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Metal scavenging by calcium carbonate at the Eyjafjallajökull volcano: A carbon capture and storage analogue

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ABSTRACT

The reaction of CO_2 and water with basaltic rock can release trace heavy metals, which pose a serious threat to the quality of surface waters. The pH of the carbonated water increases during dissolution of the host rock or dilution by pore fluids. This leads to precipitation of carbonate and other secondary minerals that often scavenge the released heavy metals. However, very little is known about uptake capacity of the precipitates in natural systems or how much divergence there could be, compared with behavior in laboratory experiments. The spring 2010 eruption of the Eyjafjallajökull volcano, Iceland, provides a unique opportunity to study the mobility of heavy metals that are released during CO_2 injection into shallow basaltic aquifers and the ensuing precipitation of carbonate minerals.

Following the Eyjafjallajökull eruption, rapid and constant travertine formation was discovered in the Icelandic river, Hvanná, in the vicinity of the volcano. The river water emerged from under the lava flow and was heavily charged with cations and dissolved CO_2. The concentration of the major dissolved constituents was: dissolved inorganic carbon (DIC), 33.08 mM; calcium, 6.17 mM; magnesium, 4.27 mM; sodium, 2.78 mM and sulfur, 1.92 mM. Carbon dioxide degassing of the river water increased pH from 6.6 to 8.5 and travertine precipitated for hundreds of meters downstream, rendering the stream bed white with calcite. Rapid crystallization rate produced dendritic structures or sometimes very porous material. Boxwork textures were observed within the porous calcite that probably originated from transformation of a metastable phase such as ikaite ($CaCO_3 \cdot 6H_2O$). A gradual decrease of conductivity from 1.8 mS/cm at the river water outlet to 1.1 mS/cm downstream and a clear drop in dissolved metal concentration strongly correlated with the precipitated calcite. Considering the complexity of the natural system, the estimated partition coefficients for Ba, Cd, Co, Cu, Mg, Mn, Na, Ni, Sr and Zn are in good agreement with the values derived from laboratory experiments under rather ideal conditions. Other elements were also scavenged from the river water, including Al, Fe, K, P, S, Si, Ti, V and the rare earth elements (REE). Our thermodynamic modeling suggests that, in addition to calcite and ikaite, silica, clay minerals, ferrihydrite, gibbsite and amorphous Ca, Mg carbonate minerals were supersaturated as the spring water degassed its CO_2. Our results provide a valuable base for assessing the environmental impact of volcanic eruptions in basaltic terrain and carbon capture and storage (CCS) in basaltic rock.

1. Introduction

The capture and storage of anthropogenic carbon dioxide in basaltic rock is a promising way of reducing CO_2 emissions (Seifritz, 1990; Bachu et al., 1994; Lackner et al., 1995; McGrail et al., 2006, 2011; Alfredsson et al., 2008, 2013; Goldberg et al., 2008; Oelkers et al., 2008; Gislason et al., 2010; Aradottir et al., 2012; Power et al., 2013; Gislason and Oelkers, 2014). Injection of CO_2 into rock formations in natural and engineered systems creates corrosive, CO_2 charged fluids with pH of 3 to 4 (Gislason et al., 2010; McGrail et al., 2011; Alfredsson et al., 2013). This occurs for example following an intrusion of magma at a shallow level in the crust, with the ensuing release of CO_2, or following the injection of CO_2-water mixtures for carbon capture and storage (CCS). These corrosive fluids dissolve the host rock and release the major cations, Ca^{2+}, Fe^{2+} and Mg^{2+}, but they can also mobilize toxic metals, especially in the early stages of water–rock interaction while the pH is still low (Aiuppa et al., 2000a,b, 2003, 2005; Rogers et al., 2006; Flaathen et al., 2009; Gislason et al., 2010; Alfredsson et al., 2013; Galeczka et al., 2013a,b; Olsson et al., 2013). Dissolution, especially of mafic rock, dilution by the original fluids in the pores and fissures of

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the host rock and CO_2 degassing would raise pH and lead to precipitation of carbonate and other secondary minerals (Rogers et al., 2006; Kelemen and Matter, 2008; Flaathen et al., 2009; Olsson et al., 2012; Alfredsson et al., 2013; Bickle et al., 2013; Galeczka et al., 2014). The question remains, to what extent are the toxic metals sequestrated by precipitation in, or adsorption on secondary minerals? Uptake of trace metals would minimize pollution of ground and surface waters in volcanic terrain and in the vicinity of CO_2 injection wells in engineered systems.

After the 2010 eruption of the Eyjafjallajökull volcano in Iceland, travertines precipitated from the basic solutions that resulted from water percolation through the fresh basalt as CO_2 degassed from them. These travertines offer a unique opportunity to investigate the uptake of heavy metals that would likely result from CO_2 injection into shallow basaltic aquifers. Coprecipitation experiments conducted in laboratory settings provide data but it is quite possible that they do not reflect the true behavior of more complex, natural systems. The study of the natural travertine formation in the Hvanná River would give insight into how carbonate minerals take up heavy metals in the environment, which is certain to be closer to what would happen during carbon storage in basaltic rock.

After 18 years of deformation and earthquake activity, Eyjafjallajökull began an effusive flank eruption at the Fimmvörðuháls ridge on March 20, 2010 and it lasted until April 12 (Pedersen and Sigmundsson, 2004, 2006; Sigmundsson et al., 2010). An explosive summit eruption started on April 14, 2010 and ended in May 2012 (Fig. 1a). Eyjafjallajökull produces lava flows with basaltic to intermediate composition and the material from the 2010 eruption was relatively primitive and mildly alkaline basalt (Sigmarsson et al., 2011). Prior to eruption in the spring of 2010, the main riverine CO_2 flux from the volcano was via Gigjökull, the runoff stream from the caldera (Gislason et al., 1995). In July 2010, new measurements showed high concentrations of dissolved inorganic carbon in the river water of Hvanná. The CO_2 probably originated from a southeast tilted dyke intruded in March 2010 directly beneath the Hvanná valley, that did not reach the surface (Fig. 1a) (Sigmundsson et al., 2010). In the stream bed of the Hvanná, a layer of white travertine precipitated that was observed for the first time on April 2, 2010. At some places, it was already several centimeters thick in July 2010, covering rocks and twigs, and it extended for hundreds of meters downstream. The dissolved concentration of a wide range of elements decreased downstream, in parallel with the formation of the travertine so our hypothesis was that they were being taken up by the precipitating travertine.

The purpose of this study was to characterize the precipitated material by (1) identifying the phases, (2) characterizing the changes in crystal habit and morphology and (3) estimating the concentration of the scavenged elements. We have derived partition coefficients for the coprecipitated metals and compared their values with those from the literature. Our results provide a valuable base for assessing the environmental impact of volcanic eruptions and magma intrusion at shallow levels in the crust, as well as for carbon capture and storage (CCS) in basaltic rock, such as the Icelandic CarbFix project at the Hellisheiði injection site in Southwest Iceland and the Wallula project in Southeastern Washington.

2. Description of the field site and sample collection

2.1. Field site

A new spring outlet was observed emerging from under the lava flow of the Eyjafjallajökull 2010 flank eruption. The water had high

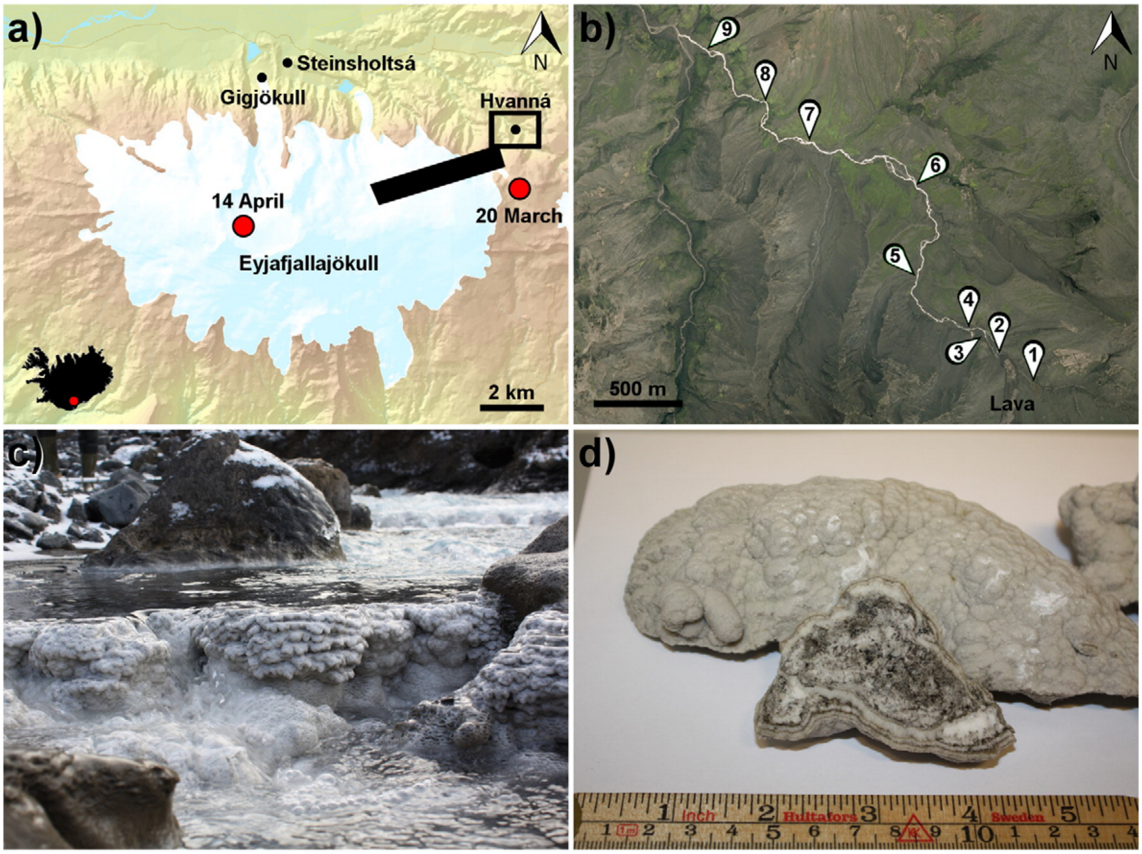

Fig. 1. Sample area and samples. (a) Map of the Eyjafjallajökull volcano. The red dots mark the eruption sites, the solid bar represents the area of an expected dyke intrusion based on deformation data (Sigmundsson et al., 2010) and the box outlined in black shows the sample area of (b), a modified satellite image from SAMSÝN, July, 2010 showing the sample locations; the white travertine shows as a heavy white demarcation of the Hvanná; (c) a photograph of sampling Site 6. (d) Travertine Sample HV03 from Site 6, showing the dark layers of altered ash that were captured as the travertine precipitated.