Tracing impact of pedogenic processes on soil solutions with Si and Mg isotopes

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Abstract

During weathering, stable isotopes of Si and Mg are fractionated in soils, directly impacting soil solutions and river signatures. In a monolithological catchment, isotopic variations in rivers would rather be related to pedogenic processes such as mineral dissolution, sequestration in secondary minerals via neoformaton or adsorption, and plant uptake. However, separating inorganic from biologically driven isotopic fractionation remains complex. The present study investigates Mg and Si isotope fractionation in soil solutions from four typical Icelandic soils from a basaltic catchment (Borgarfjördur): Histic Andosol, Histosol, Gleyic Andosol, Brown andosol. When compared to the basaltic host rock, soil solutions were found to be enriched in heavy Si isotopes and in light Mg isotopes. This observation supports the current view of preferential sequestration of light Si isotopes and heavy Mg isotopes in secondary minerals leading to a dissolved phase enriched in heavy Si and light Mg. Although our results seem to support the idea of weathering induced fractionation, we need to stress that isotopic variations in surface horizons still need to be investigated in relation to plant uptake. The combination of these two isotope systems will contribute to a better understanding of the influence of inorganic versus biological fractionation in a natural system.

Key Words

Andosol, basaltic catchment, weathering, MC-ICP-MS, Iceland

Introduction

Continental weathering does not only play a pivotal role in long-term climate and CO_2 regulation, it also sustains the biosphere by providing nutrients. Understanding weathering and associated rates is therefore important to understand the rates at which weathering-climate feedback mechanisms operate. Stable isotopes of Si and Mg are fractionated during weathering processes and might help to assess solute-solid interaction rates on small (soils) and large scales (catchments). The riverine isotopic composition of above elements in a monolithological catchment can be related to pedogenic processes, such as mineral dissolution, sequestration in secondary minerals via neoformation or adsorption, and plant uptake (Georg *et al.,* 2007). However, separating inorganic from biologically driven isotopic fractionation remains complex, owing the tight coupling of biology and weathering within the “critical zone”.

Silicon stable isotopes were used in small catchments to relate isotopic variations to soil processes, e.g. neoformation of secondary minerals (Ziegler *et al.,* 2005; Opfergelt *et al.,* 2010), Si adsorption onto oxides (Delstanche *et al.,* 2009; Opfergelt *et al.,* 2009), and Si isotope fractionation during weathering on larger scales (Georg *et al.,* 2007). All these studies have shown the preferential upake of light Si isotopes into secondary products, such as clays. Similarly, plant uptake was shown to favour light Si isotopes (Ding *et al.* 2005; Opfergelt *et al*., 2006). Magnesium isotopes are also fractionated by plant uptake favouring heavy Mg isotopes (Black *et al.,* 2008) and during neoformation of secondary minerals, likely favouring heavy Mg (Tipper *et al.,* 2006). However, Icelandic rivers were found to display a large range of Mg isotopic variations both lighter and heavier relative to the parental basalt, and few measured soils were shown to be isotopically lighter than basalt (Pogge von Strandmann *et al.,* 2008), suggesting isotope fractionation pattern similar to those Si.

This present study investigated the Si and Mg isotope fractionation in Icelandic soil solutions from four soil profiles (Borgarfjördur catchment), in order to elucidate the potential impact of soil weathering on riverine Mg and Si isotopic compositions. The combination of these two isotope systems will contribute to a better understanding of weathering derived fluxes to rivers and hence oceans.

Materials and Methods

Study site in Iceland

The Borgarfjördur catchment is located in West Iceland and is dominantly basaltic (Gislason *et al.,* 1996). Four typical Iceland soil types (Arnalds, 2004) were selected and described following FAO guidelines (FAO, 2006): Histic Andosol (HA), Histisol (H), Gleyic Andosol (GA), Brown Andosol (BA) (Figure 1).
Among the four soil profiles, ten soil solutions were collected in September 2009 using macro rhizon soil moisture samplers (length 9cm, diameter 4.5mm, porosity 0.2µm) connected with plastic syringes (30ml) in order to cover surface and deeper horizons.

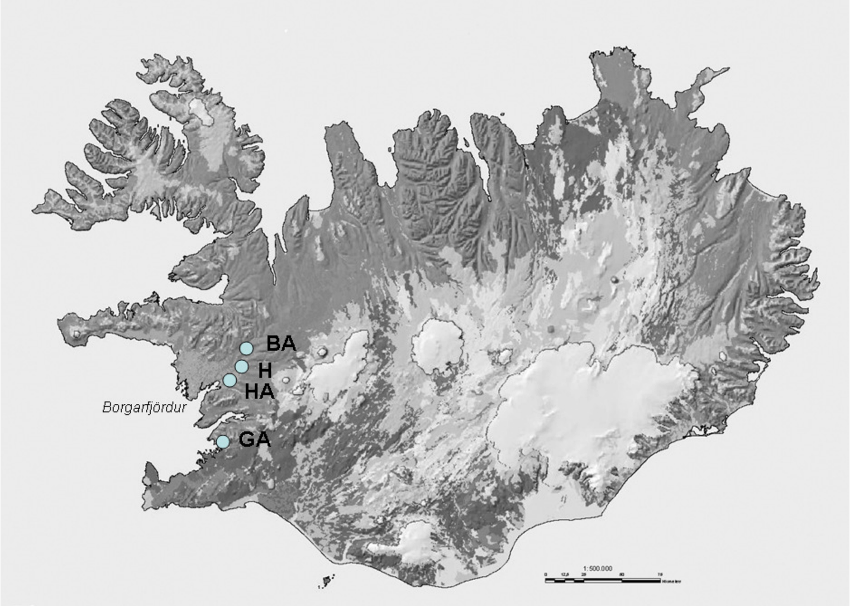

Figure 1. Location of soil sampling sites in Borgarfjördur catchment, West Iceland, 1:500.000 (map modified from Arnalds and Gretarsson 2001). GA = Gleyic andosol, HA = Histic andosol, H = Histosol, BA = Brown andosol.

Soil solutions characterization and isotope analysis

Temperature and pH of soil solutions were measured on the field. Major anion and cation concentrations were analysed at the Department of Earth Sciences in Oxford using the following instrumentation; Anion contents were measured by means of ion-chromatography (861 Advanced Compact IC) using conductivity detection following separation on a Metrohm A-Supp5 (4x50mm) column and a sodium carbonate/bicarbonate solution as mobile phase. Cation concentrations were analysed by quadrupole ICP-MS (Perkin Elmer ELAN 6100 DRC) and Si concentrations by photospectrometry (Hach, DR2800).
Soil solutions were purified for isotopic measurements through cationic exchange resin for Si (Georg *et al.,* 2006) and for Mg (adapted from Wombacher *et al.,* 2009). Silicon and Mg isotope compositions were determined by MC-ICP-MS (NuPlasma HR) and expressed in relative deviations in ‰ from NBS-28 (for Si) and DSM-3 (for Mg) using the common δ-notation. Accuracy was checked on international standards Diatomite (δ^{30}Si = +1.28±0.23‰, n=29) and Cambridge-1 (δ^{26}Mg = -2.61±0.15‰, n=563), and USGS rock standards BHVO-2 (δ^{30}Si = -0.20±0.16‰, n=25; δ^{26}Mg = -0.23±0.21‰, n=18) and BCR-2 (δ^{26}Mg = -0.24±0.26‰, n=23). Recovery for Mg was always better than 98%.

Results and discussion

The pH in soil solutions ranged from 3.6 to 6.2, with temperature varying from 10.9 to 13.1°C. Anion mean concentrations were as follows; F ~0.2ppm (±5%), Cl ~17ppm (±2%), NO_3 ~15ppm (±2%) and SO_4 ~31ppm (±2%). Silicon concentrations (±2%) ranged from 5 to 31ppm with a mean value of 15ppm. Magnesium concentrations were between 1 and ~16ppm with a mean value of 5ppm (±2%). Mean Al and Fe concentrations were 2.6ppm (±1%) and 4ppm (±3%), respectively.

Soil solutions displayed δ^{30}Si from -0.2 to +1.26‰ and δ^{26}Mg from -0.5 to -1.1‰. When comparing dissolved Si and Mg isotopes with the respective isotope composition of the parental basalt, with δ^{30}Si of -0.33±0.07‰ (mean between measured and Georg *et al.,* 2007) and δ^{26}Mg of -0.23‰ (Pogge von Strandmann *et al.,* 2008), our data suggest an enrichment in heavy Si isotopes, but light Mg isotopes in soil solutions relative to the parental material (see Figure 2 for the Histosol). Surface horizons showed a slight isotope shift, which might be related to plant uptake. This still needs to be investigated in more details.

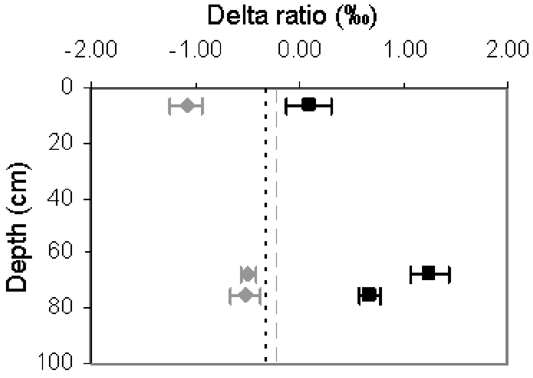

Figure 2. Distribution of δ^{30}Si (black square) and δ^{26}Mg (grey diamond) in soil solutions with depth within the Histosol ($2\sigma_{SD}$ error bar). Parental basalt δ^{30}Si (black dotted line; measured and Georg *et al.*, 2007) and δ^{26}Mg (grey dashed line; Pogge von Strandmann *et al.,* 2008) are given for comparison.

Those preliminary results indicate that soil solutions are enriched in light Mg isotope and heavy Si isotopes relative to the parental basalt. These effects can be related to the preferential sequestration of light Si isotopes in secondary minerals (Ziegler *et al.,* 2005; Opfergelt *et al.,* 2010; Georg *et al.,* 2009), and likely sequestration of heavy Mg isotopes in secondary minerals based on few data available (Tipper *et al.,* 2006).

Conclusion and perspectives

These preliminary results indicate that Mg and Si isotopes are very promising proxies to trace the effect of pedogenic processes on small-scale solute-solid interactions in soils. These data will be complemented by a mineralogical and isotopic characterization of the bulk soil (fraction <2mm) and clay fraction (fraction<2µm) in order to better constraint the isotope composition of these individual pools and the interaction between them. In the broader picture, our results will contribute to a better understanding of small-scale weathering processes, associated solute-solid interactions and resulting material fluxes in rivers draining basaltic catchments.

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