The chemistry and saturation states of subsurface fluids during the in situ mineralisation of CO$_2$ and H$_2$S at the CarbFix site in SW-Iceland

Sandra Ó. Snæbjörnsdóttir
Institute of Earth Sciences
University of Iceland
Askja
Sturlugata 7
101 Reykjavík, Iceland
tel. 354-525-5414
fax. 354-525-4499
sos22@hi.is
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Sandra Ó. Snæbjörnsdóttir$^1$, Eric H. Oelkers$^{1,2,3}$, Kiflom Mesfin$^1$, Edda Sif Aradóttir$^4$, Knud Dideriksen$^5$, Ingvi Gunnarsson$^4$, Einar Gunnlaugsson$^4$, Juerg M. Matter$^{6,7}$, Martin Stute$^7$, Sigurdur R. Gislason$^1$

$^1$Institute of Earth Science, University of Iceland, Iceland
$^2$CNRS/UMR 5563, Université Paul Sabatier, France
$^3$Earth Science, University College London, UK
$^4$Reykjavik Energy, Iceland
$^5$Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark
$^6$Ocean and Earth Science, University of Southampton, UK
$^7$Lamont-Doherty Earth Observatory, Columbia University, USA

Abstract

In situ carbonation of basaltic rocks could provide a long-term carbon storage solution, which is essential for the success and public acceptance of carbon storage. To demonstrate the viability of this carbon storage solution, 175 tonnes of pure CO$_2$ and 73 tonnes of a 75% CO$_2$-24% H$_2$S-1% H$_2$-gas mixture were sequentially injected into basaltic rocks at the CarbFix site at Hellisheidi, SW-Iceland from January to August 2102. This paper reports the chemistry and saturation states with respect to potential secondary minerals of sub-surface fluids sampled prior to, during, and after the injections. All gases were dissolved in water during their injection into permeable basalts located at 500-800 m depth with temperatures ranging from 20 to 50°C. A pH decrease and dissolved inorganic carbon (DIC) increase was observed in the first monitoring well, HN-04, about two weeks after each injection began. At storage reservoir target depth, this diverted monitoring well is located ~125 m downstream from the injection well. A significant increase in H$_2$S concentration, however, was not observed after the second injection. Sampled fluids from the HN-04 well show a rapid increase in Ca, Mg, and Fe concentration during the injections with
a gradual decline in the following months. Calculations indicate that the sampled fluids are saturated with respect to siderite about four weeks after the injections began, and these fluids attained calcite saturation about three months after each injection. Pyrite is supersaturated prior to and during the mixed gas injection and in the following months. In July 2013, the HN-04 fluid sampling pump broke down due to calcite precipitation, verifying the carbonation of the injected CO₂. Mass balance calculations, based on the recovery of non-reactive tracers co-injected into the subsurface together with the acid-gases, confirm that more than 95% of the CO₂ injected into the subsurface was mineralised within a year, and essentially all of the injected H₂S was mineralised within four months of its injection. These results demonstrate the viability of the in situ mineralisation of these gases in basaltic rocks as a long-term and safe storage solution for CO₂ and H₂S.

**Introduction**

Attenuating the current increasing atmospheric CO₂ concentration is one of the greatest challenges of this century (e.g. Broecker, 2007; Broecker and Kunzig, 2008; Global CCS Institute, 2015; Hoffert et al., 2002; International Energy Agency, 2015; IPCC, 2005, 2014; Lackner, 2003; Oelkers and Schott, 2005; Oelkers and Cole, 2008; Pacala and Socolow, 2004). One potential solution to this challenge is carbon capture and storage (CCS). A critical step in CCS is identifying locations and methods for secure subsurface CO₂ storage.

This paper follows two previous reports on the CarbFix injection, 1) a detailed description of the injection method and data from the injection well was presented by Sigfússon et al. (2015) and 2) the monitoring of tracers, carbon and pH in the first monitoring well downstream from the injection well was reported by Matter et al. (2016). The CarbFix project is focussed on CO₂ and H₂S injected into basaltic rocks. Carbon storage in basaltic rocks offers several advantages, due to their ability to promote permanent CO₂ storage by mineralisation and due to their large potential storage volume (Gislason and Oelkers, 2014; Goldberg and Slagle, 2009; Goldberg et al., 2010; McGrail et al., 2006; Snæbjörnsdóttir et al., 2014). As such, a large number of past studies have focussed on developing the technology to safely store CO₂ in basaltic rocks (Assayag et al., 2009; Bacon et al., 2014; Flaathen et al., 2009; Galeczka et al., 2014; Goldberg et al., 2013; Goldberg et al., 2008; Gudbrandsson et al., 2011; Gysi and Stefánsson, 2012a; Matter et al., 2007; McGrail et
al., 2012; McGrail et al., 2006; McGrail et al., 2011; Rogers et al., 2006; Rosenbauer et al., 2012; Sigfusson et al., 2015; Stockmann et al., 2011; Van Pham et al., 2012). Basaltic rocks are rich in divalent cations such as Ca$^{2+}$, Mg$^{2+}$, and Fe$^{2+}$. Acidic gas-charged water accelerates the release of these metals, promoting the formation of carbonate minerals such as calcite, magnesite, and siderite (Gislason et al., 2014; Gislason and Oelkers, 2014; Olsson et al., 2014; Gislason et al., 2010; Gunnarsson et al., 2011; Oelkers et al., 2008; Stefánsson et al., 2011). About 10% of the continents and most of the oceanic floor are comprised of basaltic rocks, including the mid-ocean ridges. The largest basaltic storage potential lies offshore; theoretically all CO$_2$ from the burning of fossil fuel carbon (~5000 GtC; Archer, 2005) could be stored by mineral carbonation along the mid-ocean ridges (Snæbjörnsdóttir et al., 2014). The flanks of the ridges contain highly fractured and permeable basaltic layers (Fisher, 1998) with a pervasive circulation of about 1,000 Gt seawater/yr (Harris and Chapman, 2004). The potential for using these systems for carbon storage is confirmed by the results of Wolff-Boenisch et al. (2011), who demonstrated the rapid dissolution basaltic rocks in CO$_2$ charged seawater.

About 90% of Icelandic bedrock is basaltic (Hjartarson and Sæmundsson, 2014). In total, Iceland produced 1.6 MtCO$_2$ by industrial processes in 2012 and about 0.2 MtCO$_2$ by geothermal energy production (Wöll et al., 2014). Iceland is the largest (103,000 km$^2$) part of the mid-ocean ridge systems exposed above sea level. Iceland, therefore, provides an excellent opportunity to explore the feasibility of mineral storage of CO$_2$ and gas mixtures in basaltic rocks at the oceanic ridges since drilling and detailed monitoring of injected gas and water by reactive and non-reactive tracers is much less costly onshore than offshore.

The potential advantages in storing carbon by the *in situ* carbonation of Icelandic basalts motivated creation of the CarbFix project, which was designed to inject CO$_2$ into subsurface adjacent to the Hellisheidi geothermal power plant. Extensive research was carried out prior to the injection of acid gases at the CarbFix site. Gislason et al. (2010) described the thermodynamics and kinetic basis for carbon storage at this site. Alfredsson et al., (2013) characterised the geology, and rock and water chemistry of the CarbFix site. Wiese et al. (2008) determined the amount and spatial distribution of naturally mineralised CO$_2$ within the Icelandic geothermal systems. The dissolution and precipitation rates of the subsurface rocks at the site were investigated in mixed
flow reactors (e.g. Gudbrandsson et al., 2011; Gysi and Stefánsson, 2012a; Stockmann et al., 2013), in pressurised plug flow experiments (e.g. Galeczka et al., 2014), by hydrological modelling (Khalilabad et al., 2008), and using reactive transport modelling (Aradóttir et al., 2012).

The CarbFix project is unique in that it injects CO$_2$ into basalts as a dissolved aqueous phase. In contrast, most subsurface carbon storage projects have injected CO$_2$ as a separate phase into large sedimentary basins; this method requires high integrity cap-rocks to keep the injected buoyant gas in the subsurface (Gislason and Oelkers, 2014; Rutqvist et al., 2007). However, there are numerous advantages of injecting CO$_2$ into the subsurface within an aqueous phase. First, many of the risks associated with buoyancy can be mitigated by dissolving the gases into water during their injection (Gislason et al., 2010; Sigfusson et al., 2015). Once dissolved, the injected gases are no longer buoyant, making it possible to inject CO$_2$ into fractured rocks, such as basalts along the ocean ridges and on the continents. Furthermore, this injection method may also make it possible to simultaneously store a number of acid gases including SO$_2$ and H$_2$S as sulphide minerals such as pyrite and pyrrhotite, lowering substantially gas capture/storage costs (Gislason et al., 2014; Gislason and Oelkers, 2014; WorleyParsons and Schlumberger, 2011).

Large SO$_2$ emissions are associated with fossil fuel power production and heavy industry such as metal smelters (Smith et al., 2011). These emissions peaked in 1970-1980 at about 80 Mt per year in the USA and Europe leading to acid rain and Al mobilisation, degrading aquatic and terrestrial ecosystems (Gensemer and Playle, 1999; Gislason and Torssander, 2006). Due to intervening regulations, these emissions have been in decline, and were less than 11 Mt in 2011 (European Environment Agency, 2014; United States Environmental Protection Agency, 2015) due, in large part due to SO$_2$ capture. This SO$_2$ capture could potentially be combined with CO$_2$ capture in water, and this water-soluble gas mixture injected into reactive rocks for mineral storage.

Emissions of H$_2$S are an inevitable consequence of geothermal energy exploitation, pulp and paper production and the use of fossil fuels (e.g. World Health Organization, 2000). Regulations for H$_2$S emissions have obliged Icelandic geothermal energy producers to reduce their emissions of this gas (Aradóttir et al., 2015; Gunnarsson et al., 2011). One mitigation option is to
capture H\textsubscript{2}S and inject it into the subsurface. This approach has been adopted by an ongoing carbon storage project at Weyburn Canada in connection with enhanced oil recovery, which has been co-injecting supercritical CO\textsubscript{2} and H\textsubscript{2}S into subsurface sedimentary rocks (Bachu and Gunter, 2005). The behaviour of co-injecting H\textsubscript{2}S has not been studied to the same extent as injection of pure CO\textsubscript{2}. Some work has, however, been done in terms of geochemical modelling and laboratory experiments (e.g. Bacon et al., 2014; Gudbrandsson and Stefánsson, 2014; Gunnarsson et al., 2011; Stefánsson et al., 2011; Knauss et al., 2005). One goal of the CarbFix project is to assess the feasibility of co-injecting dissolved H\textsubscript{2}S and CO\textsubscript{2} into basalts which can provide a cost effective storage solution for both of these gases.

This paper reports on our further efforts to develop the technology to store CO\textsubscript{2} through the \textit{in situ} carbonation of basaltic rocks at the CarbFix storage site in southwest Iceland. Two field injections were carried out at this storage site. In January to March 2012, 175 tonnes of pure CO\textsubscript{2} were injected into the CarbFix site. In June to August 2012, 73 tonnes of a gas mixture from the Hellsheidi geothermal power plant were injected, consisting of 75 mol\% CO\textsubscript{2}, 24 mol\% H\textsubscript{2}S and 1 mol\% H\textsubscript{2}. In each case, the gases were dissolved into formation water during their injection, releasing a single aqueous fluid into the storage formation. Here we report the compositions and saturation states of fluid samples collected from a diverted monitoring well located 125 m in the down-flow direction of the injection well at target storage reservoir depth, before, during, and after the CO\textsubscript{2} and CO\textsubscript{2}-H\textsubscript{2}S injections, and use these results to better understand the fate of these injected gases in the subsurface.

\textbf{Methods}

\textbf{Description of the CarbFix site}

The CarbFix injection site is located in SW-Iceland, about 30 km east of Reykjavik. The site is ~260 m above sea level and located 3 km SW of the Hellsheidi geothermal power plant (Fig. 1), which is owned and operated by Reykjavik Energy. During 2015, the power plant generated 303 MW of electricity and 133 MW of thermal energy using hot water and steam from a high temperature reservoir located at 800-3000 m depth E and NE of the power plant. The
power plant annually produces 40,000 tonnes CO\textsubscript{2} and 12,000 tonnes H\textsubscript{2}S. These gases are of magmatic origin produced as a by-product of the geothermal energy production.

Acidic gases injected at the CarbFix site were dissolved into water collected from HN-01, a well located about 1 km west of the 2001 m deep HN-02 injection well (Fig. 1). Well HN-01 is 1306 m deep; water collected from this well was transported via pipeline to HN-02 where the HN-01 water was injected through a pipe as described in detail by Sigfusson et al. (2015). The injected gas was released into the down flowing water via a sparger at a depth of 340 m. The gas dissolved in the water as it was carried down a mixing pipe to a depth of 540 m, where the hydrostatic pressure is above 40 bars, ensuring complete dissolution of the CO\textsubscript{2} before it was released into the subsurface rocks (Aradóttir et al., 2012; Gislason et al., 2010; Sigfusson et al., 2015).

The geology of the CarbFix site was described in detail by Alfredsson et al. (2013). The subsurface rocks at the injection site are primarily olivine tholeiite basalts, consisting of post-glacial lava flows and glassy hyaloclastite formations, formed beneath the ice-sheet during glaciations (Fig. 1). The bedrock down to about 200-300 m depth consists of relatively unaltered olivine tholeiite lava flows that host an oxygen-rich groundwater system with a static water table at about 100 m depth. Below the lava flows lies a 200 m thick, slightly altered hyaloclastite that separates the near surface water system from a deeper system, which is oxygen depleted. The site follows an approximately linear temperature gradient of 80°C/km. The target injection formation consists of a series of altered lava flows from about 400 m to 800 m depth overlain by the low permeability hyaloclastites (Alfredsson et al., 2013; Helgadóttir, 2011). The lateral and vertical intrinsic permeabilities of the storage formation were estimated to be 300 and 1700 x 10\textsuperscript{-15} m\textsuperscript{2}, respectively, having an effective matrix porosity of 8.5\% and a 25 m/year estimated regional groundwater flow velocity (Aradóttir et al., 2012). The most abundant alteration minerals from 200 m to 1000 m depth are smectites, calcite, and Ca- and Na-rich zeolites (Alfredsson et al., 2013; Helgadóttir, 2011).

The injection site is equipped with eight monitoring wells ranging from 50 to 1300 m depth. Six of the eight wells are located downstream from the HN-02 injection well. Four of the
wells penetrate the groundwater system in the topmost 200-300 m and four are drilled down through the target storage formation. These deeper wells are cased down to 400 m depth and serve as monitoring wells of the deeper system. All monitoring wells were sampled during the experiment, but evidence of tracers from the injections has only been found, to date, in samples collected from well HN-04, which is the closest to the injection well as shown in Figure 1. Well HN-04 is located about 10 m west of HN-02 at the surface, but it is diverted in the subsurface such that the distance between the wells is 125 m at 520 m depth, where the target carbon storage aquifer is located (Alfredsson et al., 2013; Aradóttir et al., 2012). Field injections at the CarbFix site were performed from 2008 to 2012. Tracer tests were conducted both under natural and forced flow conditions from 2008 to 2011 to define the system hydrology and for scaling reactive transport models (Aradóttir et al., 2012; Gislason et al., 2010; Khalilabad et al., 2008; Matter et al., 2011).

**Acid Gas Injections at the CarbFix site**

The injection of acid gases at the CarbFix site was performed in two phases during 2012 (Table 1):

**Phase I** began in late January 2012 with the injection of 175 tonnes of pure CO$_2$. The CO$_2$ was stored in a 30 m$^3$ reservoir tank pressurised at 26-28 bars and co-injected with water collected from well HN-01 into well HN-02, as described by Sigfusson et al. (2015). The predicted *in situ* pH and DIC concentrations of the injected fluid during Phase I were 3.85 and 0.823 mol kg$^{-1}$ respectively, based on the mass flow rates of water and gas into the injection well, chemical speciation calculations (Parkhurst and Appelo, 2013), and direct measurement (Sigfusson et al., 2015). The chemical tracers listed in Table 1 were co-dissolved into the injected water as described by Sigfusson et al. (2015) to aid in determining the fate of the dissolved CO$_2$ as described by Matter et al. (2016). The Phase I injection ran continuously until it was terminated on the 9$^{th}$ of March 2012.

**Phase II** began in mid-June 2012 with the injection of 73 tonnes of a gas mixture containing 75 mol% CO$_2$, 24 mol% H$_2$S, and 1 mol% H$_2$ originating from the Hellisheidi power plant. The gas mixture was obtained by diverting power plant emissions to a gas abatement plant, where it was
separated into water soluble gases (CO$_2$, H$_2$S), and less soluble gases (N$_2$, CH$_4$, H$_2$, Ar). The power plant emission gas contained about 20% H$_2$; a small fraction of this dissolves in the water along with the CO$_2$ and H$_2$S according to the solubility and partial pressure of the gases. Subsequently the soluble gas mixture was co-injected into the surface with HN-01 water. The predicted \textit{in situ} pH, DIC, H$_2$S, and H$_2$ concentrations of the injected water during the Phase II, based on the mass flow rates of water and gas into the injection well and chemical speciation calculations performed using PHREEQC (Parkhurst and Appelo, 2013) were 4.03, 0.43 mol kg$^{-1}$, 0.14 mol kg$^{-1}$ and less than 0.01 mol kg$^{-1}$, respectively. The chemical tracers listed in Table 1 were co-dissolved into the injected water as for the pure CO$_2$ injection to monitor subsurface reactivity. The gas mixture injection rate was less stable than that of the pure CO$_2$ injection and was stopped several times due to injection problems. The injection was terminated on the 1st of August 2012.

**Analytical methods**

Sampling of the fluids from the HN-04 first monitoring well began in 2008. Water samples for chemical analysis were collected several times prior to the Phase I injection in January 2012 (Alfredsson et al., 2013). During the injections and until mid-September 2012 this well was sampled twice weekly. Weekly sampling continued until mid-July 2013 with few exceptions.

Water was pumped from the monitoring well at the rate of 3.5 m$^3$/h throughout this study, to maintain a constant head from the injection to the monitoring well. The pump used was a 163 cm long, submersible Grundfos model SP3A-60 made of stainless steel, located at 303 m depth and ~200 m below the water table. This pump was connected to a 53 mm diameter steel pipe to the surface where the effluent was deposed via a service pipe extending east of the injection site and eventually re-injected into a deep geothermal system.

Fluid samples were collected via a 10 m long, 10 mm diameter stainless steel pipe connected to the 53 mm diameter monitoring well lining pipe extending down to the pump. The 10 mm sample pipe was connected directly to a sampling valve inside an on-site field laboratory. After flushing the sampling pipe, the sampled waters were immediately filtered through 0.2 µm
Millipore cellulose acetate membranes using silicon tubing and a 140 mm Sartorius® polypropylene filter holder. All air in the filtration system was expelled through a valve prior to sampling and at least 3 L of water was pumped through the system before the samples were collected in distinct bottles depending on the subsequent chemical analysis. Amber glass bottles were used to collect samples for pH and alkalinity. Acid washed high density polyethylene bottles were used to collect samples for cations and trace metals. These samples were acidified using Suprapur® HNO$_3$, 1% (v/v). Acid washed low density polypropylene bottles were used to collect samples for Fe-species measurement. These samples were acidified with Suprapur® HCl, 1% (v/v) immediately after collection. Low density polypropylene bottles were used for collecting samples for anion concentration measurements. Acid washed polycarbonate bottles were used to collect samples for dissolved organic carbon (DOC). These samples were acidified with 1.2 M concentrated HCl 2% (v/v). All sample bottles were rinsed three times by half filling them with the filtrated water and then emptying them prior to sample collection.

Temperature and conductivity were measured at the sampling site using a Eutech Instruments Oakalon 2-cell Conductivity meter. The in situ temperature of the sampled fluid was determined using down-hole temperature logging at the depth of the main feed-point of well HN-04, at about 420 m depth (Alfredsson et al., 2013; Thorarinsson et al., 2006). The pH was determined on site with a Eutech InstrumentsTM CyberScan pH 110 electrode and again in the laboratory a few hours after sampling with a Cole Parmer combined glass electrode together with an Orion pH meter. The uncertainty of the analyses is estimated to be ±0.02. The pH was then recalculated at in situ conditions using PHREEQC (Parkhurst and Appelo, 2013). Alkalinity was measured in the laboratory by alkalinity titration using the Gran function to determine the end point of the titration (Stumm and Morgan, 1996). Total dissolved inorganic carbon (DIC) was calculated with PHREEQC (Parkhurst and Appelo, 2013) using measured pH, alkalinity, temperature and total dissolved elements concentrations. The uncertainties of the DIC calculations are estimated to be within 10%.

Dissolved oxygen was fixed on site and later determined by Winkler titration. This method has a precision of 1 µmol/L O$_2$ (0.03 ppm) for the 50 ml sample bottles, but there is a risk of atmospheric contamination for samples containing no or little oxygen. Such is the case for
the samples collected from HN-04, which are oxygen depleted. The O$_2$ concentrations of the
sampled fluids ranged from 2-24 µmol/L. The difference between the O$_2$ concentration in the
samples and the reagents was determined using the method described by Arnórsson (2000). The
results show that the oxygen measured in the samples is mostly derived from the reagents. Some
oxygen contamination during sampling was also inevitable.

Dissolved hydrogen sulphide was measured by titration on site using mercury and
dithizone as an indicator (Arnórsson et al., 2000). The sensitivity of this method is about 0.29
µmol/L H$_2$S (about 0.01 ppm) when using a 50 ml sample aliquot.

The major elements Si, Ca, K, Mg, Na, and S and the trace metals Fe and Al were
analysed using a Spectro Ciros Vision Inductively Coupled Plasma Optical Emission
Spectrometer (ICP-OES) using an in-house multi-elements standard checked against the SPEX
Certified Reference standard at the University of Iceland. The samples were analysed again using
a Agilent 725 ICP-OES for major elements and an ELEMENT XR Inductively Coupled Plasma
Sector Field Mass Spectrometer (ICP-SFMS) from ThermoScientific for the trace elements Fe
and Al at ALS Scandinavia, Luleå, Sweden. Analytical measurements for the major elements had
an inter-laboratory reproducibility within 12%. The average difference between corresponding
concentration measurements is 3.7% with a standard deviation of 2.3%. Analytical
measurements for the trace elements Fe and Al had an inter-laboratory reproducibility within
19%. The average difference in corresponding Fe and Al concentration measurements was 4.9%.
Dissolved F$^-$, Cl$^-$, and SO$_4^{2-}$ concentrations were quantified using a DIONEX, ICS-2000 Ion
Chromatograph. The addition of zinc-acetate to the SO$_4$ sample was not needed for its analysis
since the H$_2$S concentrations were small compared to the SO$_4$ concentrations as shown below.
Concentrations of Fe$^{2+}$ and Fe$^{3+}$ were measured using a DIONEX IC-3000 Ion Chromatograph.
Due to ambiguities in the Fe$^{3+}$ measurements, the Fe$^{2+}$ measurements were used along with the
Fe$_{total}$ concentrations measured by ICP-SFMS at ALS Scandinavia to calculate Fe$^{3+}$
concentrations. Analysis of dissolved organic carbon (DOC) was carried out at Umeå Marine
Science Center in Umeå, Sweden using a Shimadzu TOC-VcPH total organic carbon analyser.
The precipitates collected from the pump recovered from the HN-04 monitoring well were analysed by X-ray Powder Diffraction (XRD) at ISOR, Iceland for phase identification. The samples were measured using a Bruker AXS D8 Focus X-ray diffractometer with Cu kα radiation at 1.54Å wavelength, set at 40 kV and 40 mA using 1° divergence and receiving slits. The chemical composition of the precipitates was also analysed by ALS, Scandinavia. The precipitates were digested in HNO₃ and HCl with a trace of HF in a microwave oven. The resulting fluids were then analysed using both ICP-OES and High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS). Detection limits were in the range of 0.01 ppm for trace elements to single ppm for major elements, and uncertainties for concentrations 10 times these detection limits are within 10% of the reported value.

Precipitates from samples collected from an air-lift of the HN-02 injection well in June 2013, were analysed for phase identification by XRD at the University of Copenhagen, Denmark with a Bruker D8 Discover equipped with a Co tube. 1L slurries collected from the air-lift were sealed immediately after sampling, transported to Denmark, where they were kept in an anaerobic chamber prior to analysis to minimise oxidation. Within the chamber, the samples were centrifuged, dried, crushed and mounted on low-background sample holders that were then covered with X-ray transparent cups to minimise oxidation during measurements.

**Mass balance calculations**

The fate of injected gases in this study are evaluated with the aid of mass balance calculations based on the injected non-reactive tracers SF₆ and SF₅CF₃ (Assayag et al., 2009; Matter et al., 2007; Matter et al., 2016). All collected water samples consist of a mixture from three sources; the original groundwater, that injected during Phase 1 and that injected during Phase 2. In the absence of reactions that remove or add material to the mixed fluid, mass balance requires that the concentration of chemical component \( i \) in the monitoring well samples \( (c_i) \) to be

\[
c_i = c_{i,GW}X_{GW} + c_{i,1}X_{i,1} + c_{i,2}X_2
\]  

(1)
where $c_i, GW, c_i, 1$, and $c_i, 2$ refers to the concentration of the $i$th chemical component in the original groundwater, the Phase 1 injection and the Phase 2 injection, respectively, whereas and $X_{GW}, X_i,$ and $X_2$ designate the fraction of the these three fluid sources in each monitoring sample.

The fraction of each water source in each monitoring sample was determined from the measured concentrations of the two non-reactive tracers, SF$_6$ and SF$_2$CF$_3$ together with the requirement that

$$X_{GW} + X_1 + X_2 = 1$$

(2)

Comparison of values based on the assumption of non-reactive mixing, obtained from Eqns. (1) and (2), with those measured in the monitoring wells provides an estimate of the percentage of injected gases fixed by chemical reactions, and the mass of elements added or removed from the fluid by mineral dissolution and precipitation reactions due to the injections. The background concentration of SF$_6$ in Eqn. 1 ($c_{i, GW}$) was not constant with time since SF$_6$ had been used in previous hydrological tests. This background concentration was corrected by taking account of the sample sodium fluorescein tracer concentrations; this tracer was co-injected with the SF$_6$ in the previous tests as described by Matter et al. (2016).

Sample 12KGM06 (Table 2) of the injected water from well HN-01 was used to constrain the elemental concentrations of the injected fluid, apart from the elements C and S, which were determined by accounting for the concentration of CO$_2$ and H$_2$S added to these injected fluids. Sample 12KGM01 (Table A1 in the electronic supplements) collected from well HN-04 before injection was used for representing the ambient groundwater concentrations. Mass balance calculations were performed for the major elements Ca, Mg, Si, Na, K, and Cl, and the trace elements Fe and Al.

**Geochemical modelling**

Modelling of the water chemistry, including the calculation of percent error in charge balance, the *in situ* saturation state of the water with respect to mineral and gas phases, and the effect of CO$_2$ and CO$_2$-H$_2$S-H$_2$ gas injection on the aqueous chemistry of the subsurface fluids
was performed using PHREEQC (Parkhurst and Appelo, 2013). In no case did the charge imbalance exceed 6.1%. The standard PHREEQC database was used in all calculations after including revised thermodynamic data on secondary minerals taken from Gysi and Stefánsson (2011), and pyrrhotite and greigite taken from the MINTEQ and the llnl databases, respectively, as described in Alfredsson et al. (2013). Dissolved inorganic carbon (DIC) was calculated for each water sample using measured alkalinity, pH and temperature defined at 35°C at the in situ conditions. All saturation indices were calculated assuming the oxygen fugacity was controlled by equilibrium with the $\text{H}_2\text{S}/\text{SO}_4^{2-}$ as a redox couple. For samples having no measured excess $\text{H}_2\text{S}$, the $\text{H}_2\text{S}$ concentration was assumed to be equal to the detection limit of the $\text{H}_2\text{S}$ titration, as geothermal waters always contain a small fraction of $\text{H}_2\text{S}$ although below the detection limit.

**Results**

The compositions of all sampled fluids are shown in Figures 2, 3, and 8, Table 2 and Table A1 in the electronic supplements. An increase in the non-reactive sulphur hexafluoride ($\text{SF}_6$) tracer, indicating the initial arrival of the migrating dissolved $\text{CO}_2$ plume in the HN-04 monitoring well, occurred about two weeks after the start of the Phase I injection (Fig. 2a). The concentration of this tracer increased until a maximum 56 days after the Phase 1 injection started (Matter et al., 2016). The $\text{SF}_6$ tracer concentration again increased about 100 days after the injection started, reaching an overall maximum about 13 months after Phase I was started (see Fig 2a; Matter et al., 2016). This is the same pattern observed during the previous tracer test (Khalilabad et al., 2008), indicating that the storage formation consists of relatively homogenous porous media intersected by a low volume and fast flow path that channels about 3% of the tracer flow between wells HN-02 and HN-04. The same pattern was observed for Phase II, with the first arrival of the non-reactive trifluoromethyl sulphur pentafluoride ($\text{SF}_5\text{CF}_3$) tracer observed about two weeks after the start of the mixed-gas injection (Fig. 2a), with an initial smaller maximum about 60 days after the injection began (Matter et al., 2016). A further increase in $\text{SF}_5\text{CF}_3$ was noted about 150 days after Phase II injection began (Fig. 2a), consistent with the behaviour of $\text{SF}_6$ (Matter et al., 2016). The second $\text{SF}_5\text{CF}_3$ concentration maximum was not observed due to a breakdown of the submersible pump in the monitoring well HN-04, resulting in a three month gap in the monitoring data as described below.
Fluid pH, carbon, and sulphur

Prior to the injections, the pH of the HN-04 monitoring well samples was 9.5-9.6, the DIC was 1.3-1.4 mmol/L, and the total S concentration was 0.09-0.11 mmol/L (see Fig. 2b-c, Table A1 in the electronic supplements, and Alfredsson et al. (2013)). The measured pH and DIC before, during and after the two injection phases are shown in Figure 2b. The pH of the sampled fluids is extremely sensitive to the injection of dissolved gases. The pH in situ (35°C) decreases from 9.6 prior to each injection to approximately 7 near the end the injection then subsequently recovers to a value higher than 9. The decrease starts about two weeks after the start of Phase I, contemporary with the first arrival of the non-reactive tracer. The lowest pH following Phase I was 6.6 and occurred at the same time as the highest DIC value of 4.4 mmol/L, about 50 days after the Phase I injection was started, but ten days before the first reactive tracer maximum. Subsequently, both DIC and pH trended back towards their initial values (Fig. 2b). A similar pattern was observed during Phase II; the pH began to drop about two weeks after the injection was started, with the lowest pH of 7.1 measured at the same time as the highest DIC value of 3.3 mmol/L, about 60 days after the Phase II injection was started and concurrent the first SF₅CF₃ tracer maximum (see Fig 2).

No corresponding increase in DIC was observed during the second and larger SF₆ tracer maximum. This suggests significant mineral storage of the injected carbon; the difference between measured and calculated DIC indicate that >95% of the injected CO₂ was mineralised in less than two years, as previously reported by Matter et al. (2016). The second and larger SF₅CF₃ tracer maximum was not observed due to a pump failure in the HN-04 monitoring well, but an increase was noted in this concentration approximately one year after the start of the Phase II injection, consistent with the increase during the second breakthrough of SF₆. No corresponding increase in DIC was observed. Analysis of dissolved organic carbon (DOC) show continuous decrease in DOC concentrations from the start of Phase I, and throughout the monitoring period, except for a small increase shortly after the termination of the Phase II, from August to September 2012 (Table A1 in the electronic supplements). The measured DIC concentration is more than two orders of magnitude greater than the measured DOC concentration throughout most of the monitoring period after the Phase I injection (Fig. 2b and Table A1 in the electronic supplements).
The measured sulphur concentrations (SO$_4^{2-}$, H$_2$S, and S total) from before, during and after the Phase II injection are shown in Figure 2c and Table A1 in the electronic supplements. The concentrations are close to constant throughout this two year study. The average SO$_4^{2-}$ concentration measured by IC-2000 during the period was 0.10±0.01 mmol/L, with a standard deviation of 0.005. The average total S concentration measured by ICP-OES was 0.10±0.02 mmol/L, with standard deviation of 0.003. The H$_2$S concentrations were, in most cases, close to the 0.3 µmol/L detection limit. The highest H$_2$S concentration, 1.5 µmol/L, was measured during the Phase II injection. The H$_2$S sulphur species always comprised less than 1.5% of the total dissolved S measured by the ICP-OES. This suggests an even more rapid mineralisation of the injected H$_2$S than the injected CO$_2$; no significant increase in sulphur concentrations was noted during this field injection experiment, indicating that all of the injected sulphur was mineralised before the first reactive tracer maximum of the SF$_5$CF$_3$ was observed in the monitoring well HN-04, or within 60 days of the start of the injection.

Major and trace elements

The release of the divalent cations Ca$^{2+}$, Mg$^{2+}$, and Fe$^{2+}$ from the host basalt is essential for the mineralisation of the injected gases. The chemical compositions of the HN-04 monitoring samples demonstrate the rapid increase in Ca, Mg, and Fe concentration during the two injection phases with a gradual decline in the following weeks and months (see Fig. 3a-c). The increases in these concentrations were first observed concurrently with the first appearance of the non-reactive tracers. The Fe$^{2+}$ was not detected in any sample after early April 2013, or about 6 weeks after the major part of the injected Phase 1 fluid arrived in well HN-04 and the Fe$^{2+}$ concentrations were close to the detection limit for the two months following the start of the gas mixture injection.

In contrast, dissolved Si concentrations were close to constant throughout the monitoring period (Fig. 3d). An increase in Na concentration was most prominent at the beginning of the Phase I injection when its concentration increased from 2.1-2.2 mmol/L to about 2.3-2.4 mmol/L (Fig. 3e). Another increase was observed during the Phase II injection to about 2.5 mmol/L. The Na-concentration at the end of the monitoring period was about 2.6-2.7 mmol/L. A similar trend
is evident for K, but the increase in its concentration was somewhat lower than that of Na (Fig. 3f). The only major difference between the responses of these concentrations to the dissolved gas injections was the presence of a small concentration peak in K during October 2012. The origin of this peak is unclear. The Al concentrations were strongly pH dependent, consistent with its solubility dependence on pH from neutral to basic conditions (e.g., Drever, 1982). As such, a strong correlation was observed between Al concentrations and pH before, during, and after the injections (Fig. 3g). The Cl concentrations were generally constant throughout the monitoring period with a concentration of 2.4 mmol/L (Fig. h).

**Calcite precipitates**

In July 2013, about one and a half years after the start of the Phase I injection, the submersible pump in well HN-04 broke down. When the pump was brought to the surface, it was found to be clogged and coated with a green precipitate as shown in Figure 4. No precipitation was observed on the pump prior to the injections. The bulk chemical compositions of the precipitate samples are shown in Table 3. The cation concentration of the precipitates consisted mostly of calcium (>94%) with some iron (<3%), silica (<2%) and magnesium (<1%). The XRD-analysis (Fig. A2 in the electronic supplements) confirmed that calcite was the dominant mineral phase of this precipitate and no other crystalline phases were identified. A $^{14}$C analysis of the carbon in the precipitates confirms that they originated from the injected $^{14}$C labelled CO$_2$ (Matter et al., 2016).

**Mineral saturation states of C- and S-bearing minerals**

The saturation indices (SI) of calcite (CaCO$_3$), magnesite (MgCO$_3$) and siderite (FeCO$_3$), as calculated using PHREEQC, are shown in Figure 5a. Calculations show that calcite was saturated both before and after the Phase I and Phase II injections. This mineral was, however, strongly undersaturated just after these injections concurrent with the drop in monitoring fluid pH below 8, even though the DIC and Ca concentrations were relatively high (Figs. 2a and 3a). Note that calcite was identified by XRD-analysis on drill-cuttings from the area prior to the injections (Alfredsson et al., 2013) and within and on the pump in the monitoring well at the end of the monitoring period (Figs. 4 and A2 in the electronic supplements). The monitoring fluid samples attained calcite saturation at the end of April 2012, about seven weeks after the Phase I
injection was terminated, and at end of August, about four weeks after the Phase II injection was terminated, when the fluid pH had increased to >8. In contrast, the monitoring fluid samples were calculated to be supersaturated with respect to siderite shortly after both injections, whereas magnesite was strongly undersaturated during this time (Fig. 5a). Magnesite and siderite were not identified at the Hellisheidi site prior to the injections, but both minerals have been identified by XRD-analysis of drill-cuttings from the Svartsengi geothermal field in SW-Iceland (Franzson, 1983; Richter et al., 1999), which has a significantly higher salinity and higher temperature gradient than the CarbFix site. Magnesite-siderite solid solutions were identified in low temperature CO₂ metasomatised basalts in Nuussuaq, West Greenland (Rogers et al., 2006).

There calcite appears at a relatively low CO₂ partial pressure, and magnesite-siderite at higher partial pressures (Fig. 6), as predicted by the PHREEQC modelling (Fig. 5a).

The calculated saturation indices of a number of other carbonate minerals are shown in Figure 5b. Ankerite (CaFe(CO₃)₂) is the only carbonate-phase that was supersaturated during the whole monitoring period, that is while Fe²⁺ concentrations are above the detection limit of the spectroscopic method. Ankerite has not been identified in the area. It was however identified during basaltic glass-CO₂ charged water interaction experiments performed at 75°C by Gysi and Stefánsson (2012b), and during basalt, water, supercritical CO₂ interaction experiments reported by McGrail et al. (2006). Similar to calcite, the sampled fluids were calculated to be supersaturated with respect to aragonite (CaCO₃) throughout the monitoring period, with the exception of several weeks near the end of, and shortly after both injections (see Fig. 5b).

Aragonite was identified by XRD-analysis of drill-cuttings from the area prior to the injections (Alfredsson et al., 2013). Although the fluids were calculated to be supersaturated with respect to dolomite (CaMg(CO₃)₂) following both injections, this mineral has not been observed at the CarbFix site. It has been observed however by XRD-analysis as a secondary mineral in drill-cuttings from the saline Svartsengi high-temperature geothermal field in SW-Iceland, as is the case for magnesite and siderite (Franzson, 1983). The calculated saturation indices of three different Ca-Mg-Fe-solid solutions are shown in Figure 5c. All three show similar trends as calcite and aragonite. The Mg₀.₅₀-Fe₀.₅₀-CO₃ is the least saturated of the three, but attained saturation after both injections.
The calculated saturation indices for some sulphur-bearing minerals are shown in Figure 5d. The monitoring well fluids were calculated to be undersaturated with respect to native sulphur during the whole monitoring period. In contrast, pyrite (FeS$_2$), which is one of the most abundant secondary minerals at Hellisheiði at elevated temperature, and was identified at 780 m depth within the HN-02 injection well (Helgadóttir, 2011), was calculated to be supersaturated in all the monitoring fluid samples, showing a slight decrease in its saturation index at the beginning of the Phase II injection and a peak mid-August 2012 concurrent with the first maximum in SF$_3$CF$_3$ concentration, indicating the initial breakthrough of the injected Phase II fluids (Fig. 5d). As previously mentioned, calcite was the only crystalline phase identified in the precipitates forming on the pump from well HN-04. Pyrite was, however, identified by XRD-analysis on samples collected from an airlift of the injection well HN-02, confirming formation of pyrite during or after the Phase II injection (Fig. A3 in the electronic supplement). Greigite (Fe$_3$S$_4$) showed a similar behaviour as pyrite, as this mineral was supersaturated in all monitoring well fluid samples. This mineral was not identified in the area previously, and was not identified by XRD analysis on the airlift samples collected from the injection well HN-02. It is, however, a metastable phase that may be a precursor of pyrite (Deer et al., 1992). Pyrrhotite (Fe$_7$S$_8$-FeS) was slightly supersaturated in the fluids sampled during the first weeks of the Phase II injection but undersaturated in all other samples (Fig. 5d). Pyrrhotite was previously identified within the high-temperature system in the Hellisheiði area (e.g. Gunnarsdóttir, 2012), but was not found at the CarbFix site nor identified in XRD analysis on the airlift samples from the injection well HN-02 (Fig. A3 in the electronic supplements). Gunnlaugsson and Arnórsson (1982) reported that below 180°C, geothermal waters in Iceland equilibrate with marcasite (FeS$_2$) instead of pyrite; marcasite is a pyrite dimorph generally found at lower temperatures (Deer et al., 1992). There was no evidence of marcasite in samples from the CarbFix site, either prior to the injections or in the XRD-analysis from the airlift pumping of well HN-02 (Fig. A3 in the electronic supplement). Mackinawite ((Fe,Ni)$_9$S$_8$) became supersaturated in the fluids sampled at the beginning of the Phase II injection, during the initial breakthrough of the injected Phase II fluid, and it is near to saturation in some monitoring samples collected from October to April 2013 (Fig. 5d). Mackinawite was not been identified in the area, and was not detected by XRD-analysis on the airlift samples from HN-02 (Fig. A3 in the electronic supplement).
However, mackinawite typically forms as a nanocrystalline material, whose broad peaks in XRD would be complicated to identify.

**Saturation indices for other minerals**

Saturation indices for other selected minerals are shown in Figure 7. Chalcedony (SiO$_2$) was slightly undersaturated in the monitoring fluid samples prior to the injections, but becomes saturated during Phase I; it then remains saturated for the rest of the monitoring period (Fig. 7a). Chalcedony is a common secondary mineral in the area (e.g. Alfredsson et al., 2013)

The mineral saturation states for those zeolites that are common in the area are shown in Figure 7b. Analcime, a common Na-zeolite found as an alteration phase at the CarbFix site, was undersaturated in the sampled fluids until about two months after the beginning of the Phase II injection, and then it is subsequently saturated (Fig. 7b). The samples were supersaturated with respect to other zeolites previously found in the area; and the general trend was a decrease in the monitoring fluid saturation index during the Phase I injection with an increase 6-8 weeks after Phase I was started. A slight dip was observed during the Phase II injection and an increase was observed during the second breakthrough of the injected fluid from Phase I (Fig. 7b).

The mineral saturation states for common clay minerals are shown in Figure 7c. Kaolinite (Al$_2$Si$_2$O$_5$OH$_4$) remained strongly supersaturated in the fluids sampled during the entire monitoring period (Fig. 7c), but increasingly so when the samples had a pH <8, during the injections and in the first weeks thereafter. Kaolinite was identified as a surface alteration product in geothermal areas (e.g. Markússon and Stefánsson, 2011) but has not been identified in subsurface samples collected from wells at Hellisheidi. The saturation state of gibbsite (Al(OH)$_3$) is depicted with the clay minerals; its behaviour was similar to kaolinite, except that it was undersaturated prior to the injections and became saturated when pH dropped below 8 during Phase I. It remained slightly supersaturated during the rest of the monitoring period (Fig. 7c). The saturation states of two other members of the kaolinite group; imogolite (Al$_2$SiO$_3$OH$_4$) and allophane (Al$_2$O$_3$SiO$_2$*H$_2$O), were also calculated. Imogolite was undersaturated prior to the injections but became strongly supersaturated during Phase I when the pH drops below 8, and remained supersaturated for the rest of the monitoring period, but decreasingly so as the pH
increased (Fig. 7c). Allophane was undersaturated during the whole monitoring period. Smectite was supersaturated in all samples except for the samples taken during, and shortly after the two injections while the pH was <8 (Fig. 7c). Smectite is one of the most abundant secondary minerals in basaltic rocks and has been identified in all wells drilled at Hellisheidi (e.g. Schiffman and Fridleifsson, 1991).

Discussion

Concentrations for the major elements Ca, Mg, Si, Na, K and Cl and the trace elements Fe and Al calculated using equations (1) and (2), based on the assumption of non-reactive conservative fluid mixing, are shown in Figure 3 together with their corresponding measured concentrations. Corresponding plots for the injected constituents are shown in Figure 2. Measured concentrations, greater than those calculated based on conservative fluid mixing, suggest net dissolution, lower concentrations suggest net precipitation (i.e. “fixation”). Measured Ca, Mg, and Fe concentrations were much higher during the injections and the subsequent days and weeks than that calculated assuming non-reactive conservative mixing. This indicates a net-input of these elements to the fluid consistent with the dissolution of the basalt originally present in the reservoir. The measured concentrations of these elements eventually became lower, and in the case of Mg, measured concentrations became lower than that calculated from non-reactive mechanical mixing (Fig. 3b) about 300 days after the start of the Phase 1 injection, suggesting net-precipitation into secondary minerals after these times.

Measured and calculated non-reactive conservative mixing concentrations of Si were approximately identical during the first breakthrough of Phase I, but the measured concentrations were lower during the second breakthrough (Fig. 3d). Measured Na and K concentrations were higher than the calculated from non-reactive conservative mixing, with a continuous increase up until the second breakthrough of Phase I, indicating net-release of these elements from the rock to the fluid (Fig. 3e-f). Na and K are the most mobile major elements during the weathering and low temperature alteration of basaltic rocks (Alfredsson et al., 2013; Eiriksdottir et al., 2015; Gislason et al., 1996). Measured Al concentrations were much lower during Phase I than corresponding calculated non-reactive conservative mixing concentrations indicating net Al precipitation during the injection and during the following weeks, while the pH of the samples
from well HN-04 was below 8 (Fig. 3g). Subsequently, the measured Al concentration rises slowly, with a small drop during the Phase II injection. From about 300 days after the start of the Phase I injection, and throughout the sampling period, the measured Al concentration in the samples exceeded the corresponding calculated concentrations, indicating a net release of this element from the rocks. Chlorine is a trace element in basaltic rocks (Sigvaldason and Oskarsson, 1976), but is sparingly taken up by secondary minerals, providing an example of a mobile element that behaves conservatively during mechanical mixing and moderate water rock interactions (Arnórsson and Andrésdóttir, 1995; Gislason and Eugster, 1987; Olsson et al., 2014). Measured and calculated conservative mixing concentrations of Cl were approximately identical, except during the second breakthrough of Phase I, when the measured concentrations were slightly lower than the calculated values (Fig. 3h) suggesting its possible uptake into carbonates (Olsson et al., 2014).

**The fate of the injected carbon**

The results and calculations presented above provide insight into the fate of the injected dissolved CO$_2$ gas. As previously reported by Matter et al. (2016), the difference between the measured and calculated non-reactive mixing DIC concentration (Fig. 8a), indicates its loss along the flow-path towards the monitoring well. Matter et al. (2016) also suggest that the dissolution of pre-existing carbonates at the onset of the CO$_2$ injection may have contributed to the neutralisation of the injected CO$_2$-rich water, along with dissolution of other phases such as basaltic glass, primary minerals of the host rock and other secondary minerals. This liberation of cations and neutralization of the originally acidic gas-rich injected aqueous fluid lead to the precipitation of carbonate minerals; Matter et al. (2016) concluded that over 95% of the carbon injected during Phase I was fixed as carbonate minerals in less than two years.

These previous conclusions are supported by the observations reported in this study. Shortly after the injections, the measured concentrations of dissolved Mg, Fe, and Ca increased substantially (Fig. 3a-c), and were greatly above that computed for non-reactive mixing, consistent with the rapid dissolution of the original reservoir rock. The dissolved concentration of Ca in these fluids was far greater than that of Mg and Fe, suggesting the preferential dissolution of calcium bearing minerals, such as calcite, during and shortly after both injection
phases. Indeed, the saturation state of calcite, the major carbonate phase present in the basaltic reservoir became undersaturated during and just after the Phase I injection (Fig. 5a), consistent with the initial dissolution of the calcite originally present in the host rock. Approximately 100 days after the start of the Phase I injection the monitoring fluid samples became supersaturated with respect to calcite with a saturation index of 0.6; this degree of supersaturation would be sufficient to grow calcite on the surfaces of the silicate minerals present in the reservoir (Stockmann et al., 2014). A similar variation of the calcite saturation state was evident following the Phase II injection. Moreover, calcite was observed to have precipitated within the monitoring well following the injection.

The saturation state of the monitoring fluid samples with respect to the carbonate phases magnesite and dolomite followed a similar pattern as calcite (Fig. 5b), but these were not identified in the study area. Such minerals have been reported to be kinetically inhibited from forming abiotically at temperatures less than 80 °C (Higgins and Hu, 2005; Kessels et al., 2000; Lippmann, 1973; Saldi et al., 2009, 2012). Similarly, siderite was calculated to be supersaturated in the sampled fluid but has not been found at the study site to date.

The fate of the injected sulphur

A noteworthy observation in this study is that the dissolved sulphur concentrations in the monitoring well samples remained close to constant during and after the injection of the H$_2$S-rich phase II injection. In contrast, non-reactive mixing calculations suggest these concentrations should have been as high as 0.6 mmol/L in the absence of sulphur precipitation (Fig. 8b). This indicates that vast majority of the sulphur injected into the subsurface was fixed within several weeks, before the Phase II fluids arrived at the first monitoring well. Indeed, numerous sulphur-bearing minerals, including pyrite, pyrrhotite, mackinawite, and greigite were supersaturated during the first weeks of Phase II injection (Fig. 5d).

Pyrite was strongly supersaturated favouring its nucleation and subsequent precipitation. The pyrite formation was confirmed by XRD-analysis on solids collected from the water samples taken during airlift from the injection well HN-02 in the spring of 2013. The analysis showed peaks from pyrite, amounting to 5-10 weight% of the solid material present in the air-lift
samples, based on Rietveld analysis using the software Topas (Fig. A3 in the electronic supplement). No other well-crystalline sulphides were identified in these airlift samples. Moreover, sulphide minerals were not identified in the precipitates recovered from the HN-04 monitoring well pump, which supports the conclusion that the H$_2$S mineralises prior to the arrival of the injection fluid at the first monitoring well. This rapid mineralisation of the injected H$_2$S is also in agreement with experimental studies on H$_2$S sequestration in basaltic rocks (Gudbrandsson and Stefánsson, 2014).

**The timescale of carbon and sulphur mineralisation: Carbon storage in sedimentary basins versus basaltic rocks.**

Carbon storage in sedimentary basins typically proceeds via the injection of pure CO$_2$ into porous sedimentary rocks (Fig. 9a). For common geothermal gradients, CO$_2$ is a supercritical fluid below 800 m in sedimentary basins. As supercritical CO$_2$ is less dense than the formation waters near this depth, it is buoyant and tends to rise to the surface. Ideally this CO$_2$ is trapped below an impermeable cap rock via structural or stratigraphic trapping. Eventually some of this CO$_2$ becomes stuck in small pores, limiting its mobility (residual trapping). Over time, CO$_2$ dissolves in the formation water (solubility trapping). As CO$_2$ charged water is denser than the original formation water, this CO$_2$-charged water will tend to sink. Some of this dissolved CO$_2$ may react to form stable carbonate minerals (mineral trapping). As one progresses from structural to mineral trapping, the CO$_2$ becomes more immobile and thus the storage more secure, though this process can take thousands of years or more as summarized in Figure 9a (Benson and Cole, 2008; Benson et al., 2005). Mineral trapping in sedimentary basins is slow and sometimes limited because of a lack of the calcium, magnesium, and iron bearing minerals required to mineralise the injected CO$_2$ (Gilfillan et al., 2009; Gislason and Oelkers, 2014).

In contrast during the CarbFix method, CO$_2$ is dissolved into water during its injection into porous basaltic rocks. No cap rock is required because the dissolved CO$_2$ is not buoyant and will not tend to migrate back to the surface. Solubility trapping occurs within 5 minutes during the CO$_2$ injection process (Sigfusson et al., 2015), and due to the reactivity of the basaltic rocks the bulk of the carbon is trapped in minerals within two years as shown in Figure 9b (this study; Matter et al., 2016). This rapid carbonation of injected CO$_2$ provides a permanent and safe
carbon storage option; once fixed into a carbonate mineral, the risk of leakage is minimal and little if any further monitoring of the site will be necessary.

The results of this study suggest that the co-injection of H$_2$S with CO$_2$ into the subsurface both rapidly fixes this gas through pyrite precipitation and does not detrimentally effect the carbonation of the injected CO$_2$. Indeed, the results from this study indicate that this pyrite mineralization is even faster than the carbonate mineralization; the bulk of the sulphur is trapped in minerals within four months from injection. The co-injection of these two acid gases may provide a number of advantages, most notably, it may lower substantially the energy and cost required to capture and separate the CO$_2$ from industrial exhaust. This possibility is now being explored in the SulFix-CarbFix project, where a CO$_2$-H$_2$S gas mixture is being captured and separated from the gas stream of the Hellisheidi power plant by its dissolution in water at the surface at about 5 bars pressure and 20°C. The resulting gas charged water is directly injected to 700 m depth and 200 - 270°, aiming to store 8,000 - 10,000 tonnes of the gas mixture annually.

The degree to which the CarbFix method can be applied at other sites will depend on the availability of suitable host-rocks, sufficient water to dissolve the CO$_2$ during its injection, and economic considerations. This on-shore CarbFix project, demonstrates the feasibility of carbon storage in basaltic rocks. Nevertheless, the largest geological storage potential for CO$_2$ lies offshore (Goldberg and Slagle, 2009; Goldberg et al., 2010; Goldberg et al., 2008; Snæbjörnsdóttir et al., 2014), where the mid-oceanic ridges contain permeable basaltic layers and the oceans provide an unlimited reservoir for the required water (Snæbjörnsdóttir and Gislason, 2016).

**Conclusions**

This paper reported the chemical composition and mineral saturation states of fluids collected prior to, during and after the injection of 175 tonnes of pure CO$_2$ and 73 tonnes of a gas-mixture consisting of 75 mol% CO$_2$, 24 mol% H$_2$S and 1 mol% H$_2$, into basaltic rocks at the CarbFix site in SW-Iceland. All results indicate that the vast majority of injected CO$_2$ and H$_2$S were rapidly fixed within minerals in subsurface basalts. The results presented above confirm that this fixation occurred by the initial dissolution of the host basalts due to the injection of
acidic gas-charged water; mass balance indicates the net input from host rock dissolution of Mg, Fe, and Ca following each injection. The dissolution of host basalts and fluid mixing neutralized the pH of the injected fluid such that calcite became supersaturated approximately 100 days after the start of each injection favouring the fixation of the injected CO₂ within this mineral. This results, which supports those of Matter et al. (2016) who concluded that CO₂ mineralization fixed over 95% of the injected carbon within 2 years, was further validated by observations of calcite precipitation within the monitoring well itself. Although other metal carbonate minerals, notably, ankerite, siderite and mixed Ca, Mg, Fe-carbonates, were also supersaturated in the monitoring fluids these were not observed to form during this study.

Similar results support the even more rapid mineralization of injected H₂S as pyrite, as this mineral is supersaturated before, during and after the injection of a mixed CO₂-H₂S charged water into the basalts. The rapid fixation of H₂S into this mineral is further evidenced by the observation of pyrite precipitation in the injection well but not in the first monitoring well. Such observations suggest that H₂S fixation by pyrite precipitation was essentially complete before the injected mixed-gas plume arrived at the monitoring well. Notably there appears to have been little difference in the chemical response in the subsurface of the mixed H₂S-CO₂ gas mixture injection compared to that of the pure CO₂ injection. Their similar success towards the CO₂ mineralization suggests that the injection of mixed gases might prove to be a simpler and more cost-effective approach to subsurface carbon storage than the injection of pure CO₂.

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References


Table 1. Characteristics of the two gas injections into the CarbFix storage site considered in this study.

<table>
<thead>
<tr>
<th></th>
<th>Phase I: Injection of 100% CO₂</th>
<th>Phase II: Injection of 75% CO₂, 24% H₂S, 1% H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Period:</strong></td>
<td>24th of January to 9th March 2012</td>
<td>15th of June to 1st of August 2012</td>
</tr>
<tr>
<td><strong>Injection period (days)</strong></td>
<td>45</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>Active: 40</td>
<td>Active: 29</td>
</tr>
<tr>
<td><strong>Mass of injected gas (Tonnes)</strong></td>
<td>175</td>
<td>73</td>
</tr>
<tr>
<td><strong>Tracers:</strong></td>
<td></td>
<td></td>
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<tr>
<td><strong>Reactive</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration:</td>
<td>40.0 Bq/L*</td>
<td>6 Bq/L*</td>
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<tr>
<td>¹⁴C/¹²C ratio</td>
<td>2.16 x 10⁻¹¹*</td>
<td>6.5 x 10⁻¹²*</td>
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<tr>
<td><strong>Non-reactive</strong></td>
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<td></td>
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<tr>
<td>SF₆</td>
<td></td>
<td>SF₆,CF₃</td>
</tr>
<tr>
<td>Concentration:</td>
<td>2.33 x 10⁻⁸ ccSTP/cc*</td>
<td>2.24 x 10⁻⁸ ccSTP/cc*</td>
</tr>
</tbody>
</table>

*From Matter et al. 2016
Table 2. The measured chemical composition of water collected from well HN-01, and co-injected with pure CO$_2$ gas or CO$_2$/H$_2$S gas mixtures into the CarbFix storage site.

<table>
<thead>
<tr>
<th>Date</th>
<th>Sample ID</th>
<th>pH</th>
<th>Conductivity</th>
<th>H$_2$S</th>
<th>O$_2$</th>
<th>Alk.</th>
<th>DIC</th>
<th>S$_{\text{total}}$</th>
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<td>292</td>
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<td>0.051</td>
<td>2.109</td>
<td>1.460</td>
<td>0.118</td>
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<td>4.7.2012</td>
<td>12SOS03</td>
<td>9.21</td>
<td>300</td>
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<th>Mg</th>
<th>Fe</th>
<th>Si</th>
<th>Na</th>
<th>K</th>
<th>Al</th>
<th>Cl</th>
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<td>1.83</td>
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*Measured on 12th of July
Table 3. The measured chemical composition of the major elements of two solid samples collected from the water pump recovered from well HN-04 on the 13\textsuperscript{th} of August 2013.

<table>
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<tr>
<th></th>
<th>Si (mmol/L)</th>
<th>Na (mmol/L)</th>
<th>K (mmol/L)</th>
<th>Ca (mmol/L)</th>
<th>Mg (mmol/L)</th>
<th>S (mmol/L)</th>
<th>Al (mmol/L)</th>
<th>Fe (mmol/L)</th>
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<td>10230</td>
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Figure 1. Geological cross section of the CarbFix injection site, modified from Alfredsson et al. (2013). Blue indicates lava flows and brown indicates hyaloclastic (glassy) formations. The CO$_2$-H$_2$S-H$_2$O gas mixture used in the second injection was separated from other geothermal gases at the power plant and transported via gas pipe to the injection site where it was dissolved in water from well HN-01 within the injection well HN-02. The gas charged water enters the basalt as a single phase. Water was pumped from well HN-01 to the injection well HN-02 at the rate of 7.2 m$^3$/h. Water was pumped from the monitoring well at the rate of 3.5 m$^3$/h, throughout this study. Graphic work by Sölvi Snæbjörnsson.
Figure 2. Concentrations of a) SF$_6$ and SF$_5$CF$_3$ non-reactive tracers; b) dissolved inorganic carbon (DIC) along with fluid pH calculated at *in situ* temperature (35°C), c) total dissolved sulphur and H$_2$S(aq) in samples from monitoring well HN-04 prior to, during, and after the injection of pure CO$_2$ and mixed CO$_2$/H$_2$S gas into the CarbFix Storage site. The timing of both gas injections is indicated by grey bars. The detection limit of the H$_2$S concentration measurements is 0.3 µmol/L and is indicated as a dotted line.
Figure 3. Concentrations of Ca, Mg, Fe, Si, Na, K, Al, Cl and F collected from monitoring well HN-04 prior to, during, and after the injection of CO$_2$ and CO$_2$/H$_2$S into the CarbFix Storage site. The timing of both gas injections is indicated by grey bars. Note the pH of the fluid samples is plotted together with the Al concentrations. The results of mass balance calculations depicting expected values for these concentrations, assuming pure mechanical mixing of the injected solution is also shown in these plots.
Figure 4. Photograph illustrating the presence of precipitates on the water sampling pump recovered from monitoring well HN-04 on the 13\textsuperscript{th} of August 2013. The diameter of the pump is 101 mm.
Figure 5. Saturation indices (SI) of collected HN-04 well water samples with respect to A) magnesite siderite and calcite; B) dolomite, aragonite and ankerite, C) Mg-Fe and Ca-Mg-Fe solid solutions, and D) pyrrhotite, pyrite, sulphur and mackinawite prior to, during, and after the injection of pure CO$_2$ and a CO$_2$/H$_2$S gas mixture into the CarbFix Storage site. All saturation indices were calculated assuming the oxygen fugacity was controlled by equilibrium of the H$_2$S/SO$_4^{2-}$ as a redox couple. Note that positive, negative, and zero SI values correspond to aqueous fluids that are supersaturated, undersaturated, and at equilibrium with the indicated mineral. The timing of both gas injections is indicated by grey bars.
Figure 6. Partial pressures of CO$_2$ and H$_2$S prior to, during and after both injection experiments.
Figure 7. Saturation indices (SI) of collected HN-04 well water samples with respect to A) chalcedony, B) the zeolites previously identified in the area, and C) selected clay-minerals prior to, during, and after the injection of pure CO₂ and a CO₂/H₂S gas mixture into the CarbFix Storage site. Note that positive, negative, and zero SI values correspond to aqueous fluids that are supersaturated, undersaturated, and at equilibrium with the indicated mineral. The timing of both gas injections is indicated by grey bars.
Figure 8. Comparison of measured and calculated non-reactive mixing concentrations of DIC and sulphur – see text. The timing of both gas injections is indicated by grey bars.
Figure 9. Schematic illustration of the contribution of various trapping mechanisms to the geologic storage as a function of time, a) injection of buoyant supercritical CO₂ into sedimentary rocks, modified from Benson et al. (2005), b) injection of CO₂ dissolved in water into basaltic rocks via the CarbFix method.