

Suspended basaltic glass–seawater interactions

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Abstract

The objective of this study was to quantify by experiments the initial seawater–suspended basaltic glass interactions following the 1996 outburst flood from the Vatnajökull glacier, Iceland. The altered basaltic glass dissolved in seawater as recorded by the Si release from the glass. The dissolved concentrations of Na, Ca, Si, Ba, Cd, Co, Cu, Hg, Mn, Ni and total dissolved inorganic N increased with time but the concentrations of Mg, K, S, Sr, Fe, Pb and Zn decreased. Calculated 1 to 10 day fluxes for Si range from 38,000 tons/day to 70,000 tons/10 days. The fluxes for other major elements are more uncertain, but the positive flux (release from suspended matter to seawater) of Ca and Na, and negative flux of Mg, K and S are greater than the Si flux.

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1. Introduction

The Gjálp subglacial eruption 1996 within the Vatnajökull Glacier, Iceland (Fig. 1) triggered a catastrophic outburst flood, bringing at least 180 million tonnes of suspended solids to the sea in only 42 h. This amounts to 1% of the total annual global river suspended flux to the oceans (Milliman and Syvitski, 1992). The estimated discharge at the peak of the flood was around 55,000 m³/s (Snorrason et al., 2002), making it the second largest river in the world for a few hours. In the last 200 years, 15 catastrophic jökulhlaups have emerged on the Skeidarársandur floodplain, usually in connection with volcanic eruptions (Thórarinnsson, 1974). Owing to

its frequency and size, these floods are important for the total flux of suspended and dissolved solids from Iceland to the North Atlantic.

The specific BET-surface area of the suspended solids was measured to be 11.8–18.9 m²/g (Stefánsdóttir and Gíslason, 2005). The total mass of the suspended material and its specific surface area yield the average total BET-surface area of 2.8 × 10⁹ km². This is about 100 times the geographic area of Africa. Thus, the suspended solids provide enormous potential for adsorption/desorption and precipitation/dissolution fluxes at the suspended solids–ocean water interface.

The aim of this study was to quantify by experiments the initial seawater–suspended matter interaction following the 1996 jökulhlaup and to estimate the overall flux of readily dissolved nutrients and metals from the suspended material to seawater during the first hours and days of its presence in the sea. Some of the

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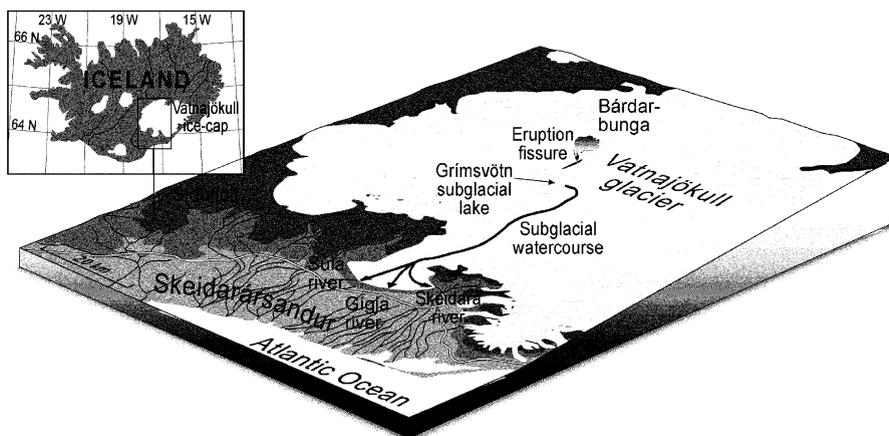


Fig. 1. Iceland in the North Atlantic. The Gjalp eruption site, the Grímsvötn caldera and subglacial lake within the Vatnajökull glacier. Also shown is the flood path within the glacier, the rivers Sula, Gígja and Skeidará and the Skeldararsandur floodplain.

metals are determinant in the primary production rate in the North Atlantic.

2. Methods

Seawater, used in the experiments, was collected in spring 1999 from the Selvogsgrunn section south of the Reykjanes peninsula in SW Iceland, filtrated through 0.2 μm pore cellulose acetate filter and stored in the dark before the experiments (Stefánsdóttir and Gíslason, 2005). A total of 16 experiments were run in 250 ml polypropylene batch reactors that were placed in a temperature controlled water bath at $25\text{ }^\circ\text{C} \pm 0.5\text{ }^\circ\text{C}$ for 16 min to 6 days. Two freeze dried samples from peak suspended matter flux (96-S059) and maximum flood-water discharge (96-S062) were used. At the end of each experiment, the water samples were filtered through 0.2 μm pore cellulose acetate filter and acidified with concentrated suprapure HNO_3 acid. The elements Ca, Mg, Na, K, S, Si, Sr were analyzed with ICP-AES (Inductively Coupled Atomic Emission Spectrometry), Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, Ti and Zn were analyzed with High Resolution Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Hg was analyzed using atom fluorescence (Rodushkin and Ruth, 1997; Rodushkin et al., 1998; Stefánsdóttir and Gíslason, 2005).

3. Results

Altered basalt glass was the major component (80%) of the suspended matter, accompanying secondary minerals (11%), such as zeolites and calcite, but only 5% of the total suspended material during the jökulllauf was fresh volcanic glass (Stefánsdóttir and Gíslason, 2005).

The BET specific surface areas of the samples ranged from $11.9\text{ m}^2/\text{g}$ to $18.9\text{ m}^2/\text{g}$ (Stefánsdóttir and Gíslason, 2005). The results of selected

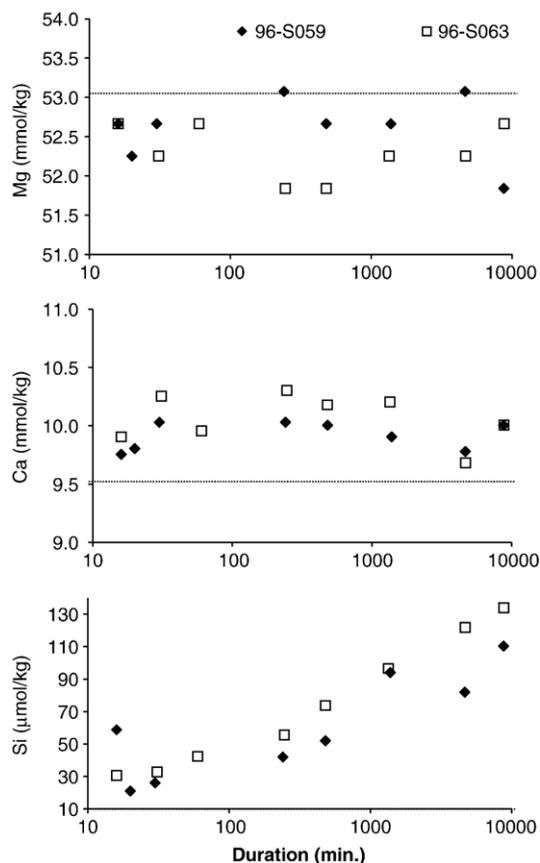


Fig. 2. The concentration of selected elements in seawater during the experiments with suspended material sample 96-S059 and 96-S063 versus the logarithm of time. The dotted line represents the original composition of the seawater.

chemical analysis of the seawater, before (horizontal bar on the diagrams) and after the experiments are presented in Fig. 2. Note that the timescale on the horizontal axis is logarithmic and that each sample represents one reactor and all the water in each reactor was used for chemical analyses for the indicated time span. Thus the water/rock ratio varies somewhat from one reactor to the other. This accounts for some of the scatter in Fig. 2. With the exception of one sample, pH did not change significantly from the initial 7.80 during the experiments. The concentrations of the elements Na, Ca, Si, Ba, Cd, Co, Cu, Hg, Mn, Ni and total dissolved inorganic N increased considerably when the suspended solids came into contact with the seawater, but the concentrations of Mg, K, S, Sr, Fe, Pb and Zn decreased (Fig. 2). The concentration of other elements did not change much with time. Note that some elements are in very high concentration in seawater, thus it is difficult to detect water/rock exchange because of the high background concentration. The concentrations of Si, Mn, Ba, Ni, Co and Cd increased rapidly at the beginning and then at a slower rate, appearing linear on the concentration log time diagrams like the one for Si in Fig. 2. These rates were scaled to the total BET-surface area of the suspended matter and water mass in each reactor (Stefánsdóttir and Gíslason, 2005), enabling calculations of dissolved element mass transfer from the surface of the suspended matter to the sea during the first hours or days of the jökulhlaup.

4. Discussion

The seawater experimental data yielded non-steady state rates of $\log r_{\text{BET,Si}}$ (mol/m²/s) release, from -9.4 at the beginning to -11.9 after 6 days at 25 °C. Compared with “far from equilibrium steady state” rates for basaltic glass which are -10.9 to -10.6 \log mol Si/m²/s at 25 °C and pH 7 and 8 respectively (Oelkers and Gíslason, 2001; Gíslason and Oelkers, 2003). The basalt glass that Gíslason and Oelkers (2003) used in their experiments had the same silica content, 48 wt.% SiO₂, but a BET-surface area of 2.3 m²/g. Its grain size was 40–120 μm, it was unaltered and cleaned ultrasonically. The solids used in this study were quite different, with a BET-surface area of 11.9 and 18.9 m²/g, their grain size was generally around 30–300 μm, they were mostly altered basalt glass, their surface covered with secondary minerals, and they were not ultrasonically cleaned. Consequently the long term BET-surface area normalized dissolution rate ($\log r_{\text{BET,Si}}$ (mol/m²/s) = -11.9) would be expected to be slower as was confirmed by this study.

There were two major dissolved element fluxes to the ocean after the flood: (1) the flux resulting from the dissolved elements in the flood waters (Gíslason et al., 2002) and (2) the flux resulting from floodwater suspended matter–seawater interactions after arrival to the ocean. The flood fluxes stemming from suspended matter–seawater interactions can be calculated from: (1) the rate expressions for sample 96-S059, (2) the total BET-surface area calculated from the total mass of suspended matter (180 Mtons) times the specific BET-surface area of the suspended matter at the highest flux of suspended matter and (3) the duration of the suspended matter–seawater interactions. The results are shown in Fig. 3 for Si, Ba, Co, Mn, Cd, the elements which increased continuously in the experiments (Fig. 2 for Si). The fluxes for other elements are more uncertain. However it is clear that the positive flux (release from suspended matter to seawater) of Ca and Na, and negative flux of Mg, K and S are greater than the flux of Si. The direction of these fluxes are in agreement with experimental fluxes at 50 °C (Crovisier et al., 1983), and interstitial water–volcanic ash fluxes (Gieskes and Lawrence, 1981; Perry et al., 1996); namely, release of Ca to seawater and interstitial water but uptake of Mg and K.

The release of elements from the suspended material to seawater during 1 day are more important than the dissolved ones carried by the flood (Gíslason et al., 2002; Stefánsdóttir and Gíslason, 2005) for several elements (i. e. Mn, Ba, Ni, Co, Cd). If the grains are in active contact with seawater without deep burial for more than 1 day, the importance of the dissolution flux from the suspended matter increases. The world’s major deltas act like fluidized bed reactors; the sediments are in active contact with seawater due to, for example, repeated re-suspension, for months after their arrival to the delta and similar processes occur on smaller scales in most estuarine–shelf systems (Aller, 1998). This observation underscores further the importance of dissolved fluxes stemming from river suspended material to ocean waters.

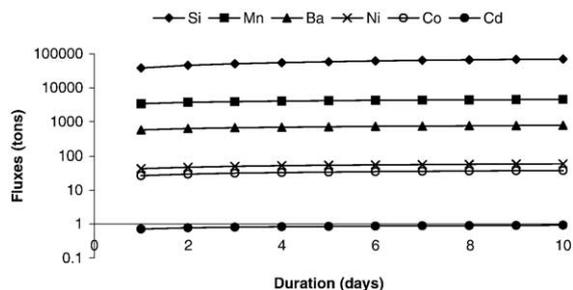


Fig. 3. The logarithm of the desorption/dissolution fluxes versus time for the indicated elements.

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