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An experimental study of basalt–seawater–CO₂ interaction at 130 °C

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Abstract

Over millions of years, the interaction of marine basalt with percolating seawater in low-temperature ocean floor hydrothermal systems leads to the formation of calcite and aragonite. The presence of these minerals in marine basalts provides evidence for substantial CO₂ fixation in these rocks. Here, we report on laboratory experiments to study this process under enhanced CO₂ partial pressures ($p\text{CO}_2$) at 130 °C. Mid-ocean-ridge-basalt (MORB) glass was reacted with North Atlantic Seawater charged with CO₂ in batch experiments lasting up to 7 months. For experiments initiated with seawater charged with ~ 2.5 bar $p\text{CO}_2$, calcite and aragonite are the first carbonate minerals to form, later followed by only aragonite (\pm siderite and ankerite). For experiments initiated with seawater charged with ~ 16 bar $p\text{CO}_2$, magnesite was the only carbonate mineral observed to form. In total, approximately 20 % of the initial CO₂ in the reactors was mineralized within five months. This carbonation rate is similar to corresponding rates observed in freshwater-basalt-CO₂ interaction experiments and during field experiments of the carbonation of basalts in response to CO₂-charged freshwater injections in SW-Iceland. Our experiments thus suggest that CO₂-charged seawater injected into submarine basalts will lead to rapid CO₂ mineralization. Notably, at $p\text{CO}_2$ of tens of bars, magnesite will form, limiting the formation of Mg-rich clays, which might otherwise compete for the Mg cation and pore-space in the submarine basaltic crust. This suggests that the injection of CO₂-charged seawater into subsurface basalts can be an efficient and effective approach to the long-term safe mineral storage of anthropogenic carbon.

1 Introduction

The urgent need for large scale carbon dioxide removal (CDR) to limit global warming is increasingly evident. It is estimated that between 100 and 1000 Gt of CO₂ will have to be removed from the atmosphere by the end of the 21st century to limit global warming to 1.5 °C compared to pre-industrial levels (Rogelj et al., 2018). Carbon capture and storage (CCS) technologies are an intriguing CDR method as CO₂ can be captured from exhaust streams or directly from the atmosphere. As of 2020, only 40 Mt CO₂ are captured from concentrated

44 sources and stored in geological formations per year (Global CCS Institute, 2020), while global
45 annual CO₂ emissions amounted to 42 Gt CO₂ in 2019 (Friedlingstein et al., 2020). The
46 imbalance between current CCS and anthropogenic CO₂ release highlights the need for
47 research and development of efficient CCS techniques.

48 Carbon dioxide storage through its mineralization in the subsurface is a low risk
49 technique as carbon bound in stable carbonate minerals has minimal leakage risk (e.g., Matter
50 et al., 2016; Snæbjörnsdóttir et al., 2020). The CarbFix project demonstrated the mineralization
51 of 95% of freshwater-dissolved CO₂ injected into fresh basalts within two years at 20-50 °C
52 and the mineralization of up to 60% of freshwater-dissolved CO₂ injected into altered basalts
53 within several months at 250-270 °C (Matter et al., 2016; Gunnarsson et al., 2018; Clark et al.,
54 2020). A second field project was conducted in the Columbia River Basalt near Wallula
55 (Washington) at 30-45 °C in 2013, where supercritical CO₂ was injected into the subsurface.
56 Hydrological modelling suggests mineralization of up to 60% of the injected CO₂ within two
57 years (McGrail et al., 2017; White et al., 2020).

58 While the injection method employed in the CarbFix project, i.e. injection of water-
59 dissolved CO₂, drastically reduces the risk of CO₂ leakage to the surface (the injection fluid is
60 not a buoyant fluid), substantial amounts of water are required. At 30 bar pressure and 20 °C,
61 around 22 metric tons of freshwater are needed to dissolve one ton of CO₂ (e.g.,
62 Snæbjörnsdóttir et al., 2020). Therefore, the large-scale application of this method requires
63 large amounts of fresh water and faces potential usage conflicts. The use of seawater as a solute
64 is a potential alternative to fresh water. Vast quantities of seawater are available in the
65 immediate vicinity of the basaltic oceanic crust, a reservoir with a storage potential of ~ 3x10⁵
66 Gt CO₂ (Marieni et al., 2013). The capacity of submarine basalts to store vast quantities of CO₂
67 is supported by the observations of substantial carbonate mineral formation through seawater-
68 basalt interaction. For example, Gillis and Coogan (2011) and Coogan and Gillis (2013)
69 reported that the basaltic oceanic crust can contain ~0.5 to 4.0 wt% of carbonate minerals.
70 These carbonate minerals are formed by the percolation of CO₂-bearing seawater through off-
71 axis hydrothermal systems below the seafloor at temperatures < 100 °C. Moreover, the
72 weathering of marine silicate sediments can result in the formation of as much as ~1 wt%
73 carbonate minerals (Wallmann et al., 2008). While these processes represent an important
74 carbon sink over geological timescales and influence long-term climate regulation (Staudigel
75 et al., 1989; Brady and Gíslason, 1997; Coogan and Gillis, 2013; Isson et al., 2020), only
76 limited data are available on conditions that could enhance and/or accelerate such carbon
77 mineralization processes. Young (< 3 Ma) oceanic crust typically contains only minor amounts
78 of carbonate minerals, suggesting that only limited carbonate precipitation occurs in high
79 temperature mid-ocean ridge hydrothermal systems (Gillis et al., 2001; Heft et al., 2008;
80 Coogan and Gillis, 2018). This is likely related to early uptake of seawater Ca by rapid
81 anhydrite precipitation (Voigt et al., 2018b) and higher stability of non-carbonate Ca and Mg
82 bearing minerals at such conditions. In contrast, carbonate minerals are abundant in the
83 Reykjanes geothermal system, a seawater-dominated on-shore hydrothermal system in
84 southwest Iceland (Wiese et al., 2008; Marks et al., 2010).

85 Most experimental studies focusing on the chemical reactions during water-basalt-CO₂-
86 interaction have been performed using freshwater (Gysi and Stefánsson, 2012a, b, c;
87 Stockmann et al., 2013, 2014; Galeczka et al., 2013, 2014; Menefee et al., 2017, 2018; Kumar
88 et al., 2017; Clark et al., 2019). Less experimental data are available for seawater systems as
89 shown in Table 1 and described below. A number of experimental studies reacting basalt with

90 seawater under hydrothermal conditions have been published to better understand silicate
91 weathering phenomena and element cycling patterns in mid-ocean ridge systems (e.g.,
92 Seyfried, 1977; Bischoff and Seyfried, 1978; Mottl and Holland, 1978; Seyfried and Bischoff,
93 1979; Mottl et al., 1979; Seyfried and Bischoff, 1981; Seyfried and Mottl, 1982; Voigt et al.,
94 2018b, 2020). However, mineralization of CO₂ was not considered in these studies. Brady and
95 Gislason (1997) found that increasing the *p*CO₂ in equilibrium with seawater increased basalt
96 dissolution rates slightly, although it remained unclear whether this increase was due to higher
97 dissolved CO₂ concentrations or to a lower liquid phase pH. Wolff-Boenisch et al. (2011)
98 performed a series of far-from-equilibrium basalt dissolution experiments with seawater at
99 25 °C, and found that the basalt dissolution rates were significantly higher in the presence of
100 seawater compared to freshwater. Similarly, Marieni et al. (2020) measured dissolution rates
101 of submarine basalts and altered gabbro in CO₂-charged seawater, and found that these rates
102 were faster than those measured in freshwater of low dissolved inorganic carbon (DIC) content.
103 Rosenbauer et al. (2012) performed experiments reacting different basalts with CO₂-charged
104 NaCl brines at 50, 100 and 200 °C. The results indicated that 8 to 26% of the available CO₂
105 was mineralized within ~ 4 months at 100 °C, while lower carbon uptakes were observed at 50
106 and 200 °C, respectively. The only carbonate mineral product identified in this study was
107 ferroan magnesite (Fe^{II} bearing MgCO₃), and the CO₂ uptake correlated with the magnesium
108 content of the rock. In contrast, Shibuya et al. (2013) performed two experiments reacting CO₂-
109 charged aqueous NaCl solutions with basalt. These authors found that the initial 400 mM of
110 dissolved CO₂ was reduced to 0 and 100 mM due to calcite (CaCO₃) formation after ~ 3
111 months, at 250 °C and 350 °C, respectively. In a further study, Luhmann et al. (2017) flooded
112 basalt cores with CO₂-rich NaCl brines. Siderite (FeCO₃) formation was suspected based on
113 the calculated liquid saturation states. However, in the three aforementioned studies, no other
114 seawater component (e.g. Mg, Ca, K, ...) was introduced to the experiments. The
115 concentrations of such solutes can significantly alter reaction paths. In contrast, Rigopoulos et
116 al. (2017) reacted artificial seawater, initially equilibrated with atmospheric CO₂, with either
117 very fine grained basalt or peridotite at room temperature. In their ~ 2 month long experiments,
118 they detected carbon mineralization in the form of aragonite (CaCO₃) only in the peridotite
119 experiments. Finally, Wolff-Boenisch and Galeczka (2018) induced calcite, magnesite, and
120 other Ca/Mg-carbonate precipitation at 90 °C by injecting seawater that was highly
121 supersaturated with respect to carbonate minerals, by the addition of ammonium bicarbonate,
122 into a reactor containing basalt powder.

123 Although most of these experimental studies demonstrated the potential of using CO₂-
124 charged brines or seawater for carbon mineralization by reacting them with mafic or ultramafic
125 rocks, we are not aware of any experiments that achieved carbon mineralization by reacting
126 CO₂-charged seawater with basalt. To explore and quantify such reactions, a series of batch
127 experiments were run in the present study to mimic the reactions of CO₂-charged seawater
128 injected into a reservoir of basaltic glass at 130 °C. The purpose of the present study is to
129 explore the potential of injecting CO₂-charged seawater into basalt formations for accelerated
130 mineral carbon storage.

131 2 Methods

132 2.1 Experimental design

133 Either natural North Atlantic seawater or synthetic Mg-free seawater (see section 2.2)
134 was reacted with basaltic glass powder and CO₂ in batch experiments at 130 °C. The effects of

135 distinct initial CO₂ partial pressure ($p\text{CO}_2$), water/rock ratio, and the presence or absence of
136 calcite seed crystals were investigated in experiments that ran from 2 to 228 days. All
137 experimental conditions are listed in Table 2. Individual closed system batch experiments were
138 run for each selected sampling duration instead of sampling the liquid repeatedly from single
139 experiments to (1) avoid either CO₂ degassing from the liquid due to an increased headspace
140 after sampling or buffering the solution at low pH if more CO₂ was added to the reactor to
141 maintain $p\text{CO}_2$, (2) obtain a sample of the solids at the same time as obtaining the liquid sample,
142 and (3) maintain a nearly constant water/rock ratio during the experiment.

143 Three main series of individual experiments were performed to explore the reaction
144 paths and efficiency of carbon mineralization. Most of the experiments were run in the low-
145 $p\text{CO}_2$ series. Experiments in this series are labelled ‘Low-#’ (where # is the duration in days)
146 in Table 2 and throughout this text. Experiments in this series were started with approximately
147 2.5 bar $p\text{CO}_2$, resulting in ~ 26 mM DIC in the initial aqueous phase. This DIC concentration
148 is similar to that of the CO₂-charged injection water in the first phase of the CarbFix2 project
149 (Clark et al., 2020). Another experimental series was started with ~ 16 bar $p\text{CO}_2$ in the reactors,
150 resulting in ~ 125 mM DIC in the initial aqueous phase. This is the high- $p\text{CO}_2$ series, and these
151 experiments are labeled ‘High-#’. The third experimental series was run using synthetic Mg-
152 free seawater instead of natural seawater and at approximately 2.5 bar $p\text{CO}_2$. This experimental
153 series is referred to as the MgFree series, and these experiments are labeled ‘MgFree-#’. Note
154 that some of the individual experiments of the low- $p\text{CO}_2$ series were initiated with different
155 water/rock ratios, lower stirring rates (experiment ‘Low- $p\text{CO}_2$ -Slow’), and in the presence of
156 calcite seeds (experiment ‘Low- $p\text{CO}_2$ -Calcite’) to test the effect of these parameters. A single
157 experiment (‘Low-66-146’) was sampled once during the experiment to induce degassing of
158 the aqueous phase in the reactor.

159 An experimental temperature of 130 °C was chosen for this study i) to achieve sufficient
160 reaction progress within reasonable timespans while ii) limiting anhydrite precipitation from
161 the seawater, which occurs at temperatures above ~ 150 °C for standard seawater (Bischoff and
162 Seyfried, 1978) and at lower temperatures for seawater enriched in Ca²⁺ and/or SO₄²⁻. Such
163 temperature conditions can be found in the margins of coastal geothermal systems such as in
164 Reykjanes, Iceland (e.g. Marks et al., 2010), making the experiments directly applicable to
165 such settings. In addition, batch reactors, as opposed to open systems, were used in this study
166 to achieve sufficient solid reaction products to quantify carbon mineralization when starting
167 directly from CO₂-charged seawater. This is in contrast to many previous carbonation
168 experiments that were initiated at close to neutral or alkaline pH to artificially accelerate the
169 formation of secondary carbonates. Here we allow the initial acidic liquids that are
170 undersaturated with respect to carbonate minerals to evolve towards conditions suitable for
171 carbonation in each individual experiment.

172 All experiments were conducted in 300 mL or 600 mL Parr titanium reactors as
173 illustrated in Figure 1. The reactor vessels, inner magnetic drive rotors and housings, as well
174 as all parts of the reactor system in contact with liquid during the experiments were made of
175 titanium. All reactors were equipped with Ashcroft G2 500 psig or Omega PX4202 600 psig
176 pressure transducers, type J thermocouples placed in a thermowell, and stirrer tachometers.
177 These sensors were all connected to Parr process controllers and a computer, allowing
178 continuous monitoring of the reactor pressure and temperature, as well as controlling the
179 heating jackets. Pressure readings were converted to absolute pressures by assuming a constant
180 laboratory pressure of 1 atm.

181 Before starting an experiment, the reactor assemblage was cleaned mechanically and
182 ultrasonically. The reactors were then filled with ~ 0.1 M HCl (where M denotes molality
183 throughout this study, defined as mol per kg water) and heated to the experimental temperature
184 for at least 24 h. The reactors were then emptied, and the same procedure was repeated using
185 ~ 0.1 M HNO₃ and finally with ultrapure H₂O (18.2 M Ω ·cm at 25 °C). All reactor assemblages
186 were tested for leaks by filling them with > 20 bar gas and monitoring pressure over at least 48
187 h.

188 Experiments were initiated by placing the desired amount of basaltic glass and reactive
189 liquid into the reactor and closing it. The reactor headspace was flushed with pure CO₂ for \sim
190 30 min by connecting the gas inlet to a CO₂ cylinder and pressure regulator and adjusting
191 reactor pressure to ~ 1.1 bar. The reactor contents were stirred at 600 rpm at room temperature
192 leaving a plug in the reactor head slightly open. Preliminary tests found that this stirring rate
193 was sufficient to maintain the basaltic glass powder in suspension for the employed water/rock
194 ratios. Subsequently, the reactor was closed and heated to the desired experimental temperature
195 within ~ 30 min. Finally, the desired total pressure was set by addition of CO₂ through the gas
196 inlet for ~ 2 h, allowing for CO₂ dissolution into liquid, after which the inlet was closed again,
197 so that the reactors were completely sealed during the experiments.

198 A single liquid sample was taken from the reactor before ending an experiment. For
199 this, a water-cooled titanium tube with a 0.2 μ m cellulose acetate (CA) membrane filter at the
200 end was connected to the sampling outlet. During sampling, a CO₂ cylinder with pressure
201 regulator was connected to the gas inlet again and was set to maintain the same pressure as
202 observed before sampling was initiated. This maintained a constant p CO₂ during sampling.
203 After flushing the outlet with at least 5 mL of liquid, approximately 10 mL of liquid was
204 sampled into a polypropylene (PP) bottle of known mass containing ~ 90 mL of ultrapure water
205 for alkalinity measurements. This immediate 1:10 dilution avoids the possibility of
206 precipitation of solids from the liquid before the analysis. Another 10 mL of liquid was sampled
207 into an acid (HCl) washed PP bottle and acidified with a known amount of Suprapur HNO₃ for
208 analysis by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). An
209 untreated liquid sample of at least 10 mL was taken for fluorine measurements. In several
210 experiments, a 10 mL sample of liquid was collected directly into an Erlenmeyer flask
211 containing a mixture of 5 mL of 5 M NaOH and 5 mL acetone using Norprene tubing for H₂S
212 titrations. Additional liquid samples for redox potential measurements were sampled into a 10
213 mL PP syringe from some experiments. In experiment Low-66-146, a liquid sample was taken
214 after 66 days to reduce the p CO₂ (and thus increase pH) during the second part of this
215 experiment.

216 Experiments were stopped by quenching them to room temperature in less than 2 h.
217 The reactor contents were not stirred while cooling to minimize retrograde water-rock
218 interaction. After opening the reactors, the remaining liquid was decanted. The reacted solids
219 were placed in a vacuum filtration system with a 0.2 μ m CA membrane filter. The solids were
220 then rinsed a minimum of three times with ultrapure water for ~ 30 to 60 s to remove any
221 remaining experimental liquid. The cleaned solids were dried at room temperature or at
222 temperatures up to 35 °C. Any solids remaining in the reactor (e.g. stuck at the bottom, or
223 precipitated on stirrer shaft, thermowell, or walls) were also collected, cleaned and dried
224 separately.

225 Thermodynamic calculations were carried out using PHREEQC v3.6.2 (Parkhurst and
226 Appelo, 2013) and the carbfix.dat database v1.1.0 (Voigt et al., 2018a). Quenching simulations

227 were performed to assess the potential for any carbonate mineral precipitation during the
228 cooling of the reactor system (Wolff-Boenisch et al., 2016). In the quenching simulations, the
229 known *in-situ* liquid composition was cooled together with the gas phase contained in the
230 reactor headspace, accounting for pressure changes. Thermodynamic calculations indicate that
231 the liquid was not supersaturated with any carbonate minerals of interest during the quenching
232 procedure (Figure S-1 in the Supplementary Material). Although these calculations predict the
233 supersaturation of the reactor liquid with carbonate minerals after opening the reactors as the
234 $p\text{CO}_2$ decreased to below 1 atm, this is unlikely to have occurred in the few seconds between
235 opening the reactor and decanting the liquid.

236 2.2 Reactants

237 The basaltic glass used in this study originated from the Stapafell volcano located
238 within the first fissure swarm of the Reykjanes peninsula where the Mid-Atlantic Ridge comes
239 onshore in SW-Iceland. This basaltic glass is of similar composition as Mid-Ocean-Ridge-
240 Basalt (MORB; Oelkers and Gíslason, 2001; Gíslason and Oelkers, 2003). This material has
241 been extensively characterized and studied (e.g. Wolff-Boenisch et al., 2011; Gysi and
242 Stefánsson, 2012b; Galeczka et al., 2014; Příkryl et al., 2018; Clark et al., 2019). The basaltic
243 glass was ground and sieved to obtain the 45-100 μm size fraction. This size fraction was then
244 ultrasonically cleaned in ultrapure water before it was dried at room temperature. Its chemical
245 composition was determined to be consistent with
246 $\text{SiTi}_{0.02}\text{Fe}_{0.17}^{2+}\text{Fe}_{0.02}^{3+}\text{Mg}_{0.28}\text{Ca}_{0.26}\text{Na}_{0.08}\text{K}_{0.008}\text{O}_{3.45}$ by Oelkers and Gíslason (2001), and its
247 specific surface area was measured by Clark et al. (2019) using the BET technique (Brunauer
248 et al., 1938) and determined to be 1240 cm^2/g . Powdered basaltic glass (> 90 wt.% glass; < 10
249 wt.% forsterite) was used instead of larger pieces to increase the chemical reactivity so that
250 sufficient reaction progress is achieved during the experiments.

251 Most experiments were started using natural seawater collected from the Faxaflói 9
252 station, located offshore west of Iceland (64° 20' N, 27° 58' W), at 3 m depth during February
253 2011 (Jones et al., 2012). The seawater was filtered and acidified using HCl upon collection
254 and stored in the dark at < 10 °C. Prior to each experiment, sufficient aqueous 1 M NaOH
255 solution was added to an aliquot of this seawater so that its alkalinity was ~ 2.3 meq/kg (Table
256 2), corresponding to that of standard seawater (Millero et al., 2008). Other experiments used
257 synthetic Mg-free seawater, prepared by weighing reagent grade NaCl, Na₂SO₄, CaCl₂·2H₂O,
258 KCl, NaHCO₃, Na₂CO₃ and NaF into a container with ultrapure water, followed by thorough
259 mixing and storage at < 10 °C in the dark until use. Similar to the natural seawater, a final
260 adjustment of the alkalinity to ~ 2.3 meq/kg was done by adding small amounts of a 1 M NaOH
261 solution.

262 2.3 Analysis of liquids

263 Alkalinity titrations of liquid samples were carried out with an aqueous ~ 0.001 M HCl
264 solution and a Cole Parmer double junction glass pH electrode using the Gran (1952) method.
265 Alkalinity titrations were performed in duplicate. The 95% confidence interval, used for stated
266 uncertainties throughout this text, was determined to be approximately ± 0.5 % based on
267 repeated measurements.

268 The concentrations of Na, Ca, S, Mg, Cl, Fe, K, Al, and Si in all liquid samples were
269 determined using a Spectro Ciros Vision ICP-OES. All measurements were carried out in
270 duplicate on samples diluted 10-, 100-, and 1000-fold in an aqueous 1% HNO₃ solution.
271 Uncertainties were estimated from repeated measurements to be approximately ± 3 % for major

272 elements. Detection limits were $\sim 4 \mu\text{M}$ for Al, $\sim 1 \mu\text{M}$ for Fe, and $\sim 20 \mu\text{M}$ for Si. The
273 concentrations of all other elements were above detection limits for all samples. Fluorine
274 concentrations were determined using a F^- selective electrode, and corrections were made for
275 the presence of aqueous MgF^+ complexes based on the procedure described in Kleine et al.
276 (2020).

277 The pH and DIC values at experimental temperatures were calculated using measured
278 alkalinities, the elemental composition of the liquid, and the pressure recorded by the pressure
279 transducers mounted on the reactors via thermodynamic calculations. This approach makes use
280 of the fact that the total pressure in the reactor is determined by the equilibrium of H_2O and
281 CO_2 between the liquid and gas phases. The pH and DIC calculated for the experimental
282 temperature are estimated to have an uncertainty of approximately 0.07 pH units and 3 mM,
283 respectively, based on propagating uncertainties using Monte Carlo methods (e.g. Anderson,
284 1976). For this, the uncertainty of pressure measured using the transducer was assumed to be
285 0.1 bar. In some cases, the pH of a liquid aliquot sampled from the reactor at shut-down was
286 measured using a Thermo Fisher Scientific Eutech double junction plastic combination pH
287 electrode. Although these measurements are affected by degassing of the liquid, their values
288 are similar to those calculated using the measured total pressure when corrected to the
289 experimental temperature using thermodynamic calculations. Some comparisons of measured
290 and calculated pH values are provided in Figure S-2 in the Supplementary Material.

291 Samples for total sulfide sulfur ($\text{S}^{\text{II}-}$) concentration measurement were first taken up in
292 aqueous NaOH and acetone solutions. The resulting liquid was then passed through filter paper
293 to remove precipitates formed due to the pH increase of the seawater. The recovered liquids
294 were then titrated with an aqueous $(\text{CH}_3\text{COO})_2\text{Hg}$ solution using dithizone as indicator as
295 described by Arnórsson et al. (2006). The detection limit of these measurements was
296 approximately $1 \mu\text{M S}^{\text{II}-}$.

297 A Microelectrodes MI-800 Ag-AgCl Micro Combination Redox Electrode was used
298 for redox potential measurements at ambient temperature and pressure conditions.
299 Measurements were converted to the standard H_2 electrode reference state using the equations
300 of Wolkersdorfer (2008) for the specific electrode type. The redox potential at *in situ* pressure
301 and temperature conditions were then calculated using the same thermodynamic data as in other
302 calculations.

303 2.4 Analysis of solids

304 The basalt powder used as reactant and the solid reaction products collected at the end
305 of each experiment were analyzed using a Zeiss Leo Supra 25 Scanning Electron Microscope
306 (SEM) equipped with an energy-dispersive spectrometer (EDS) located at the Innovation
307 Center Iceland. Samples were gold-coated and analyzed using an acceleration voltage of 20
308 kV, an aperture of $30 \mu\text{m}$, and a working distance of 8.5 mm.

309 Total inorganic carbon (TIC) contents of the solids were determined using a system
310 originally designed for DIC analysis located at the GET Laboratory, Toulouse, France
311 (Bénezeth et al., 2011). This system uses a non-dispersive infrared (NDIR) CO_2 gas analyzer
312 to measure the mass of CO_2 released from a sample upon addition of a 1 M aqueous HCl
313 solution. A CO_2 -free carrier gas transports the released gas phase to the NDIR detector. The
314 detection limit is approximately 0.0005 wt% CO_2 , and the relative uncertainty of measurements
315 was $\sim 6 \%$, as determined by repeated measurements. Note that sample heterogeneity likely
316 contributes significantly to this value. Measurement of the TIC content of solids collected from
317 the high- $p\text{CO}_2$ experiment was not possible using this method, as the dissolution of the

318 magnesite present in these samples is slow even in concentrated acids. TIC was also measured
319 by heating the solids to 1000 °C in a furnace in a pure nitrogen environment and detecting the
320 released carbon with a solid-state infrared cell using an ELTRA CW-800 at Activation
321 Laboratories Ltd., Canada. This latter method has a higher detection limit of 0.01 wt% CO₂
322 and higher relative uncertainties equal to 100% at the detection limit, which decreases to 20%
323 at 0.1 wt% CO₂ in a sample. Nevertheless, this approach allowed the determination of the CO₂
324 contents of the samples containing magnesite.

325 X-ray diffractometry (XRD) measurements were carried out to characterize the identity
326 of alteration minerals in reacted samples using a PANalytical X'Pert PRO diffractometer fitted
327 with a Co-sourced X-ray tube (40 kV, 40 mA) and a high-speed Scientific X'Celerator detector.
328 The solids were analyzed without grinding and applying the top-loading technique to allow the
329 identification of trace amounts of secondary carbonates. This approach enhances the intensities
330 of carbonate-diagnostic reflections due to crystal size effects (Baldermann et al., 2020). The
331 solids were examined between 4 and 85 °2 θ with a step size of 0.008 °2 θ and a count time of
332 40 s per step. The recorded XRD patterns were analyzed by the PANalytical Highscore Plus
333 software suite (version 3.0.4) and its pdf-4 database (Baldermann et al., 2018).

334 3 Results

335 3.1 Evolution of liquid compositions

336 The composition of all collected liquid samples is provided in Table 3 and shown as a
337 function of experiment duration in Figure 2. The *in situ* pH increased rapidly during the
338 experiments, from ~ 5.1 in the low-*p*CO₂ experiments or ~ 4.3 in the high-*p*CO₂ experiments
339 to ~ 5.6 and 5.0, respectively. The pH in the experimental liquids remained relatively stable at
340 these levels after the initial increase. Alkalinity increased in the liquids of all experiments from
341 an initial ~ 2.3 meq/kg. Within the first two hours, while the experiments were charged and
342 equilibrated with CO₂ before disconnecting the reactor from the CO₂ source, alkalinity rose to
343 ~ 7.3 meq/kg. The highest alkalinities were recorded in experiments of < 100 days and those
344 in the high-*p*CO₂ series, where 9.4 meq/kg was reached. Calculated DIC concentrations at the
345 beginning of the experiments, after charging the reactors with CO₂, were ~ 26 mM in the low-
346 *p*CO₂ experiments and ~ 125 mM in the high-*p*CO₂ experiments. These values decreased to a
347 minimum of 12 mM and 105 mM, respectively, during these experiments.

348 During the low-*p*CO₂ experiments, the Mg concentrations of the reactive liquids
349 significantly decreased from an initial 54 mM to a minimum of 16 mM, while Ca
350 concentrations gradually increased from 10 mM to 31 mM. Silica and Fe concentrations
351 increased rapidly from below the detection limit to ~ 4 mM and 0.06 mM, respectively, and
352 stayed relatively constant afterwards. Sulfate sulfur (S^{VI}) decreased over time in the
353 experiments, from 29 mM down to a minimum of 7 mM. Sulfide sulfur (S^{II-}) was only analyzed
354 in longer duration experiments and its concentrations were above the detection limit only in
355 experiment 'Low-*p*CO₂-Slow', where 9.5 μM was measured. Fluoride concentrations increased
356 significantly from the initial 40 μM to 277 μM after 5 days, but were systematically lower in
357 the longer duration experiments with a minimum of 8 μM. Similarly, Al concentrations
358 increased initially to 8 μM, but were at or below the detection limit of ~ 1 μM in the samples
359 collected at the end of the longer duration experiments.

360 During the high-*p*CO₂ experiments, the liquid composition evolved in a similar
361 direction as in the low-*p*CO₂ experiments, although the magnitude differed. Magnesium
362 decreased only to 46 mM and Ca increased to 12 mM. On the other hand, Si and Fe increased

363 to a greater extent in the high- $p\text{CO}_2$ experiments compared to the low- $p\text{CO}_2$ experiments, to
364 6.6 mM and 0.19 mM, respectively. Sulfate sulfur decreased slightly less, to 16 mM, and Al
365 and F evolutions are similar to the trends seen in the low- $p\text{CO}_2$ experiments.

366 In the experiments conducted with synthetic Mg-free seawater, the opposite trends
367 were observed for some elements. Magnesium in the liquid increased from below detection
368 limit to 5 mM, while Ca concentrations decreased initially to 4 mM before increasing again to
369 8 mM after 150 days. Furthermore, S^{VI} decreased less strongly in these experiments, to a
370 minimum of 23 mM. The liquids collected from the longest duration experiment in this series
371 had a F concentration of 897 μM , and an Al concentration of 11 μM , which is significantly
372 higher than in the other experiments. On the other hand, Si and Fe show similar increases in
373 this series compared to other experiments.

374 The highest Ca concentration was measured in experiment ‘Low- $p\text{CO}_2$ -Calcite’, which
375 was started in the presence of 102 mg of calcite seeds, corresponding to ~ 0.1 wt% of the total
376 solid mass. These seeds were added to accelerate the initial pH increase and alkalinity
377 generation and to assess the effect of the presence of small quantities on carbonation rates. The
378 presence of these seeds added up to 4.7 mM of Ca and 9.5 meq/kg of alkalinity to the liquid.
379 Similar effects potentially occur in natural systems where calcite is present in the host rocks.
380 For example, the basaltic oceanic crust can contain ~ 0.5 to 4.0 wt% carbonates (Gillis and
381 Coogan, 2011; Coogan and Gillis, 2013), and initial calcite dissolution likely occurred during
382 CO_2 -charged freshwater injection into basaltic rocks in Iceland (Snæbjörnsdóttir et al., 2017).

383 Liquid K, Na, and Cl concentrations remained close to constant throughout the
384 experiments as shown in Table 3 and the Figure S-3 in the Supplementary Material.
385 Nevertheless, the strong positive correlation between the Na and Cl concentrations of the
386 reacted seawater, with a Pearson r value of 0.89, suggests some water evaporation during the
387 experiments. As the gas in the reactor headspace contained relatively little water vapor, this
388 evaporated water was most likely present in condensed form in the inner magnetic drive rotors
389 and other accessories of the upper reactor assemblage, and/or evaporated during the initial
390 flushing of the reactor with CO_2 (see section 2.1). Significant loss of H_2O from the reactor
391 system is unlikely to have occurred because: (1) No significant correlation was found between
392 the experiment duration and Na or Cl concentrations, (2) the loss of water vapor would have
393 been accompanied by a CO_2 loss of a similar magnitude, and (3) all reactors were tested for
394 leaks by pressurizing them to a pressure significantly above those used during the experiments.

395 The redox potential of the sampled liquids decreased from the initially oxidizing
396 conditions ($p\text{E} \sim 4$ to 5) to moderately reducing $p\text{E}$ of around zero. This redox potential
397 evolution is shown in Figure 3. Assuming thermodynamic equilibrium of the redox couples,
398 these redox potentials indicate that practically all the aqueous iron is present as Fe^{II} (Figure 3).
399 This dominance of Fe^{II} suggests that the relatively small amounts of Fe^{III} released from the
400 basaltic glass were taken up by secondary phases such as clays and hematite (see below). At
401 this $p\text{E}$, practically no H_2S is expected to be present in the reactor, which agrees with the
402 measured H_2S concentrations, which were mostly below the detection limit (Table 3). It is
403 unclear, however, if redox equilibrium was achieved during the experiments as they were run
404 at 130 $^\circ\text{C}$ (e.g., Stumm and Morgan, 1996; Kaasalainen and Stefánsson, 2011). This prevents
405 a more detailed interpretation of these measurements.

406 3.2 Solid reaction products

407 The solids recovered from the reactors at the end of the experiments were markedly
408 altered. The bulk of the solids were found to be present as loose powder after the experiments.

409 SEM images, in conjunction with EDS and XRD analyses, revealed that significant amounts
 410 of the initially smooth and clean basaltic glass grain surfaces of the basalt were covered with a
 411 honeycomb-shaped layer of saponite, a trioctahedral smectite rich in Mg (Figure 4 A, C, D,
 412 Figure 5). The identity of these clays was verified by XRD as ferrous saponite, as indicated by
 413 broad and asymmetric reflections at $\sim 15 \text{ \AA}$ (d_{001}), 6.1 \AA (d_{002}), 4.5 \AA (d_{020}), 3.2 \AA (d_{004}), 2.6 \AA
 414 ($d_{13,20}$), 1.7 \AA ($d_{15,24,31}$) and 1.53 \AA (d_{060}) (\AA) (Decarreau et al., 2008; Baldermann et al., 2014). In
 415 some cases, the initial stages of smectite growth could be seen (Figure 4 D), and some basaltic
 416 glass grains almost completely covered by smectite were also found. In places the underlying
 417 glass surfaces could be seen beneath the smectite precipitate (Figure 4 C). Furthermore,
 418 rounded grains suggest significant dissolution of the initial basaltic glass (Figure 4 B).
 419 Anhydrite appears as elongated or platy particle shapes attached to existing basalt grains
 420 (Figure 4 E). Based on EDS spectra and the evidence from XRD (see below), precipitates with
 421 a pseudo-hexagonal form, twinning (c.f. Sand et al., 2012) and Ca, C and O composition were
 422 identified as aragonite (cf. Figure 4 F, from the experiment ‘Low-66-146’).

423 In addition to the minerals identified by SEM, XRD patterns of the retrieved powders
 424 indicate the presence of small amounts of aragonite in the solids recovered from most of the
 425 long-term experiments. Calcite was identified in the solids collected in experiments ‘Low-44’,
 426 ‘Low-57’, and siderite in experiments ‘Low-148’ and ‘Low- $p\text{CO}_2$ -Slow’. Ankerite was
 427 identified in the solids collected from experiment ‘Low-148’. Magnesite was identified in the
 428 solids collected after the longer high- $p\text{CO}_2$ experiment ‘High-140’ (see Figure 5 and the Figure
 429 S-6 in the Supplementary Material). Furthermore, XRD data show that zeolites and hematite
 430 were present in small amounts in the solids collected from some experiments. The only primary
 431 crystalline mineral phase detected by XRD was forsterite (in both the initial basalt as well as
 432 the reacted samples), while the majority of all samples is the basaltic glass starting material.

433 In some cases, material was found to be stuck to the reactor bottom in the form of a
 434 cone. This is likely due to the slower fluid dynamics below the stirrer. This was most
 435 pronounced in the experiment ‘Low- $p\text{CO}_2$ -Slow’, where stirring was reduced to 20 rpm for
 436 most of the experiment. No other correlations between the presence of powder stuck to the
 437 reactor bottom and experimental parameters were found. Furthermore, minor amounts of light-
 438 colored precipitates were found on reactor walls, thermowells, sampling dip-tubes and stirrer
 439 shafts. EDS spectra and XRD patterns suggest that these solids are mainly comprised of
 440 anhydrite and smectite.

441 3.3 Carbon content of the solids and carbon mass balance

442 The TIC present in the reacted solids measured by both methods described above are presented
 443 in Table 4 and Figure 6. These results show significant carbon uptake by the solids during the
 444 experiments. The agreement between both analytical methods is good, but the significant
 445 uncertainties of the furnace method at low CO_2 contents, as well as its higher detection limit,
 446 lead to small differences for some experiments. A further approach to estimating the amount
 447 of carbon mineralized during the experiments is via the determination of carbon remaining in
 448 the fluid phases at the end of each experiment. The total amount of carbon present in the reactor
 449 fluids (liquid and gas) can be estimated using thermodynamic principles from the temperature,
 450 total pressure, volumes of the respective phases, and the composition of the liquid including its
 451 alkalinity. This mass balance relation can be expressed as

$$452 \quad n_{\text{CO}_2}^{\text{Fluids}} = n_{\text{CO}_2}^{\text{Liquid}} + n_{\text{CO}_2}^{\text{Gas}} = \text{DIC} \cdot m^{\text{Liquid}} + \frac{p_{\text{CO}_2}}{P} \cdot \frac{V^{\text{Gas}}}{V_m}$$

453 where $n_{\text{CO}_2}^x$ stands for the molar amount of CO_2 in x , m^{Liquid} refers to the mass of liquid, P
454 designates the total pressure, and V^{Gas} and V_m denote the volume of the headspace and the molar
455 volume of the gas, respectively. Similar to other thermodynamic calculations in this study, p_{CO_2}
456 and V_m were calculated using PHREEQC. The difference between the carbon calculated to be
457 in the fluid phases at the beginning and end of the experiments equals that mineralized during
458 the experiments. These results of this calculation are provided in Table 4.

459 All methods used to determine the mass of carbon incorporated into the solids during
460 the experiments show a trend of increasing CO_2 mineralization with experiment duration. In
461 the low- $p\text{CO}_2$ series, around 19% of the total mass of carbon present in the reactor was
462 mineralized after 150 days. In comparison, the Mg-free experimental series exhibits ~ 33%
463 mineralization after 150 days (experiment MgFree-150). The solids recovered from both high-
464 $p\text{CO}_2$ experiments exhibited slow CO_2 release during acidification-TIC measurements
465 indicating the presence of magnesite. Furnace-TIC measurements indicate ~ 14% of the CO_2
466 mineralized after 140 days in the high- $p\text{CO}_2$ experimental series. This is slightly less than that
467 over this time frame during the low- $p\text{CO}_2$ experiments. However, the absolute amount of CO_2
468 mineralized in the high- $p\text{CO}_2$ experiments is significantly higher due to the higher mass of CO_2
469 introduced into the reactor at the beginning of these experiments. Expressed as CO_2 wt% in the
470 solids, the longest duration high- $p\text{CO}_2$ experiment had 0.37 wt% CO_2 in the recovered solids
471 while the longest duration low- $p\text{CO}_2$ experiment had only ~ 0.11 wt% CO_2 in the recovered
472 solids.

473 The highest mineralization of $55 \pm 9\%$ CO_2 was measured in the experiment ‘Low-
474 $p\text{CO}_2$ -Calcite’ which was ran with calcite seeds. The calcite seeds rapidly dissolved under the
475 acidic conditions prevailing at the beginning of the experiments, increasing the liquid pH, Ca
476 concentration, and alkalinity. XRD or SEM analysis indicates the initial calcite seed crystals
477 were completely dissolved during the experiments. A similar high carbon mineralization ($53 \pm$
478 4% CO_2) is suggested by mass balance calculations for the ‘Low- $p\text{CO}_2$ -Slow’ experiment.
479 While the three methods for measuring carbon mineralization generally show a relatively good
480 agreement with each other, differences exist. A notable example is the experiment MgFree-
481 140, where mass balance calculations suggest minor CO_2 mineralization, while both methods
482 for quantification of carbonates in the solids revealed a higher CO_2 mineralization. The reason
483 for these differences is unclear.

484 4 Discussion

485 4.1 General trends of seawater-basalt- CO_2 interaction

486 As evident in Figure 2, basalt dissolution causes a rapid initial increase in alkalinity and
487 pH in all experiments. Subsequently, the pH is buffered by a balance between basalt dissolution
488 and secondary mineral precipitation as well as by the presence of bicarbonate. Otherwise, the
489 evolution of the aqueous chemistry differs among the experimental series due to distinct
490 secondary mineral formation behaviour. In the low- $p\text{CO}_2$ series, substantial smectite clay
491 precipitation, as seen in XRD and SEM observations (Figure 4 and Figure 5), leads to a strong
492 decrease in aqueous Mg concentrations and low aqueous Fe concentrations. At higher $p\text{CO}_2$,
493 smectite clay precipitation is significantly less pronounced, as suggested by the smaller
494 decrease in aqueous Mg concentrations and higher Fe concentrations. As aqueous Al
495 concentrations remain low in both of these experimental series, it is likely that a poorly
496 crystalline aluminosilicate phase such as allophane or amorphous Al-hydroxides formed
497 consuming aqueous Al. In many experiments, aqueous Al concentrations were below the

498 detection limit of $\sim 1 \mu\text{M}$, allowing only the calculation of maximum saturation indices (SI)
499 for relevant aluminosilicates (Figure S-4 in the Supplementary Material). Nevertheless,
500 allophane was potentially at saturation, and Mg-saponite was potentially significantly
501 oversaturated, but less so in the high- $p\text{CO}_2$ series, in agreement with the trends described
502 above. Thermodynamic calculations also suggest that chalcedony is slightly oversaturated in
503 the sampled liquids (Figure 7), indicating that this phase potentially formed even though it was
504 not detected by XRD. This may be due to the fine-grained nature of this phase (Gíslason et al.,
505 1997). In both experimental series run in natural seawater, basalt dissolution releases Ca to the
506 liquid, eventually leading to anhydrite precipitation. This results in a decrease in aqueous S^{VI}
507 concentrations. The rapid anhydrite precipitation is further evidenced by the saturation indices
508 at the end of the experiments, which were close to equilibrium with respect to anhydrite (see
509 Figure 7). Although Fe is mostly released from the basalt in reduced form, the reduction of S^{VI}
510 to S^{II} appears to be negligible (Table 3), preventing Fe-sulfide mineral precipitation.
511 Furthermore, the aqueous solutions became supersaturated with respect to different carbonate
512 minerals due to increases in pH, alkalinity, and aqueous Ca (and Fe) concentrations (Figure 7).
513 This leads to carbonate mineral precipitation, which is discussed in detail in the following
514 sections.

515 Experiments run in the presence of Mg-free seawater exhibit several differences
516 compared to those run in natural seawater. While the pH is buffered at similar or slightly higher
517 values compared to natural seawater, no strong decrease in alkalinity was observed. The lack
518 of Mg in the liquid leads to the formation of zeolite minerals instead of smectite clays as seen
519 in the XRD data (Figure 5). The formation of zeolite minerals consumes aqueous Ca. The high
520 aqueous Al concentration measured in liquids of this series after 150 days is likely a
521 consequence of the formation of Al-F aqueous complexes due to elevated aqueous F
522 concentrations (Tagirov and Schott, 2001).

523 4.2 Reaction path simulations

524 Reaction path calculations were performed to estimate the mass of secondary minerals
525 precipitated during the individual experiments. This was not possible to determine directly
526 from the experiments due to the large number of reacting phases and their variable composition.
527 The reaction path models were calibrated against the first 150 days of data from each
528 experimental series. The calibrations took account of the observed identity of secondary
529 phases, the liquid compositions, and the amount of CO_2 mineralized in the three experimental
530 series: low- $p\text{CO}_2$, high- $p\text{CO}_2$, and Mg-free. While two experiments were run for 204 and 228
531 days (experiments Low- $p\text{CO}_2$ -Slow and Low- $p\text{CO}_2$ -Calcite), both of these represent special
532 conditions. One was run at slow stirring rates, and one contained 102 mg calcite seeds to
533 accelerate initial reactions. As it is unclear how much influence these conditions had on the
534 reaction progress, they were not included in the calibration of the reaction path calculations.

535 The secondary phases considered in the models were restricted to those observed by
536 SEM and XRD analysis, notably Mg-Mg and Mg-Fe saponite, anhydrite, hematite, Ca-stilbite,
537 aragonite or magnesite for low- and high- $p\text{CO}_2$, respectively. Chalcedony and allophane were
538 included as well, although these phases are not detectable by XRD. The total amount of basaltic
539 glass dissolved was adjusted to fit the observed liquid compositions for the reaction progress
540 during the ~ 5 month experiments. A slight adjustment of the solubilities of some phases was
541 made to improve the fit of the measured liquid compositions. A list of the revised equilibrium
542 constants is provided in Table S-1 in the Supplementary Material. These adjustments of mineral
543 solubility are within the uncertainties associated with the thermodynamic data under such

544 conditions (e.g., Voigt et al., 2018a). Furthermore, the equilibrium constants for secondary
545 aluminosilicate precipitation reactions had to be increased substantially compared to those of
546 the Voigt et al. (2018a) database to reproduce the observed liquid composition trends of the
547 experiments (see Table S-1 in the Supplementary Material). This is most likely due to the
548 sluggish precipitation kinetics of these minerals compared to the other secondary phases.
549 Without these equilibrium constant changes, these aluminosilicates are predicted to rapidly
550 consume most of the alkalinity generated by the basaltic glass dissolution, impeding carbonate
551 mineral precipitation. This observation highlights the importance of slow aluminosilicate
552 precipitation vs faster carbonate mineral precipitation for carbon mineralization. Note that it is
553 unclear if aluminosilicate precipitation would become dominant over timescales beyond those
554 of our experiments, as proposed by Rigopoulos et al. (2017). It was not possible to accurately
555 reproduce the observed experimental trends assuming secondary phases precipitated at local
556 equilibrium together with a laboratory-measured basaltic glass dissolution rate equation. This
557 suggests that secondary silicate mineral precipitation is the overall rate determining process of
558 the coupled basalt dissolution/carbonate precipitation process. Note that secondary
559 aluminosilicate precipitation removes substantial Si and Al from the liquid and lowers the pH,
560 which both cause the reactive liquid to remain strongly undersaturated with respect to hydrated
561 basaltic glass, promoting its dissolution. This is consistent with the observation that doubling
562 the amount of basalt in the reactor, i.e. a reduction of the water/rock (W/R) ratio, did not
563 significantly increase the amount of CO₂ mineralization (Figure 6). This indicates that the
564 reactive surface area of the basalt is not directly correlated to the degree of CO₂ mineralization
565 observed in our experimental series.

566 To compare and calibrate the results of the reaction path models to the experiments,
567 reaction time was calculated as a linear function of dissolved basaltic glass. To achieve a good
568 fit to the experimental data, between 40% to 80% faster dissolution was assigned to the first 50
569 days of the models compared to the subsequent days. This model approach reflects the natural
570 environment in so far that secondary clay precipitation on altered basalt surfaces potentially
571 slows dissolution. After such adjustments, the resulting calculated liquid concentrations and
572 carbonation rates reproduce the observed experimental trends relatively well (see Figure S-5
573 in the Supplementary Material). Nevertheless, some differences exist, such as a poor estimation
574 of pH and thus also alkalinity in the low-*p*CO₂ simulation.

575 The results of the calculations, as shown in Figure 8, suggest that different amounts of
576 basaltic glass dissolution were required to achieve the experimentally observed liquid
577 compositions and mass of CO₂ mineralization after 5 months. Specifically, the dissolution of
578 12.5 g of basalt per kg of water was required to reproduce the observations of the low-*p*CO₂
579 experiments, 6.7 g of basaltic glass dissolution was required per kg of water to reproduce the
580 observations of the high-*p*CO₂ experiments, and 3.3 g of basaltic glass dissolution was required
581 per kg of water to reproduce the observations of the Mg-free seawater experiments. These
582 differences may stem from the significantly larger amount of saponite precipitation in the low-
583 *p*CO₂ experiments; saponite precipitation removes Si and Al from the liquid promoting further
584 basaltic glass dissolution. The only (alumino)silicate minerals predicted to form in significant
585 amounts during the high-*p*CO₂ experiments are allophane and chalcedony. The only
586 (alumino)silicate mineral predicted to form in significant amounts during the Mg-free
587 experiments is Ca-stilbite (see Figure 8). Such computed results are consistent with
588 observations from the solids recovered after the experiments. Small amounts of anhydrite
589 formation are predicted in all experimental systems due to the release of Ca from the basaltic

590 glass. Rapid early anhydrite formation is only predicted to occur from basaltic glass interaction
591 with the synthetic Mg-free seawater at 130 °C due to the lack of aqueous Mg-SO₄
592 complexation; this complex increases anhydrite solubility in natural seawater.

593 The reaction path models give new insights into the mineralogical and chemical
594 differences of the solids and liquids observed among the different experiment series. The lack
595 of saponite precipitation from the synthetic Mg-free seawater experiments leads to higher
596 alkalinity and thus a higher degree of carbon mineralization during the experiments (Figure 8).
597 As saponite formation is also largely suppressed in the high-*p*CO₂ experiments, and aqueous
598 Mg is consumed by magnesite precipitation, as seen in the experiments, the absolute amount
599 of CO₂ mineralization is significantly higher under these conditions. At the same time,
600 however, the degree of CO₂ mineralization during the high-*p*CO₂ experiments is comparable
601 to the low-*p*CO₂ series, as significantly more CO₂ was introduced into the system in the former.

602 4.3 Identity of carbonate minerals

603 The predominant carbonate mineral identified in the reacted solids of most experiments
604 was aragonite, with some experiments also producing calcite, siderite, ankerite, and magnesite
605 (Figure 5). The predominance of aragonite over calcite as CaCO₃ polymorph is in agreement
606 with studies of young (< 15 Ma) marine sediments and hydrothermal crustal aquifers showing
607 the widespread presence of aragonite (Coogan and Gillis, 2018). Older marine carbonates are
608 dominated by calcite. This is interpreted to be caused by a lower Mg/Ca concentration ratio of
609 seawater during the time of mineral formation (Morse et al., 1997; Stanley and Hardie, 1998,
610 1999). No such correlation could be found in our experiments, as aragonite was formed in
611 experiments performed in either natural seawater or synthetic Mg-free seawater. Calcite was
612 observed only from the solids recovered from the relatively short duration experiments, while
613 aragonite was predominant in longer experiments. This observation is potentially due to
614 slightly higher initial supersaturation of the liquid with respect to calcite during the shorter
615 experiments (Figure 7), although this could also be affected by the precipitation kinetics of
616 these two minerals. The results of this study contrast with that of Shibuya et al. (2013), who
617 reacted a CO₂-charged NaCl brine with basalt at 250 °C and 350 °C and an initial DIC of 400
618 mM. The carbonate mineral formed during these experiments was calcite even after ~ 3 months
619 of experiment. It is unclear if the difference between the results of the Shibuya et al. (2013)
620 experiment and those of the present study is due to their higher temperature, higher initial DIC,
621 or different initial reactive solution composition. Similarly, calcite was the only authigenic
622 carbonate mineral found in drill cores recovered from the Surtsey geothermal system, a
623 seawater-dominated and basalt with fluid temperatures of 40-141 °C (Kleine et al., 2020). As
624 Mg and Ca concentrations observed in this system are similar to those in our experiments, the
625 reason for this difference is unclear. Calcite is also the only carbonate mineral found in the
626 Reykjanes system, where fluids close to seawater composition circulate through a basaltic
627 hydrothermal system (Wiese et al., 2008; Marks et al., 2010). The fact that the fluids in the
628 Reykjanes system are heated and undergo fluid-rock interaction at temperatures of ~ 260 to
629 310 °C, much higher than in our experiments, make the identification of the reason for this
630 difference difficult. Potential reasons for the difference in carbonate mineralogy between this
631 natural system and our experiments include i) the depletion of the fluids in Mg or other
632 elements due to fluid-rock interaction before carbonate precipitation occurred, and ii) the
633 presence of minerals such as illite, chlorite, epidote, garnet, and pyrite in the system (Marks et
634 al., 2010).

635 Thermodynamic calculations indicate that the final reactive liquids in all of our
636 experiments were close to or supersaturated with respect to aragonite, ankerite, and siderite
637 (Figure 7), while the initial CO₂-charged seawater was undersaturated with respect to these
638 minerals. This change is mainly due to the increase in pH, associated with changes in the
639 speciation of DIC. Similar saturation index evolutions are observed for calcite, magnesite, and
640 dolomite. The absence of the latter two minerals from the solids recovered from all experiments
641 other than those performed at high-*p*CO₂ could stem from kinetic inhibition. Magnesite
642 precipitation was only observed in the higher *p*CO₂ experiments performed in this study. It is
643 unclear whether this observation stems from the higher DIC, lower pH, and/or the lower
644 amount of smectite precipitation of these experiments. As smectite precipitation reduces
645 dissolved Mg concentrations in natural marine hydrothermal fluids at temperatures above ~ 60
646 °C (Coogan and Gillis, 2018), the low amount of smectite formed in our experiments is likely
647 a key for magnesite formation. This conclusion is consistent with that of Rosenbauer et al.
648 (2012), who observed ferroan magnesite formation during the reaction between a CO₂-charged
649 NaCl brine with basalt at ≥ 1 M DIC and temperatures from 100 to 200 °C.

650 No correlation between the observation of siderite/ankerite in some solids and
651 experimental conditions or liquid compositions is evident, as these two carbonate minerals only
652 precipitated during two experiments. Thermodynamic calculations indicate that the
653 experimental liquids showed the highest supersaturation with respect to dolomite, and, in
654 descending order, ankerite, magnesite, siderite, calcite, and aragonite. The fact that the most
655 abundant mineral found in the experimental solids is aragonite, and magnesite for the high-
656 *p*CO₂ experiments, highlights the importance of factors other than thermodynamics influencing
657 the identity of precipitating carbonate minerals.

658 4.4 Comparison to freshwater systems

659 Although no experiments with fresh or pure water were performed in this study, the
660 results can be compared to previous studies. Gysi and Stefansson (2012b) performed two batch
661 experiments at 150 °C, reacting CO₂ charged freshwater with basaltic glass powder of the same
662 origin as in this study (Stapafell, Iceland) at an initial water/rock ratio of 5 for 26 and 123 days,
663 respectively. The DIC concentration of their reactive liquid decreased from ~ 100 to ~55 mM
664 during their 123 day experiment, and to ~70 mM during their 26 day experiment. While this
665 decrease in DIC is of the same magnitude as the CO₂ mineralization rates observed in the
666 present study under comparable conditions (the high-*p*CO₂ series), the DIC decrease reported
667 by Gysi and Stefansson (2012b) was not exclusively due to carbon mineralization. Gysi and
668 Stefansson (2012b) sampled their batch reactors periodically to monitor the liquid phase
669 composition, thereby increasing the headspace volume. This leads to a degassing of the
670 aqueous solution, lowering its DIC concentration. As a result, the pH of the reactive liquids in
671 the Gysi and Stefansson (2012b) experiments increased to pH 6.4 at the end of their 123 day
672 experiment, while the pH remained close to constant at pH ~5 in our high-*p*CO₂ experiments.
673 This difference is potentially related to the low Mg concentration of their initial freshwater,
674 such that less clay mineral precipitation occurred. Clay mineral precipitation buffers pH and
675 alkalinity as it liberates protons to the liquid phase (e.g., Voigt et al., 2020). Note, however,
676 that a number of other studies reported substantial clay mineral formation in experiments using
677 freshwater for CO₂ mineralization studies of basalts and anorthite (e.g., Hangx and Spiers,
678 2009; Munz et al., 2012; Hellevang et al., 2017; Gadikota et al., 2020). A further difference
679 between the seawater and freshwater experiments can be seen in the carbonate mineralogy.
680 While only calcite formation was observed at 150 °C in the freshwater experiments of Gysi

681 and Stefansson (2012b), our study observed calcite formation only in some shorter duration
682 experiments, while the majority of the experiments show mostly aragonite or magnesite
683 formation. This observation is in agreement with field evidence. Carbonate mineral formation
684 during freshwater-basalt-CO₂ interaction during the CarbFix injections (Matter et al., 2016;
685 Snæbjörnsdóttir et al., 2017; Strandmann et al., 2019) is dominated by calcite formation,
686 whereas aragonite formation is predominant in young marine sediments and hydrothermal
687 settings (Coogan and Gillis, 2018). The absence of magnesite in the aforementioned freshwater
688 experiments is most likely due to the lack of Mg in the initial liquid, suggesting that the use of
689 seawater for CO₂ mineralization efforts could be advantageous if the dissolved Mg is consumed
690 by carbonation reactions instead of or along with aluminosilicate formation reactions.

691 4.5 Implications for mineral carbon storage

692 The formation of carbonate minerals due to interaction of CO₂-containing seawater with
693 basaltic rocks is a natural process leading to the drawdown and storage of globally significant
694 amounts of CO₂, and thus climate regulation, over geologic timescales (Staudigel et al., 1989;
695 Brady and Gíslason, 1997; Alt and Teagle, 1999; Coogan and Gillis, 2013; Isson et al., 2020).
696 This occurs in low-temperature hydrothermal systems in the basaltic oceanic crust, where
697 carbonate abundances reach up to ~ 4 wt% (e.g., Gillis and Coogan, 2011; Coogan and Gillis,
698 2013), mostly precipitating during the first 20 million years after crust formation. In this study,
699 we presented experimental evidence that this process can be significantly accelerated by
700 reacting seawater charged with high *p*CO₂ with basalt at 130 °C, leading to substantial CO₂
701 mineralization within several months. The effect of different initial conditions, most
702 importantly *p*CO₂ and seawater composition (standard seawater vs. Mg free seawater), was
703 studied in different sets of experiments. Up to around 20% of the total CO₂ contained in the
704 reactor was mineralized after 5 months both at ~ 2.5 bar and ~ 16 bar initial *p*CO₂ (26 and 125
705 mM DIC, respectively). CO₂ mineralization of over 50 % was observed after > 200 days in
706 experiments that started in the presence of ~ 0.1 wt% calcite or run with reduced stirring rates.
707 However, it is unclear how much of this increased mineralization can be attributed to longer
708 run times as opposed to these experimental conditions. Nevertheless, such an effect would be
709 relevant to natural basalt reservoirs containing pre-existing carbonate minerals formed by
710 natural weathering and fluid-rock reactions. In the high-*p*CO₂ experiments, magnesite was
711 formed as opposed to aragonite at lower initial *p*CO₂, and significantly less voluminous
712 smectite clay formation was observed. This, in combination with the higher absolute amounts
713 of CO₂ mineralization, makes such conditions particularly attractive for mineral carbon storage
714 applications. Furthermore, a higher initial DIC concentration allows injection of the same
715 quantity of CO₂ with fewer wells due to the reduced amount of liquid injected. This will reduce
716 the significant costs for the drilling of wells.

717 A temperature of 130 °C was chosen for our experiments to avoid rapid anhydrite
718 formation when seawater is heated to temperatures exceeding 150 °C (Bischoff and Seyfried,
719 1978). Observations and reaction path modelling suggest only limited anhydrite formation at
720 130 °C. Therefore, this temperature should be regarded as the upper limit to avoid rapid
721 anhydrite formation that could potentially lead to fluid pathway clogging close to CO₂ injection
722 wells. The Mg-free seawater experiments were designed to see if the formation of voluminous
723 smectite clays could be avoided at low-*p*CO₂ conditions. This appears to be the case, as zeolites
724 where formed instead of clays, and CO₂ mineralization was higher compared to experiments
725 started with natural seawater (see Figure 8). However, rapid anhydrite precipitation occurs in

726 this case due to the lack of Mg-SO₄ complexation, potentially leading to clogging of fluid
727 pathways close to the injection site.

728 The magnitude of mineralization observed in the CO₂ charged seawater experiments
729 performed in this study is comparable to that observed in experiments conducted with
730 freshwater (Gysi and Stefánsson, 2012b). This suggests that subsurface carbon storage using
731 seawater, similar to existing injections in freshwater systems (Matter et al., 2016; Clark et al.,
732 2020) is feasible. As opposed to freshwater, injection of CO₂-charged seawater has the
733 advantage of a lower price, much greater availability, and avoidance of potential water use
734 conflicts. Furthermore, vast amounts of CO₂ can be stored in the basaltic oceanic crust; Marieni
735 et al. (2013) estimated that $\sim 3 \times 10^5$ Gt CO₂ can be potentially stored in deep-sea basalt at water
736 depths > 5000 m. Finally, offshore storage could reduce public acceptance and political issues
737 associated with onshore CCS projects, as such offshore mineral carbon storage through CO₂-
738 charged seawater injection has the potential to significantly increase the global relevance of
739 such techniques.

740 The extrapolation of the results of this study to natural and/or engineered subsurface
741 sites is complicated by large uncertainties of reactive surface areas in natural rocks as well as
742 the effect of fluid dynamics on rates. To address such issues, it is common to adjust reaction
743 rates by up to several orders of magnitude when fitting reactive transport models to field results
744 (Aradóttir et al., 2012; Beckingham et al., 2016, 2017). Nevertheless, our experimental results
745 indicate that different initial W/R ratios did not significantly change the amount of CO₂
746 mineralization (Figure 6, section 4.2). This highlights the importance of secondary mineral
747 precipitation rates as opposed to the reactive surface area of the primary basalt. Therefore,
748 similar timescales of mineralization might be realized on laboratory vs. field scales even if
749 reactive surface areas of the primary rocks are substantially different. Our reaction path models
750 indicate slowing reactions over time during the experiments, which may be due to secondary
751 aluminosilicate precipitation on primary basaltic glass surfaces. Similar processes might occur
752 on field scales. However, it remains to be clarified to what degree secondary mineral
753 precipitation slows mineralization processes over the long term. In the field, the formation of
754 voluminous secondary minerals potentially modifies or clog fluid flow pathways. Evidence
755 from altered oceanic crust, however, suggests that substantial porosity is maintained despite
756 such clogging processes (e.g., Fisher, 1998; Jarrard et al., 2003; Johnson and Pruis, 2003).

757 5 Conclusions

758 This study demonstrated the efficiency of carbon mineral formation from CO₂-charged
759 seawater during its interaction with fresh basaltic glass. If a similar efficiency of this reaction
760 can be demonstrated in the field, it may provide a powerful approach for the safe, long-term,
761 and cost-effective storage of CO₂ at many sites around the world. Due to the widespread
762 availability of seawater in the vicinity of basalt and its low cost, such reactions could enable
763 significant upscaling of CCS through mineral carbon storage. CO₂ mineralization of over 30
764 % was observed in experiments after > 150 days. These rates were potentially further
765 accelerated in the presence of ~ 0.1 wt% calcite seeds. As small quantities of calcite are
766 common in basaltic rocks, such acceleration might be at work in many subsurface systems.

767 The experimental results also provide insight into the role of non-carbonate secondary
768 minerals in subsurface mineral carbonation efforts. Pore clogging secondary minerals such as
769 smectite can be detrimental to the long-term efforts as they may limit well injectivity over time.
770 Experimental results in this study suggest that the precipitation of such minerals can be delayed

771 or even avoided by controlling the composition of the injected CO₂-charged liquid.
772 Specifically, raising the *p*CO₂ from ~ 2.5 bar to ~ 16 bar resulted in the formation of magnesite
773 as the exclusive carbonate mineral while smectite formation was largely suppressed. Also,
774 experiments started with synthetic Mg-free seawater resulted in the formation of zeolites
775 instead of clay minerals and higher CO₂ mineralization rates. Further efforts could be made to
776 explore how to best limit the formation of such pore clogging minerals to better exploit
777 subsurface pore space for geologic carbon storage.

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1062

1063 **Tables**1064 Table 1: Summary of previous experimental studies on basalt-CO₂-seawater or NaCl-brine
1065 interaction.

Study	Reactor type	Aqueous matrix	T / °C	DIC / mM	pH	Carbonate precipitation
Brady and Gíslason (1997)	Flow-through	Seawater	25-50	~ 0.01 – 0.1		No
Wolff-Boenisch et al. (2011)	Mixed flow	Seawater	25	~ 100	3.6	No
Rosenbauer et al. (2012)	Reaction cell	NaCl brine	50 – 200	1000		Magnesite
Shibuya et al. (2013)	Reaction cell	NaCl brine	250, 350	400	7.6, 8.7	Calcite
Luhmann et al. (2017)	Flow-through	NaCl brine	150	650	3.3	Siderite indicated by modelling
Rigopoulos et al. (2017)	Batch reactor	Seawater	~ 25	< 1	8.6	Aragonite
Wolff-Boenisch and Galeczka (2018)	Mixed flow	Seawater	90	40 – 400	7 – 7.7	Calcite, magnesite, Ca/Mg-carbonates
Marieni et al. (2020)	Batch reactor	Seawater	40	~ 30	~ 4.7	No

1066

1067

1068 Table 2: Initial conditions of all experiments with their durations. W/R = water/rock ratio.

Exp.	Duration / days	$T / ^\circ\text{C}$	$P_{\text{Start}} / \text{bar}$	$p\text{CO}_{2,\text{Start}} / \text{bar}$	pH ^a	SW / g	Basalt / g	W/R	Alk. / meq/kg
Low-0.1 ^b	0.08	130	4.81	2.54	5.10	216	86.0	2.5	2.24
Low-5	5	130	4.89	2.63	5.09	230	46.1	5.0	2.24
Low-19	19	130	4.65	2.38	5.13	461	92.0	5.0	2.24
Low-44	44	130	4.59	2.32	5.18	461	92.1	5.0	2.46
Low-57	57	130	4.70	2.43	5.12	461	92.0	5.0	2.25
Low-102	102	130	4.71	2.44	5.13	214	86.0	2.5	2.29
Low-148	148	130	4.78	2.51	5.12	230	46.0	5.0	2.29
Low-150	150	130	5.02	2.75	5.07	216	86.0	2.5	2.25
High-56	56	130	18.22	15.81	4.35	216	86.0	2.5	2.25
High-140	140	130	18.11	15.69	4.35	216	86.1	2.5	2.22
MgFree-60 ^e	60	130	4.77	2.49	5.21	461	92.0	5.0	2.25
MgFree-150 ^e	150	130	4.73	2.46	5.21	216	86.4	2.5	2.25
Low-66-146	66,146	130	4.48	2.22	5.17	462	92.0	5.0	2.29
Low- $p\text{CO}_2$ -Slow ^d	204	130	4.64	2.38	5.12	217	86.0	2.5	2.16
Low- $p\text{CO}_2$ -Calcite ^c	228	130	4.94	2.67	5.09	215	86.0	2.5	2.29

1069 ^a Calculated for experimental conditions from P_{Start} , alkalinity, liquid composition, and
1070 thermodynamic relationships. ^b Experiment stopped after ~ 2 h to estimate amount of basalt
1071 dissolution during CO_2 addition, before reactors were completely sealed ^c 102 mg calcite seed crystals
1072 (Riedel-de Haën puriss. p.a.) were added to the reactor. ^d Stirring rate was decreased to 20 rpm after
1073 69 days. ^e synthetic Mg-free seawater was used as the initial reactive liquid
1074

Table 3: Compositions of initial liquids used as reactant and aqueous solutions in mM sampled at the end of each batch experiment. pH and pE are given for *in situ* conditions. Uncertainties of values are approximately $\pm 3\%$ (95% confidence interval) of their values except for alkalinity ($\pm 0.5\%$), pH (± 0.06), DIC (± 3 mM), pE (± 0.2), and explicitly stated uncertainties for Fe and Al. Quantification limits were $\sim 4 \mu\text{M}$ for Al, $\sim 1 \mu\text{M}$ for Fe, ~ 0.02 mM for Si, and $\sim 1 \mu\text{M}$ for $\text{S}^{\text{II-}}$, below which values are shown as ‘BQL’. NA = not analyzed.

Sample	Na	Mg	S^{VI}	Ca	K	Si	Fe	\pm	Al	\pm	$\text{S}^{\text{II-}}$	Cl	F	Alk. / meq/kg	DIC	pH	pE
Initial Seawater	513	54	28.9	10.3	10.6	BQL	BQL	BQL	BQL	BQL	NA	584	0.040				
Synthetic Mg-free SW	452	0.0114	26.7	9.4	10.5	BQL	BQL	BQL	BQL	BQL	NA	429	0.051				
Low-0.1	524	54	29.6	12.8	10.5	2.82	0.082	0.002	BQL	BQL	NA	598	0.045	7.33	27	5.61	NA
Low-5	548	54	29.2	14.5	11.1	3.11	0.0174	0.0006	0.0078	0.0004	NA	614	0.227	7.27	28	5.58	4.22
Low-19	540	44	20.7	16.0	11.0	3.17	0.0321	0.001	BQL	BQL	NA	606	0.017	8.55	26	5.72	4.87
Low-44	541	32.0	16.1	23.4	10.9	3.4	0.037	0.001	BQL	BQL	NA	604	0.009	7.37	25	5.66	NA
Low-57	520	29.3	13.7	22.4	10.7	3.4	0.0317	0.0010	BQL	BQL	BQL	591	0.010	7.12	24	5.66	5.23
Low-102	574	24.3	9.8	26.4	11.8	3.5	0.0339	0.001	0.00099	0.0002	NA	662	0.016	4.86	21	5.50	3.28
Low-148	568	24.0	10.0	25.1	11.7	3.7	0.0304	0.0010	BQL	BQL	NA	650	0.016	4.37	21	5.45	NA
Low-150	556	27.7	19.3	30.9	11.2	3.8	0.056	0.002	BQL	BQL	NA	626	0.014	5.72	21	5.60	4.65
High-56	528	50	26.1	10.9	10.5	5.4	0.170	0.005	BQL	BQL	BQL	614	0.082	10.90	121	5.04	5.03
High-140	524	46	16.1	12.3	10.3	6.6	0.189	0.006	BQL	BQL	BQL	618	0.101	9.38	105	5.03	1.73
MgFree-60	490	4.2	23.3	3.5	10.6	3.15	0.00278	0.0001	BQL	BQL	BQL	461	0.113	8.35	24	5.87	4.65
MgFree-150	543	5.4	25.9	8.3	11.7	3.9	0.036	0.001	0.0112	0.0005	BQL	502	0.897	9.24	27	5.83	-0.16
Low-66	536	30.1	16.4	26.5	10.6	3.9	0.036	0.001	0.00171	0.0002	NA	627	0.010	6.60	22	5.67	NA
Low-146	570	19.4	13.2	31.4	11.2	3.7	0.0265	0.0008	BQL	BQL	NA	644	0.008	4.14	14	5.66	1.73
Low- <i>p</i> CO ₂ -Slow	506	16.2	6.9	25.8	11.4	3.5	0.0314	0.0010	BQL	BQL	0.0095	591	0.011	3.51	12	5.66	0.19
Low- <i>p</i> CO ₂ -Calcite	583	17.3	17.0	41	11.7	4.3	0.040	0.001	BQL	BQL	NA	698	0.041	5.15	17	5.66	NA

Table 4: Total inorganic carbon (TIC) contained in the solids retrieved at the end of each batch experiment, expressed as wt% of the solid and as the percentage of the original total CO₂ in the reactor contained in the solids at the end of the experiment. Values were measured by acidification and NDIR, heating in a furnace and solid state IR, and estimated by mass balance calculations (see text). Relative uncertainties for the acidification method are ~ 6%. BDL = Below detection limit; NA = not analyzed; Acidif. = Acidification.

Exp.	CO ₂ / wt% of solids					CO ₂ mineralization / %				
	Acidif.	Furnace	±	Mass balance	±	Acidif.	Furnace	±	Mass balance	±
Initial	0.00133	BDL	BDL							
Low-0.1	0.00026	BDL	BDL	0.00	0.03	0.053	BDL	2	0	6
Low-5	0.00020	BDL	BDL	0.00	0.06	0.021	BDL	BDL	0	5
Low-19	0.00049	BDL	BDL	0.01	0.05	0.057	BDL	BDL	1	6
Low-44	0.056	0.08	0.02	0.02	0.05	6.6	9	3	2	7
Low-57	0.044	0.08	0.02	0.06	0.06	5.0	9	3	7	6
Low-102	0.073	0.12	0.03	0.08	0.03	15.4	25	6	17	5
Low-148	0.084	BDL	BDL	0.18	0.06	9.0	BDL	BDL	19	5
Low-150	0.099	0.23	0.04	0.14	0.04	19	44	8	28	5
High-56	NA	0.09	0.03	0.14	0.05	NA	3.5	1.0	5	1
High-140	NA	0.37	0.05	0.44	0.10	NA	14	2	17	1
MgFree-60	0.0166	0.12	0.03	0.14	0.06	1.8	13	3	16	6
MgFree-150	0.155	0.15	0.03	0.02	0.03	33	32	7	3	6
Low-66-146	0.147	0.03	0.01	0.14	0.06	18	4	2	17	6
Low- <i>p</i> CO ₂ -Slow	0.100	0.16	0.03	0.24	0.05	22	35	8	53	4
Low- <i>p</i> CO ₂ -Calcite	0.27	0.31	0.05	0.26	0.05	48	55	9	47	3

Figures

Figure 1: Schematic illustration of the reactor assemblage used for experiments in this study.

Figure 2: Composition of reacted seawater after its interaction with basalt powder and CO₂ at 130 °C in batch experiment of various durations. pH and DIC were calculated from measured alkalinity and pressure for *in situ* temperature conditions. The arrows show major trends observed in the compositions. Note that individual experiments were run at distinct conditions varying initial *p*CO₂, seawater composition, and stirring rate accounting for some of the scatter among these trends. Analytical uncertainties (95% confidence level) are smaller than the symbol size in all cases.

Figure 3: Redox potential, reported as pE, of the sampled reactive liquids, re-calculated for *in situ* temperature conditions, and fraction of Fe²⁺ in total Fe in these reactive liquids calculated based on this redox potential assuming thermodynamic equilibrium. The dashed line shows the Fe²⁺ fraction of the dissolving basaltic glass. Analytical uncertainties (95% confidence interval) are similar to the symbol size.

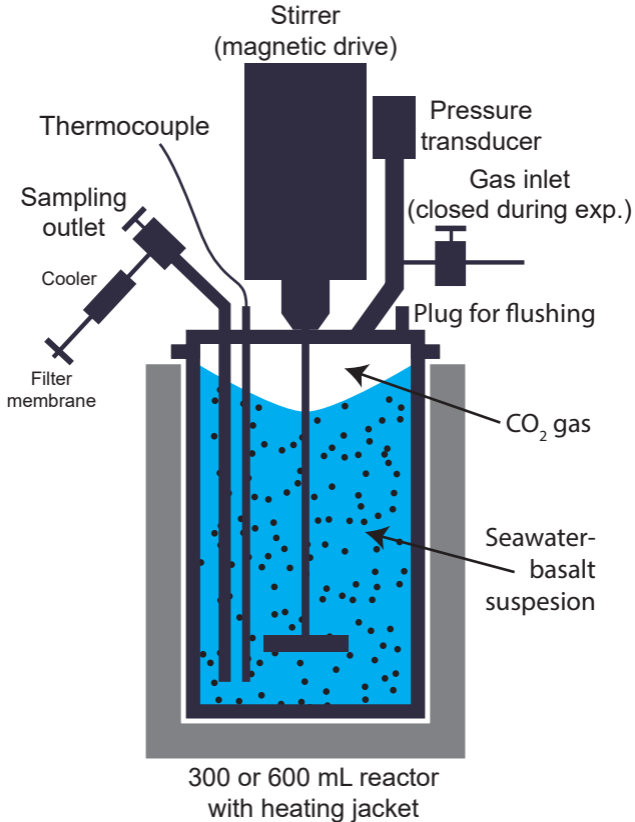
Figure 4: Secondary electron microscopy (SEM) microphotographs of (A) the initial basaltic glass powder used as reactant, and the solid reaction products collected after experiments (B,C) Low-148, (D) High-140, (E) Low-148, and (F) Low-66-146. The last image also shows an overlay of the morphology of pseudo-hexagonal aragonite twins, modified after Sand et al. (2012).

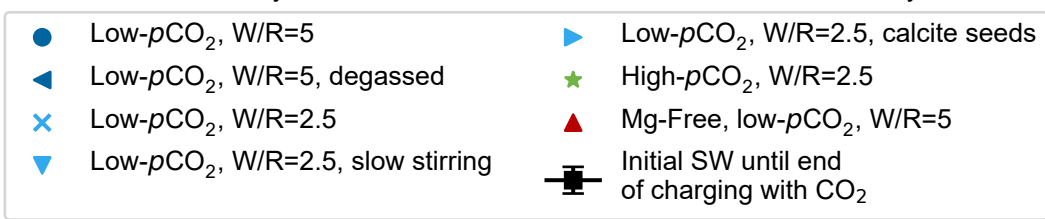
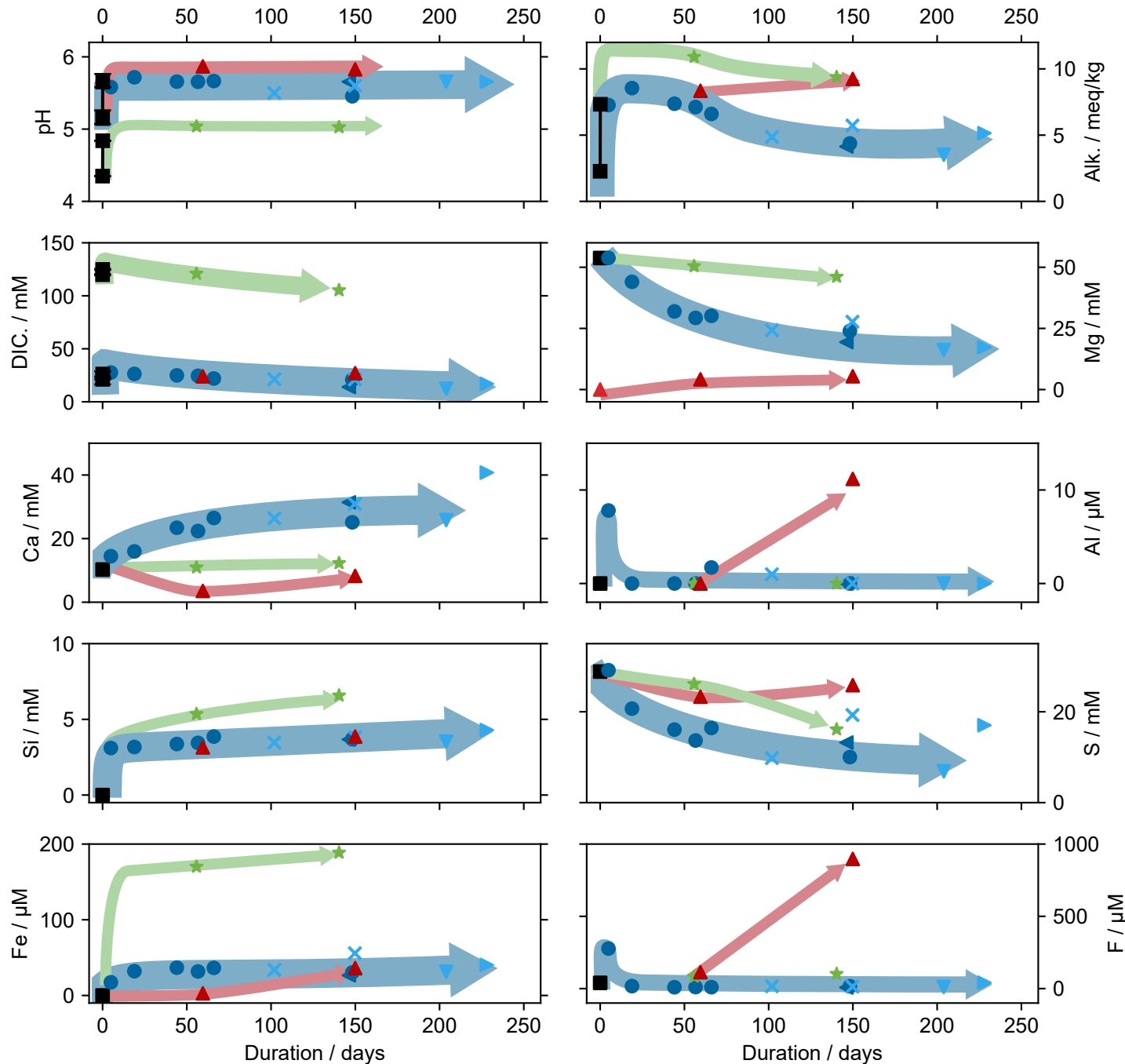
Figure 5: Diagram showing the development of alteration and pristine minerals identified in the basalt powder after each experiment by XRD and SEM. In all samples, the majority of the solids was amorphous material (basaltic glass, not shown), while the phases shown in the diagram were present in minor to moderate amounts.

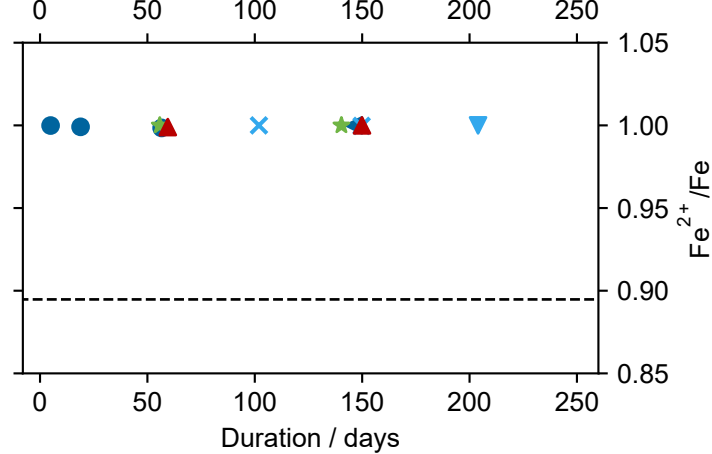
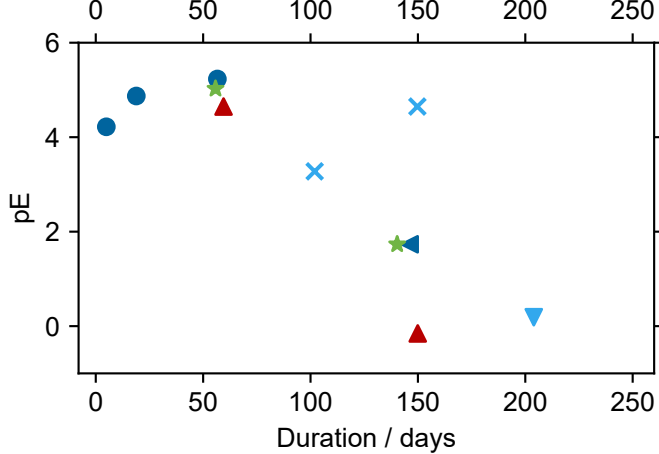
Figure 6: Comparison of total inorganic carbon (TIC) content in the solids determined after each batch experiment, expressed as percentage of total initial carbon present in reactor (a) as measured by NDIR after acidification, (b) as measured by solid state IR after heating in a furnace, and (c) as estimated by fluid mass balance calculations (see text for details). Shown confidence intervals (95%) of mass balance calculations are those propagated from measured values (mainly pressure, alkalinity) using Monte Carlo methods.

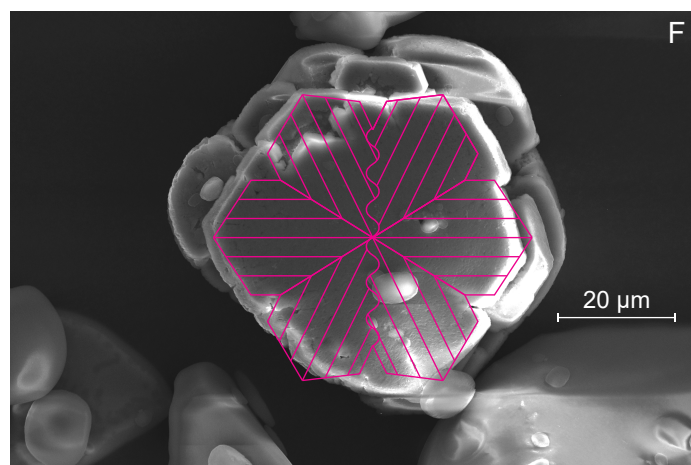
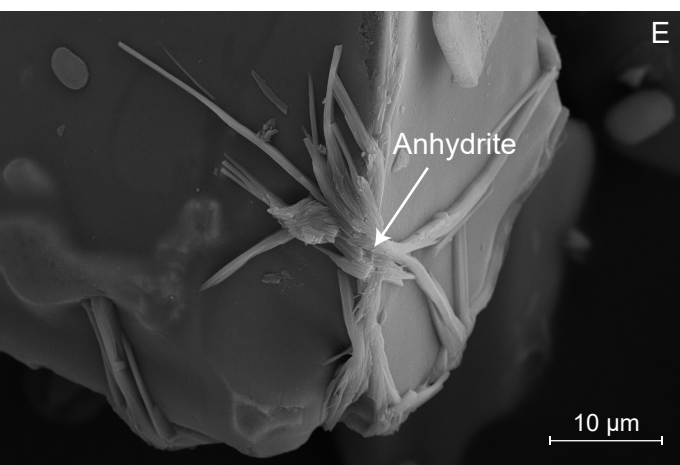
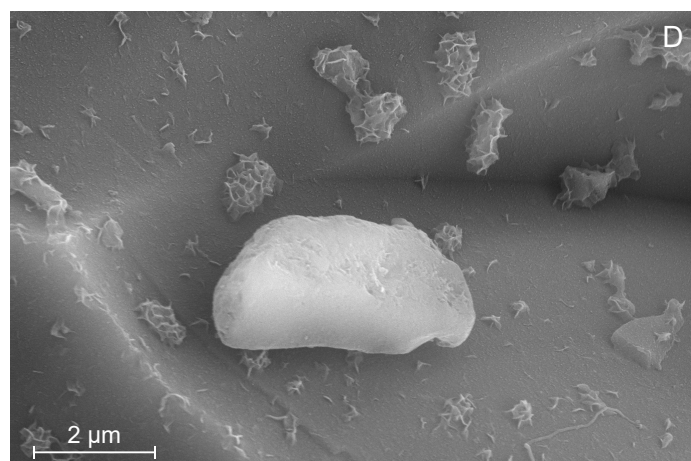
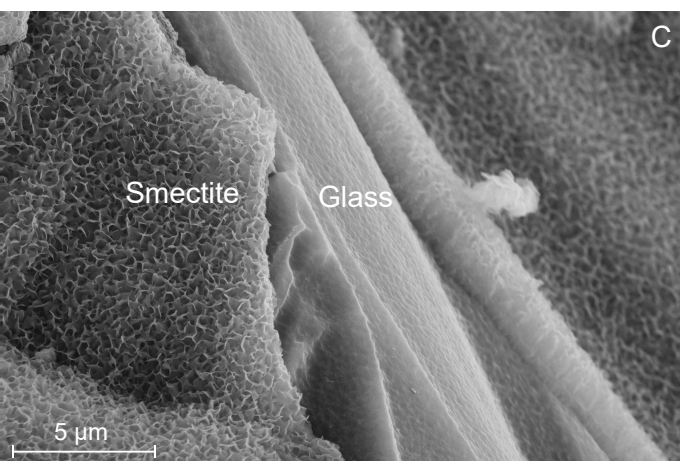
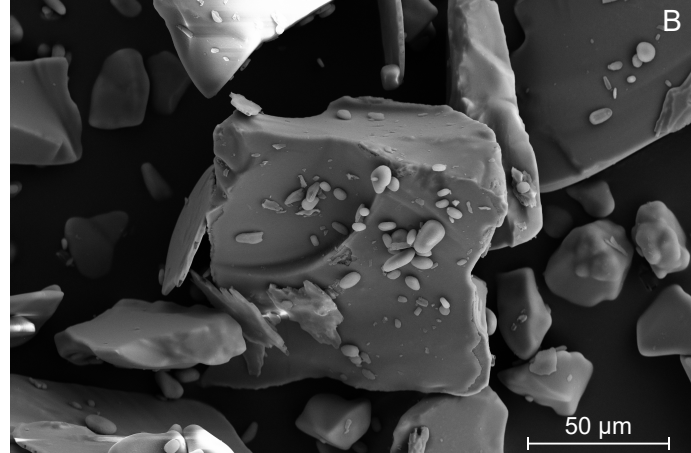
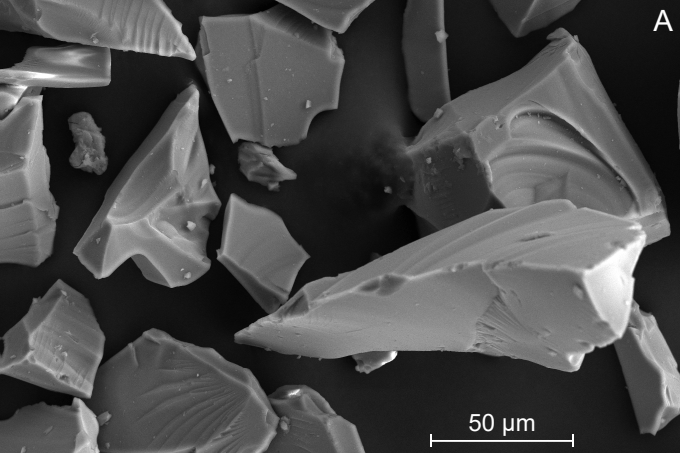
Figure 7: Calculated saturation indices (SI) of the reacted liquids collected at the end of each batch experiment with respect to selected alteration minerals. For ankerite and siderite, it was assumed that all aqueous Fe was present as Fe^{II} (see Figure 3 and text). Uncertainties (95% confidence level) propagated from analytical uncertainties are smaller than the symbol size in all cases. Maximum SI of minerals containing Al are presented in Figure S-4 in the Supplementary Material.

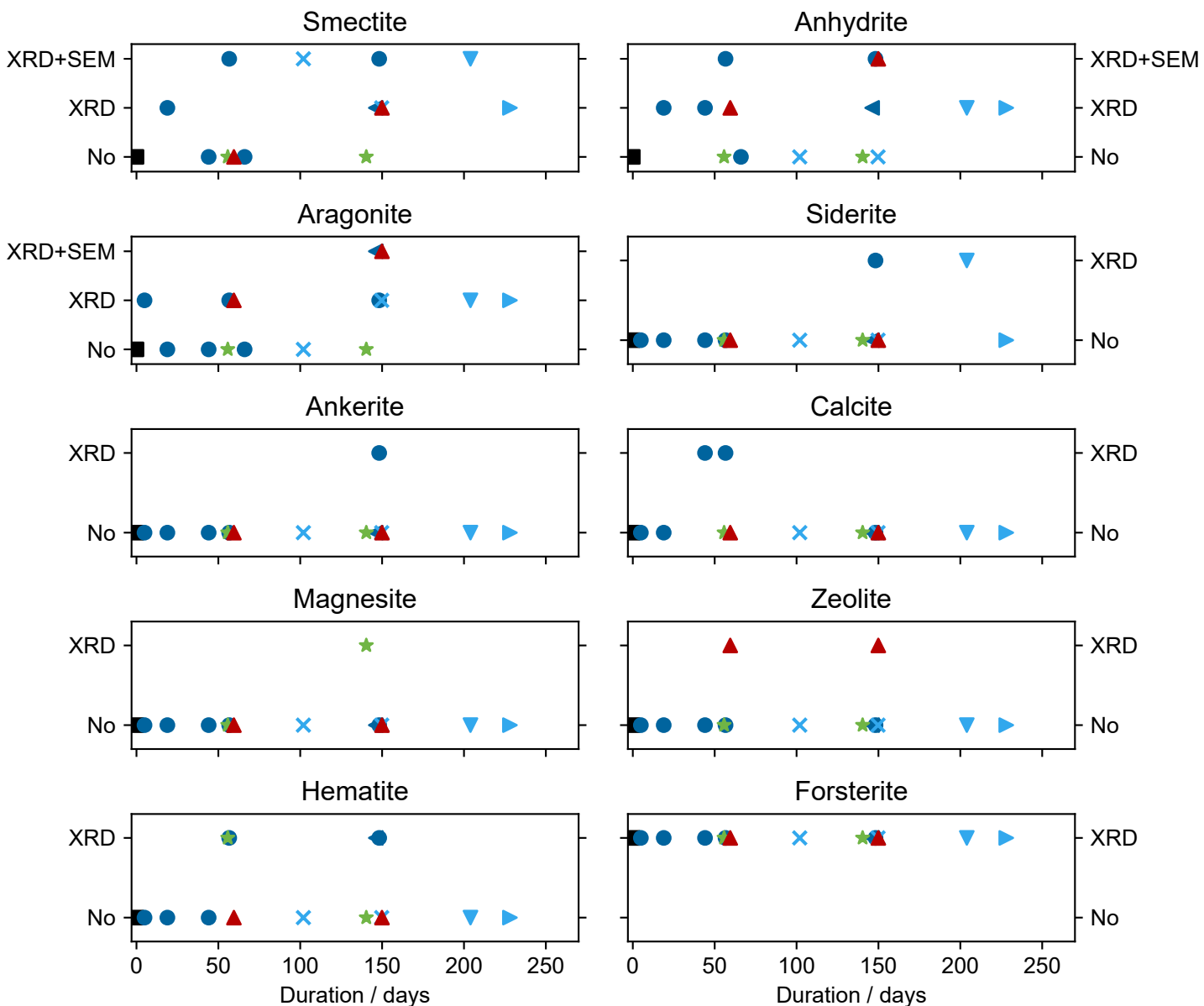
Figure 8: Results of reaction path calculations of basalt-seawater-CO₂ interaction at the experimental conditions of this study (initial water/rock ratio of 5 at 130 °C). Reaction progress is shown as function of basalt dissolution in units of g of basaltic glass dissolved per kg seawater (kgw). The length of the horizontal axis corresponds to the mass of basaltic glass dissolved during the ~ 5-month duration of the longest experiments. Note the difference scale of the horizontal axis in the three experimental series. The top plots show the predicted change in solid volume in cm³ per kgw; the middle plots show the calculated percentage of initial total CO₂ mineralized and the bottom plots show the total g of CO₂ mineralized per kgw. The symbols show the observed percentage of CO₂ mineralized as determined from the CO₂ content of the solids collected at the end of the batch experiments reported in this study by acidification (low pCO₂ and Mg free experiments) and heating methods (high pCO₂ experiments).



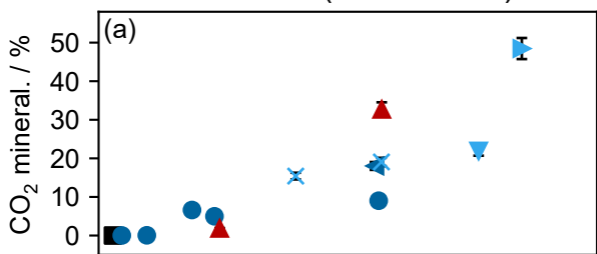




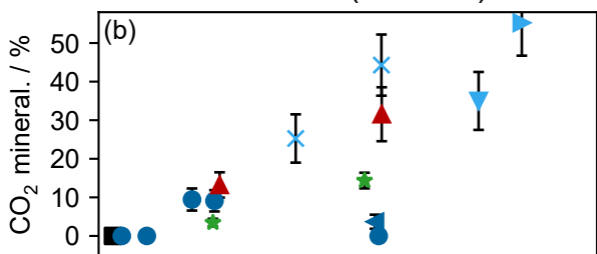




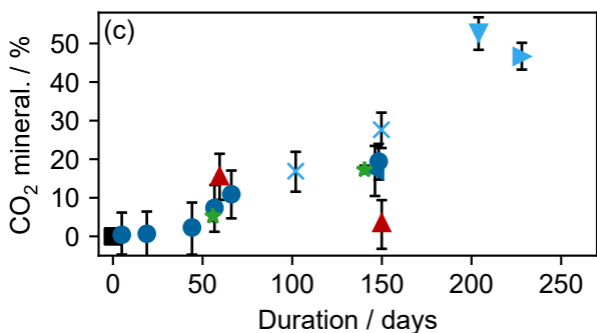
Solid TIC (Acidification)



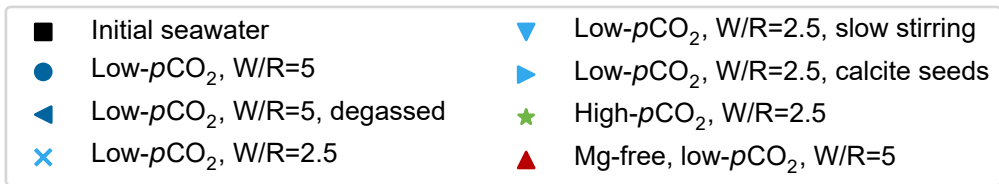
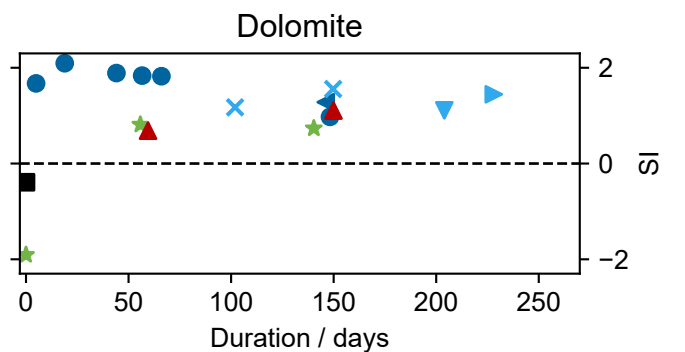
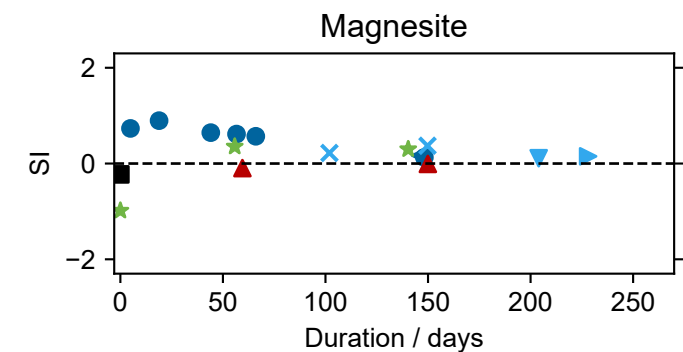
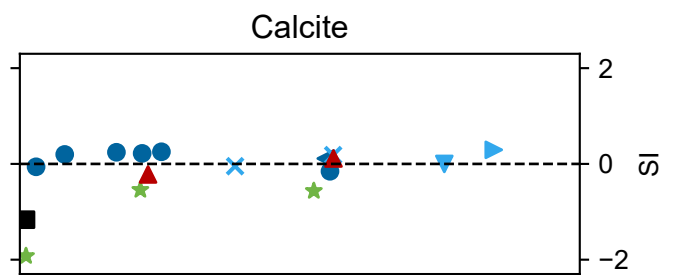
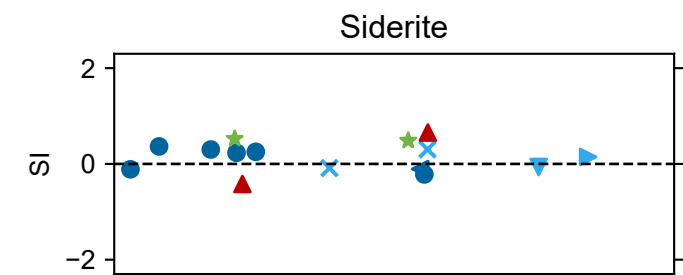
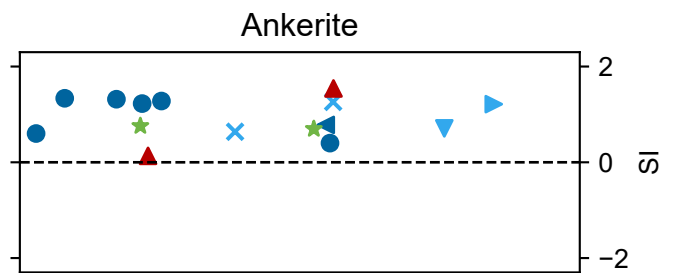
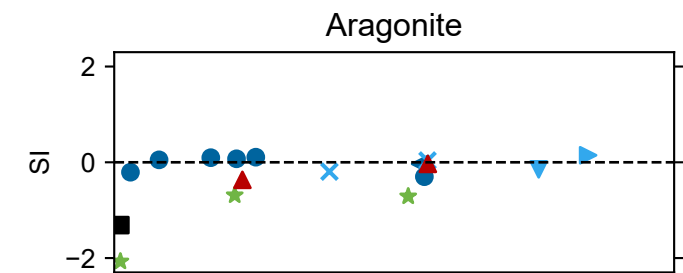
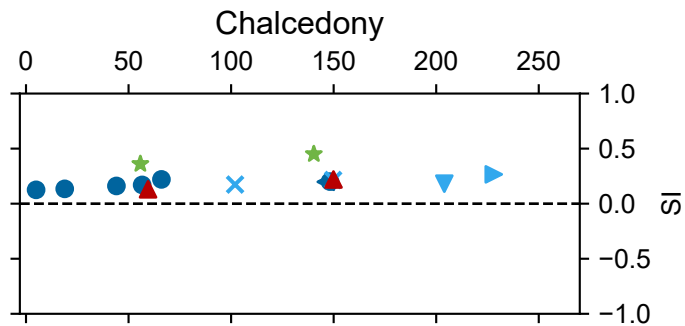
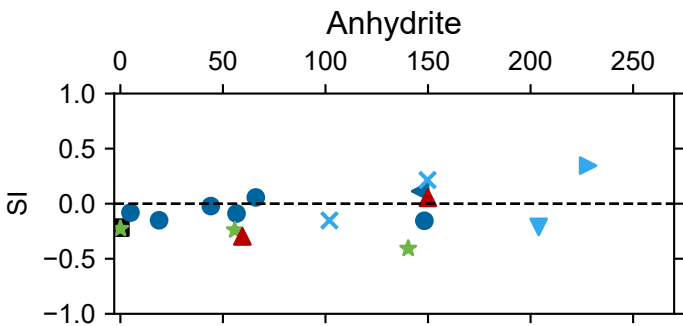
Solid TIC (Furnace)

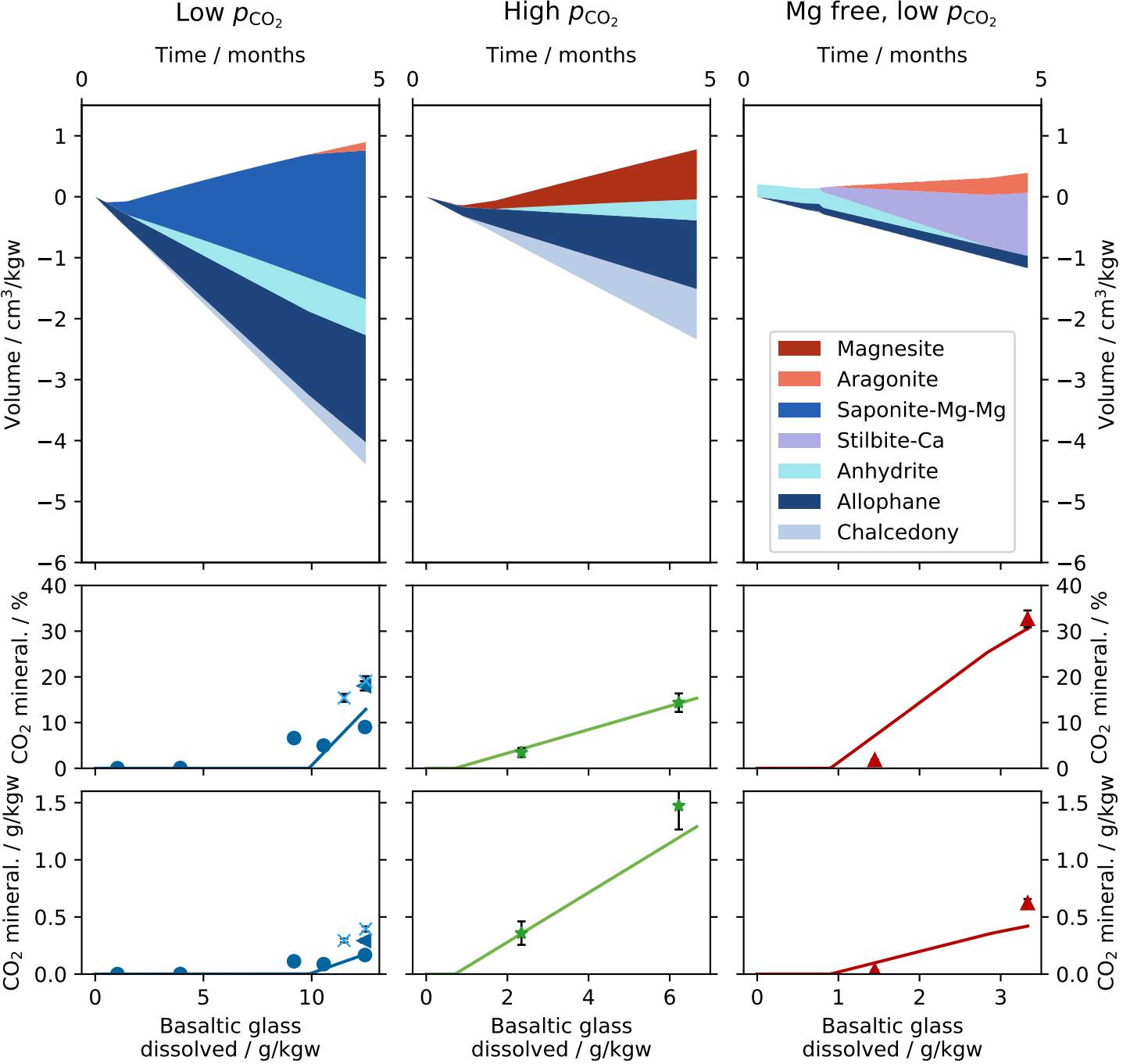


Fluid mass balance



- Initial basalt
- Low-*p*CO₂, W/R=5
- ▲ Low-*p*CO₂, W/R=5, degassed
- × Low-*p*CO₂, W/R=2.5
- ▼ Low-*p*CO₂, W/R=2.5, slow stirring
- ▶ Low-*p*CO₂, W/R=2.5, calcite seeds
- ★ High-*p*CO₂, W/R=2.5
- ▲ Mg-free, low-*p*CO₂, W/R=5





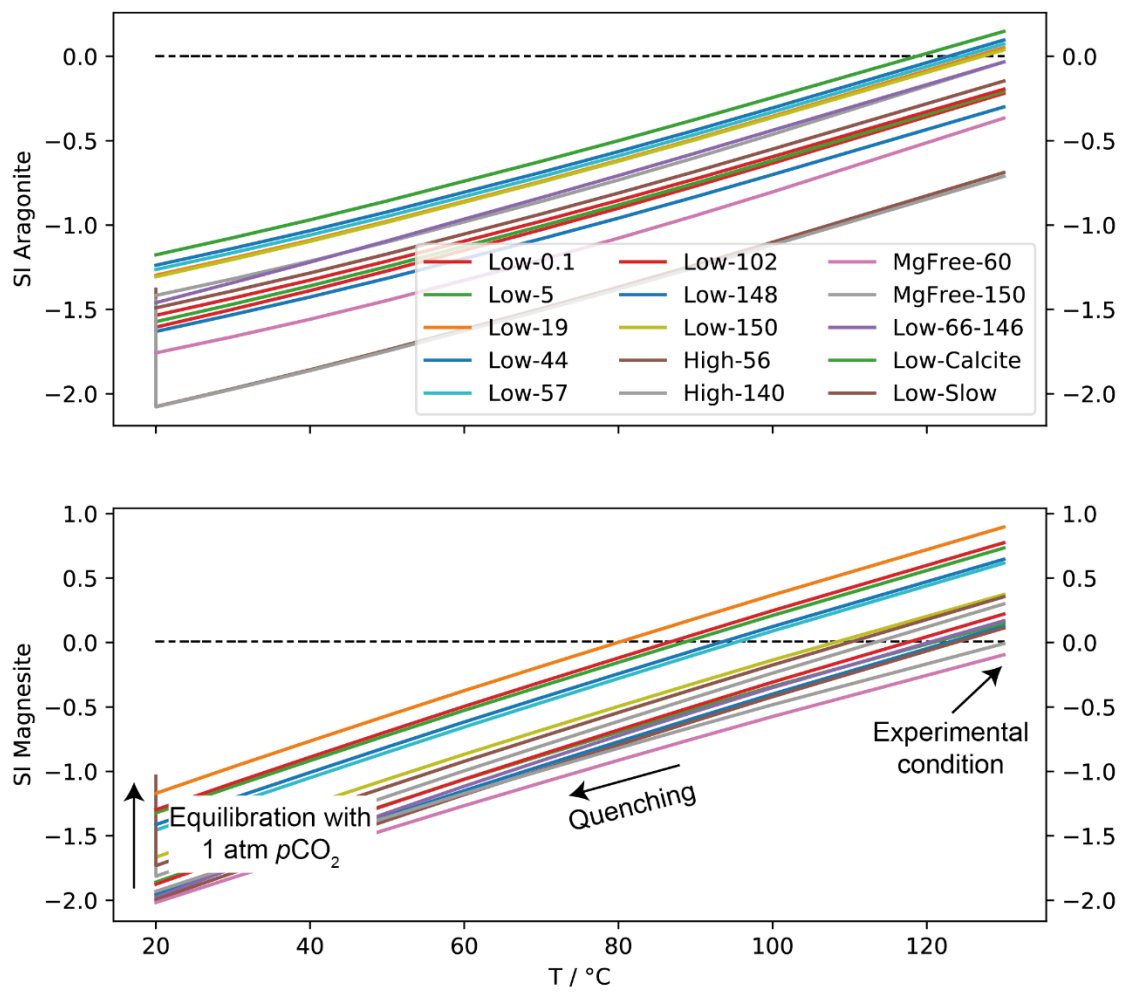


Figure S-1: Saturation indices (SI) of aragonite and magnesite, as predicted by thermodynamic calculations during quenching of the reactors and equilibration to 1 atm $p\text{CO}_2$.

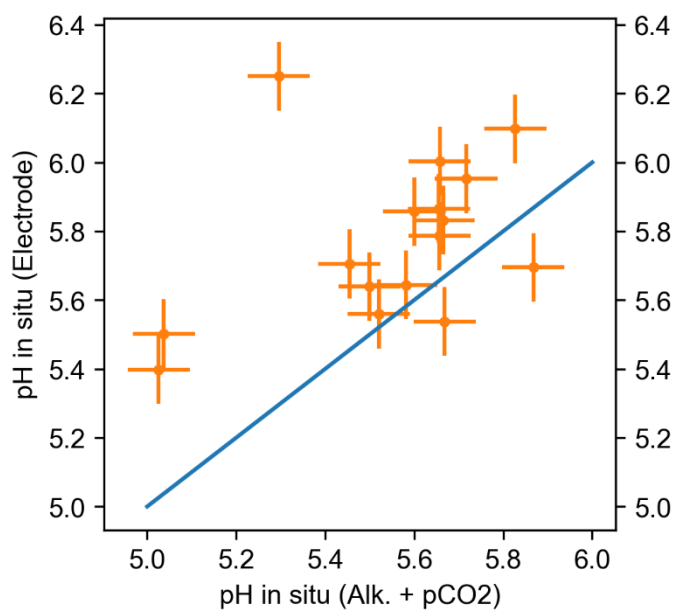


Figure S-2: Comparison between pH calculated for in situ conditions from measured alkalinities, pressure, and fluid composition, versus the pH measured using a pH combination electrode during sampling. Note that degassing of CO₂ from the solution during sampling likely affected the latter pH measurements, which is consistent with these measurements giving slightly higher pH values in most cases.

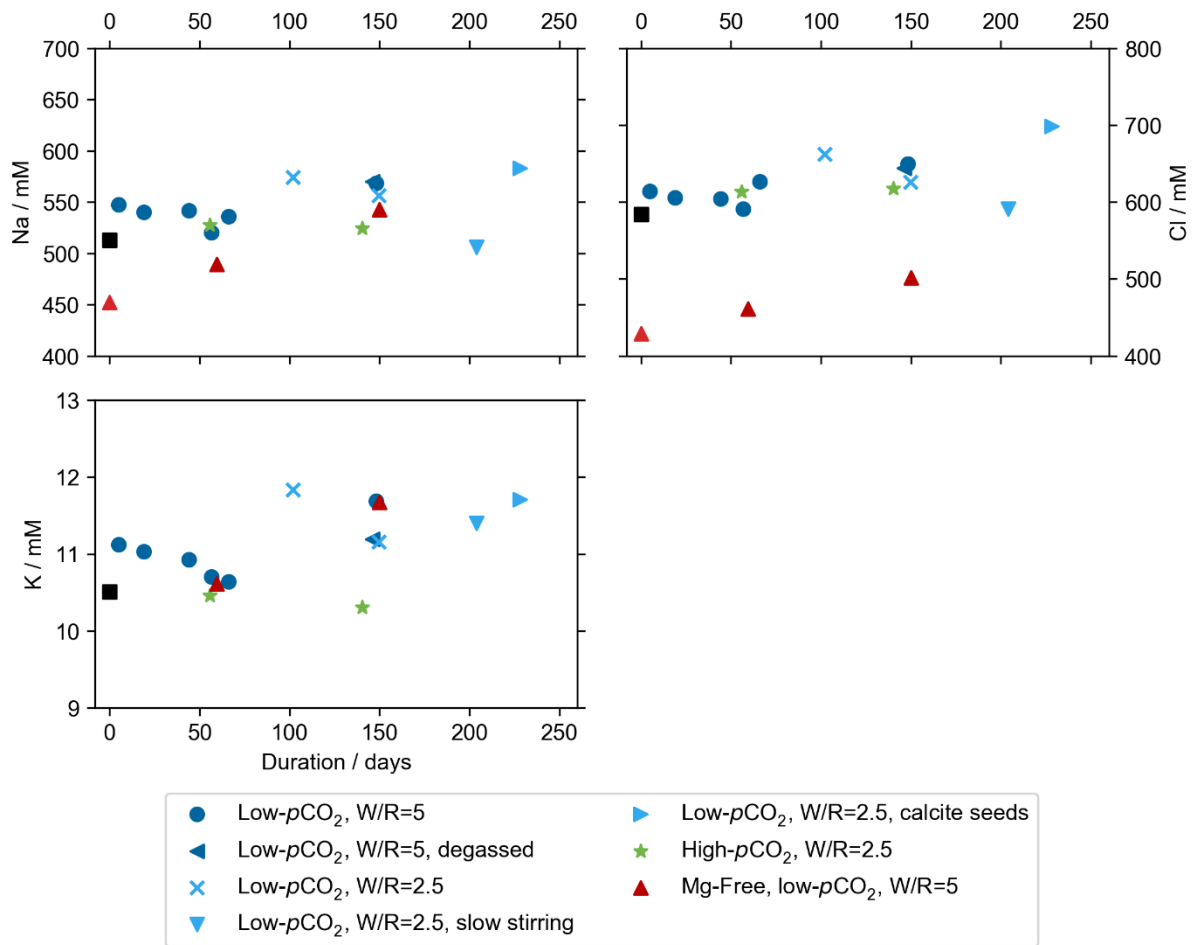


Figure S-3: Plots of measured fluid Na, Cl, and K concentrations of the experiments.

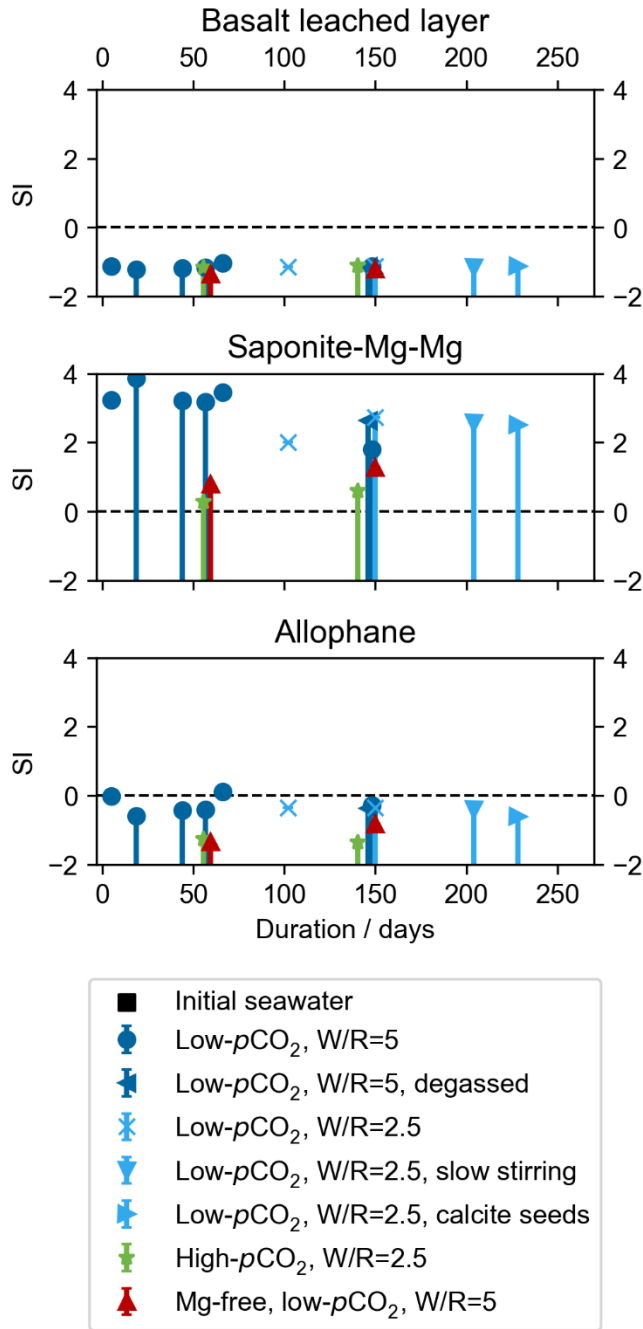


Figure S-4: Diagram showing calculated saturation indices (SI) of the reacted seawater with respect to different aluminosilicate minerals. Since aqueous Al concentrations were below the detection limit of $\sim 1\mu\text{M}$ in most cases, SI for those experiments were calculated using $1\mu\text{M}$ Al and thus represent maximum values, indicated by the error bars below the symbols.

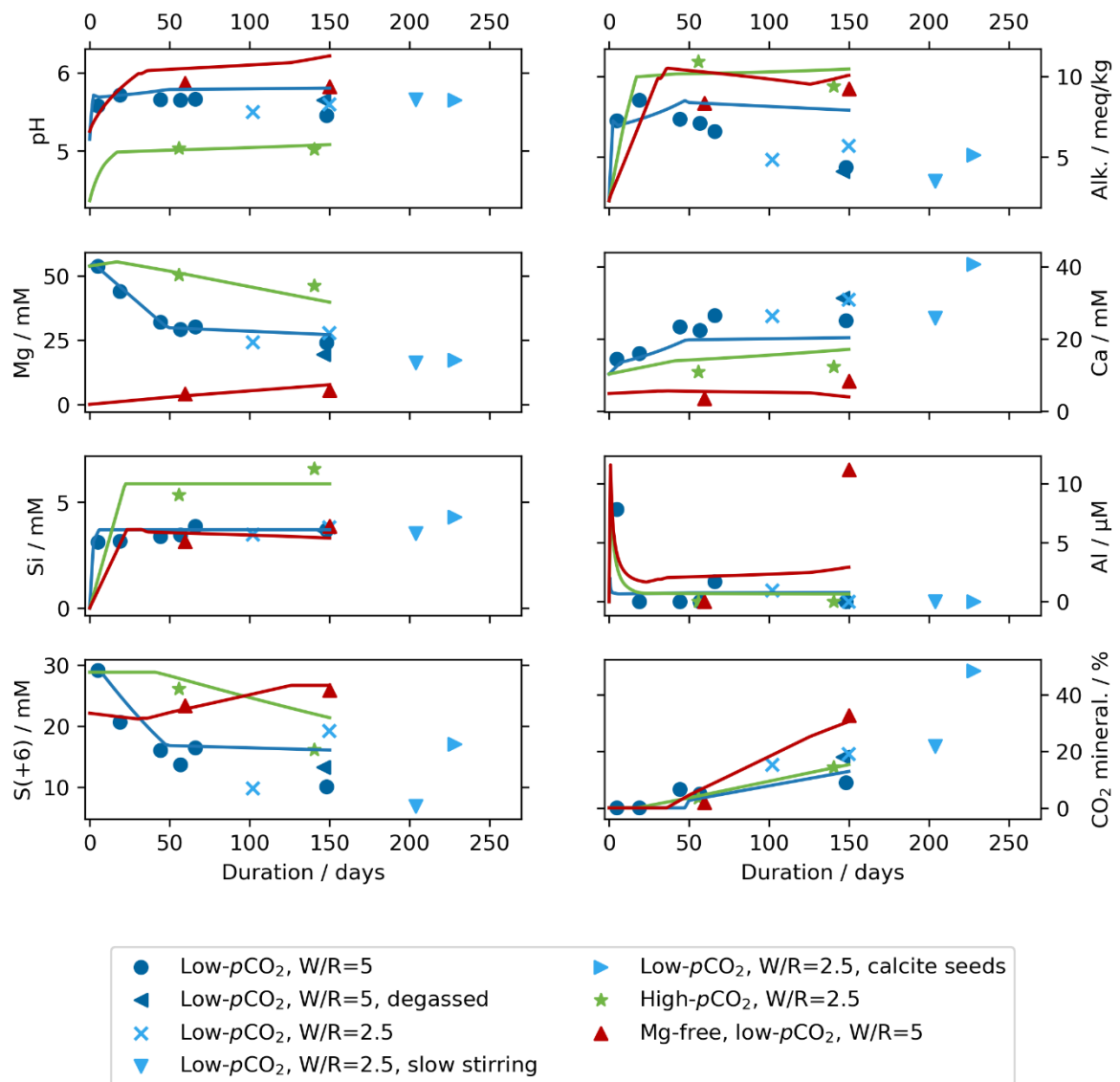


Figure S-5: Plot showing the fit of the reaction path model (solid lines) to the observed fluid composition (points) and CO_2 mineralization (as calculated from measured TIC contents of the solids).

Table S-1: Secondary minerals whose solubility was adjusted during the calibration of the reaction path model and their dissolution reactions. The adjustment is expressed in terms of change of logarithm of the solubility constant $\log K$ relative to the values in *carbfix.dat*.

Mineral	Dissolution reaction	$\log K$ used
Mg-Mg-Saponite	$\text{Mg}_{3.175}\text{Al}_{0.35}\text{Si}_{3.65}\text{O}_{10}(\text{OH})_2 + 7.4 \text{H}^+ = 0.35 \text{Al}^{3+} + 3.175 \text{Mg}^{2+} + 3.65 \text{SiO}_2 + 4.7 \text{H}_2\text{O}$	+4
Mg-Fe-Saponite	$\text{Fe}_{0.175}\text{Mg}_3\text{Al}_{0.35}\text{Si}_{3.65}\text{O}_{10}(\text{OH})_2 + 7.4 \text{H}^+ = 0.175 \text{Fe}^{2+} + 0.35 \text{Al}^{3+} + 3 \text{Mg}^{2+} + 3.65 \text{SiO}_2 + 4.7 \text{H}_2\text{O}$	+4
Ca-Stilbite	$\text{CaAl}_2\text{Si}_7\text{O}_{18} \cdot 7 \text{H}_2\text{O} + 8 \text{H}^+ = 2 \text{Al}^{3+} + \text{Ca}^{2+} + 7 \text{SiO}_2 + 11 \text{H}_2\text{O}$	+1
Anhydrite	$\text{CaSO}_4 = \text{Ca}^{2+} + \text{SO}_4^{-2}$	-0.1
Aragonite	$\text{CaCO}_3 + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^-$	+0.1
Chalcedony	$\text{SiO}_2 = \text{SiO}_2$	+0.2
		+0.4 (high- $p\text{CO}_2$)
Allophane	$\text{Al}_2\text{O}_3(\text{SiO}_2)_{1.22} \cdot 2.5 \text{H}_2\text{O} + 2.5 \text{H}_2\text{O} = 2 \text{Al}(\text{OH})_4^- + 2 \text{H}^+ + 1.22 \text{SiO}_2$	-1
		-0.5 (Mg-free)