



## The behaviour of magnesium and its isotopes during glacial weathering in an ancient shield terrain in West Greenland

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### ABSTRACT

The magnesium (Mg) isotope composition of rivers is sensitive to changes in the balance of primary mineral dissolution and secondary mineral formation. As these processes are regulated by climate then changes to the Earth's climate system, such as the onset of glaciation, could potentially alter the isotopic behaviour of Mg in rivers. To investigate how Mg isotopes behave during glacial weathering, we have determined the Mg concentration and Mg isotope ratio for the dissolved, suspended and bedload phases of glacial and non-glacial rivers in west Greenland. This region is essentially monolithological and there is little biological activity; hence isotope variations largely result from differences in weathering processes. Dissolved Mg in rivers is always enriched in the light Mg isotopes relative to the bedload ( $\delta^{26}\text{Mg} = -0.4\text{‰}$ ), and the glacial rivers have lighter Mg isotope compositions ( $\delta^{26}\text{Mg} -1$  to  $-1.3\text{‰}$ ) than the non-glacial rivers ( $\delta^{26}\text{Mg} \sim -0.6\text{‰}$ ). Enrichment of light Mg in the dissolved load is consistent with the preferential uptake of heavy Mg from solution during the formation of secondary silicate minerals. However, evidence from saturation state modelling suggests that little secondary mineral formation is likely to have occurred in the glacial rivers because the concentration of dissolved solids is very low. Moreover, the glacial derived suspended sediment has identical Mg isotope ratios to the bedload. These observations suggest that the formation of secondary weathering minerals is not controlling the behaviour of Mg isotopes in these rivers. Rather, variations in the  $\delta^{26}\text{Mg}$  value of the dissolved load are attributed to incongruent weathering of the solid phase: preferential dissolution of carbonate minerals, which have low  $\delta^{26}\text{Mg}$  ( $-1.1$  to  $-5.2\text{‰}$ ), imparts a more negative  $\delta^{26}\text{Mg}$  signal to the glacial river waters. Although our study indicates that the Mg isotopic composition of the dissolved load is sensitive to changes in weathering congruence, it is unlikely that glaciation will result in major changes in the  $\delta^{26}\text{Mg}$  composition of continental runoff.

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### 1. Introduction

The transfer of magnesium (Mg) from the continents to the oceans, by chemical weathering, and its removal from seawater through hydrothermal exchange at mid-ocean ridges, plays a major role in the global carbon cycle, and temporal variations in the Mg concentration of seawater have been invoked as a controlling factor on the carbonate mineralogy of the ocean (Albarède and Michard, 1986; Berner et al., 1983; Tipper et al., 2006a,b; Wilkinson and Algeo, 1989). Magnesium is removed from the ocean during hydrothermal

reaction at mid-ocean ridges, via its combination with  $\text{HCO}_3^-$  to form dolomite (Holland, 2005), and ion exchange reactions involving the substitution of Mg for Ca in clays (Elderfield and Schultz, 1996). The major input of Mg to the oceans is from the weathering of continental rocks, principally delivered by rivers and groundwaters (Berner and Berner, 1996; Burnett et al., 2001; Holland, 2003). At the present-day the oceans have a uniform Mg concentration of 53 mmol/l (Carpenter and Manella, 1973) and a uniform  $\delta^{26}\text{Mg}$  isotope value of  $-0.82 \pm 0.1\text{‰}$  (Chang et al., 2004; Tipper et al., 2006b; Young and Galy, 2004), consistent with a long residence time of between  $\sim 10$  and 14 Myr (Berner and Berner, 1996; De Villiers et al., 2005).

The principal controls on river and groundwater Mg isotope compositions are rock type, secondary mineral formation, and biological incorporation. In large rivers, that drain diverse rock types, the Mg abundance and isotope composition of waters appears to be dominantly controlled by weathering reactions that reflect a balance between the dissolution of primary minerals and the formation of secondary minerals (Tipper et al., 2006a,b). The

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liberation of Mg from primary phases is dependent upon the mineral dissolution rate, while the incorporation into secondary minerals is dependent upon the nature of the phase being formed. For example, heavy Mg isotopes are preferentially incorporated into the secondary clay smectite (Tipper et al., 2006a,b) driving the residual waters to light isotope compositions. In contrast, light Mg isotopes are preferentially incorporated into calcium carbonate, leaving heavy isotopes in the residual waters (Galy et al., 2002). In smaller, monolithological catchments, the importance of rock types is evident, and catchments that are dominated by carbonate rocks generally yield waters with lighter Mg isotope compositions than those that drain silicates (Brenot et al., 2008; Tipper et al., 2006a,b). Recent work has also shown that Mg isotopes are sensitive to biological uptake (Bi et al., 2008; Black et al., 2006; Ra and Kitagawa, 2007). Cyanobacteria preferentially extract light Mg from solution into chlorophyll-a (Black et al., 2006), while marine phytoplankton and higher plants preferentially incorporate heavy Mg from their growth medium (Bi et al., 2008; Ra and Kitagawa, 2007).

Silicate weathering rates are primarily controlled by temperature and runoff (Bluth and Kump, 1994; Dessert et al., 2003; Gaillardet et al., 1999a,b; Gislason et al., 2009; White and Blum, 1995; White and Brantley, 1995). High temperatures and high water–rock ratios enhance the dissolution rates of primary phases, liberating elements for potential incorporation into secondary minerals. Therefore, it is reasonable to assume that during glacial intervals, when temperatures are cooler and continental runoff is lower, the Mg isotope composition of the riverine flux may be very different from that at the present-day.

At the present-day glacial regions supply a small proportion of the total riverine flux of water to the oceans, just ~1% (Tranter, 2003). However, models suggest that at the height of last deglaciation [7–12 ka (Petit et al., 1999)], glacial regions supplied as much as ~18% of total global runoff (Jones et al., 2002). Although glacial rivers are usually characterised by a low dissolved elemental concentration (Tranter, 2003), the total flux of material may still be significant. Chemical weathering rates from glacial regions have been shown to be similar to (Anderson et al., 1997) or higher than (Sharp et al., 1995) non-glacial catchments with a similar runoff. This is because glacial regions produce significant quantities of fine grained sediment that is highly susceptible to chemical weathering (Petrovich, 1981). The chemistry of glacial waters is also often distinctive due to low water–rock contact times and the highly incongruent nature of weathering. For example, glacial rivers are characterised by relatively high levels of Ca, K and  $\text{SO}_4^{2-}$ , irrespective of the underlying bedrock (Tranter, 2003), because of the preferential dissolution of phases such as carbonate, biotite and sulphide. Therefore, one approach to quantifying the impact of climate change on the Mg elemental and isotope flux to the oceans is to compare the chemistry of the signal seen in glacial rivers with that of non-glacial rivers in the same or similar terrains (cf. Pogge Von Strandmann et al., 2008).

This study aims to investigate how the chemical and physical weathering processes in an actively glaciated ancient shield terrain affect the behaviour of Mg isotopes. Glacial and non-glacial rivers have been investigated adjacent to the ice sheet in western Greenland, near the town of Kangerlussuaq. This region is essentially monolithological (Escher and Pulvertaft, 1995) and, in general, sparsely vegetated (Anderson et al., 1997) hence biological influences are minimal. Consequently, the Mg isotope data can be interpreted in terms of the major mineral reactions, i.e. the balance between primary mineral dissolution and secondary mineral formation. The chemical composition of these Greenland samples, together with their lithium isotopic composition, is the subject of a companion paper (Wimpenny et al., 2010). That study demonstrates that the intensity of chemical weathering in the glacial versus the non-glacial rivers is very different. In the glacial rivers the water–rock contact times are short because the volume of water and the flow rate are high so the time that water

molecules interact with sediment grains is relatively short. For this reason, the rivers are diluted, mineral saturation states are low and secondary mineral formation is suppressed. Conversely, the non-glacial rivers have higher water–rock contact times, higher elemental concentrations, higher saturation states, and secondary mineral formation is more likely to occur. This difference in the nature of chemical weathering between glacial and non-glacial rivers should be apparent in the elemental and isotopic composition of dissolved Mg, enabling an assessment of impact of glacial weathering on the continental Mg flux delivered to the oceans.

## 2. Geology, climate and river settings

The studied area lies between the town of Kangerlussuaq in SW Greenland and the ice sheet some 35 km inland, and the samples measured here are the same as those described in a companion study (Wimpenny et al., 2010). The underlying bedrock is essentially monolithologic, comprising Archean gneiss metamorphosed to amphibolite facies, with a common mineral assemblage of biotite–garnet–cordierite–sillimanite–quartz (Escher and Pulvertaft, 1995; Wells, 1979). The climate in this region is Arctic and arid; the mean annual temperature is  $-5\text{ }^\circ\text{C}$  and the sample area is underlain by a layer of continuous permafrost (Jorgensen and Andreasen, 2007). However, due to its continental location, the annual temperature range is high; in winter, temperatures can be as low as  $-50\text{ }^\circ\text{C}$  while summers can be relatively mild with temperatures exceeding  $20\text{ }^\circ\text{C}$  (Russell, 2007). Kangerlussuaq lies in a region of negative precipitation where evaporation exceeds precipitation by ~150 mm each year; these relatively high levels of evaporation have led to the formation of numerous saline lakes.

River samples were taken from the Watson River and its glacially and non-glacially sourced tributaries (see Fig. 1). For the purposes of this study ‘glacial’ rivers are those that are directly sourced from ice sheet melting, while ‘non-glacial’ rivers are those that are sourced from surface runoff and lake waters. Glacial river samples were taken at a range of distances from the ice sheet; for example, GR9 and GR1 were taken adjacent to the glacial outflow while sample GR5 was taken 30 km downstream in Kangerlussuaq. Consequently these river samples will reflect different degrees of mixing with non-glacial sources depending on their distance from the ice sheet. However, the flux of water delivered by non-glacial tributaries is relatively low and any effect on the glacial river chemistry should be limited. Non-glacial river waters were taken from a number of streams and small rivers, some of which were strongly coloured (GR11 and GR12), suggesting that they contain relatively high levels of dissolved organic matter. Overland flow from the ice sheet to the lakes is limited and, although subsurface mixing between glacial and non-glacial waters is possible, this is likely to be minimal due to the continuous layer of permafrost (Jorgensen and Andreasen, 2007). Finally, one water sample (GR3) was taken from the ice sheet itself: because it has had no contact with bedrock it represents the lowest chemical weathering endmember and is referred to as a ‘supraglacial’ throughout this study.

## 3. Methods

### 3.1. Sample collection and preparation

At each sample location between 15 and 20 l of river water was collected along with samples of the bedload sediment. In situ measurements of pH, temperature and total dissolved solids (TDS) were taken using pre-calibrated pH and TDS monitors (Hanna Instruments). Around 100 ml of river water was filtered ( $0.2\text{ }\mu\text{m}$ ) in situ using preweighed filters, which were later dried at  $40\text{ }^\circ\text{C}$  and reweighed in order to calculate the amount of total suspended sediment (TSS) per litre of river water. Each water sample was filtered ( $0.2\text{ }\mu\text{m}$ ) within 12 h of sampling using a Sartorius frontal filtration

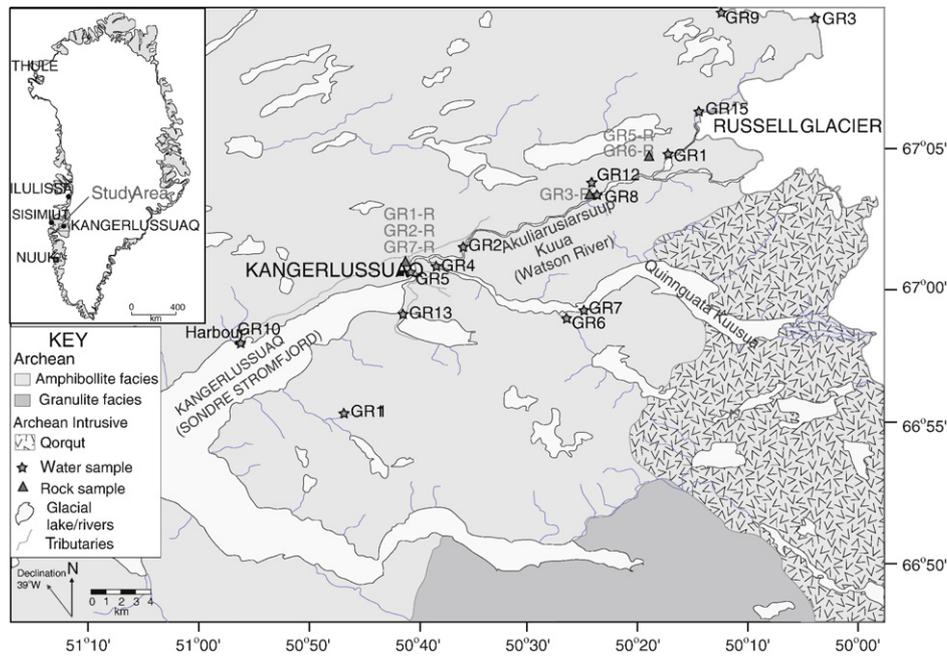


Fig. 1. Location map showing geology and river sample sites from the Kangerlussuaq region of SW Greenland (after Wimpenny et al., 2010).

unit, and suspended particulate material was kept for analysis. The alkalinity of each filtered river sample was calculated by titrating against 0.01 M HCl and plotting the volume of acid used versus the Gran function. Between 5 and 10 l of the filtered water was filtered again (10 kD) using a Sartorius tangential ultrafiltration system. The resulting solutions are a retentate which is a mixture of initial filtrate and colloidal sized particles ( $<0.2 \mu\text{m}$ ,  $>10 \text{kD}$ ), and the filtrate which contains “dissolved” material ( $<10 \text{kD}$ ).

On return from the field the bedload sediments were dried and crushed to a fine powder using an agate mill. Samples of the powdered bedload and suspended sediment ( $\sim 0.1 \text{g}$ ) were dissolved in a mixture of  $\text{HNO}_3$  and HF, and after drying the final sample was redissolved in 2%  $\text{HNO}_3$  for analysis by inductively coupled plasma mass spectrometry (ICP-MS). A number of rock standards were also prepared using this technique for use as calibration standards during ICP-MS analyses.

### 3.2. Cation analyses

Major element analyses of the bedload and rock samples were performed by X-ray fluorescence (XRF) with reference standards reproducing to within 1% of certified values. All cation concentrations in the bedload, suspended sediment, and dissolved load were determined using ICP-MS. River waters were calibrated against multi element standards of known concentration and corrected for machine drift by repeat measurements of our house river water standard Sco2/15. The external reproducibility of this approach was assessed from repeat measurements of the certified river water reference material SLRS-4 and is better than 8% ( $2\sigma$ ) for all elements. Dissolved solid samples were calibrated against the certified rock reference materials JB-2, BIR-1, BCR-2, JG-2, SDC-1 and AGV-1. One of these standards was also monitored during each sample run to correct for machine drift. Two reference materials (BIR-1 and JB-2) were also routinely measured to calculate the external reproducibility of this technique; the external error ( $2\sigma$ ) is better than 6% for all major and minor elements.

### 3.3. Mg isotope analyses

Magnesium was separated from the sample matrix by ion exchange chromatography. Two stages of column chemistry were

used; the first involved elution through an anion exchange resin (Bio-Rad AG1-X8) to remove Fe (Wiechert and Halliday, 2007), the second involved elution through a cation exchange resin (Bio-Rad AG50W-X12) to separate Mg from the other cations, in particular Al, Ca and Na. A minimum of 500 ng of Mg was loaded onto the columns during sample processing; the total procedural blank is  $\sim 50 \text{pg}$  of Mg. After column chemistry, magnesium isotope ratios were measured by multi-collector ICP-MS (Thermo-Fisher Neptune) at the Open University. Samples were diluted using 3%  $\text{HNO}_3$  to give a final Mg concentration of 500 ppb. The diluted sample was introduced to the instrument using the standard sample introduction system and all measurements were made at medium resolution. This resolution separates the  $^{12}\text{C}^{14}\text{N}^+$  signal from the  $^{26}\text{Mg}$  signal. A 500 ppb solution typically gave a  $^{24}\text{Mg}$  signal of between 10 and 12 V; the blank contribution to this signal was typically  $<0.01 \text{V}$  of  $^{24}\text{Mg}$ . The isotopic composition of the blank was measured between sample and standard measurements and this blank composition was subtracted offline during data processing. The three magnesium isotopes (24, 25 and 26) were collected and measured on Faraday cups (L3, centre and H3 respectively). Each sample run consisted of 1 block of 20 isotope measurements. The final isotopic composition ( $\delta^{26}\text{Mg}$ ) is the permil difference between the isotopic ratio of the sample and the isotopic ratio of the bracketed DSM-3 standard:

$$\delta^{26}\text{Mg} = \left( \frac{\left( \frac{^{26}\text{Mg}}{^{24}\text{Mg}} \right)_{\text{Sample}}}{\left( \frac{^{26}\text{Mg}}{^{24}\text{Mg}} \right)_{\text{DSM-3}}} - 1 \right) \times 1000 \quad (1)$$

Typically the internal precision of  $\delta^{26}\text{Mg}$  measurements was better than 0.05‰, and the internal precision of  $\delta^{25}\text{Mg}$  measurements was better than 0.03‰. DSM-3 and CAM-1 are now widely used as standard reference materials for the magnesium system (Galy et al., 2003). Relative to DSM-3, CAM-1 has a  $\delta^{26}\text{Mg}$  composition of  $-2.58\% \pm 0.14$  (Galy et al., 2003). As a measure of external reproducibility CAM-1 was routinely measured throughout this study, multiple times during each analytical session. The average  $\delta^{26}\text{Mg}$  composition of CAM-1 ( $n=24$ ) was  $-2.62 \pm 0.13\%$  ( $2\sigma$ ) while the average  $\delta^{25}\text{Mg}$  composition was  $-1.35 \pm 0.06\%$  ( $2\sigma$ ). The Mg

isotopic composition of IAPSO seawater (that has passed through column chemistry) was also measured routinely throughout this study. The average  $\delta^{26}\text{Mg}$  composition was  $-0.87 \pm 0.08\%$  ( $2\sigma$ ,  $n=9$ ) while the average  $\delta^{25}\text{Mg}$  composition was  $-0.45 \pm 0.05\%$  ( $2\sigma$ ). These values are within error of published values for seawater [ $\delta^{26}\text{Mg} \sim -0.82\%$ , e.g. Young and Galy (2004)].

## 4. Results

### 4.1. Physicochemical properties of river waters

In situ measurements of the river waters, including temperature, pH, TDS and TSS are given in Table 1 and have been discussed in detail in Wimpenny et al. (2010). In brief, glacially sourced rivers contain very low levels of dissolved solids with TDS ranging from 3 to 18  $\mu\text{S cm}^{-1}$  and high amounts of suspended sediment with TSS ranging from 0.23 to 0.6 g/l. In contrast, the non-glacially sourced rivers contain much higher levels of dissolved solid, with TDS ranging from 25 to 198  $\mu\text{S cm}^{-1}$ , and low levels of suspended sediment with TSS values between 0.004 and 0.01 g/l. The pH ranges from 6.3 to 8.5 with most rivers having a pH of between 7 and 8.2.

### 4.2. Major element concentrations

#### 4.2.1. Solid phases

The composition of the bedload is, on average, very similar to the average composition of amphibolite from the Kangerlussuaq region (see compilation by Wells, 1979). The composition of the suspended sediment is slightly different. In particular, the major cations, including  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{K}^{+}$ , have, on average, higher concentrations in the suspended sediment compared to their corresponding bedload (Table 1). For example, the average magnesium concentration in the suspended sediment is 1.9 wt.% compared to 1.1 wt.% in the bedload.

#### 4.2.2. Dissolved load

The dissolved loads of both the glacial and non-glacial rivers are dominated by  $\text{Ca}^{2+}$ . As a percentage of the cation sum ( $\text{Na}^{+} + \text{Mg}^{2+} + \text{Ca}^{2+} + \text{K}^{+}$ ) dissolved calcium accounts for an average of 57% and 44%

of the total cations in the glacial and non-glacial rivers, respectively. While the proportion of  $\text{Na}^{+}$  is quite similar in both types of river ( $\sim 16\%$ ), the proportions of  $\text{K}^{+}$  and  $\text{Mg}^{2+}$  are more variable. Glacial rivers contain relatively more  $\text{K}^{+}$  ( $\sim 12\%$ ) and less  $\text{Mg}^{2+}$  ( $\sim 16\%$ ) than the non-glacial rivers (which contain  $\sim 5\%$   $\text{K}^{+}$  and  $\sim 29\%$   $\text{Mg}^{2+}$ ).

#### 4.2.3. Colloids

As discussed in Wimpenny et al. (2010), the removal of colloids ( $<0.2 \mu\text{m}$ ,  $>10 \text{ kD}$ ) significantly reduces the concentrations of Al and Fe in the dissolved phase, but it has little effect on the concentrations of Na, Li and Mg, which are similar in the filtered ( $<0.2 \mu\text{m}$ ) and ultrafiltered ( $<10 \text{ kD}$ ) fractions.

Comparisons of the amount of Mg in the filtered water ( $<0.2 \mu\text{m}$ ), with the combined amount of Mg in the colloidal ( $<0.2 \mu\text{m}$ ,  $>10 \text{ kD}$ ) and ultrafiltered fractions ( $<10 \text{ kD}$ ), balance to within 8%, indicating that the amount of Mg present in colloids is negligible. Consequently, no Mg isotope measurements of the colloidal fraction were undertaken.

### 4.3. Magnesium isotopes

The  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values of all samples and standards measured in this study define a line with a slope of  $0.5147 \pm 0.0032$  ( $R^2 = 0.9994$ ) in a  $\delta^{26}\text{Mg}$  versus  $\delta^{25}\text{Mg}$  graph (Fig. 2). This is close to the slope of the terrestrial equilibrium mass fractionation line defined by Young and Galy (2004) (0.521).

The bedload has an average  $\delta^{26}\text{Mg}$  value of  $-0.42\%$ , by comparison the suspended sediment has an almost indistinguishable average  $\delta^{26}\text{Mg}$  value of  $-0.40\%$ . The  $\delta^{26}\text{Mg}$  value of the dissolved load is significantly lower than the  $\delta^{26}\text{Mg}$  value of both the bedload and the suspended sediments. Dissolved  $\delta^{26}\text{Mg}$  values range from  $-1.31\%$  in the supra-glacial sample (GR3) to  $-0.58\%$  in the non-glacial rivers. The non-glacial rivers always have higher concentrations of Mg with higher  $\delta^{26}\text{Mg}$  values relative to the glacial and supraglacial waters. On average the  $\delta^{26}\text{Mg}$  value of the dissolved fraction in the glacial rivers is  $-1.12 \pm 0.06\%$  compared to  $-0.63 \pm 0.04\%$  in the non-glacial rivers (Fig. 3). In comparison, the average global riverine  $\delta^{26}\text{Mg}$  value for rivers has been estimated to be  $-1.09\%$  (Tipper et al., 2006a,b); extending from values of  $-2.5$  to  $-0.3\%$  (Tipper et al., 2006a,b).

**Table 1**

Major cation concentrations, and Mg isotope ratios from the dissolved, suspended (SP) and bedload (S) phases in Greenland rivers.

Sample	Origin	TDS ( $\mu\text{S cm}^{-1}$ )	TSS (g/l)	Si ( $\mu\text{mol/l}$ )	Na ( $\mu\text{mol/l}$ )	Ca ( $\mu\text{mol/l}$ )	K ( $\mu\text{mol/l}$ )	Mg ( $\mu\text{mol/l}$ )	$\delta^{26}\text{Mg}$ (‰)	$\delta^{25}\text{Mg}$ (‰)
GR1	Glacial	9.21	0.435	19.6	11.6	24.8	12.2	8.28	-1.04	-0.52
GR2	Glacial	14.4	0.598	21.6	29.9	32.9	18.2	11.0	-1.07	-0.54
GR3	Supraglacial	2.6	0.229	6.14	2.99	11.1	4.54	3.3	-1.31	-0.67
GR4	Glacial	17.8	0.846	25.7	32.2	40.8	20.2	11.6	-1.12	-0.56
GR5	Glacial	9.77	0.399	24.8	30.2	39.2	18.6	11.4	-1.17	-0.58
GR7	Glacial	12.7	0.545	28.7	35.4	42.4	21.6	13.7	-1.19	-0.64
GR8	Glacial	10.7	0.444	42.1	37.7	40.6	22.9	14.4	-1.18	-0.59
GR9	Glacial	6.77		21.7	8.01	31.1	9.75	9.71	-1.06	-0.54
GR11	Non-glacial	25.1	0.004	76.1	99.1	105	15.6	86.3	-0.66	-0.35
GR12	Non-glacial	198	0.014	323	539	665	142	775	-0.58	-0.32
GR13	Non-glacial	55.3		6.88	136	148	40.5	116	-0.65	-0.34
GR15	Non-glacial	106		4.17	171	181	82.7	202	-0.62	-0.32
				(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)		
GR1-SP	Glacial				2.47	3.12	2.15	2.07	-0.41	-0.21
GR3-SP	Glacial				2.54	3.09	1.76	1.79	-0.27	-0.13
GR5-SP	Glacial				2.83	3.24	1.95	1.92	-0.44	-0.23
GR8-SP	Glacial				2.56	3.12	2.17	1.97	-0.46	-0.24
GR1-S	Glacial			32.3	2.82	2.49	1.42	0.99	-0.53	-0.25
GR3-S	Glacial			32.0	2.70	2.45	1.11	1.17	-0.39	-0.20
GR5-S	Glacial			32.0	2.74	2.48	1.33	1.20	-0.43	-0.22
GR8-S	Glacial			33.7	2.76	1.86	1.62	0.65	-0.44	-0.22
GR11-S	Non-glacial			32.4	2.84	2.21	1.44	1.06	-0.10	-0.05
GR12-S	Non-glacial			30.7	2.35	2.17	1.24	0.94	-0.31	-0.16
GR15-S	Non-glacial			31.0	2.73	2.57	1.36	1.24	-0.34	-0.18

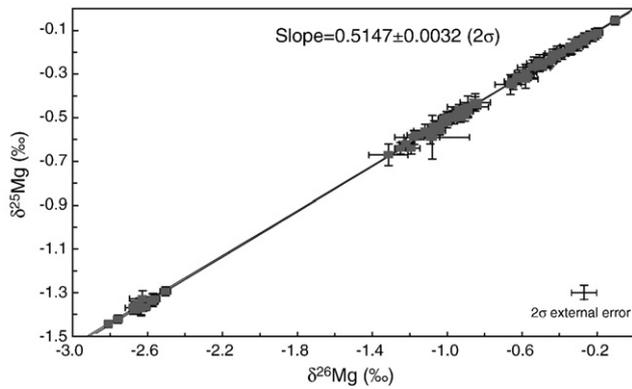


Fig. 2.  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values of all samples and standards measured in this study.

## 5. Discussion

### 5.1. Physicochemical properties

Glacial river water is sourced from surface or subsurface melting of the ice sheet (Tranter, 2003). The water–rock contact time is generally low, so the rates of chemical weathering are generally lower than in non-glacial regions (Anderson et al., 1997). Consequently, glacial river waters from Greenland are relatively dilute with an average TDS of  $\sim 11 \mu\text{S cm}^{-1}$  when compared to the global riverine average [ $\sim 50 \mu\text{S cm}^{-1}$  (Gaillardet et al., 1999a,b)]. Greenland rivers also carry significant quantities of fine grained suspended sediment ( $\sim 0.5 \text{ g/l}$ ) derived from the physical grinding of the ice sheet acting on the bedrock. Due to the volume and speed of the glacial river flow, particularly in summer when melt rates are high, glacial rivers can carry significant amounts of this sediment. Using recent estimates for the annual discharge of the Watson River [ $1.7 \times 10^9 \text{ m}^3 \text{ year}^{-1}$  (Mernild and Hasholt, 2009)], and an estimated catchment area of  $800 \text{ km}^2$ , it is possible to derive chemical and physical weathering rates for the region of  $7 \text{ t/km}^2/\text{year}$  and  $1060 \text{ t/km}^2/\text{year}$ , respectively. The chemical weathering rate is lower than the global riverine average [ $24 \text{ t/km}^2/\text{year}$  (Gaillardet et al., 1999a,b)] but is much higher than chemical weathering rates for many other shield areas [ $0.5\text{--}3 \text{ t/km}^2/\text{year}$  (Millot et al., 2003)]. This is almost certainly a consequence of the high physical weathering rate, which is comparable to the physical weathering rates of rapidly eroding mountainous regions

(Jacobson and Blum, 2003; West et al., 2005). Physical weathering has been shown to enhance the rate of chemical weathering by providing greater surface area for chemical reactions to occur (e.g. Gaillardet et al., 1999a,b).

In contrast to the glacial rivers, the non-glacial rivers carry less water so have longer water–rock contact times. They are also subject to high levels of evaporation, because they are relatively shallow and slow moving, as are the lakes that may feed in to them. These factors are reflected in the average TDS ( $100 \mu\text{S cm}^{-1}$ ) which is significantly higher than the TDS in either the glacial rivers or the global riverine average. However, the flux of water carried in these rivers is small and their impact on chemical and physical weathering rates in this region is minor.

### 5.2. Major element behaviour

#### 5.2.1. Solid phases

The chemical composition of pristine unaltered bedrock approximates that of the typical amphibolite found in this region (Wells, 1979). By comparison, the chemistry of the river bedload is similar to the bedrock in both the glacial and non-glacial rivers. However, the composition of the suspended sediment differs significantly from both the pristine bedrock and the bedload, suggesting that the suspended sediment has undergone more extensive alteration, as a result of chemical weathering. This is supported by comparisons of the molar Ca/Na and Mg/Na ratios of the suspended and bed sediments (Stallard and Edmond, 1981). As sodium is usually the most mobile major element during weathering (Gaillardet et al., 1999a,b; Gislason et al., 1996), the Ca/Na and Mg/Na ratios will be greater where more weathering has occurred. In this case the Ca/Na and Mg/Na ratios have average values of 0.69 and 0.7, respectively, in the suspended sediment, and 0.5 and 0.38, respectively, in the bedload, consistent with the suspended sediment having experienced more weathering.

#### 5.2.2. Dissolved load

Major cation concentrations in rivers often reflect the chemistry of the underlying bedrock (Meybeck, 2003). However, previous work has shown that glacial rivers are dominated by high  $\text{Ca}^{2+}$  concentrations, almost irrespective of the bedrock composition (but with the exception of basalts), and often have relatively high concentrations of  $\text{K}^+$  and  $\text{SO}_4^{2-}$  when compared to non-glacial rivers (Anderson et al., 1997; Tranter, 2003). This characteristic chemistry is thought to result from the low intensity of chemical weathering in glacial rivers, which means that weathering tends to be highly incongruent and water chemistry reflects the preferential dissolution of the phases most susceptible to weathering. As a consequence, easily weathered minerals can exert a disproportionate influence over the water chemistry. High concentrations of  $\text{Ca}^{2+}$  are likely to be caused by the preferential dissolution of carbonate minerals and by the preferential leaching of the Ca-rich aluminosilicates (White et al., 2001). This is illustrated in Fig. 4, which shows the dissolved Ca/Na and Mg/Na ratios in glacially and non-glacially sourced rivers. Glacial rivers have Ca/Na ratios that are up to 8 times higher than that of the bedload (Ca/Na  $\sim 0.5$ ), supporting the hypothesis that there has been preferential leaching of Ca rich phases. While all of the glacial rivers have Ca/Na ratios that are enriched in Ca relative to the bedload this enrichment is less evident in those samples that were taken further downstream from glacial outflow. Away from the ice sheet, water–rock contact times increase so chemical weathering is more congruent, and the weathering of silicate minerals starts to obscure the carbonate weathering signal. High concentrations of  $\text{K}^+$  are a result of the non-stoichiometric dissolution of biotite and the preferential leaching of interlayer K which is relatively rapid under glaciers and glacial soils (Sharp and Gomez, 1986; Stallard, 1995). The subglacial oxidation of sulphides is another important process in glacially sourced rivers (Tranter, 2003), leading to high  $\text{SO}_4^{2-}$

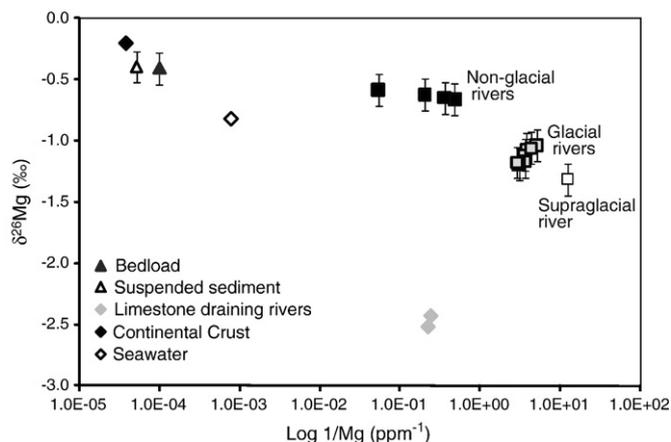


Fig. 3. Mg isotope ratios of glacially sourced, non-glacially sourced and supraglacial rivers from Greenland together with average values for the suspended and bedloads as a function of Mg concentration. Average  $\delta^{26}\text{Mg}$  values for the continental crust (Tipper et al., 2008), seawater (Bruland, 1983) and rivers draining limestone catchments (Tipper et al., 2006b) are also shown. The error bars reflect the external reproducibility of the Mg isotope measurements ( $\pm 0.13\%$ ,  $2\sigma$ ).

concentrations in waters. A by-product of this reaction is the formation of Fe-oxyhydroxides (Tranter, 2003), a process that causes the preferential uptake of  $^6\text{Li}$  from solution, which is an important control on the composition of Li isotopes in glacial rivers (Wimpenny et al., 2010). In the non-glacial rivers the intensity of chemical weathering is greater and weathering is more congruent, so the water chemistry is dominated by silicate weathering (Fig. 4). These non-glacial rivers contain, on average, 24 times more Mg than the glacial rivers due to the higher silicate weathering rates.

### 5.3. Magnesium isotope behaviour

Glacial, supraglacial and non-glacial rivers have distinct Mg isotope compositions (Fig. 3). The supraglacial water sample (GR3) has a lower  $\delta^{26}\text{Mg}$  value ( $-1.3\%$ ) than the glacial rivers ( $-1.1\%$ ) and the non-glacial rivers have the heaviest isotope composition ( $-0.6\%$ ). By contrast, excluding sample GR11-S (which has an anomalously high  $\delta^{26}\text{Mg}$  value), the suspended sediment and bedload samples have  $\delta^{26}\text{Mg} = -0.40 \pm 0.07\%$ . Thus, the dissolved load is lighter than the solid phases. In the following sections, we discuss the potential causes for these isotope variations.

#### 5.3.1. Secondary mineral formation

Secondary mineral formation plays an important role in controlling the Mg isotope composition of rivers (Tipper et al., 2006a,b). The  $\delta^{26}\text{Mg}$  composition of dissolved Mg is always lighter than that of Mg in the bedload or suspended sediment. Therefore, if secondary mineral formation is the major control over the dissolved  $\delta^{26}\text{Mg}$  composition then the results here suggest that it must involve the preferential incorporation of heavy Mg isotopes from solution. If it is assumed that the secondary mineral formation includes clays, such as smectite, then this is in accord with previous work (Tipper et al., 2006b) which indicates that silicate soils are enriched in  $^{26}\text{Mg}$  relative to the source rock. If secondary mineral formation is controlling the Mg isotope behaviour then the Mg isotope results presented here suggest that it is most significant in glacial rivers where the extent of fractionation ( $\delta^{26}\text{Mg}_{\text{bedload}} - \delta^{26}\text{Mg}_{\text{dissolved}}$ ) is the greatest.

A quantitative estimate of the potential for secondary mineral formation can be obtained from saturation state models, such as PHREEQC (Parkhurst & Appelo, 1999). Application of this model to our river water data indicates that the formation of common secondary minerals such as clays is unlikely in any of the rivers as almost all of the Greenland river waters are undersaturated. The most likely secondary mineral to form is amorphous Fe-oxide, but only in the non-glacial rivers, as the concentration of dissolved iron in glacial rivers is extremely low. Despite the higher likelihood for secondary mineral formation in these non-glacial rivers, the Mg isotopic com-

position of their dissolved load is far closer to that of the bedload ( $\delta^{26}\text{Mg}_{\text{bedload}} - \delta^{26}\text{Mg}_{\text{non-glacial}} = 0.2\%$ ) than it is in glacial rivers ( $\delta^{26}\text{Mg}_{\text{bedload}} - \delta^{26}\text{Mg}_{\text{glacial}} = 0.7\%$ ).

The Li isotopic composition of the glacial rivers appears to be affected by the uptake of Li on newly-formed Fe-oxyhydroxide minerals under the ice (Wimpenny et al., 2010). Because the supraglacial sample, GR3, has never been in contact with the bedrock under the ice, its dissolved load has a Li isotope composition that is closer to that of the bedrock than it is for the glacial rivers. By contrast, the Mg isotope composition of sample GR3 is more fractionated from the bedrock ( $\delta^{26}\text{Mg}_{\text{bedload}} - \delta^{26}\text{Mg}_{\text{supraglacial}} = 0.9\%$ ) relative to the glacial rivers. This suggests that uptake of Mg by Fe-oxyhydroxides in the subglacial environment cannot explain the enrichment of light Mg in the glacial rivers.

#### 5.3.2. Biological controls

The non-glacial rivers have low water-rock ratios, hence water is in contact for a longer time with roots and plant material. In addition, some of these rivers (GR11 and GR12) are yellow in colour, suggesting that they contain relatively high levels of dissolved organic carbon (Wimpenny et al., 2010). Consequently, it seems reasonable to surmise that biological processes are likely to be more important in these non-glacial rivers, and that such processes may exert some influence over the dissolved Mg isotope ratio. However, if biological uptake is the major control on dissolved Mg isotope ratios then, as noted in the discussion in Section 5.3.1, we would expect the greatest fractionation of Mg to occur in the non-glacial rivers. Instead, the extent of fractionation of Mg isotopes in these rivers is lower ( $\delta^{26}\text{Mg}_{\text{bedload}} - \delta^{26}\text{Mg}_{\text{non-glacial}} = 0.2\%$ ) than it is in the glacial rivers. Hence biological uptake does not appear to be an important control over the dissolved Mg composition in these rivers.

#### 5.3.3. Source controls

If the Mg isotope composition of the dissolved phase cannot be explained by fractionation processes then alternatively it may be controlled by changes in the sources of Mg to the waters. While rock weathering is the most important source of Mg to rivers (Berner, 2004), some Mg may also be derived from seawater and/or from aeolian input. In principle these inputs should be most important in the supra-glacial sample (GR3), which has had no contact with the bedrock. As a result, the proportion of Mg in this sample that is derived from rock weathering will be extremely low. Assuming that the bedload ( $\delta^{26}\text{Mg} = -0.4\%$ ) contains Mg that is representative of the underlying bedrock, then in order to account for the dissolved  $\delta^{26}\text{Mg}$  value of  $-1.3\%$  in GR3 (or a  $\delta^{26}\text{Mg}$  value of  $\sim -1.1\%$  in the glacial rivers), the seawater and/or aeolian dust must contribute Mg with  $\delta^{26}\text{Mg}$  values of  $< -1.3\%$ . Additionally, element ratios can further constrain the source of dissolved solute to these rivers. For example, Fig. 5 demonstrates that glacial river waters have relatively low  $\delta^{26}\text{Mg}$  values, and relatively high Ca/Mg ratios ( $\sim 3$ ), compared to the bedload. This suggests that, in addition to having relatively low  $\delta^{26}\text{Mg}$  values, any source of dissolved solute to glacial rivers must also contribute Ca/Mg in the ratio  $> 3$ . Seawater contains a high concentration of dissolved Mg (52 mmol/l), with a well characterised  $\delta^{26}\text{Mg}$  isotope composition of  $-0.82\%$  (Carder et al., 2004; Tipper et al., 2006a,b; Young and Galy, 2004) and a relatively low Ca/Mg ratio of  $\sim 0.19$  (Bruland, 1983). Clearly, the Mg isotopic composition of seawater is too heavy to drive sample GR3 to  $\delta^{26}\text{Mg}$  values of  $-1.3\%$  (or to drive the glacial river waters to  $\delta^{26}\text{Mg}$  values of  $-1.1\%$ ). Moreover, straightforward mixing between seawater and bedrock cannot accommodate dissolved Ca/Mg ratios of up to 3. Finally, the Cl content of the river waters indicates that  $< 3\%$  of the Mg in sample GR3 is derived from seawater. Therefore, the seawater contribution is neither large enough, nor sufficiently enriched in Ca relative to Mg, and possesses an Mg isotope composition that is not sufficiently light

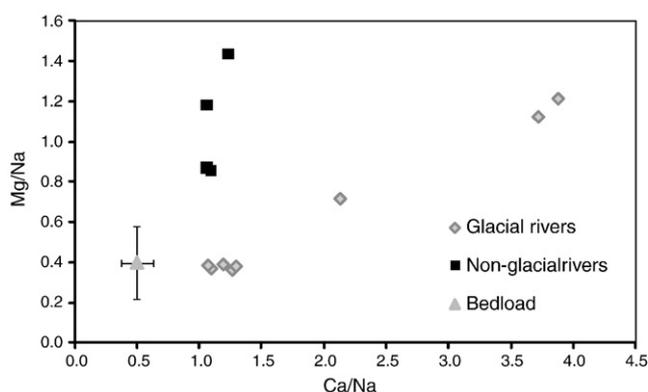


Fig. 4. Molar Mg/Na and Ca/Na ratios for the dissolved load of the glacially and non-glacially sourced rivers, uncorrected for seawater input. The average value for the bedload sediments is also shown; the error bar shows the  $2\sigma$  standard deviation from the average value.

to account for the major element chemistry and Mg isotope composition of the glacial rivers.

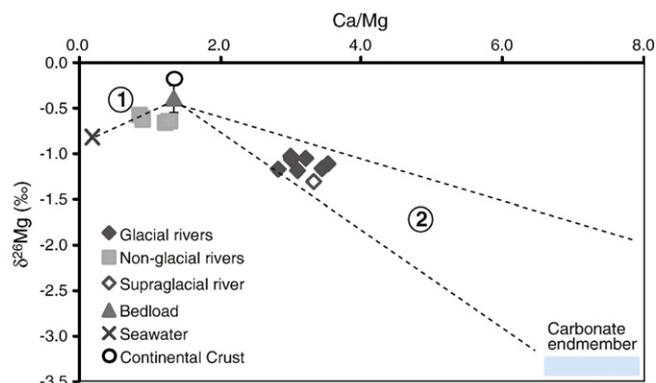
Dust is transported to Greenland via the westerly jet stream, that originates in east Asia (Biscaye et al., 1997) and north Africa (Tanaka and Chiba, 2006). The Mg isotope composition of this dust flux has not yet been measured and is difficult to estimate because of the range of possible source regions and source lithologies. A recent study has shown the Mg composition of the continental crust is heterogeneous, with I and S type granitoid rocks having a mantle like  $\delta^{26}\text{Mg}$  signature of between  $-0.14$  and  $-0.35\text{‰}$ , while sedimentary rocks such as shales and loess have higher  $\delta^{26}\text{Mg}$  (up to  $+0.92\text{‰}$ ) (Li et al., 2010). The Mg delivered by the dust flux to Greenland can be expected to have  $\delta^{26}\text{Mg}$  values that are either similar to the average continental crustal value [ $-0.22\text{‰}$ , (Li et al., 2010)] or, if weathering has occurred, slightly higher values because of preferential uptake of heavy Mg into secondary silicates (Li et al., 2010; Tipper et al., 2006a). In either case, these  $\delta^{26}\text{Mg}$  values are far too high to account for the values measured in the supraglacial water and the glacial rivers. The Ca/Mg ratio of this dust source to Greenland is also unknown but if it is assumed that the chemical composition is similar to estimates for the composition of the continental crust then the ratio is likely to be  $\sim 1.3$  (Rudnick and Gao, 2003), which is the same as the average value of the bedload in the present study. Thus estimates for both the Mg isotopic composition and Ca/Mg ratios in dust suggest that the flux of dust to Greenland is unlikely to be a major chemical control over the glacial river waters.

While an external source cannot readily explain the light Mg isotope composition of the glacial rivers, in theory the composition of dissolved Mg in the non-glacial rivers ( $-0.6\text{‰}$ ) could be produced simply by mixing Mg derived from seawater and rock weathering/dust (Fig. 5). The input of seawater could also account for non-glacial Ca/Mg ratios that are low relative to Ca/Mg ratios in the bedload, because the Ca/Mg ratio of seawater is around 0.19. However, low non-glacial Ca/Mg ratios could also be explained by the input of water from saline lakes which are numerous in the region around Kangerlussuaq and have Ca/Mg ratios of  $\sim 0.37$  (Anderson et al., 1997). While some seawater input is likely, calculations based on dissolved  $\text{Cl}^-$  concentrations suggest that the magnitude of this seawater input is too low to account for the dissolved Mg composition in non-glacially sourced rivers. As only 8% of the dissolved Mg in these rivers can be derived from seawater, then straightforward mixing of Mg from seawater ( $\sim 8\%$ ,  $\delta^{26}\text{Mg} -0.82\text{‰}$ ) and from rock weathering ( $\sim 92\%$ ,  $\delta^{26}\text{Mg} -0.4\text{‰}$ ) would result in a Mg isotope ratio of around

$-0.44\text{‰}$ . If the Mg derived from dust was then added to this mix the resulting Mg isotope ratio would be heavier still. For this reason, it is unlikely that the input of Mg from either seawater or dust flux is controlling the dissolved Mg isotope composition in any of these rivers, either glacial or non-glacial.

Another possibility is that the variations in the dissolved  $\delta^{26}\text{Mg}$  between glacial and non-glacial rivers result from differences in the susceptibility of specific phases to chemical weathering (i.e. differences in weathering congruence between minerals). As discussed previously, sub-glacial weathering often results in the preferential dissolution of phases such as carbonates, biotite and sulphide (Anderson et al., 1997; Tranter, 2003) which can dominate the chemistry of the waters. Evidence for the incongruent weathering of such phases in the glacial waters studied here is given by the relatively high concentrations of  $\text{Ca}^{2+}$  and  $\text{K}^+$  in these rivers (Section 5.2.2). The Mg isotope composition of carbonates is generally much lighter than that of silicates (Young and Galy, 2004). For example, carbonate rocks range in composition from  $-1.1$  to  $-5.2\text{‰}$ , whereas silicate rocks range from  $0.92$  to  $-1.1\text{‰}$  (Li et al., 2010; Young and Galy, 2004). It is evident from the study of small rivers draining monolithological catchments, that such differences in the composition of the bedrock will be transferred to the  $\delta^{26}\text{Mg}$  value. For example, rivers draining limestone in the Jura, have a  $\delta^{26}\text{Mg}$  isotope composition of  $-2.52\text{‰}$  (Tipper et al., 2006b). In comparison, rivers draining basaltic and felsic crystalline rock catchments have average  $\delta^{26}\text{Mg}$  compositions of between  $-0.6$  and  $-0.8\text{‰}$  (Tipper et al., 2006b). Similarly, a recent study of the Moselle River basin shows a small but significant difference of  $\sim 0.6$ – $0.8\text{‰}$  in  $\delta^{26}\text{Mg}$  compositions between water flowing in carbonate and silicate sub-catchments (Brenot et al., 2008).

In Kangerlussuaq the bedrock is Archean and has been subject to high-grade amphibolite-faces metamorphism. Primary carbonate rocks in the region have not been observed (Wells, 1979), hence any carbonate present must be disseminated throughout the silicate bedrock as a minor phase. However, the formation of this carbonate must postdate any metamorphism in order for its preferential weathering to impart distinct Mg isotope signal, otherwise the Mg in the carbonate will be in equilibrium with other phases in the bedrock. Consequently, the carbonate must be secondary, and may have formed either by the alteration of primary phases like plagioclase, or through late stage hydrothermal activity (White et al., 1999). In either case, the carbonate is likely to have acquired an Mg isotope composition lighter than that of other phases in the rock, and the preferential dissolution of this phase will liberate Mg with a light isotope composition. Carbonate minerals are also strongly enriched in Ca relative to Mg, so their dissolution would impart solute with a relatively high Ca/Mg ratio (Dessert et al., 2003). Because seawater input is relatively minor, and secondary minerals are unlikely to form, the Mg isotope composition in glacially sourced rivers probably results from two component mixing between carbonate, with light  $\delta^{26}\text{Mg}$  values [ $\sim -3.2\text{‰}$  (Young and Galy, 2004)] and high Ca/Mg ratios [6–100 (Brenot et al., 2008; Turekian and Wedepohl, 1961)], and silicate sources with heavier  $\delta^{26}\text{Mg}$  values ( $-0.4\text{‰}$ ) and lower Ca/Mg ratios (Ca/Mg  $\sim 1.3$ ) as illustrated in Fig. 5. Calculating the relative proportions of carbonate and silicate sources in the glacial rivers is difficult because the composition of the carbonate endmember is unknown. However, other studies have shown that rivers draining carbonate rocks typically have high Ca/Na and Sr/Na ratios of over 50 and 0.05, respectively (Roy et al., 1999). In contrast, rivers draining silicate rocks have lower dissolved Ca/Na and Sr/Na ratios of 0.5 and 0.003, respectively, which are almost identical to the average composition of the bedload of Greenland rivers. Using these values for the carbonate and silicate endmembers, we calculate that weathering of carbonates supplies 2–7% of the Mg in the glacial rivers, while weathering of silicates supplies the remaining 93–98%. The supraglacial river GR3 has significantly higher Ca/Na and Sr/Na ratios relative to the glacially sourced rivers, requiring a higher input



**Fig. 5.**  $\delta^{26}\text{Mg}$  plotted versus the molar Ca/Mg ratio for the dissolved load of glacially and non-glacially sourced rivers from Greenland. Also plotted are three potential sources of Mg; the bedload (i.e. rock weathering), seawater, and carbonate. The composition of Mg in non-glacial rivers derives from weathering of bedload, some secondary mineral formation, and minor mixing with Mg from seawater (1). In contrast, the composition of Mg in glacial rivers requires mixing between silicate and carbonate sources, although the exact Ca/Mg value of the carbonate endmember is unknown (2).  $\delta^{26}\text{Mg}$  values of seawater and continental crust are taken from Tipper et al. (2008); carbonates have  $\delta^{26}\text{Mg}$  values that range from  $-1.1$  to  $-5.2\text{‰}$  (Young and Galy, 2004), with an average value of  $\sim -3.2\text{‰}$  (Tipper et al., 2006b).

(~14%) from carbonate sources. This explains why the  $\delta^{26}\text{Mg}$  value of dissolved Mg in GR3 ( $-1.3\text{‰}$ ) is  $\sim 0.2\text{‰}$  lighter than Mg in the glacially sourced rivers. Calculation of the quantity of Mg derived from silicate versus carbonate sources is more difficult for the non-glacial rivers. This is because the chemical composition of the river waters has been affected by (i) secondary mineral formation and, (ii) high levels of evaporation. Nevertheless, as weathering intensity in these rivers is likely to be higher than it is in the glacial rivers, we can speculate that weathering is likely to be more congruent and dominated by inputs from weathering of silicate minerals.

Thus, to summarise, it seems most likely that the low  $\delta^{26}\text{Mg}$  values for the dissolved load of glacial (and supraglacial) rivers is the result of a greater proportion of dissolved Mg being sourced from carbonate weathering. In glacial regimes, weathering is highly incongruent, favouring the dissolution of easily weatherable minerals such as calcite. In contrast, the Li and Li isotopic composition of Greenland rivers is controlled almost exclusively by the formation of secondary Fe-oxyhydroxide phases in the subglacial environment (Wimpenny et al., 2010). Although both Mg and Li are relatively mobile during rock weathering, our data suggest that the processes controlling the Mg and Li isotopic compositions of river water in glacial environments may be very different.

#### 5.4. Implications for Mg cycling

The global average  $\delta^{26}\text{Mg}$  composition of river water is  $-1.09\text{‰}$  (Tipper et al., 2006b), with the majority of large rivers possessing compositions between  $-0.5$  and  $-1.5\text{‰}$  (Fig. 6). The only rivers to significantly deviate from this range are those that drain limestone, which have much lower  $\delta^{26}\text{Mg}$  values (Tipper et al., 2006b), and rivers from Iceland which have  $\delta^{26}\text{Mg}$  values of as high as  $0.6\text{‰}$  (Pogge Von Strandmann et al., 2008). The rivers from Iceland are unusual because they are affected by the formation of secondary carbonates at the high pH of the glacial waters (driving Mg to heavy isotope compositions), and the input of hydrothermal fluids that also have heavy Mg isotope compositions ( $0.85\text{‰}$ ) (Pogge Von Strandmann et al., 2008). At first sight, the similarity between the isotope ratios of Mg in rivers from Greenland and the global river average can be taken to suggest that glaciation is likely to have little impact on the isotope composition of the global Mg flux.

However, this simplified view does not take into account how a change to glacial conditions might affect the composition of runoff from a single catchment. In Kangerlussuaq, there is a clear difference in the  $\delta^{26}\text{Mg}$  value between glacial and non-glacial rivers of  $\sim 0.5\text{‰}$ . If this is representative of glacial regions worldwide then clearly there is the

potential for glaciation to have had a significant effect on the Mg isotope composition of continental runoff. Currently, glacial runoff accounts for only  $\sim 1\%$  of the total riverine flux; however at various times in the Earth's past the glacial flux has been far higher. During the last deglaciation glacial rivers are thought to have supplied  $\sim 18\%$  of the global riverine flux (Jones et al., 2002) and over the last 130 ka global glacial runoff is thought, at times, to have accounted for 20–30% of total global runoff (Tranter et al., 2002). During these times of enhanced glacial flow the average water–rock contact times and weathering intensities of continental runoff will have been lower, and the chemistry of the waters is likely to have been dominated by incongruent weathering. Assuming the  $0.5\text{‰}$  difference between  $\delta^{26}\text{Mg}$  in glacial and non-glacial rivers is representative of glacial rivers worldwide, then we can estimate the impact of increasing the glacial flux to 30% of the global riverine flux. In this case the  $\delta^{26}\text{Mg}$  value of the global flux would have decreased by  $\sim 0.15\text{‰}$ , only just outside of the external reproducibility of the  $\delta^{26}\text{Mg}$  measurements made in this study. However, these pulses in the magnitude of glacial runoff only occur over relatively short timescales; on the order of hundreds to thousands of years (Tranter et al., 2002). Magnesium has a residence time in the oceans of between  $\sim 10$  and  $14$  Myr (Berner and Berner, 1996; De Villiers et al., 2005) so short term pulses in glacial runoff would have limited impact on the global oceanic Mg isotope composition. On average, over the last 130 ka the global glacial flux was only  $\sim 2.8\%$  higher than today (Tranter et al., 2002). While the rivers of the Kangerlussuaq region may not be representative of glacial rivers worldwide, even if glacial rivers are, on average,  $1\text{‰}$  lighter than non-glacial rivers the impact on the global continental Mg flux over the last 130 ka would be small,  $\sim -0.03\text{‰}$  which is well within the external reproducibility of the measurements made here. This suggests that glaciation is only likely to affect the composition of the riverine Mg flux if it occurs over a prolonged period of time (i.e. a timescale of millions of years) and where the glacial flux accounts for a substantial proportion (20–30%) of total continental runoff.

## 6. Conclusions

The  $\delta^{26}\text{Mg}$  composition of rivers in Greenland varies between glacial and non-glacial rivers. Relative to the amphibolite-facies bedrock, the non-glacial rivers have a light Mg isotope composition, although the extent of fractionation is relatively low ( $\delta^{26}\text{Mg}_{\text{bedload}} - \delta^{26}\text{Mg}_{\text{non-glacial}} = 0.2\text{‰}$ ). The Mg isotope composition of the glacial rivers is also lighter than that of the bedrock, but the degree of fractionation is much greater ( $\delta^{26}\text{Mg}_{\text{bedload}} - \delta^{26}\text{Mg}_{\text{glacial}} = 0.7\text{‰}$ ). These glacial rivers are more dilute and have lower secondary mineral saturation states than the non-glacial rivers, so it is unlikely that secondary mineral formation is controlling the Mg isotope behaviour. Similarly, the low degree of biological activity in these rivers suggests that significant biological uptake of Mg is also unlikely. Instead, the results of this study suggest that changes in the source of Mg are controlling the dissolved Mg isotope composition which is, in turn, controlled by the intensity and congruence of chemical weathering. Highly incongruent weathering in the glacial and supraglacial rivers favours the dissolution of easily weatherable minerals such as carbonates. The proportion of dissolved solute derived from carbonate weathering is relatively high in these rivers (2–14%), and the Mg isotopic composition of the carbonates is relatively light, driving dissolved  $\delta^{26}\text{Mg}$  values in glacial and supraglacial rivers to, respectively,  $-1.1$  and  $-1.3\text{‰}$ .

The Mg isotope composition of the glacial rivers is indistinguishable from that of the estimated global riverine mean [ $-1.09\text{‰} \pm 0.05$  (Tipper et al., 2006b)]. However, our data suggest that glacial and non-glacial rivers, that drain the same rocks, have significantly different  $\delta^{26}\text{Mg}$  values; the  $\delta^{26}\text{Mg}$  value of glacial rivers is  $\sim 0.5\text{‰}$  lower than the average  $\delta^{26}\text{Mg}$  value of non-glacial rivers. This suggests that, in principle, glaciation could have influenced the

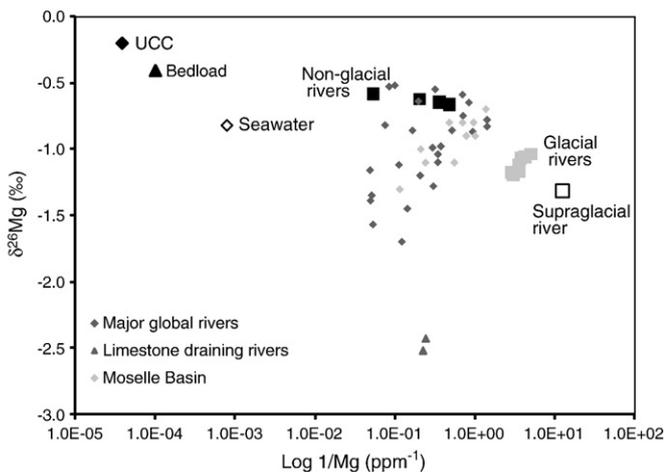


Fig. 6. Comparison of Mg isotope data in Greenland rivers with major global rivers, limestone draining rivers and rivers from a recent study of the Moselle basin (Brenot et al., 2008). Compositions of Greenland bedload sediment, seawater and an estimate for the continental crust (Tipper et al., 2008) are also plotted for reference.

composition of Mg in continental runoff in the past. However, although there have been 'pulses' of high glacial runoff (up to 30% of total runoff) in the past, these are short lived relative to the residence time of Mg in the oceans, so the long term effect on the average riverine Mg composition will be minimal.

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