Towards 'green' geothermal energy: Co-mineralization of carbon and sulfur in geothermal reservoirs

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A B S T R A C T

Geothermal fluid utilization is considered one of the green energy sources. Yet, mitigation strategies must be applied to reduce the associated pollutants like carbon dioxide (CO_2) and toxic hydrogen sulfide (H_2S) emissions. One suggested method is the re-injection of the two gases back into the geothermal reservoir wherein carbon and sulfur are expected to mineralize naturally for a long-term underground storage. However, CO_2 and H_2S mineralization rates for natural systems are not well defined. To address the feasibility of such sequestration, experiments were conducted at 250 °C for several reservoir rock types, ranging from basaltic to silicic. Analysis of solution composition and secondary mineralogy confirmed the precipitation of Fe-Ca carbonates and Fe sulfide for all the rocks within days. The measured mineralization rates indicate that ∼0.2–0.5 t of CO_2, and ∼0.03–0.05 t of H_2S can be sequestered annually per cubic meter of rock, depending on reservoir lithology and surface area. Calculations show that a total rock sequestration capacity of ∼0.03 km^3 would be sufficient to store the annual world CO_2 and H_2S geothermal emissions. These findings indicate efficient abatement of CO_2 and H_2S at field conditions, confirming the strategy potential for at least the typical 50 years-lifetime of geothermal power plants.

1. Introduction

The increasing level of carbon dioxide (CO_2) in the atmosphere is considered to cause climate change (IPCC, 2014). The fraction of anthropogenic CO_2 in the atmosphere amounts to ∼30% (∼900 Gt) (Hofmann et al., 2009), with geothermal exploitations contributing only ∼9 Mt/yr through more enhanced natural discharges (Bertani, 2016; Fridriksson et al., 2016). However, besides CO_2, geothermal activity emits hydrogen sulfide (H_2S), which is toxic and life-threatening when above 100 ppm (Agency for Toxic Substances and Disease Registry (ATSDR), 2016), and commonly contains pollutant elements such as arsenic, boron, and mercury (Barbier, 2002). If present at high concentrations in the geothermal fluids, these chemicals represent a major environmental concern once released to the environment at surface (e.g., Hansell and Oppenheimer, 2010; Kristmannsdóttir and Ármannsson, 2003). One developing method to reduce the geothermal CO_2 and H_2S emissions is the re-injection of the gases together with condensed steam and/or waste water back into the reservoir where natural fluid-rock interactions are considered to lead to mineralization of secondary carbonates and sulfides, respectively (Aradóttir et al., 2015). This option offers the advantages of avoiding major

modifications on the power plants, costly CO_2 and H_2S separation steps, and generation of waste by-products while harvesting the heat energy.

A number of laboratory and field investigations have focused on the CO_2 sequestration potential of mafic rocks, demonstrating its potential and the associated environmental and societal benefits (e.g., Galeczka et al., 2014; Gysi and Stefánsson, 2012; Matter et al., 2016, 2007; McGrail et al., 2016; Rosenbauer et al., 2012; Schaef et al., 2009; Shibuya et al., 2013). The results highlight the feasibility of long-term underground storage of greenhouse gas in a solid state. On the other hand, very few studies have considered the H_2S abatement through geological storage (e.g., Bachu and Gunter, 2005), and even less through mineralization at geothermal conditions (Přikryl et al., 2018; Stefánsson et al., 2011). Technical difficulties encountered during re-injection tests in the field, such as gas breakthrough and well casing corrosion, have led to the development of other abatement technologies (Sanopoulos and Karabelas, 1997). For instance, a more conventional and usually expensive approach commonly in use to reduce H_2S emissions from geothermal power plants is oxidation to form elemental sulfur or sulfuric acid (Rappold and Lackner, 2010; Rodríguez et al., 2014). However, the recent successful H_2S re-injection into the basaltic reservoir at the Hellisheiði power plant, SW Iceland, has put this option

under the spotlight (Gunnarsson et al., 2015). Nonetheless, considerable uncertainties remain relating to the co-mineralization potential, especially the effects of H_2S mineralization on the CO_2 sequestration, chemical variability of host-rocks, and reservoir capacity. To address these issues, we investigate the geochemical applicability of re-injection of CO_2 and H_2S into geothermal reservoirs by conducting experiments on a suite of typical host-rocks and the potentials of such sequestration method for geothermal systems worldwide.

2. Materials and methods

2.1. Solid material

Three volcanic glasses were used to account for the compositional variability of the main common rock types associated with geothermal systems worldwide: basaltic glass (BG) (Stapafell Mountain, SW Iceland); dacitic glass (DG) (Hekla volcano, S Iceland); and rhyolitic glass (RG) (Askja caldera, NE Iceland) (Oelkers and Gislason, 2001; Wolff-Boenisch et al., 2004). The solid material was ground, and then sieved to obtain a 45–125 μm size fraction, which was then used in the experiments. The material was cleaned ultrasonically in deionized water and acetone to obtain grains with smooth surfaces and no fine particles (< 10 μm) (Fig. 1).
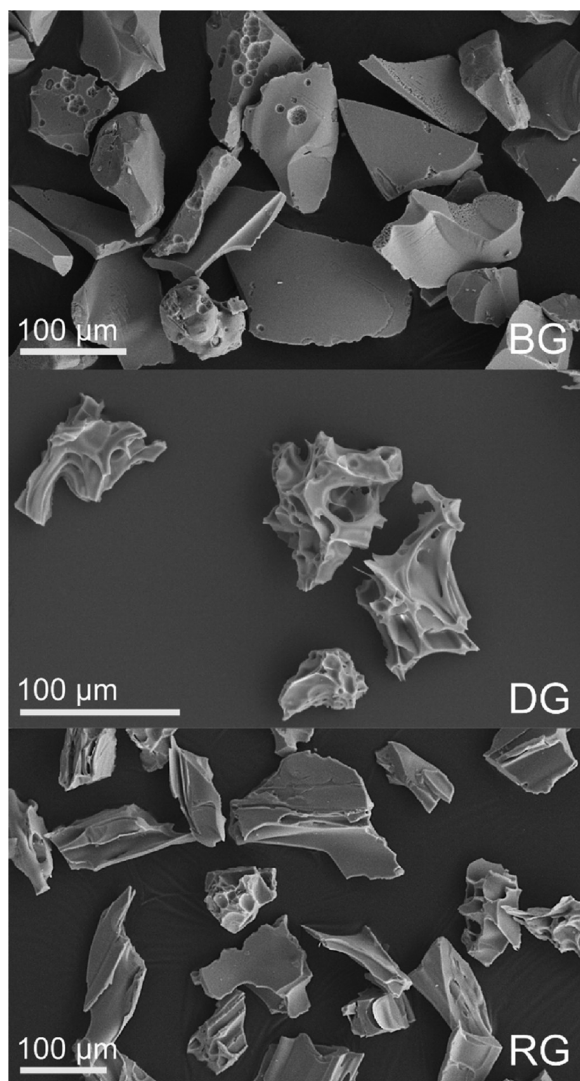

Fig. 1. Scanning electron microscope (SEM) images of pre-experiment solid grains of basaltic (BG), dacitic (DG) and rhyolitic (RG) glass.

Table 1
Glass densities, together with BET specific surface areas (A_{BET}), geometric surface areas (A_{geo}), roughness factor (A_{BET}/A_{geo}) and chemical compositions.

ID	BG-Stapafell A-BG1	RG-Askja 1875 B-RG1	DG-Dacite C-DG1
Rock density (g/cm³)	2.851[1]	2.452[2]	2.512[2]
A_{BET} (cm²/g)	23,000[3]	14,100[2]	12,100[2]
Ageo (cm²/g)	250[3]	312[2]	305[2]
Roughness factor	92	45	40
wt. %	[3]	[2]	[2]
SiO_2	48.12	69.28	66.01
TiO_2	1.56	0.90	0.42
Al_2O_3	14.62	12.42	14.65
Fe_2O_3	1.11	2.48	2.14
FeO	9.82	2.09	3.81
MnO	0.19	0.10	0.18
MgO	9.08	0.97	0.39
CaO	11.84	2.81	3.21
Na_2O	1.97	3.74	4.72
K_2O	0.29	2.21	2.07
P_2O_5	0.20	0.19	0.10
Tot	98.80	98.89	98.67

[1] Galeczka et al. (2014).
[2] Wolff-Boenisch et al. (2004).
[3] Oelkers and Gislason (2001).

The surface morphology, before and after the experiments, and the secondary mineralogical composition of the solid products were analysed using scanning electron microscopy (LEO Supra™ 25 FE-SEM) and standard energy-dispersive spectrometry (EDS). All chemical analysis was performed using an acceleration voltage of 20 kV, a beam current of 200 pA, and a beam diameter of 1–2 μm. Natural and synthetic minerals and glasses were used as standards to check for potential drift.

The bulk chemical composition and the physical characterisation of all the glasses pre-experiment are summarised in Table 1.

2.2. Solution preparation and analysis

The initial experimental solution contained ∼15.5 and ∼2 mmol/l of dissolved inorganic carbon (DIC = $[CO_2] + [HCO_3^-] + [CO_3^{2-}]$) and H_2S, respectively, and had pH ∼7 (Table 2). They were made from HCl (Sigma–Aldrich® 37%), Na_2CO_3 (Sigma–Aldrich®), and Na_2S (Sigma–Aldrich®) in N_2-deoxygenated deionized water (Millipore™). A fresh solution was made every two to three days to avoid oxidation of H_2S. For all experiments, the inlet solution was undersaturated with respect to sulfide and carbonate minerals.

Samples of inlet and outlet solutions were collected to determine their chemical composition. Samples for major dissolved elements (Si, Ti, Na, K, Mg, Ca, Fe, Al, Cl) determination were first filtered through 0.2 μm, then acidified to 1% HNO_3 (Suprapur®), and analysed using ICP-OES. Samples for SO_4 analysis were treated with 2% Zn-acetate (1 ml–100 ml sample) in order to precipitate all the residual H_2S as ZnS (s), which was filtered off prior to measuring SO_4 using IC. Determination of pH, CO_2, and H_2S was carried out on un-treated samples using a combination of a pH electrode and a pH meter, modified alkalinity titration, and precipitation titration using Hg-acetate,

Table 2
Summary of the initial experimental conditions.

#	Rock	Experimental duration days	Rock mass g	pH/25 °C	CO_2[a] mM	H_2S mM
A-BG1	Basaltic glass	8	37	7.12	15.4	2.15
B-RG1	Rhyolitic glass	7	21	7.13	15.8	1.71
C-DG1	Dacitic glass	7	12	7.09	15.8	2.42

[a] CO_2 = total dissolved carbon.