

The 1996 subglacial eruption and flood from the Vatnajökull glacier, Iceland: effects of volcanoes on the transient CO₂ storage in the ocean

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Maximum CO₂ removal from the atmosphere within the last 30 years occurred during the 2 years following the volcanic eruption of Mt. Pinatubo in the Philippines in June 1991 (Sarmiento 1993). Sarmiento (1993) has suggested a biological fixation of CO₂ caused by metal fertilization as a plausible cause for the removal of CO₂ from the atmosphere. Volcanic glass from the volcanic eruption in Mt. Pinatubo spread over the Pacific and dissolved in the oceans, releasing metals that enhance biological fixation of CO₂.

The October 1996 volcanic eruption of the Vatnajökull glacier and the associated 35 days of chemical weathering of the eruption products provide an opportunity to study the net effect of eruptions on the short term budget of CO₂ in the atmosphere and its effect on CO₂ storage in the ocean. During most volcanic eruptions, gas, volcanic ash, volatile nutrients, and soluble metallic salts are dispersed into the atmosphere and stratosphere where their fluxes are hard to define. However, during the 1996 Vatnajökull subglacial eruption these volatile elements condensed and dissolved in the meltwater that enclosed the eruption site and were eventually discharged to the ocean in a dramatic flood of 3.5 km³ that lasted for two days.

Eruption

The subglacial eruption started on September 30 at about 22 GMT within the Vatnajökull glacier (Einarsson *et al.*, 1997). It lasted for 13 days, 3 km³ of ice were melted at the eruption site and the erupted basaltic andesite magma fragmented into glass forming a hyaloclastite ridge 6–7 km long and 200–300 m high under 500–750 m of ice. At one location the eruption melted its way through the ice.

Areal dispersed volcanic glass amounted to less than 2% of the total volume erupted. Meltwater at an average temperature of at least 15–20°C flowed along a narrow channel along the glacier bed from the eruption site into the Grímsvötn subglacial lake for five weeks, before draining in a sudden flood, or jökulhlaup (Gudmundsson *et al.*, 1997).

Chemistry of snow, ice, and water at the eruption site

The ice that melted at the eruption site and the flow path in the Vatnajökull glacier was purified snow, thus the dissolved constituents in the flood water have primarily magmatic and rock origin. Volatile gases and metals condensed and dissolved in this 'purified meltwater', leading to corrosive water that interacted with the volcanic glass for less than 35 days. The water-rock interaction resulted in consumption of the acids and simultaneous release of elements from the glass. According to the concentration of S, Cl, and F in the flood water the pH of the water before interaction with the volcanic glass was as low as 2.70. According to calcite saturation calculations the temperature of the water at the eruption site ranged from 15 to 80°C. Heat and mass balance calculations yield a minimum temperature of 15 to 20°C for the water leaving the eruption site (Gudmundsson *et al.*, 1996).

Less than a 2% fraction of the erupted basaltic-andesite glass was forced through the meltwater at the eruption site within the glacier and aerielly dispersed. The surface of this glass and other volcanic aerosols enclosed in the snow on the glacier did not contain a significant amount of acid-producing aerosols since melted snow in contact with the glass had a pH of 5.55 to 5.01, nor did the snow

below the glass (pH 5.63) on the glacier in the vicinity of the eruption site. However, the melted snow in contact with the glass was enriched in some metals compared to the composition of the 1996-1997 winter precipitation on the Vatnajökull and the Langjökull glaciers in Iceland. The enrichment ratios in decreasing sequence were; Mn (262), Al (44), Co (>31), Fe (26), Cu (17), S (16), Hg (>12) Ba (8), Ca (5), Zn(4), Ni (2), and Mg, Na, Cr, Pb (1). There was no enrichment of the nutrients, NH_4 , NO_3 , NO_2 , and PO_4 , in the melted snow that was in contact with the ash. Ca was the only major element in the glass that was enriched in the snow. Despite significant enrichments, the actual concentrations in one kg of the melted snow containing 5.8 g of volcanic glass were low; Mn (16 $\mu\text{g}/\text{kg}$), Al (49 $\mu\text{g}/\text{kg}$), Fe (14 $\mu\text{g}/\text{kg}$) and Hg (12 ng/kg). These concentrations were close to 3 orders of magnitude less than the concentration of metals in melted snow in contact with volcanic ash from the 1991 eruption of Hekla, Iceland (Gíslason *et al.*, 1992). Thus, most of the volatile metals had condensed and dissolved in the meltwater at the eruption site before areal dispersion.

The flood

On November 4 the sulphur concentration of the Skeidará River increased and later that day at 21:30 GMT a sudden appearance of a continuous high frequency seismic tremor indicated that the ice barrier of the Grímsvötn subglacial lake was being lifted (Einarsson *et al.*, 1997). The water rushed along the 50 km flow path beneath the glacier down to the glacier edge. At 3:00 November 5, conductance and chemistry of the rivers at the glacier edge changed significantly without any other sign of the flood. It emerged there before 8 GMT, more than 10 hours after leaving Grímsvötn, finally reaching the ocean at 11 GMT. The drop in elevation along the flow path was 1300 m. The flood reached peak discharge of more than 50,000 m^3/sec on November 5 at 24:00 GMT. The total volume of water released from the glacier during these two days was 3.5 km^3 .

Chemistry of the flood waters

The temperature of the floodwater 10 km downstream from the glacier edge was zero and the dissolved oxygen in the water was 50% of air saturation at that temperature. There was a trace of H_2S in the water, but most of the sulphur was in the form of SO_4^{2-} and perhaps some $\text{S}_2\text{O}_3^{2-}$. The pH of the water ranged from 7.35 to 6.90 measured at 20°C and the partial pressure of CO_2 in the water at 0°C

was higher than in the atmosphere. The concentrations of Ca, Mg, Sr, and dissolved inorganic carbon reached peak concentration very early in the flood, Mg at 9:25 on November 5 but the others at 13:15; the concentrations then declined towards the end. The concentrations of Na, K, Cl, and F were high at 13:15 and remained high, or even increased, throughout the flood. There was a rise followed by a decline in the concentrations of S and Si, reaching peak concentration at 0:30 on November 6, coinciding with peak discharge. Concentrations of Fe and Mn were highest late in the flood, or between 6:45 and 10:24 on November 6, but Cu concentration was highest at the end.

The first part of the flood was heaviest with respect to the $^{18}\text{O}/^{16}\text{O}$ isotope ratio; the water was lightest shortly after peak discharge and thereafter the ratio increased. The $^{13}\text{C}/^{12}\text{C}$ flood ratio was around -2 compared to -4 in the river before the flood. The ^{14}C -BP age of the carbon before the flood ranged from 12 to 16 thousand years, but the ^{14}C -BP age of carbon in the flood water was 33 to 36 thousand years old.

Fluxes of dissolved elements and CO_2 storage in the ocean

The flux of each element at a given time in the flood can be calculated by integrating the discharge and concentration measurements. The mole flux of elements in declining sequence was: $\text{C} > \text{Ca} > \text{Na} > \text{S} > \text{Si} > \text{Mg} > \text{Cl} > \text{K} > \text{F} > \text{Mn} > \text{B} > \text{Fe} > \text{N} > \text{Al} > \text{Sr} > \text{P} > \text{Zn} > \text{Cu}$. The CO_2 flux was 0.5 million tonne, translating to a 515 mg/kg CO_2 concentration released from the magma.

Using the Redfield-type elemental composition of diatoms C:Si from Martin and Knauer (1973), and for C: Fe, Zn, Cu, Mn, Ni, Cd in planktonic organic tissue (Bruland *et al.*, 1991) the corresponding C fixation was calculated, assuming each element to be rate-determining for planktonic growth. The concentrations of Fe, Mn, and Zn in this stoichiometry are below or near their respective threshold values for optimal growth of organic material (Bruland *et al.*, 1991). Therefore it is possible that insufficient concentration of these three nutrient trace metals limits oceanic plankton production in waters otherwise having a high nutrient supply. The calculated CO_2 fixation or measured volcanic CO_2 release was in declining order: $\text{Mn} > \text{Fe} > \text{Si} > \text{CO}_2$ eruption release $> \text{Cu} > \text{Zn} > \text{P} > \text{N}$. Therefore, if any of the Mn, Fe, or Si was rate-determining for planktonic or diatom growth, a subglacial volcanic eruption and ensuing flood could lead to transient net CO_2 removal from the atmosphere.