Earth and Planetary Science Letters 301 (2011) 125–136

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

Transport and exchange of U-series nuclides between suspended material, dissolved load and colloids in rivers draining basaltic terrains

Philip A.E. Pogge von Strandmann [a,b,*], Kevin W. Burton [a,c], Don Porcelli [c], Rachael H. James [a,d], Peter van Calsteren [a], Sigurður R. Gislason [e]

[a] Department of Earth Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK
[b] Bristol Isotope Group, Department of Earth Sciences, Bristol University, Bristol, UK
[c] Department of Earth Sciences, Oxford University, Oxford, OX1 3AN, UK
[d] National Oceanography Centre, Southampton, University of Southampton Waterfront Campus, European Way, Southampton, UK
[e] Institute of Earth Sciences, University of Iceland, Reykjavik, Iceland

ARTICLE INFO

Article history:
Received 30 April 2010
Received in revised form 13 October 2010
Accepted 20 October 2010
Available online 20 November 2010

Editor: M.L. Delaney

Keywords:
uranium
thorium
U-series
weathering
erosion
clay minerals

ABSTRACT

This study presents uranium and thorium concentrations and activity ratios for all riverine phases (bedload, suspended load, dissolved load and colloids) from basaltic terrains in Iceland and the Azores. Small basaltic islands, such as these, are thought to account for ~25% of CO_2 consumed by global silicate weathering, and for ~45% of the flux of suspended material to the oceans. These data indicate that [U] and [Th] in the dissolved and colloidal fractions are strongly controlled by pH, and to a much lesser extent by levels of dissolved organic carbon (which are low in these environments). At high pH, basalt glass dissolution is enhanced, and secondary mineral formation (e.g. Fe-oxyhydroxides and allophane) is suppressed, resulting in high dissolved [U], and low colloidal [U] and [Th], indicating a direct chemical weathering control on elemental abundances. When the dissolved ($^{234}U/^{238}U$) activity ratio is >~1.3 (i.e. when physical weathering, groundwater contribution or soil formation are high), there is little isotope exchange between dissolved and colloidal fractions. At lower activity ratios, the dissolved load and colloids have indistinguishable activity ratios, suggesting that when chemical weathering rates are high, secondary clay formation is also high, and colloids rapidly adsorb dissolved U. Many of the suspended sediment samples have ($^{234}U/^{238}U$) activity ratios of >1, which suggests that uptake of U onto the suspended load is important. Identical ($^{230}Th/^{232}Th$) in suspended, dissolved and colloidal samples suggests that Th, like U, is exchanged or sorbed rapidly between all riverine phases. This particle-reactivity, combined with poorly constrained contributions from groundwater and hydrothermal water, and short-term variations in input to soils (volcanic and glacial), suggests that U-series nuclides in riverine material from such basaltic terrains are unlikely to reflect steady state erosion processes.

1. Introduction

The destruction of the continental crust by erosion and chemical weathering, and its subsequent transfer to the oceans not only affects the evolution of the continents over time, but it also plays a pivotal role in removing CO_2 from the atmosphere. In particular, the chemical weathering of continental Ca-Mg silicates results in the net sequestration of atmospheric CO_2 in the oceans and is thus Earth's dominant climate moderating process (Berner, 2003, 2004; Berner et al., 1983; Kump et al., 2000; Walker et al., 1981). Of the silicate lithologies, basalt weathering exerts a disproportionate effect on atmospheric CO_2, as it accounts for ~35% of CO_2 consumption despite only making up <5% of the continental area (Dessert et al., 2003). Weathering of small basaltic islands (e.g. Iceland, the Azores, Reunion, Hawaii and volcanic arc islands) is thought to account for the majority of basaltic CO_2 consumption, due to very high weathering rates (Gaillardet et al., 1999b) — thus chemical weathering of these islands probably accounts for ~25% of CO_2 consumed by global silicate weathering (Dessert et al., 2003; Louvat and Allegre, 1997, 1998; Louvat et al., 2008). These small basaltic islands are also typical of the high-relief, volcanic and tectonically active islands thought to contribute >45% of the river suspended material to the oceans (Gislason et al., 2006; Milliman and Syvitski, 1992). These islands dominate the suspended material flux to the oceans due to the combined effect of high runoff, the presence of rapidly weathering rocks, and an absence of sedimentary traps. This suspended material undergoes continued weathering during transport to the marine environment, thus acting as a further sink of atmospheric CO_2 (Gislason et al., 2006; Pogge von Strandmann et al., 2008b; Wallmann et al., 2008). The delivery of suspended material to the oceans appears to be far more climate dependent (i.e. sensitive to changes in river discharge/runoff) than

---

[*] Corresponding author. Bristol Isotope Group, Department of Earth Sciences, Bristol University, Bristol, UK.
E-mail address: P.PoggevonStrandmann@bristol.ac.uk (P.A.E. Pogge von Strandmann).

0012-821X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.epsl.2010.10.029

the riverine dissolved load (Gislason et al., 2006, 2009). Furthermore, there is an inverse relationship between the degree of weathering of the riverine suspended load and the suspended sediment concentration (Gaillardet et al., 1999a). Thus, during warmer and wetter climate intervals, the delivery of suspended material to the oceans will increase and the material itself will be less weathered, resulting in greater weathering in the estuarine environment, providing a strong negative feedback acting to stabilise Earth's climate (Gislason et al., 2006; Pogge von Strandmann et al., 2008b).

Understanding the relationship between continental weathering and climate change demands precise information on the timing and rate of response of weathering to climatic or tectonic forcing, or human activity. In principle, uranium series isotopes can provide key chronological constraints, because their fractionation is time-dependent. The time interval between leaching of U-series nuclides from the rock, and discharge of river water into the ocean, is recorded by radioactive decay of the nuclides. This time interval, in turn, provides information on the kinetics of U release from the rock, as well as the timescale of weathering, which depends on the residence times of sediments within a given watershed and thus on the extent and nature of soil formation (Dosseto et al., 2006a,b,c, 2008a,b; Granet et al., 2007, 2010; Moreira-Nordemann, 1980; Plater et al., 1992; Vigier et al., 2001, 2005, 2006).

The energetic α-decay of ^{238}U to ^{234}U often causes the (^{234}U/^{238}U) (where parentheses denote activity ratio) of surface waters to be greater than secular equilibrium (=1). The highest (^{234}U/^{238}U) are found in waters draining terrains with high physical weathering rates. In contrast, when chemical weathering rates are high, or soil residence times short, riverine activity ratios are usually close to those of the basement lithology (i.e. secular equilibrium) (Andersen et al., 2009; Chabaux et al., 2003; Dosseto et al., 2006a,b,c, 2008a,b; Kigoshi, 1971; Kronfeld and Vogel, 1991; Pogge von Strandmann et al., 2006, 2010; Robinson et al., 2004; Vigier et al., 2001, 2005, 2006). The same process can also cause isotope variations between U and ^{230}Th. Further decoupling of the behaviour of U and Th arises from a difference in valence and complexation behaviour: in oxidising natural waters U exists as soluble uranyl, whereas tetravalent Th is insoluble (although the solubility of U and Th changes when complexing with inorganic or organic ligands) (Chabaux et al., 2003; Faure, 1986), as a result of which U is usually more mobile than Th in the weathering environment.

A further complication arises because both U and Th bind strongly to organic, and to a lesser extent inorganic, colloids (Andersson et al., 1998, 2001; Dosseto et al., 2006c; Porcelli et al., 1997; Riotte et al., 2003). Colloids can therefore exert a strong control on U-series nuclide mobility, and thus on the distribution of radioactive disequilibria amongst different phases in river systems.

This study presents major and trace element compositions, and U and Th activity ratios for suspended, dissolved and colloidal fractions of rivers from two well-characterised, dominantly basaltic, watersheds in Iceland and Sao Miguel (Azores Archipelago) (Pogge von Strandmann et al., 2006, 2008a, 2010). These results illustrate that even inorganic colloids can strongly affect U-series mobility, and that rapid exchange of both U and Th between the different riverine phases is common. Taken together, with poorly quantified inputs from hydrothermal waters and groundwaters, these observations suggest that steady state erosion models may not be applicable in the basaltic terrains in Iceland.

2. Field areas

The dominantly basaltic terrains studied here have been described in detail elsewhere (Pogge von Strandmann et al., 2006, 2010). Briefly, samples from Iceland were collected from a catchment between the Langjökull icecap and the Borgarfjörður estuary in the west of the island (Fig. 1). Some of the rivers here receive water directly from glaciers. While other, direct-runoff, rivers mostly drain the older basaltic areas (given that Icelandic glaciers are generally present on recently erupted volcanic rocks), due to a decrease in rock permeability with rock age. This is because in the older rocks compaction and sealing by secondary minerals reduces the permeability by up to five orders of magnitude (Sigurdsson and Ingimarsson, 1990). Some samples were also taken from rivers just off the Vatnajökull icecap in the south-east of Iceland.

Samples were collected in September 2003 and August 2005. Element concentrations and Li, U, Mo and Mg isotope data for the dissolved (<0.2 μm) phase have been previously reported and discussed (Pearce et al., 2010; Pogge von Strandmann et al., 2006, 2008a).

In the Azores archipelago samples were taken from Sao Miguel island. Here the only permanent rivers are in the oldest eastern part of the island and around the calderas, which have often formed lakes (Fig. 1). The recent volcanic soils in the west and centre of the island drain too rapidly to carry permanent streams.

Samples were collected in October 2004, and concentrations and Li and U isotope data for the dissolved (<0.2 μm) phase are reported and discussed by Pogge von Strandmann et al. (2010). The primary basalt and secondary weathering mineralogy is similar in both areas: the primary rock type is basaltic, and secondary minerals comprise ubiquitous Fe oxides and oxyhydroxides, as well as clays. The stability of many of these clays is pH-dependent: for example, smectites and allophane are unstable at high pH, while chlorite and talc (which form iddingsite) are only stable at high pH (Arnalds, 2005; Arnorsson et al., 2002; Gislason and Arnorsson, 1990; Gislason et al., 1996; Pogge von Strandmann et al., 2006, 2008a, 2010; Stefansson and Gislason, 2001; Stefansson et al., 2001).

3. Methods

3.1. Sample collection and filtration

On the day of collection, water samples were initially filtered through 0.2 μm cellulose acetate filters contained in a teflon unit. Where possible, >0.2 μm material was recovered from the filters. Subsequently (also on the day of collection), aliquots of the filtered water were passed through a Sartorius tangential ultrafiltration system at 10 kD, using Sartocon polyethersulphone (PESU) slice cassettes to separate retentate (colloidal) fractions from truly dissolved (<10 kD) fractions. The nature of tangential filtration (cross-flow filtration) is that flow is directed tangentially along the surface of the membrane, with most of the solution circulated back to the feed tank. This circulation of the water means that the retentate volume gradually decreases, while the retained particle concentration remains constant, effectively concentrating the colloids in a small (known) amount of solution. This solution has the same concentrations as the dissolved load, so colloidal concentrations are further corrected for this. Total organic carbon (TOC) was measured commercially by Severn Trent. Thorium was co-precipitated with Fe-oxyhydroxide (using Fe powder purified by column chemistry) from 15 L of filtered water (Edwards et al., 1987). For the purposes of this study, and to allow direct comparison with studies that have not conducted ultrafiltration, material >0.2 μm is classified as suspended, <0.2 μm as dissolved, 10 kD<x<0.2 μm as colloidal (i.e. ultrafiltration retentate), and <10 kD as ultrafiltered.

3.2. Cation analyses

Water and colloidal samples were calibrated against a set of synthetic multi-element standards prepared gravimetrically from high purity single element standard solutions. Some colloidal material was pre-treated with dilute H_2O_2 in order to ensure dissolution. However, there was no difference in the composition of H_2O_2-treated vs. non-treated samples. The accuracy of the analyses was assessed by running the natural water certified reference material SLRS-4, as well as in-house standards. The 2σ external uncertainty of these measurements is better than ±3.2% for major elements and ±5% for trace elements.