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The stable calcium isotopic composition of rivers draining basaltic catchments in Iceland

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ABSTRACT

Calcium isotopic compositions ($\delta^{44/42}$Ca) were measured in Icelandic rivers draining a range of catchment types. The $\delta^{44/42}$Ca values of the rivers ranged from 0.45‰ to 0.67‰, which in all cases was higher than the $\delta^{44/42}$Ca value of basaltic rock standards (0.42 ± 0.03‰). A single explanation was unable to satisfactorily explain the $\delta^{44/42}$Ca values of all rivers, rather it was found that the rivers formed three distinct groups based on the extent of glacial coverage in each catchment. The Ca isotopic composition of rivers draining catchments with less than 10% glacial cover could be explained by the mixing of water sources: basalt-derived solutes, meltwater (taken to represent meteorological precipitation inputs) and hydrothermal water. However, fractionation of $\delta^{44/42}$Ca in these catchments cannot unequivocally be ruled out. In catchments with greater than 22% glacial cover, Ca isotopic compositions could not be explained by a mixture of water sources and instead reflected a fractionation process, most likely the precipitation of Ca-bearing secondary minerals or the adsorption/ion-exchange of Ca onto mineral surfaces. The fractionation factor (α) for this process was calculated to be 0.9999. The third group of rivers, with partially glaciated (10–21%) catchments, grouped with glaciated catchments with respect to their Sr geochemistry and with non-glaciated catchments with respect to their Ca geochemistry. The difference in the controls of Ca isotope fractionation between glaciated and unglaciated catchments was attributed to different weathering regimes.

1. Introduction

Silicate weathering rates are affected by changes in environmental conditions, such as temperature, runoff and erosion (e.g. White and Blum, 1995; Riebe et al., 2004; West et al., 2005). Since the magnitude of silicate weathering is thought to provide an important negative feedback in the long-term carbon cycle (Walker et al., 1981; Berner et al., 1983), through the reaction of calcium (Ca) and magnesium (Mg) silicates with carbonic acid derived from atmospheric carbon dioxide, it is important to be able to predict exactly how silicate weathering fluxes will be affected by changes in climate.

Basaltic rocks are particularly susceptible to weathering and are thought to constitute 30–35% of atmospheric drawdown by silicate rocks (Dessert et al., 2003), despite a global outcrop area of only 5% (Amiotte Suchet et al., 2003). The weathering flux from oceanic basaltic islands is thought to be particularly important due to the tendency for the islands to be geologically young and have higher meteorological precipitation and runoff, thereby enhancing weathering rates (Gíslason et al., 1996; Louvat and Allègre, 1997, 1998). A 40 year study of basalt weathering in a single locality (Iceland) has already hinted that increasing temperatures lead to increased rates of chemical weathering (Gíslason et al., 2009). This study calculated annual weathering fluxes from regular samples of river water, a common method for obtaining catchment-scale integrated weathering rates. Another approach to study the response of weathering rates and processes to changes in climate is through shorter term studies which compare river water samples taken from different catchments with the same underlying lithology, but which differ in their local environmental conditions (e.g. White and Blum, 1995;

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Gíslason et al., 1996; Oliva et al., 2003). Such an approach has been applied extensively in Iceland where the island is essentially monolithological and there are variations in meteorological precipitation, glacial cover and vegetation across the island (e.g. Gíslason et al., 1996).

Previous studies which focussed on the major ion chemistry of Icelandic rivers have shown that the formation of secondary minerals is ubiquitous in these catchments, weathering is incongruent, pH (modified by glacial cover and vegetation) is an important control on element release and glaciers affect chemical weathering rates (Gíslason and Eugster, 1987b; Gíslason et al., 1996; Arnórsson et al., 2002).

More recently, two spot sampling campaigns have focussed on isotopic studies of Icelandic river water. The use of isotope tracers has enabled additional information on and/or provided confirmation of how basaltic weathering processes are affected by local environmental conditions. For example, using silicon isotopes Georg et al. (2007) found that, due to differences in the amount of meteorological precipitation, the east and the west sides of the island had different weathering regimes. Measurements of uranium series nuclides have suggested that weathering processes are close to steady-state and the highest weathering rates are found in those catchments with the shortest weathering timescale (Vigier et al., 2006). The extent of secondary mineral formation, as controlled by several environmental factors such as pH, strongly influences weathering rates: the highest chemical weathering rates are reported from those catchments where the extent of secondary mineral formation, as measured by lithium isotopes, is low (Vigier et al., 2009).

This study investigates the Ca isotopic compositions of the aforementioned two sets of Icelandic river samples, which have previously been analysed for other isotopic systems. In basaltic rocks, calcium is typically present at around 10 wt% and is the most abundant constituent after silicon and aluminium (Arnórsson et al., 2002). The major minerals hosting Ca are plagioclase and pyroxene. As a major constituent of basalt (and all silicate rocks), understanding the release and subsequent biogeochemical cycle of Ca is crucial in order to predict how the cycle may be altered by changing environmental conditions. Nevertheless, there have been relatively few studies on Ca isotope systematics in the terrestrial environment (Bullen et al., 2004; Wiegand et al., 2005; Tipper et al., 2006, 2008; Ewing et al., 2008; Cenki-Tok et al., 2009; Holmden and Bélanger, 2010; Farkaš et al., 2011; Hindshaw et al., 2011; Moore et al., 2013). Only one of these studies (Wiegand et al., 2005) was conducted in a basaltic environment (Hawaii) and highlighted changes in the source of Ca to plants, from primary minerals to atmospheric deposition, as the age of basalt increased from 0.3 to 4100 ka. Fractionation of Ca isotopes occurs during uptake into plants, with vegetation enriched in light Ca and, depending on the extent of vegetation, the upper soil layers are depleted in light Ca (Holmden and Bélanger, 2010; Farkaš et al., 2011; Hindshaw et al., 2013). Previous studies in granitic catchments have suggested that negligible fractionation occurs during the initial stages of weathering (Hindshaw et al., 2011) but that in older sites Ca isotopic differences between soil pools (Bullen et al., 2004) and seasonal changes in the Ca isotopic composition of runoff (Cenki-Tok et al., 2009) may be observed. Although variations in riverine Ca isotopic compositions are small (Tipper et al., 2010), there is evidence that the precipitation of secondary minerals (Tipper et al., 2006) and adsorption onto clays (Ockert et al., 2013) may cause river waters to become fractionated compared to bedrock.

Variations in stable isotope ratios may arise as a result of a fractionation process or the mixing of isotopically different sources. In order to aid in the interpretation of stable Ca isotope ratios, strontium (Sr) radiogenic isotope ratios, which only trace sources, were also obtained. The radiogenic strontium isotope ratio is commonly used to trace Ca sources due to the similar geochemical behaviour of Ca and Sr (e.g. Capo et al., 1998).

The aim of this study was to investigate whether the previously reported precipitation of secondary minerals and variations in weathering processes in Iceland, inferred from other isotopic and element data, would affect the calcium isotopic composition of river water, and thus help develop the use of Ca isotopes as a viable tracer of catchment scale biogeochemical processes.

2. Sampling locations

Iceland is situated in the north Atlantic ocean on the Mid-Atlantic ridge and over the Iceland hotspot, it is therefore a geologically active island with several active volcanoes and hydrothermal springs. The climate on Iceland is maritime (cool summers and mild winters) with a mean annual temperature of 2–5 °C. Meteorological precipitation is highly variable with the highest values in the southeast (4000 mm) and the lowest values in the north (400 mm), in the rain shadow of Vatnajökull (Einarsson, 1984). Icelandic rivers have significant seasonal variation in discharge: peak discharge occurs in spring as a result of snow-melt and later in the summer if there is a significant contribution from glacier ice melt. Glaciers cover 11.5% of the area of Iceland with the Vatnajökull icecap alone accounting for 70% of the glacial cover. Vegetation cover is sparse with only 23% of the island vegetated. Iceland is composed of volcanic rocks, predominantly of basaltic composition (80%), but also includes intermediate and silicic compositions and clastic sediments of volcanic origin. As a result of crustal accretion, there is a symmetrical pattern of rocks ages about the axis of the main rift. The oldest rocks (~13 Ma) are found in the north-west and east of the island and the youngest are found near the active volcanic zones. Volcanic eruptions which occur under ice cover tend to produce predominantly basaltic glass (hyaloclastite) (Jakobsson and Gudmundsson, 2008), whereas predominantly crystalline basalt is the main product from volcanoes free of ice. Soils in Iceland are developed from volcanic material and tend to be young and immature. The majority of soils in the non-glaciated catchments are classified as Brown Andosols, which contain significant amounts of the secondary phases allophane (15–30 wt%) and ferrihydrite (1–8 wt%), whereas in the glaciated catchments the most common soil type is Vitrisols, which are dominated by volcanic glass (Arnalds, 2004).

The sources of Icelandic rivers have been grouped into four categories: direct runoff, spring-fed, glacial-fed and lake-derived, with rivers often having more than one source type. Direct runoff rivers are more common in the geologically older areas (NW and E) of Iceland due to a reduction of permeability caused by soil compaction and secondary mineral formation (Gíslason et al., 1996).

River water samples were analysed from two previous sampling campaigns in Iceland. The first (samples IS-x), sampled rivers around the island in late June/early July 2001 (Fig. 1). The rivers sampled cover a variety of ages, from 0.01 Ma (IS-14 Laxá) to 11.2 Ma (IS-19 Heiðarvatn) and represent a range of glacial coverage and runoff. Areas with known inputs of hydrothermal water were avoided. These samples have previously been analysed for Os isotopes (Gannoun et al., 2006), U-series (Vigier et al., 2006), Si isotopes (Georg et al., 2007) and Li isotopes (Vigier et al., 2009). The second sampling campaign (samples Ax and Ex), sampled two localities in September 2003 and August 2005. The 'A' set consisted of rivers draining the west of the island which are minimally glaciated, are of Tertiary age (~3.1 Ma) and are situated in one of the most vegetated parts (primarily mosses and grasses) of Iceland. The 'E' set consisted of rivers draining the Vatnajökull