbing CO_2 from the atmosphere.

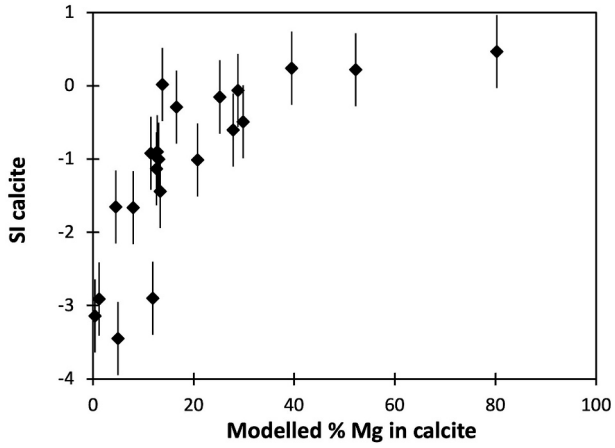

Fig. 7. The modelled % of Mg taken into calcite (calculated from the Mg isotope ratio) shown against the saturation index of calcite. The more Mg is being taken into calcite, the higher the calcite SI, suggesting a relationship between these two independent parameters.

the only precipitating secondary mineral was carbonate. If additional clay were precipitating, then this estimate of carbonate precipitation would be a minimum estimate:

$$\delta = \delta^{i} + 1000(\alpha - 1)lnf \quad \text{Eqn. 4.}$$

where δ is the δ^{26}Mg of the water and δ^{i} is the δ^{26}Mg of the starting compositions of the input Mg, in this case the Mg isotope ratio of basalt. α is the isotopic fractionation factor, and f is the fraction of Mg remaining in solution.

We calculated the partition coefficient from an experimental relationship of the partition coefficient and water Mg/Ca, and using the Mg/Ca of our river waters (Mucci and Morse, 1983). Using a published fractionation factor of $\alpha = 0.9973$ (Mavromatis et al., 2013; Saenger and Wang, 2014), the amount of dissolved Mg taken up in calcite in these samples ranges from ~ 0.4 to 80 %. This parameter also co-varies with the saturation index of calcite (Fig. 7), which was independently calculated from entirely different parameters (δ^{26}Mg and [Mg] vs. pH, alkalinity and [Ca]). Thus, when calcite is supersaturated, the Mg isotope ratios suggest that a large amount of Mg has been taken into calcite, which gives confidence that this approach works (Pogge von Strandmann et al., 2019a; Pogge von Strandmann et al., 2019c). If the fractionation factor between the leached carbonate fraction and solution δ^{26}Mg* of our glacial samples is used, then the relationship with calcite SI still exists, but the uptake of Mg into calcite ranges from a minimum of 0.5–0.8 % to a maximum of 85–96 %.

Given a "known" partition coefficient, the molar Mg/Ca of the precipitated calcite can then be calculated (Pogge von Strandmann et al., 2019a; Pogge von Strandmann et al., 2019c):

$$[x] = [(x)_{solution} - f^{*}(x)_{solution}]D \quad \text{Eqn. 5.}$$

where [x] could either be [Mg] or Mg/Ca, depending on what partition coefficient (D) is used, and ranges between ~ 0.0001 and 0.10 (average 0.008). This is a similar average to the travertines precipitated during the Eyjafjallajökull 2010 eruption (average ~ 0.01).

Some of our samples were taken next to flow gauges, or, in the south-eastern glacial rivers where river cross-sections are too variable for flow gauges, there are some generalised estimates for runoff (Pogge von Strandmann et al., 2006; Pogge von Strandmann et al., 2023; Vigier et al., 2009). This then yields calcite formation fluxes of on average ~ 0.7 t/km^2/yr for the Langjökull glacier, and 25 t/km^2/yr for the considerably larger Vatnajökull icecap, when according to the formula:

$$calcite\ formation\ flux = \frac{[x] \times runoff}{D} \quad \text{Eqn. 6.}$$

It must be noted that the Langjökull samples were taken further away from the snout of the glacier than those for Vatnajökull, and therefore the former may represent an underestimate because runoff estimates may not be fully representative of glacially-sourced water (e.g. the lowest value is a sample taken ~ 50 km from Langjökull).

The use of a Reyleigh fractionation formula is justified by some samples having a too high $\delta^{26}Mg^*$ to be explained by batch ("equilibrium") fractionation. For the other samples, if batch fractionation is used, it results in similar calcite formation fluxes of ~ 0.77 t/km^2/yr for the Langjökull glacier, and ~ 30 t/km^2/yr for the Vatnajökull icecap.

This modelled calcite precipitation rate also co-varies with pH (Fig. 8), where the model suggests that rivers with very high pH are precipitating more calcite. It should be noted that pH is not an input into these calculations, and therefore this correlation offers an independent indication that the model approach is valid.

The total uncertainty on these results includes a number of factors, including analytical uncertainty, potential effects on α such as speciation, uncertainty on the partition coefficients used, and uncertainty on the measured runoff. Of these, the last is the most poorly constrained, and we assume a 10 % error in this. Cumulatively, this conservatively yields total uncertainties of around 50 % on the final calcite precipitation rates (Fig. 8).

Samples from 2003 that were re-collected in 2012 (A8 and E5) show similar rates for E5 (Vatnajökull), while for A8 (Langjökull), rates were 1.3 t/km^2/yr in 2003 and 0.02 t/km^2/yr in 2012. This difference is solely due to the difference in measured dissolved $\delta^{26}Mg$, likely caused, as discussed above, by seasonal variations in subglacial carbonate precipitation.

Normalised to drainage area, these rates equate to 26–3800 t/yr $CaCO_3$, with a Langjökull average of 1100 t/yr (1300 t/yr for batch fractionation), and a Vatnajökull average of 1700 t/yr (2300 t/yr for batch fractionation). These relatively low estimates can be compared to those occurring when volcanic eruptions dramatically increase the DIC content and therefore the calcite precipitation rate: Olsson et al. (2014) reports ~ 9100 t/yr $CaCO_3$ precipitation for the 2010 Eyjafjallajökull eruption, and the 1996 eruption beneath Vatnajökull ice cap is estimated to have produced around 1.8×10^{10} mol of C, from which ~ 1.1×10^6 t was precipitated as carbonate in 35 days (Gislason et al., 2002), giving a rate of ~ 1.15×10^7 t/yr $CaCO_3$. During the 2002 glacial flood of the Skaftá River, 2.3×10^5 t CO_2 was drawn down due to carbonate precipitation during the 7 day flood (Galeczka et al., 2015). These cases were enhanced due to saturation changes from volcanic eruptions or geothermal melting, and therefore must be considered an upper limit to any normally occurring carbonate precipitation. A comparison to soils shows that alkalinity enhancement in a 3 m Icelandic thick soil profile that received a large dust flux for 3000 years suggests

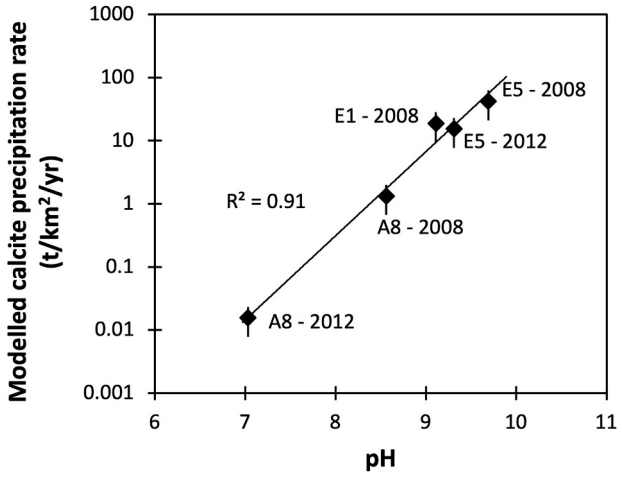

Fig. 8. The modelled calcite precipitation rate for these samples, based on Mg isotopes, plotted against the water pH (where pH is not a defining parameter on the modelled rate). The higher the pH, the more calcite is precipitating. The sample labels show the location (A = Langjökull; E = Vatnajökull), and the year. The error bars represent the propagated uncertainty as discussed in the text.

precipitation of ~ 140 t calcite/km^2/yr (Linke et al., 2023), higher than our subglacial precipitation per km^2.

In principle, basaltic groundwater- or sub-glacial carbonate formation will have an effect on CO_2 sequestration. While significantly more data are needed to address this properly, a simple calculation for the last glacial maximum (Weichselian), when Iceland was entirely glaciated (Geirsdottir and Eiriksson, 1994), would suggest a sequestration rate of ~ 1.15 ± 0.8 Mt CO_2 per year due to sub-glacial inorganic calcite precipitation, equating to sequestration of ~ 11.5 ± 5.8 Gt CO_2 for the entire ~ 10 ka long glaciation of Iceland at the Last Glacial Maximum (LGM), approximately 2 % of the total glacial-interglacial CO_2 change.

The sub-glacial carbonate would also have dissolved as it was exposed during glacial retreat (11 % of Iceland is still glaciated), also consuming atmospheric CO_2, forming bicarbonate in rivers and transporting that carbon to the oceans, following the formula $CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^-$. Hence, for every mole of subglacial carbonate dissolved, another mole of atmospheric CO_2 is withdrawn, and both are delivered to the oceans. Eventually, over geologic timescales, half of that carbon will be released back to the atmosphere, but initially that carbon is removed from the atmosphere. Therefore, this process could temporarily withdraw a further ~ 10 Gt CO_2 from the atmosphere.

5.4. Implications of Mg isotope sensitivity to carbonate formation

An interesting further outcome of this study is that secondary silicate precipitation experiments have suggested that phyllosilicate bond lengths and differences in mineral structure can drive Mg isotope fractionation in different directions (Hindshaw et al., 2020). The original interpretation of the Icelandic isotopically heavy waters was similar, in that the precipitation of different secondary silicates caused both the isotopically light and heavy river waters (Pogge von Strandmann et al., 2008b). Isotopically heavy surface waters have been reported by other studies, but only in weathering environments where dissolution-reprecipitation reactions occur, plus the potential physical removal of isotopically distinct phases (Gao et al., 2018; Ma et al., 2015). Hence, the original interpretation of the Icelandic heavy rivers was, so far, the only observational field data that suggested that fractionation direction may depend on silicate mineral structure. However this study now has refuted that possibility, meaning that a disconnect between laboratory experiments and field observations remains.

The same study suggested that trace carbonates could affect the Mg isotope ratios of rivers, even in silicate-dominated catchments, due to carbonate's faster reaction kinetics (Hindshaw et al., 2020). Indeed, prior calcite precipitation (PCP) in some settings has been shown to affect water $\delta^{26}Mg$ values (e.g. Gou et al., 2023; Immenhauser et al., 2010). This study confirms that carbonate precipitation can strongly affect riverine Mg isotope ratios, even in catchments where the initial bedrock is solely silicate, and this opens up both the necessity of considering carbonate precipitation and dissolution during Mg isotope studies, but also the intriguing possibility of using Mg isotopes as a tracer for this.

Interestingly, Mg isotopes may be a more sensitive indicator of calcite precipitation than calcium isotopes, given the amount of fractionation that occurs, and the precision of the measurement for each isotope system. For Mg isotopes, inorganic calcite precipitation causes ~ 1.3 to > 3.3 ‰ fractionation, 0.65–1.65 ‰/a.m.u. (atomic mass units) (Galy et al., 2002; Li et al., 2012; Mavromatis et al., 2013; Pogge von Strandmann, 2008; Saulnier et al., 2012), and ~ 0.6 to 1.5 ‰ $\delta^{44/40}Ca$ fractionation, 0.15–0.4 ‰/a.m.u., albeit complicated by a temperature dependence (DePaolo, 2004; Fantle and Tipper, 2014; Gussone et al., 2005)). Given reasonable external analytical precision (e.g. ± 0.07 ‰ for $\delta^{26}Mg$ (Foster et al., 2010; Pogge von Strandmann et al., 2011b) and ± 0.07 ‰ for $\delta^{44/40}Ca$ (Chen et al., 2023; DePaolo, 2004; Hindshaw et al., 2013)), Mg isotopes are ~ 3–16 times more sensitive to calcite precipitation than Ca isotopes, assuming of course that the

precipitated carbonate contains at least trace amounts of Mg.

5.5. Conclusions

This study examines the possibility of sub-glacial carbonate precipitation as the mechanism for generating heavy riverine Mg isotope ratios in Iceland, which hitherto were explained as the formation of hydrothermal-temperature Mg-rich minerals, such as chlorite. However, the high pH conditions in sub-glacial waters and groundwaters are also conducive to precipitating carbonates.

In our samples, $\delta^{26}Mg^*$ (corrected for rainwater input) values co-vary with both the calcite saturation index and pH, suggesting that calcite precipitation is one of the key controls in driving solution $\delta^{26}Mg$ high, specifically in high-pH waters.

This then allows the Mg isotope ratios to be used to calculate the calcite precipitation rates, using calculations based only on the riverine isotope composition, and "known" carbonate fractionation factors and partition coefficients. The amount of Mg taken in calcite calculated thus also co-varies with the calcite saturation index and pH, with more calcite precipitation as pH increases. This also shows that it is possible to use Mg isotopes to calculate such precipitation rates.

Therefore, high river $\delta^{26}Mg$ values in these glaciated basaltic terrains are most likely due to carbonate formation. Extrapolated, subglacial carbonate formation in the last glacial maximum on Iceland could have accounted for ~ 2 % of the total pCO_2 change.

Data availability

Data are available through the Gutenberg Open Science repository at https://openscience.ub.uni-mainz.de/handle/20.500.12030/13780 or https://doi.org/10.25358/openscience-13759.

CRediT authorship contribution statement

Philip A.E. Pogge von Strandmann: Investigation. **Xianyi Liu:** Writing – review & editing, Formal analysis. **Chun-Yao Liu:** Writing – review & editing, Investigation, Formal analysis. **Sigurður R. Gíslason:** Writing – review & editing, Investigation. **Kevin W. Burton:** Writing – review & editing, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

The supplement contains the data tables, including concentrations and isotope ratios of the river waters, leaches of the bedload and parameters used for model calculation. Supplementary material to this article can be found online at https://doi.org/10.1016/j.gca.2025.12.017.

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