



HAL
open science

Mineralization potential of water-dissolved CO₂ and H₂S injected into basalts as function of temperature: Freshwater versus Seawater

Chiara Marieni, Martin Voigt, Deirdre E Clark, Sigurður R Gíslason, Eric H Oelkers

► To cite this version:

Chiara Marieni, Martin Voigt, Deirdre E Clark, Sigurður R Gíslason, Eric H Oelkers. Mineralization potential of water-dissolved CO₂ and H₂S injected into basalts as function of temperature: Freshwater versus Seawater. *International Journal of Greenhouse Gas Control*, 2021, 109, pp.103357. 10.1016/j.ijggc.2021.103357 . hal-03386376

HAL Id: hal-03386376

<https://hal.science/hal-03386376>

Submitted on 19 Oct 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Mineralization potential of water-dissolved CO₂ and H₂S injected into basalts as**
2 **function of temperature: Freshwater versus Seawater**

3

4 **Author names and affiliations:** Chiara Marieni ^{a,*}, Martin Voigt ^b, Deirdre E. Clark ^c,
5 Sigurður R. Gíslason ^b, Eric H. Oelkers ^{a,b}

6 ^a Géosciences Environnement Toulouse (GET), CNRS UMR 5563, 14 Avenue Edouard
7 Belin, Toulouse 31400, France

8 ^b Institute of Earth Sciences, University of Iceland, Sturlugötu 7, 102 Reykjavík, Iceland

9 ^c Iceland GeoSurvey (ÍSOR), Grensásvegur 9, 108 Reykjavík, Iceland* Corresponding
10 author, chiara.marieni@get.omp.eu

11

12

13 **Highlights**

- 14 • Reaction path models quantified gas-charged waters/basalt interactions
- 15 • Gas-charged freshwater and seawater compared
- 16 • Geochemical reactions modelled at temperatures from 25 to 260 °C
- 17 • Optimal conditions for subsurface mineralization of CO₂ and H₂S identified

18

19 **Abstract**

20

21 Mineralization of freshwater-dissolved gases, such as CO₂ and H₂S, in subsurface
22 mafic rocks is a successful permanent gas storage strategy. To apply this approach globally,
23 the composition of locally available water must be considered. In this study, reaction path
24 models were run to estimate the rate and extent of gas mineralization reactions during gas-
25 charged freshwater and seawater injection into basalts at temperatures of 260, 170, 100, and
26 25 °C. The calculations were validated by comparison to field observations of gas-charged
27 freshwater injections at the CarbFix2 site (Iceland). The results show that more than 80% of
28 the injected CO₂ dissolved in freshwater or seawater mineralizes as Ca and Fe carbonates at
29 temperatures ≤170 °C after reaction of 0.2 mol/kgw of basalt, whereas at 260 °C much lower
30 carbon mineralization rates are observed in response to the same amount of basalt
31 dissolution. This difference is due to the competition between carbonate versus non-
32 carbonate secondary minerals such as epidote, prehnite, and anhydrite for Ca. In contrast,
33 from 80 to 100% of the injected H₂S is predicted to be mineralized as pyrite in all fluid
34 systems at all considered temperatures. Further calculations with fluids having higher CO₂
35 contents (equilibrated with 9 bar pCO₂) reveal that i) the pH of gas-charged seawater at
36 temperatures ≤170 °C is buffered at ≤6 due to the precipitation of Mg-rich aluminosilicates,
37 which delays CO₂ carbonation; and ii) the most efficient carbonation in seawater systems
38 occurs at temperatures < 150 °C as anhydrite formation is likely significant at higher
39 temperatures.

40

41

42 **Keywords**

43 Mineral storage / Carbon Dioxide (CO₂) / Hydrogen Sulfide (H₂S) / Reaction path modelling /

44 Freshwater / Seawater

45 1. Introduction

46 The 2018 IPCC report concluded that all pathways that limit global warming to 1.5 °C
47 above pre-industrial levels require some carbon capture and storage technology (Rogelj et
48 al., 2018). Permanent storage by *in situ* mineral carbonation, a strategy enhancing a natural
49 process, is one long-term carbon dioxide (CO₂) storage option (e.g., Metz et al., 2005;
50 Oelkers et al., 2008; Pacala and Socolow, 2004; Power et al., 2013; Sanna et al., 2014).
51 Mafic and ultramafic rocks provide the best candidates for such storage due to their relatively
52 fast dissolution rates and their high content of divalent cations, such as Mg²⁺, Ca²⁺ and Fe²⁺,
53 required for the carbonate mineral formation (Gislason and Oelkers, 2014; Kelemen and
54 Matter, 2008; McGrail et al., 2016; Schaef et al., 2010). The effects of rock composition and
55 crystallinity, extent of reactions, and water chemistry on secondary mineralogy have been
56 explored by a number of past experimental studies focused on freshwater-basalt-CO₂
57 interactions (Galeczka et al., 2014; Gislason and Oelkers, 2003; Gudbrandsson et al., 2011;
58 Gysi and Stefánsson, 2012a, b; Luhmann et al., 2017; Marieni et al., 2018; Oelkers and
59 Gislason, 2001; Peuble et al., 2015; Schaef and McGrail, 2009; Schaef et al., 2009;
60 Sissmann et al., 2014; Wolff-Boenisch et al., 2004a, 2006; Wolff-Boenisch et al., 2004b).
61 Reaction path simulations have provided insight into these basalt alteration processes and
62 the effects of high CO₂ partial pressures ($p\text{CO}_2$) on dissolution and precipitation reactions
63 (Gysi and Stefánsson, 2008; Rosenbauer et al., 2012). Field observations of alteration
64 products and the related changes in aqueous solutions at sites where CO₂ is injected into the
65 subsurface have advanced our understanding of the timescales of such fluid-rock
66 interactions. For example, the CarbFix process, where gases are dissolved into water before
67 or during their injection into subsurface reactive basalts, has been demonstrated to be a safe
68 and cost-effective approach to limiting CO₂ and hydrogen sulfide (H₂S) emissions as the
69 gases are mineralized within two years (Gunnarsson et al., 2018; Matter et al., 2016;
70 Snæbjörnsdóttir et al., 2018a). Large volumes of water, however, are required to dissolve the
71 gases using this method; approximately 32 tons of freshwater are needed to dissolve each
72 ton of CO₂ at 25 °C and 25 bar $p\text{CO}_2$ (Snæbjörnsdóttir et al., 2020). This requirement limits

73 the CarbFix approach geographically to where ample freshwater resources are located near
74 suitable reactive rock formations. On the other hand, porous basalts near the continental
75 margins have huge potential storage capacities adjacent to nearly unlimited supplies of
76 seawater (Goldberg et al., 2008; Marieni et al., 2013; Snæbjörnsdóttir and Gislason, 2016).
77 This observation suggests that the CarbFix approach could be applied to these regions by
78 the injection of gas-charged seawater into submarine basalts. Yet, the use of seawater
79 instead of freshwater for this purpose is not straightforward because the high amount of salts
80 and sulfates present in seawater can dramatically alter the reaction paths and rates of both
81 gas capture from point sources and the mineralization of CO₂ injected into the subsurface
82 (e.g., Rosenbauer et al., 2012; Xu et al., 2007). For example, injection of seawater during
83 industrial processes often leads to pipe clogging (e.g., Bader, 2007; Dai et al., 2017), and
84 reactions between seawater and basalts can lead to the formation of permeability-destroying
85 clay minerals in submarine basalt formations (e.g., Wolff-Boenisch and Galeczka, 2018;
86 Wolff-Boenisch et al., 2011).

87 This study was designed to assess the potential of extending the CarbFix approach for
88 the capture and subsurface mineral fixation of carbon and sulfur. Reaction path models were
89 created to predict the rate and extent of subsurface geochemical reactions in basaltic
90 reservoir rock in response to the injection of CO₂- and H₂S-charged freshwater and seawater
91 as a function of temperature. These model calculations focus on i) identifying the main
92 differences between the use of freshwater versus seawater for the injection of CO₂ and H₂S
93 into subsurface basalts for mineral carbonation, ii) investigating the temperature limits of
94 CO₂-charged injections, and iii) identifying the optimal temperature and fluid composition for
95 the mineralization of CO₂ and H₂S gas mixtures within basaltic reservoirs.

96

97 **2. Model calculations**

98 **2.1. Reaction path modelling**

99 This study is largely based on thermodynamics via reaction path calculations. The
100 reaction path models created in this study are used to predict the distribution of mineral

101 reaction products occurring in response to the injection of gas-charged aqueous fluids while
102 these fluids travel through a basaltic reservoir (**Figure 1**). Focus is made to determine the
103 effect of varying temperature (from 25 to 260 °C) and fluid composition (freshwater or
104 seawater) on the mineral-fluid interactions. Four distinct temperatures were chosen to give
105 an overview of the effect of this parameter on carbonation potential. The modelled system
106 was divided into ten sequential reaction steps to track fluid-rock interactions as a function of
107 basalt dissolution. In each step, a fixed quantity of basalt was dissolved into the injected fluid
108 and secondary minerals were allowed to precipitate until the system attained local
109 thermodynamic equilibrium. The identity of secondary minerals allowed to form in the
110 calculations was based on thermodynamic constraints and past field observations (see
111 below). Precipitated minerals were not allowed to react in subsequent reaction steps, i.e.
112 their precipitation was considered non-reversible. This was done to simulate fluids flowing in
113 a reservoir, which constantly moves away from the minerals precipitated from this fluid.

114 All the calculations in this study were performed using the PHREEQC software
115 package (v3) (Parkhurst and Appelo, 2013) together with the *carbfix.dat* (v1.1.0)
116 thermodynamic database (Voigt et al., 2018a). Reaction path calculations were performed
117 rather than the more detailed reactive transport calculations to generate site independent
118 results, as well as to avoid uncertainties introduced by the estimation of mineral-fluid
119 interfacial surface areas and the use of laboratory measured mineral dissolution and
120 precipitation kinetics.

121 The reaction path model was parameterized and validated using the results from the
122 ongoing CarbFix2 injection (Clark et al., 2018; 2020; Gunnarsson et al., 2018). In the
123 CarbFix2 project, gas-charged water from the Hellisheiði geothermal power plant (SW
124 Iceland) is injected into a hydrothermally altered basaltic reservoir with temperatures of ~260
125 °C (Clark et al., 2020; Gunnarsson et al., 2018; Snæbjörnsdóttir et al., 2018b). During the
126 first phase of the CarbFix2 injection, up to July 2016, approximately 25% of the water-soluble
127 gases from the power plant's exhaust gas stream containing 63 vol% CO₂, 21 vol% H₂S, 14
128 vol% H₂, and 2 vol% of other gases such as Ar, CH₄, and N₂ were dissolved in a scrubbing

129 tower into 20 °C condensed steam collected from the power plant's turbines. The resulting
130 gas-charged water was then transported to injection wells. Effluent water was co-injected into
131 the wells with the gas-charged water, and these two water streams mixed in the well before
132 entering the host rock. Three geothermal wells are used to monitor the geochemical
133 evolution of fluids and assess the magnitude of gas mineralization. These wells are located
134 984 m (HE-31), 1356 m (HE-48), and 1482 m (HE-44) downstream from the dominant
135 injection well (Clark et al., 2020; Gunnarsson et al., 2018). Mass balance calculations on
136 sampled well fluids, taking account of non-reactive chemical tracers, were used to determine
137 the fraction of the injected and formation water reaching each monitoring well, assuming non-
138 reactive mixing. For field validation, a mixing final step was performed on the modelled fluid
139 with formation waters (**Figure 1**). This accounts for fluid mixing within the reservoir near the
140 monitoring wells as each monitoring well passes through three distinct hyaloclastite water
141 feedzones (Snæbjörnsdóttir et al., 2018b). The mixing ratio used in the validation model
142 calculation was chosen to be that of the fluids sampled from the monitoring well HE-31 on 3
143 November 2015, which contained 84 vol% formation water and 16% injected water based on
144 tracer test results reported by Gunnarsson et al. (2018). Data from the other monitoring wells
145 were not used for model validation because of the uncertainties on the various fluid flow
146 paths (e.g., different injected water paths to each monitoring well and/or variable reactive
147 paths depending on time).

148 The secondary mineralogy in the freshwater injection models was constrained by the
149 mineralogy of alteration phases described in the literature for on-shore basalt formations
150 (Alfredsson et al., 2013; Helgadóttir, 2011; Kristmannsdóttir, 1979; Larsson et al., 2002;
151 Schiffman and Fridleifsson, 1991; Snæbjörnsdóttir et al., 2018b; Thien et al., 2015). The
152 seawater injection models were validated using observations of alteration mineral zones
153 described in the literature for the oceanic crust (Alt, 1995) and further field observations (e.g.,
154 Alt et al., 1996; Davis et al., 1997; Fisher et al., 2011).

155 Note that Daval (2018) speculated, based on some observations of Trias et al. (2017),
156 that part of the carbon fixation during the original CarbFix injection could be due to biologic

157 activity leading to the formation of subsurface organic material. The analysis of carbon
158 isotopes at the original CarbFix injection site, where the injected carbon was mineralized at
159 35 °C, indicates, however, that bio-fixing was negligible. Moreover, it is highly unlikely that
160 biologic activity influenced to any extent the carbon fixation during the ongoing CarbFix2
161 injections, as carbon fixation in this system is occurring at temperatures in excess of 250 °C.
162 As such, the potential carbon fixation by subsurface biota has not been considered in this
163 study.

164

165 **2.2. Thermodynamic dataset and reactant compositions**

166 All reaction path calculations reported in this study were performed using the
167 *carbfix.dat* thermodynamic database (Voigt et al., 2018a). The *carbfix.dat* database is based
168 on the *core10.dat* database (Neveu et al., 2017), which itself is largely derived from the
169 widely used *llnl.dat* database compiled at the Lawrence Livermore National Laboratory. The
170 *carbfix.dat* database corrects several errors, only contains thermodynamics data for
171 reactions for which equilibrium constants, K , were available (as opposed to constants
172 estimated based on the assumption of constant reaction enthalpy change, Δ_rH), and only
173 contains phases and species for which molar volumes are available, allowing the PHREEQC
174 computer code to estimate the pressure dependence of equilibrium constants. The molar
175 volumes listed in this database were also used to calculate the volume of the secondary
176 minerals as a function of reaction progress.

177 The bulk chemical composition of Stapafell basaltic glass (Gysi and Stefánsson, 2011;
178 Oelkers and Gislason, 2001) normalised to one mol of Si, was used as the only phase
179 initially present in the rock formation; the composition of such glass is provided in **Table 1**.
180 This basaltic glass composition is in agreement with normalized field data and was used in
181 all the reaction path models to allow direct comparison of computed results. The freshwater
182 composition used in some of the calculations was set to that of the pre-injection effluent
183 water collected near the Hellisheiði power plant as reported by Gunnarsson et al. (2018),
184 whereas the seawater composition used in the other calculations was taken from Millero et

185 al. (2008). The compositions of these waters are provided in **Table 2** together with the
186 average composition of the formation waters sampled from monitoring well HE-31 before the
187 gas-charged water injections (Clark et al., 2020), which was used in the final mixing step of
188 the modelling to match model results to the observed monitoring well water composition.

189 In all the reaction path calculations, the power plant exhaust gases were first dissolved
190 in pure water, consistent with the composition of condensed steam. This gas-charged water
191 was subsequently mixed with either freshwater or seawater in the molar ratio of 0.3 parts
192 gas-charged water to 0.7 parts either fresh or seawater; this ratio is based on the mixing ratio
193 of the fluids injected during the CarbFix2 project (Clark et al., 2018). The resulting diluted
194 gas-charged water contains either 30.8 or 32.0 mmol/kgw of dissolved inorganic carbon
195 (DIC) and 22.4 or 42.4 mmol/kgw of dissolved sulfur (DS), for freshwater or seawater
196 dilution, respectively (**Table 3**). These DIC values correspond to a fluid equilibrated with 1
197 bar of $p\text{CO}_2$. In the case of freshwater, almost all the carbon and sulfur in the injected mixture
198 originates from the dissolved gas; in the case of seawater, almost all the carbon but only
199 21.9 mmol/kgw of sulfur (~52% of the total injected DS) are derived from the dissolved gas,
200 with the remaining originating from the natural sulfate content of seawater. The choice to first
201 dissolve the gases in pure water prior to their dilution in freshwater or seawater was made to
202 enable clear comparisons among the model results.

203 The use of model input parameters replicating those from the CarbFix2 gas-charged
204 water injection allows the validation of model results with field observations. In addition, the
205 injection of more concentrated CO_2 fluids was also explored. For these latter calculations,
206 identical fluids were used as in the original calculations other than they contained a higher
207 CO_2 concentration. This higher concentration was taken equal to that of freshwater or
208 seawater equilibrated with 9 bar CO_2 (**Table 3**), which is the injection pressure at the
209 CarbFix2 injection well head (Clark et al., 2020). This results in injected dissolved CO_2
210 concentrations of ~127 and ~116 mmol/kgw, respectively, for the freshwater and seawater
211 injections. In all calculations, carbon dioxide solubility was determined with the Peng-

212 Robinson equation of state (Peng and Robinson, 1976) as implemented in PHREEQC
213 (Appelo et al., 2014).

214 The compositions, chemical formulas, molar volumes and thermal stability fields of the
215 secondary phases considered in the reaction path calculations are listed in **Table 4**. The
216 thermal stability field defines the temperature range in which a mineral has been observed in
217 experimental and/or field studies. Consistent with field observations, dolomite was not
218 allowed to precipitate, and the formation of reduced aqueous carbon species, C^{-4} or methane
219 (CH_4), was restricted. The volume of the dissolving basaltic glass was calculated using a
220 molar weight of 123 g/mol and density of 2.851 g/cm³ (Galeczka et al., 2014). The rock
221 volume changes reported below are defined as the difference between the volume of the
222 dissolved rock and the total volume of the precipitated secondary minerals. As such, these
223 do not correspond to rock porosity changes. Rock porosity changes would depend on the
224 amount of basalt dissolved and secondary minerals formed at each point in the system,
225 which will be a function of fluid rates, rock-fluid interfacial surface area, and mineral reaction
226 rates. Such factors are not explicitly considered in this study. Also, the effect of the presence
227 of dissolved gas in the fluid phase on reservoir rock volume changes was determined by
228 comparing each gas-charged reaction path calculation to a corresponding reaction path
229 calculation result with either gas-free freshwater or seawater (**Table 2**).

230

231 **3. RESULTS**

232 **3.1. Reaction path field validation**

233 The results from the reaction path calculations, performed for the injection of
234 freshwater-dissolved CO_2 into basalts at 260 °C and thereby mimicking the CarbFix2
235 injection are shown in **Figure 2** along with the corresponding field observations reported by
236 Clark et al. (2020). Ten steps of 0.02 mol basalt dissolution per kg H_2O were required prior to
237 the non-reactive mixing of the resulting fluid with the background water to obtain the fluid
238 composition measured at monitoring well HE-31. A total of 0.2 mol basalt dissolution was
239 chosen for this calculation to match the results of Clark et al. (2020). This 0.2 mol/kgw

240 basaltic glass corresponds to a mass of 25 g or a volume of 8.6 cm³ of basalt dissolved per
241 kg water.

242 The calculated final pH of 7.36 obtained in this calculation after fluid-rock interaction is
243 in close agreement with the measured field *in situ* pH of 7.31 (**Figure 2a**). A close match is
244 also found between calculated and measured DIC and DS (**Figure 2b**); the calculated final
245 fluid values were 9.93 and 1.86 mmol/kgw, whereas the corresponding field measured
246 values were 10.58 and 2.14 mmol/kgw, for DIC and DS, respectively. Similarly, the
247 calculated major element fluid concentrations match well with the corresponding field values,
248 with no significant systematic differences (**Figure 2c**). Note, however, an underestimate of
249 ~20% in the Si concentrations and a ~15% overestimate of the Na values were obtained in
250 the calculation. The model results indicate the formation of calcite, albite, prehnite, Mg-
251 chlorite (clinochlore) and epidote (**Figure 2d**), which is in agreement with the geochemical
252 calculations based on monitoring data as well as the geological description of the CarbFix2
253 site (Snæbjörnsdóttir et al., 2018b). The model-field comparison of the saturation indices of
254 all the secondary minerals listed in **Table 4** for temperature conditions of 260 °C shows that
255 most are in close agreement other than for those of Fe-bearing phases, which are
256 underestimated by the model calculations.

257

258 **3.2. Reaction path calculations for gas-charged waters at 260 °C**

259 A comparison of the results from the gas-charged freshwater and the gas-charged
260 seawater reaction path model calculations at 260 °C are shown in **Figure 3**. In the freshwater
261 system, the pH increases from 5.8 to 7.7, whereas in the seawater system the pH follows a
262 different trend, decreasing from 5.5 to 4.1 in response to the dissolution of the first 0.02 mol
263 of basaltic glass, and then slowly rising back to ~5.4 after the dissolution of 0.14 additional
264 moles of basaltic glass.

265 The DIC and DS mineralized are shown as a percentage of the amount of these gases
266 originally injected in **Figure 3 c and d**. A substantial amount of the originally injected sulfur is
267 mineralized in response to 0.2 mol basalt dissolution per kg of injected solution, with

268 freshwater mineralizing around 80% (~17.4 mmol/kgw), and seawater almost 100% (~41.9
269 mmol/kgw, of which 22.4 mmol/kgw originates from the gas-charged solution) of the injected
270 dissolved sulfur. In contrast, the efficiency of DIC mineralization is substantially different if
271 injected via freshwater compared to seawater after the dissolution of 0.2 mol of basalt. Gas-
272 charged freshwater-basalt interaction is estimated to mineralize ~40% of the originally
273 injected DIC (~11.6 mmol/kgw), whereas gas-charged seawater-basalt interaction removes
274 only ~10% (~3.2 mmol/kgw) of the originally injected DIC. This lower CO₂ uptake by the
275 solids in the latter case is the result of the stability and formation of non-carbonate Ca-
276 bearing minerals (see below).

277 In both the freshwater and the seawater systems, the CO₂ is mineralized as calcite,
278 whereas dissolved sulfur precipitates only as pyrite in freshwater, and as pyrite and anhydrite
279 in seawater. The other minerals observed as secondary phases during the dissolution-
280 precipitation reaction path in freshwater, in descending order of molar abundance, are
281 quartz, epidote, Mg-chlorite (clinochlore), albite, prehnite, ilmenite, magnetite, and K-
282 feldspar. In the seawater reaction path model, the secondary minerals are quartz, Mg-
283 chlorite, albite, epidote, hematite, ilmenite, and magnetite. Prehnite and K-feldspar are
284 observed only during the freshwater injection and hematite only during the seawater
285 injection. Furthermore, quartz, epidote, and magnetite are more abundant during the
286 freshwater injection, clinochlore and albite more abundant during the seawater injection,
287 while ilmenite shows similar abundances from either injection. In these 260 °C calculations,
288 chlorites were allowed to precipitate rather than smectites consistent with the observations
289 by Alt (1995) and Snæbjörnsdóttir et al. (2018c) for seawater and freshwater injections,
290 respectively.

291 The efficiency of CO₂ mineralization can be visualized by assessing the distribution of
292 Ca among the various secondary phases (**Figure 3 g and h**). In the freshwater system, Ca is
293 taken up, in descending order of abundance, by epidote, prehnite, and calcite, with prehnite
294 being predominant compared to the other phases during the initial reaction path steps. In the
295 seawater system, most of the Ca is taken up by anhydrite. It is only after the injected sulfate

296 is consumed, after 0.12 mol of basaltic glass dissolution, that epidote and calcite begin to
297 form, with epidote being predominant over calcite.

298 The combined dissolution-precipitation reactions predicted to occur leads to an
299 increase in the rock volume per kg of injected solution in both systems: +1% for the
300 freshwater case, and +11% for seawater. Moreover, the gas-charged seawater-basalt
301 system shows a rock volume increase during the first reaction step, whereas the rock volume
302 increase in the freshwater system begins only after the dissolution of 0.10 mol of basaltic
303 glass. This volume increase is largely the result of the formation of hydrated minerals, such
304 as chlorites, where the water included in the structure increases the mineral volume.

305

306 **3.3. Reaction path calculations for gas-charged waters at 170 °C**

307 The results from both the gas-charged freshwater and the gas-charged seawater
308 reaction path calculations at 170 °C are illustrated in **Figure 4**. In the freshwater system, the
309 aqueous solution pH increases almost linearly from 5.0 to 9.7 with increasing basaltic glass
310 dissolution, whereas in the seawater system the pH first sharply increases from 4.8 to 5.6 in
311 response to the dissolution of the first 0.02 mol of basaltic glass, followed by a slow rise to
312 6.0.

313 At this temperature, both the freshwater and seawater injections indicate a similarly
314 high percentage of injected sulfur mineralization, with the freshwater mineralizing around
315 96% (~21.5 mmol/kgw) of the initial DS, and the seawater mineralizing almost 95% (~40.2
316 mmol/kgw, of which 22.4 mmol/kgw originated from the dissolved gas) of the initial DS.
317 Similarly, the mole percent of initial DIC sequestered is above 90% during both the
318 freshwater and seawater system (~99% and ~92%, respectively). In the case of the
319 freshwater injection, most of the DIC is mineralized before the first 0.12 mol of basaltic glass
320 is dissolved, whereas about twice as much basalt dissolution (0.2 mol) is required to reach a
321 similar DIC mineralization value in the seawater system.

322 As in the 260 °C reaction path calculations, the CO₂ is mineralized as calcite, whereas
323 the DS precipitates as pyrite during the freshwater injection, but as both pyrite and anhydrite

324 during the seawater injection. The other secondary phases calculated to form during the
325 reaction path calculations in the freshwater systems, in descending order of abundance, are
326 Mg-smectites, Ca-zeolites (laumontite and mordenite), ilmenite, Na-zeolite (analcime), Fe-
327 smectites, K-smectites, magnetite, and K-feldspar. In the seawater system, the secondary
328 minerals are Mg-smectites, hematite, ilmenite, and Fe-smectite. Zeolites, magnetite, K-
329 smectites and K-feldspar are observed only during freshwater injection, whereas hematite
330 only during seawater injection. Fe-smectites are more abundant during the freshwater
331 injection, whereas Mg-smectites are more abundant during the seawater injection.

332 At this temperature in the freshwater system, Ca is taken up, in descending order of
333 abundance, by calcite, mordenite and laumontite, with more than 60% of Ca being
334 incorporated into calcite throughout the whole reaction path. During the seawater injection,
335 calcite and anhydrite compete for Ca, with anhydrite taking up to ~75% of the available Ca in
336 the initial reaction step, and ~35% after 0.06 mol of basaltic glass has dissolved. The results
337 of these calculations suggest a similar increase in rock volume in both modelled gas-charged
338 water injections as a function of basalt dissolution: +18% for the freshwater system, and
339 +14% for the seawater system. This volume increase is mostly due to the formation of clay
340 minerals and zeolites, which are hydrated minerals.

341

342 **3.4. Reaction path calculations for gas-charged waters at 100 °C**

343 The results from both the gas-charged freshwater and the gas-charged seawater
344 reaction path calculations at 100 °C are shown in **Figure 5**. In the freshwater system, the pH
345 increases almost linearly from 4.7 to 10.4, whereas in the seawater system, the pH first
346 increases sharply from 4.6 to 5.8 in response to the dissolution of the first 0.02 mol of
347 basaltic glass, and then increases more slowly to 6.9.

348 Both injected fluids show comparable high percentages of the injected carbon
349 mineralization, with gas-charged freshwater-basalt interaction mineralizing almost 100%
350 (~30.8 mmol/kgw) of the initial DIC and gas-charged seawater-basalt interaction mineralizing
351 almost 99% (~31.6 mmol/kgw) of the initial DIC. The DS is nearly completely mineralized

352 during the injection of gas-charged freshwater, but only ~74% of this sulfur is mineralized
353 during the injection of gas-charged seawater; yet, almost 100% of the injected H₂S is
354 mineralized even during seawater injection. The sulfur remaining in the fluid phase is in the
355 form of sulfate. For both the gas-charged freshwater and seawater injections, most of the
356 DIC is mineralized before 0.14 mol of basaltic glass has dissolved, whereas only half of this
357 basalt is required to mineralize most of the H₂S.

358 At this temperature, in both the freshwater and seawater systems, the CO₂ is
359 mineralized mainly as calcite, with lesser amounts of ankerite precipitating near the end of
360 the calculations. The DS is mineralized as pyrite during both the freshwater and seawater
361 injections, with only a minor amount of anhydrite formed due to gas-charged seawater
362 injection at this temperature. The other minerals observed as secondary phases throughout
363 the dissolution-precipitation reaction path during freshwater injections, in descending order of
364 molar abundance, are Mg-smectites, Ca-zeolites (mordenite and thomsonite), ilmenite, Fe-
365 smectites, K-smectites, and celadonite. In the seawater system, the secondary minerals are
366 Mg-smectites, hematite, ilmenite, and Ca-zeolites (mordenite and thomsonite). Fe-smectites,
367 K-smectites and celadonite are observed only in the freshwater system, whereas hematite
368 was only observed to form in the seawater system. Ca-zeolites are more abundant during the
369 freshwater injection, whereas Mg-smectites are more abundant during the seawater injection.

370 In the freshwater system, calcium is consumed in descending order of molar
371 abundance by calcite, ankerite, mordenite and laumontite, with ~57% of Ca incorporated into
372 calcite throughout the whole path, ~3% by ankerite, and ~40% by zeolites. In the seawater
373 system, the same minerals compete for Ca, with calcite consuming ~55% of the available Ca
374 throughout the whole reaction, and about ~15% each is consumed by zeolites, ankerite, and
375 anhydrite.

376 The volume of the precipitating phases is +18% larger than that of the dissolving basalt
377 during the freshwater injection but only +14% during the seawater injection. This volume
378 increase can be related to the abundance of both the smectitic clay minerals and the
379 zeolites.

380

381 **3.5. Reaction path calculations for gas-charged waters at 25 °C**

382 The results from both the gas-charged freshwater and the gas-charged seawater
383 reaction path models at 25 °C are illustrated in **Figure 6**. In the freshwater system, the pH
384 increases almost linearly from 4.9 to 11.9 with increasing basaltic glass dissolution, whereas
385 in the seawater system the pH increases linearly from 4.7 to 8.3 as 0.14 mol basalt is
386 dissolved per kg of injected solution, but from this point on the pH remains nearly constant.

387 Both the freshwater and seawater injections mineralize more than 90% (~28.4 and 32.0
388 mmol/kgw, respectively) of the injected DIC. In contrast, the DS is almost completely
389 mineralized during the freshwater injection, but only ~62% during the seawater injection
390 (~26.4 mmol/kgw total, of which 22.4 mmol/kgw comes from the dissolved gas). Most of the
391 DIC is mineralized in response to the first 0.12 mol of basaltic glass dissolution, whereas only
392 half of this basalt dissolution is required to mineralize most of the DS. The sulfur remaining in
393 the aqueous solution at the end of the calculation is mainly in the form of sulfate.

394 The injected CO₂ is primarily mineralized as calcite, while some ankerite is predicted to
395 form in the seawater system. The DS precipitates as pyrite during both the freshwater and
396 seawater injections. The other minerals observed as secondary phases during the
397 dissolution-precipitation reaction path in freshwater, in descending order of molar
398 abundance, are Mg-smectites, Ca-zeolites (chabazite and thomsonite), ilmenite, Fe-smectite,
399 Na-smectite, K-smectite, and celadonite. In the seawater system, the secondary minerals are
400 Mg-smectites, celadonite, hematite, ilmenite, K-smectite, Ca-zeolite (thomsonite), and Na-
401 smectite. Fe-smectites are formed only in response to the injection of gas-charged
402 freshwater, whereas hematite precipitates only in the response to the injection of gas-
403 charged seawater. Ca-zeolites are more abundant during the injection of freshwater, with
404 Mg-smectites and celadonite more abundant during the injection of seawater.

405 In the freshwater system, aqueous calcium is consumed, in order of abundance,
406 calcite, chabazite and thomsonite, with ~70% of the Ca precipitating as calcite, and the rest
407 as Ca-zeolites. During the seawater injection, calcite, ankerite and thomsonite compete for

408 Ca, with calcite consuming ~65% of the available Ca over the reaction path, but significant
409 amounts of ankerite and zeolite are also calculated to form. As was the case for the higher
410 temperature models, the formation of these minerals leads to a net volume increase in the
411 solid phases in both freshwater and seawater systems of 9 and 12%, respectively.

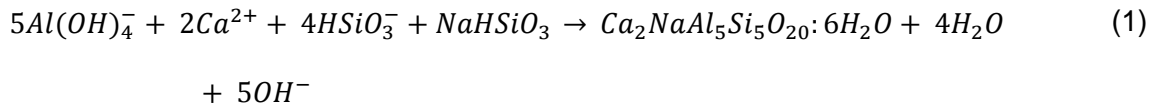
412

413 **3.6. Reaction path calculations for CO₂-rich waters**

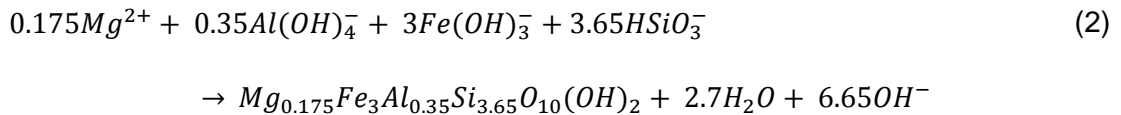
414 The results from the additional reaction path calculations run for systems having higher
415 DIC concentrations are summarized in **Figure 7**. In these calculations, the freshwater or
416 seawater was first equilibrated with 9 bar CO₂ at 67 °C prior to its injection. For these
417 calculations, 1 kg of initial gas-charged freshwater or seawater was reacted in 70
418 consecutive reaction steps, each adding 0.02 mol of basaltic glass. This increased mass of
419 basaltic glass dissolution was necessary to mineralize the CO₂ in the injected waters, which
420 have substantially higher carbon concentrations than in the previous model calculations.

421 In the case of the injection of either CO₂-rich freshwater or CO₂-rich seawater at
422 temperatures ≤170 °C, the dissolution of 0.4 mol of basaltic glass was sufficient to mineralize
423 ~90% of the injected CO₂, whereas around 4 times more basaltic glass dissolution was
424 required for this mineralization at 260 °C due to the formation of other Ca-bearing secondary
425 minerals. The fluid pH of the injected waters after 90% of the injected DIC was mineralized
426 differed between the freshwater and the seawater system. For the freshwater injection this
427 pH ranged from between 8.8 and 9.8, depending on temperature. The pH of the injected
428 CO₂-rich seawater was more strongly buffered; the pH of the fluid phase after ~90% of the
429 DIC had mineralized ranged from 5.7 to 6.4 at temperatures ≤170 °C but was 8.1 at 260 °C.
430 As further DIC mineralized, the calculations for both the freshwater and seawater systems
431 suggest that the pH continues to increase to above 10, which is higher than the maximum pH
432 around 9 typically observed for groundwater isolated from the atmosphere in contact with
433 alumino-silicate minerals (Langmuir, 1997). These anomalous high pH are due to the
434 continued calculated precipitation of zeolites and clay at alkaline conditions. For example,

435 thomsonite (**Equation 1**) and saponite-Fe-Mg (**Equation 2**) are predicted to form at pH 10
436 according to



437 and



438 The continued precipitation of these minerals at elevated pH in the calculations suggests
439 some inconsistencies in the thermodynamic database for one or more of these phases or the
440 aqueous species of their constituent metals at high pH.

441 The solid phases predicted to form according to the reaction path calculations were
442 compared to the results of corresponding experimental data reported in a number of studies
443 of high pCO_2 gas-charged water-basalt interaction (e.g., Gysi and Stefánsson, 2012a; Gysi
444 and Stefánsson, 2012b; Kanakiya et al., 2017; Schaef et al., 2010; Shibuya et al., 2013;
445 Sissmann et al., 2014), and to observations of mineral assemblages in CO_2 -rich natural
446 systems (Freedman et al., 2009; Nakamura and Kato, 2004; Neuhoff et al., 1999; Rogers et
447 al., 2006; Schiffman and Fridleifsson, 1991; Shibuya et al., 2012). Similar to these past
448 studies, our calculations exhibit the precipitation of carbonates and other non-carbonate
449 phases such as chlorites, zeolites and clay minerals as the fluid pH increases (see
450 **Appendix A**). Some differences are nevertheless evident. In contrast to the previous studies,
451 amorphous silica was not predicted to precipitate during the 100 °C CO_2 -rich freshwater
452 reaction path calculations, despite it having been observed upon CO_2 input to the
453 experimental systems at 75 and 150 °C by Gysi and Stefánsson (2012c), at 150 °C by
454 Sissmann et al. (2014), and in West Greenland basalts altered at 80-125 °C by Rogers et al.
455 (2006). Epidote was predicted to form in the model calculations during both the freshwater
456 and seawater injections at 260 °C, similar to its presence as a secondary mineral reported in
457 field studies of hydrothermally altered mafic systems (e.g., Freedman et al., 2009; Schiffman
458 and Fridleifsson, 1991). Yet, this mineral was not detected at comparable temperatures

459 during water-dissolved CO₂-basalt experimental studies (e.g., Gysi and Stefánsson, 2012b;
460 Shibuya et al., 2013) or other field observations (e.g., Nakamura and Kato, 2004).

461

462 **3.7. Reaction path model results for gas-free waters**

463 Reaction path calculations with gas-free freshwater or seawater were included to better
464 constrain the effect of the presence of injected gases on the rock volume changes. For the
465 reaction path run in the presence of seawater at 170 °C, kaolinite was allowed to precipitate
466 in addition to the already listed secondary minerals in the gas-charged system as it was
467 computed to be supersaturated at times in the fluids phase. For the purpose of this study,
468 only the output results on the rock volume changes were discussed below; yet all the
469 reaction path calculation outputs were summarized and made available in **Appendix B**.

470

471 **4. DISCUSSION**

472 **4.1. Gas-charged water injection: comparison with field data**

473 The results of the reaction path calculations based on the CarbFix2 gas injection
474 conditions (**Figure 2**) are in close agreement with the chemical composition of the fluid
475 sampled from the field monitoring well HE31 during this injection (Clark et al., 2020). The
476 modelled pH of this 260 °C freshwater injection matches the pH of the CarbFix2 monitoring
477 fluids after the dissolution of about 0.2 mol of basalt. Also, the computed saturation states
478 determined from the calculations agree well with the monitoring results for most minerals
479 although they underestimate those of the Fe-bearing phases such as ankerite, pyrite,
480 daphnite, and epidote. This underestimation is most likely related to the assumption of full
481 oxidation-reduction (redox) equilibrium in the model calculations, while measured
482 sulfide/sulfate redox couple concentrations were used to interpret the field-obtained
483 monitoring data. These differences suggest that full redox equilibrium might not have been
484 achieved in the CarbFix2 system in the field.

485 The mineral assemblages predicted to form by the reaction path calculations shown in
486 **Figure 3** are similar to the observed secondary mineralogy produced by the freshwater

487 hydrothermal alteration of basaltic rocks in natural analogues (e.g., Kristmannsdóttir, 1979;
488 Snæbjörnsdóttir et al., 2018b), and gas-water-basalt interaction experiments performed at
489 250 °C (Stefánsson et al., 2011; Thien et al., 2015). Calculations indicate Mg-chlorite
490 (clinochlore) precipitation throughout the whole reaction path, while epidote is calculated to
491 precipitate only at pH >7, consistent with the mineralogy seen on the top of the chlorite-
492 epidote zone of basalt alteration in the Hellisheiði reservoir (Snæbjörnsdóttir et al., 2018b).
493 Albite formation reflects the process of albitization associated with the alteration of Ca-rich
494 plagioclase as expected to occur at this temperature (Franzson et al., 2008; Snæbjörnsdóttir
495 et al., 2018b). Model results also confirm field observations that DS mineralizes as pyrite
496 earlier, in terms of the amount of basaltic glass dissolved, compared to the carbonation of
497 DIC as calcite. Pyrite forms during the first reaction path steps up until the pH reached ~7,
498 when its precipitation is slowed by epidote formation (Stefánsson et al., 2011). Significant
499 amounts of calcite are calculated to begin forming at pH >7.3, consistent with the
500 observations reported by Clark et al. (2020) where calcite only precipitated when sufficient
501 basaltic glass has dissolved to neutralize the acidic injection fluids. At lower pH, the Ca-
502 bearing mineral prehnite is predicted to precipitate. Another Ca-bearing phase potentially
503 competing with calcite for aqueous calcium is tremolite (the Ca-Mg end-member of
504 actinolite), which was found to be supersaturated in both the modelled and monitored fluids
505 (**Figure 2**). Note, however, that actinolite is found in Icelandic geothermal systems only when
506 temperatures exceed 280 °C (Kristmannsdóttir, 1979), so that its precipitation during the
507 reaction path calculations was not allowed.

508 The results of DIC mineralization in the gas-charged seawater calculations can be
509 compared with field studies of oceanic crust alteration (Alt and Teagle, 1999; Coggon et al.,
510 2004; Coogan and Gillis, 2013; Gillis and Coogan, 2011; Rausch et al., 2013; Staudigel et
511 al., 1989). On average, the carbonate content as CaCO₃ within the upper 600–700 m of
512 global oceanic crust, equal to 10% of the average thickness of this crust, is ~1.5 wt%
513 (Rausch, 2012). Though, within the uppermost 300 m of submarine volcanic basalts the
514 carbonate abundance can reach as much as ~11 wt%, mainly as calcite, with carbonate

515 veins commonly filled at temperatures below 100 °C during the Cretaceous, when the
516 atmospheric CO₂ concentration was higher than at present (Alt and Teagle, 1999; Staudigel
517 et al., 1989). Note, the results from the reaction path calculations at 25 and 100 °C for the
518 seawater system suggest the mineralization of CO₂ via the precipitation of mainly calcite, but
519 also some ankerite (**Figures 5 and 6, h**). Coogan and Gillis (2013) suggested that the higher
520 CO₂ content in Cretaceous seawater led to an enhanced alkalinity production during fluid-
521 rock reaction in the oceanic crust, allowing for substantially more CO₂ to be taken up as
522 calcite, similarly to what has been suggested during the injection of CO₂-charged freshwater
523 at Hellisheiði (Clark et al., 2020). Studies of hydrothermally altered reservoirs also
524 demonstrate that in seawater charged with up to ~6 bar pCO₂, such as in Reykjanes,
525 Iceland, calcite contents can reach ~13 wt% (Freedman et al., 2009; Wiese et al., 2008).

526

527 **4.2. Effect of dissolved gas injection on reacted rock volume changes**

528 Water-basalt interaction in natural systems, even without any added gases, generates
529 significant rock volume changes. The addition of gases to the injected fluid enhances the
530 physical and chemical alteration of primary basalt, as observed in field and modelling studies
531 (e.g., Snæbjörnsdóttir et al., 2018a; Thien et al., 2015). Changes in rock volume determined
532 for each reaction path system in the more dilute gas calculations corresponds to the
533 response of the water-rock system to the dissolution of 0.2 mol of basaltic glass into 1 kg of
534 gas-charged water over time and distance. The relative effect of gas injection on reservoir
535 rock volume changes was estimated by comparing model outputs from corresponding gas-
536 charged and gas-free injection calculations (see **Appendix B**). The results of such a
537 comparison are shown in **Figure 8**.

538 A notably higher final rock volume change is predicted for gas-charged freshwater
539 injection compared to gas-free freshwater injection at all temperatures except for 170 °C. In
540 contrast, the addition of gas to seawater leads to significantly higher rock volume changes
541 only at 25 °C. At 100 °C, the rock volume change in response to the gas-free seawater
542 injection is comparable to that observed in response to the gas-charged seawater injection

543 (12% and 14%, respectively). This result is due to the decreased formation of zeolites
544 minerals in the latter case. At 170 and 260 °C, lower rock volume changes are predicted for
545 the gas-charged seawater injection compared to the gas-free seawater injection due to the
546 decreased precipitation of voluminous kaolinite, Na-zeolite and chlorite in the presence of
547 CO₂ and H₂S. At 260 °C, more chlorite precipitation is calculated to occur during the injection
548 of seawater compared to the injection of freshwater leading to a larger increase in rock
549 volume in the former. On the other hand, smaller rock volume changes are observed during
550 gas-charged seawater injection compared to gas-charged freshwater injection at
551 temperatures ≤170 °C. It should also be noted that during all the gas-charged injections other
552 than gas-charged seawater at 260 °C a negligible change (<3%) to the rock volume is
553 predicted during the dissolution of the first 0.02 mol of basaltic glass, which limits the risk of
554 clogging in the proximity of the injection well.

555

556 **4.3. Effects of reservoir temperature on injected gas mineralization**

557 A comparison of the model results from the more dilute gas calculations shows that the
558 secondary phase mineralogy, and thus the mineralization of DIC and DS, varies as a function
559 of temperature. At 260 °C, the majority of aqueous Ca is consumed by epidote and prehnite,
560 as well as anhydrite in the case of the seawater systems, while most aqueous Ca is
561 consumed by carbonate formation at lower temperatures, leading to more efficient DIC
562 mineralization. The amount of H₂S-mineralization does not change substantially with
563 temperature, with calculations showing that even at 25 °C, most of the added DS from the
564 injected gas-charged fluid is mineralized after no more than 0.2 mol/kgw of basaltic glass
565 dissolution. In addition to H₂S storage, a generally increasing desulfurization trend is
566 observed during gas-charged seawater injection as a function of increasing temperature; the
567 amount of sulfate originally contained in the seawater fixed by mineral reactions increases
568 from 20 to 100% with increasing temperature from 25 to 260 °C. This sulfate removal is due
569 to both redox reactions and precipitation of anhydrite (see Section 4.4).

570 In the 260 °C systems, chlorite minerals were allowed to precipitate during the
571 calculations rather than smectite. Note, however, that there is an ongoing debate
572 surrounding smectite formation temperatures and stabilities, with some experimental
573 observations suggesting smectite formation at temperatures as high as at 300 °C in the
574 presence of seawater (Seyfried and Bischoff, 1979; Seyfried and Bischoff, 1981; Voigt et al.,
575 2018b). One possibility is that smectite is a meta-stable phase at these (and even lower)
576 temperatures and slowly transforms to mixed-layer clays, and eventually to chlorite
577 (Schiffman and Fridleifsson, 1991). The formation of clays and zeolites is pervasive at
578 temperatures below 260 °C, and the precipitation of these minerals consumes pore space,
579 increasing the potential of clogging flow paths in the reservoir at some distance from the
580 injection well, but, leaves Ca available in solution for carbon mineralization.

581 All calculations suggest that lower temperatures mineralize the injected carbon and
582 sulfur more efficiently, as fewer Ca-bearing non-carbonate minerals and fewer Fe-bearing
583 non-sulfide minerals form (**Figure 9**). However, as illustrated in **Figure 9c**, reaction rates
584 change dramatically with temperature. Based on the activation energy of 25.5 kJ/mol
585 (Gislason and Oelkers, 2003), and the Arrhenius (1889) equation, the basaltic glass
586 dissolution is estimated to proceed at rates almost two orders of magnitude slower at 25 °C
587 than at 260 °C. As such, almost two orders of magnitude more reaction time might be
588 required for the same mass of basalt to dissolve at the lower temperature. Therefore, at low
589 temperatures, slow reaction kinetics will have to be compensated by longer flow paths or
590 slower flow rates than at higher temperatures for the complete mineralization of the injected
591 gases.

592

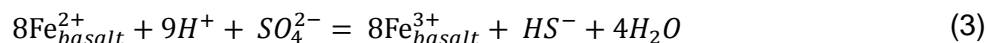
593 **4.4. Effects of fluid composition on injected gas mineralization.**

594 The calculations presented above for different fluid compositions (**Figures 3-6**) suggest
595 that the efficiency of gas-charged seawater carbon mineralization is somewhat lower than
596 that of freshwater for temperatures ≥ 170 °C, but similar for temperatures ≤ 100 °C at the
597 lower considered initial DIC concentration. For example, at 260 and 170 °C, to reach the

598 same amount of CO₂ mineralization obtained during the gas-charged freshwater injection
599 due the dissolution of 0.2 mol/kgw of basaltic glass requires 0.36 and 0.22 mol/kgw of
600 basaltic glass dissolution during the gas-charged seawater injection, respectively. At
601 temperatures ≥ 170 °C, the mineralization of DIC within carbonates in the presence of
602 seawater is slowed because of extensive early anhydrite formation decreasing the Ca
603 availability for carbonate mineral formation. This upper temperature limit for gas-charged
604 seawater injection can be further constrained by experimental observations of significant
605 amounts of anhydrite when heating seawater to temperatures above 150 °C (Bischoff and
606 Seyfried, 1978). At temperatures ≤ 100 °C, DIC mineralization is calculated to be similar for
607 both injected fluids in response to the dissolution of 0.2 mol/kgw basaltic glass, although the
608 calculations suggest somewhat different pH evolutions. In the presence of seawater, the
609 system pH is buffered at pH ≤ 6 due to enhanced clay mineral precipitation. As carbonate
610 formation is expected to begin at pH approaching neutrality, depending on the temperature,
611 the time required for the system to increase the pH towards more alkaline conditions might
612 slow DIC mineralization somewhat in the presence of seawater. The early formation of Mg-
613 chlorite at 260 °C, and clay minerals at temperatures ≤ 170 °C are the main processes
614 buffering the pH in the presence of seawater due to the production of H⁺ associated with their
615 precipitation. The precipitation of these minerals, therefore, could slow the onset of the Ca-
616 carbonate precipitation. This is qualitatively similar to what has been observed during some
617 CO₂- and H₂S-free seawater-basalt interaction experiments (Seyfried and Bischoff, 1977;
618 1979; 1981; Voigt et al., 2018b). In these experiments the pH initially drops, most likely due
619 to the formation of hydrated silicates.

620 The efficiency of DS mineralization in response to seawater injection is predicted to be
621 similar to that of freshwater at ≥ 170 °C, but lower at 100 °C or below (**Figures 3-6**). Note,
622 however, the total initial DS in the gas-charged seawater includes the sulfur naturally present
623 in seawater itself as sulfate. Almost all of the dissolved H₂S is mineralized during the
624 seawater injection at both 25 and 100 °C, in each case requiring the dissolution of only 0.08
625 mol/kgw basaltic glass. On the other hand, most of the sulfate in the seawater is removed by

626 anhydrite precipitation at temperatures ≥ 170 °C, and only up to 10% by sulfate reduction
627 reactions (**Figure 10**). Several factors influence the reduction of seawater sulfate in the
628 modelled system as this process depends on ferrous iron, proton, and sulfate availability
629 according to



630 where $\text{Fe}_{\text{basalt}}^{2+}$ and $\text{Fe}_{\text{basalt}}^{3+}$ correspond to the aqueous ferrous and ferric ions, respectively,
631 released by the dissolution of the basaltic glass.

632 The H^+ required for this reaction in natural hydrothermal systems has been attributed to Mg-
633 silicate formation reactions in previous experimental studies (e.g., Shanks et al., 1981). In the
634 reaction path calculations presented in this study, the formation of Mg-bearing phases does
635 not always provide sufficient protons to allow the completion of reaction (3). In addition to H^+
636 availability, seawater sulfate reduction can proceed only if sufficient oxidizable ferrous iron is
637 released from the basalt as 8 Fe^{2+} are required to be oxidized to reduce one S^{6+} .
638 Furthermore, the early precipitation of anhydrite and its separation from the flowing fluids
639 limits sulfate reduction in the model calculations performed for gas-charged seawater-basalt
640 interaction at 260 °C (**Figure 10**). Finally, the greater reduction potential of ferric iron
641 compared to that of sulfate leads to the oxidation of some H_2S in response to the release of
642 Fe^{3+} from the basalt, as can be seen in the initial reaction steps shown in **Figure 10**. The
643 associated oxidation of sulfide into sulfate is observed at every considered temperature until
644 less than at least 1 mmol/kgw of H_2S is left in the aqueous solution after which the reverse
645 redox reaction start to take place, in accord with **Eqn. 3**. Due to mass balance
646 considerations, 0.47 mmol/kg sulfate reduction is calculated for each 0.02 mol/kgw of
647 basaltic glass dissolved, assuming that all the iron in basalt is available as ferrous iron and
648 no Fe^{2+} -rich solid phase forms. The kinetics of the Fe-S redox reaction, however, may be a
649 limiting factor for this process. As described by Ohmoto and Lasaga (1982) and Shanks et al.
650 (1981), inorganic sulfate reduction rates are fast enough to become detectable and
651 geochemically important only at temperatures above 200 °C.

652 The injected fluid composition also affects the rock volume increase due to the coupled
653 dissolution-precipitation reactions in the lower considered DIC concentration systems as
654 shown in **Figure 9b**. At 260 °C, the rock volume increase during gas-charged seawater
655 injection is larger than that estimated for gas-charged freshwater injection due to the
656 formation of both chlorite and anhydrite. At 170 and 100 °C, a significantly smaller rock
657 volume increase is calculated for the seawater injection compared to the freshwater injection.
658 This latter difference stems from the enhanced precipitation of zeolites during the freshwater
659 injection. In contrast to the results at higher temperatures, reactions at 25 °C in response to
660 seawater injection led to a similar rock volume increase compared to the corresponding
661 freshwater injection. Note that most of the rock volume increases take place after substantial
662 basalt dissolution occurs, likely avoiding flow path clogging near the injection well (**Figures**
663 **3-6 k and l**).

664

665 **4.5. Effects of CO₂ concentration on mineralization**

666 Calculations of basaltic glass interaction with fluids charged with higher CO₂
667 concentrations were run to provide insight into applying the CarbFix method to other gas
668 emitting industries, such as coal, gas-fired, and oil-fired power plants (Kagel and Gawell,
669 2005; U.S. Environmental Protection Agency, 2010; Xu et al., 2003). The CO₂ concentrations
670 for the injection fluids considered in these calculations were those equal to the fluid at
671 equilibrium with 9 bar CO₂ and the injecting pressure at the well head of Hellisheiði (Clark et
672 al., 2020).

673 No significant change in carbonate mineralogy was observed due to the increasing fluid
674 $p\text{CO}_2$, with Ca-carbonate being the dominant CO₂-bearing precipitating mineral phase. This
675 is in agreement with several experimental and modelling studies (e.g., Gysi and Stefánsson,
676 2012c; Rosenbauer et al., 2012; Sturmer et al., 2020). These studies showed that the
677 precipitation of Mg- and Fe-carbonates occurs *i*) from fluids with $p\text{CO}_2$ higher than 25 bar,
678 and *ii*) in presence of Mg-rich silicates such as olivine.

679 Relatively efficient CO₂-mineralization is found in all CO₂-rich freshwater and seawater
680 model calculations for temperatures ≤170 °C, with only 0.4 mol/kgw of basaltic glass required
681 to mineralize the CO₂ contained in these more gas-concentrated fluids (**Figure 7**). Note,
682 however, the time required for this carbonation will depend strongly on the mineral reaction
683 kinetics, which are not considered in these calculations. Given that the reaction path
684 calculations do not consider reaction rates, pH higher than 10 was also reached (**Figure 7**)
685 due to zeolite and clay minerals precipitation (**Equations 1 and 2**). The observation of such
686 high pH is uncommon in natural systems and as suggested above is due to the precipitation
687 of zeolites and clay minerals at extremely alkaline conditions in the model calculations. Such
688 computed results may be an effect of the uncertainty on the thermodynamic properties of
689 sheet silicates (Voigt et al., 2018a).

690 Both freshwater experiments (Gysi and Stefánsson, 2012c) and observations of basalt-
691 hosted petroleum reservoirs in the presence of brines (Rogers et al., 2006) suggested that
692 the mineralization of CO₂ at temperatures <100 °C was favoured by the formation of a
693 number of different carbonate minerals, including calcite, ankerite, and magnesite. The
694 formation of these carbonates in nature apparently stems from the formation of amorphous
695 silica instead of the zeolites and smectites seen in the model calculations. The formation of
696 these latter minerals may be inhibited kinetically at some conditions. To assess this
697 possibility, CO₂-rich reaction path calculations were run at 100 °C in both freshwater and
698 seawater systems without allowing zeolites and smectites to form. The results of these
699 additional calculations shows that amorphous silica is expected to form in the absence of Ca-
700 zeolites formation. Similarly, slow precipitation kinetics may explain the absence of epidote in
701 high pCO₂ laboratory experiments (e.g., Gysi and Stefánsson, 2012c; Shibuya et al., 2013),
702 as the reactive path calculations suggest epidote precipitation at 260 °C in response to CO₂-
703 rich water injections. Also, based on the study of relatively fresh and strongly altered Archean
704 basaltic rocks, Nakamura and Kato (2004) suggested that the absence of Ca-Al silicate
705 minerals such as epidote and actinolite in strongly altered rocks was due to the continued
706 presence of CO₂-rich hydrothermal fluids inhibiting their growth. The absence and/or delayed

707 formation of epidote and Ca-zeolites would favour the carbon mineralization as more Ca
708 would be available in the fluid phase to form Ca-carbonate minerals.

709

710 **5. SUMMARY AND CONCLUSIONS**

711 Reaction path model calculations were used in this study to assess the potential use of
712 gas-charged seawater injection into basalts for subsurface CO₂ and H₂S mineralization. The
713 model calculations were validated by the comparison of model results for gas-charged
714 freshwater-basalt interaction at 260 °C with major elemental concentrations, mineralization
715 percent of DIC and DS, and secondary mineral assemblages observed from the ongoing
716 CarbFix2 injection. The results of the reaction path calculations presented above suggest
717 that:

- 718 • 260 °C or higher temperatures are not optimal for carbon mineralization, in particular
719 when injecting gas-charged seawater: i) relatively more basaltic glass dissolution is
720 necessary compared to lower temperatures to increase the pH sufficiently to enable CO₂
721 mineralization, and ii) early anhydrite formation consumes most of the Ca available in the
722 solution and increases the risk of clogging near the injection well in seawater systems;
- 723 • Below 260 °C, most Ca is predicted to be consumed by carbonate minerals, i.e. used for
724 mineralization of CO₂ (mainly as calcite and in some cases ankerite);
- 725 • For gas-charged freshwater injections, the best conditions for the subsurface
726 mineralization are at temperatures between 25 and 170 °C, where high degrees of CO₂
727 and H₂S mineralization have been predicted;
- 728 • For gas-charged seawater injection, the upper temperature limit for the mineral
729 carbonation process is likely dictated by the anhydrite thermal stability field (which is
730 above ~150 °C), below which the efficient mineralization of CO₂ and H₂S is observed.

731 Overall, these results indicate that the main limiting factor constraining mineral carbonation at
732 high temperatures is the competition of secondary minerals for Ca, the main cation required
733 for DIC mineralization, whereas at low temperatures the formation of silicate phases can
734 uptake a significant portion of pore space within the potential reservoir. Calculations

735 performed for the injection of more CO₂ concentrated fluids found that the injection of CO₂-
736 rich freshwater was more efficient for carbon mineralization than CO₂-rich seawater at 260
737 °C, but similar efficiencies were found for temperatures ≤170 °C. At these lower
738 temperatures, however, the fluid chemistry reaction pathway of the CO₂-rich freshwater
739 injection differs from that of the CO₂-rich seawater. In the seawater systems, the pH is
740 buffered at ≤6 for substantial time due to clay mineral formation, which may lead to
741 somewhat slower carbonation rates.

742 Key factors controlling the rates of carbon storage via mineralization will likely be a) the
743 rates of basalt dissolution and secondary mineral precipitation, which at 25 °C is likely
744 around two orders of magnitude lower than at 260 °C, and b) the possible absence of
745 zeolites and clay minerals in the presence of high pCO₂ fluids, which could favour an earlier
746 precipitation of carbonates.

747 The mineralization of sulfate injected into the subsurface during gas-charged seawater
748 injections can be influenced by oxidation-reduction reactions. Five major factors influencing
749 this redox process were identified: i) availability of H⁺, added to the fluid by Mg-phase
750 precipitation; ii) availability of Fe²⁺, associated with the basalt dissolution; iii) availability of
751 sulfate, associated with the early anhydrite precipitation; iv) presence of H₂S in the fluid
752 phase; and v) rate of Fe-S redox reactions relative to the rates of Fe²⁺-rich secondary
753 phases. Calculations suggested that the highest degree of sulfate reduction occurs at 170
754 °C, mainly due to a relatively low amount of anhydrite precipitation compared to higher
755 temperatures, and to a higher availability of Fe²⁺ compared to lower temperatures, where
756 several other Fe²⁺-rich secondary phases are predicted to form.

757 It should be noted that all the reaction path models presented in this study were run
758 assuming local geochemical equilibrium of the precipitated phases. Such may be only partly
759 achieved in real systems, as reaction kinetics may play a role, particularly at lower
760 temperatures. Nevertheless, the highest carbon and sulfur mineralization potential seems to
761 lie at temperatures ≤170 °C, warranting investigations of the rates of carbonation reactions at
762 these conditions.

763 Most significantly, the results of this study suggest that the carbonation of gas-charged
764 seawater may be in many cases as efficient as the carbonation of gas-charged freshwater.
765 As the CarbFix approach requires substantial quantities of water for injection, the successful
766 mineralization of CO₂-charged seawater will extend this method's applicability. For example,
767 submarine basalts as well as large igneous provinces (Snæbjörnsdóttir et al., 2020) nearby
768 the coast could be suitable reservoirs for additional pilot injections using this approach.

769

770 **Acknowledgements**

771 We thank Editor Charles Jenkins, Daniel Sturmer, and the anonymous reviewer for their
772 constructive comments that have improved the paper. This work is part of the CarbFix project
773 and has received funding from the European Union's Horizon 2020 research and innovation
774 programme under grant agreement No. 764760. We also thank Thomas Ratouis and the
775 whole Reykjavik Energy-Carbfix team for providing technical feedback and access to drilling
776 reports during the article preparation.

777

778 **Appendix A**

779 Results of reaction path calculations with CO₂-rich fluids at 25 (Fig. A1), 100 (Fig. A2), 170
780 (Fig. A3), and 260 °C (Fig. A4) of pH, mineralized proportion of DIC and DS, cumulative
781 secondary mineral abundance per kg of injected fluid, Ca distribution, cumulative total
782 volume of minerals per kg of injected fluid and their volume change for freshwater (left) and
783 seawater (right) injections.

784 **Appendix B**

785 Results of reaction path calculations with gas-free fluids at 25 (Fig. B1), 100 (Fig. B2), 170
786 (Fig. B3), and 260 °C (Fig. B4) of pH, mineralized proportion of DIC and DS, cumulative
787 secondary mineral abundance per kg of injected fluid, Ca distribution, cumulative total
788 volume of minerals per kg of injected fluid and their volume change for freshwater (left) and
789 seawater (right) injections.

790

791 **References**

- 792 Alfredsson, H.A., Oelkers, E.H., Hardarsson, B.S., Franzson, H., Gunnlaugsson, E.,
793 Gíslason, S.R., 2013. The geology and water chemistry of the Hellisheidi, SW-Iceland carbon
794 storage site. *International Journal of Greenhouse Gas Control* 12, 399-418.
- 795 Alt, J.C., 1995. Subseafloor processes in mid-ocean ridge hydrothermal systems. *Seafloor*
796 *Hydrothermal Systems: Physical, chemical, biological, and geological interactions*, 85-114.
- 797 Alt, J.C., Kinoshita, H., Stokking, L.B., Allerton, Bach, Becker, K., Boehm, Brewer, Dilek,
798 Filice, Fisk, Fujisawa, Fumes, Querin, Harper, Honnorez, Hoskins, Ishizuka, Laveme,
799 McNeill, Magenheim, Miyashita, Pezard, Salisbury, Tartarotti, H., T.D.A., Vanko, Wilkens,
800 Worm, 1996. *Proc. ODP, Sci. Results*, 148, Ocean Drilling Program, College Station, TX.
- 801 Alt, J.C., Teagle, D.A.H., 1999. The uptake of carbon during alteration of ocean crust.
802 *Geochimica et Cosmochimica Acta* 63, 1527-1535.
- 803 Appelo, C.A.J., Parkhurst, D.L., Post, V.E.A., 2014. Equations for calculating
804 hydrogeochemical reactions of minerals and gases such as CO₂ at high pressures and
805 temperatures. *Geochimica et Cosmochimica Acta* 125, 49-67.
- 806 Arrhenius, S., 1889. About the heat of dissociation and the influence of temperature on the degree
807 of dissociation of electrolytes. *J. Phys. Chem.* 4, 96-116.
- 808 Bader, M.S.H., 2007. Sulfate removal technologies for oil fields seawater injection
809 operations. *Journal of Petroleum Science and Engineering* 55, 93-110.
- 810 Bischoff, J.L., Seyfried, W.E., 1978. Hydrothermal chemistry of seawater from 25 degrees to
811 350 degrees C. *American Journal of Science* 278, 838-860.
- 812 Blounot, C.W., Dickson, F.W., 1969. The solubility of anhydrite (CaSO₄) in NaCl-H₂O from
813 100 to 450°C and 1 to 1000 bars. *Geochimica et Cosmochimica Acta* 33, 227-245.
- 814 Clark, D.E., Gunnarsson, I., Aradóttir, E.S., Þ. Arnarson, M., Þorgeirsson, Þ.A.,
815 Sigurðardóttir, S.S., Sigfússon, B., Snæbjörnsdóttir, S.Ó., Oelkers, E.H., Gíslason, S.R.,
816 2018. The chemistry and potential reactivity of the CO₂-H₂S charged injected waters at the
817 basaltic CarbFix2 site, Iceland. *Energy Procedia* 146, 121-128.
- 818 Clark, D.E., Oelkers, E.H., Gunnarsson, I., Sigfússon, B., Snæbjörnsdóttir, S.Ó., Aradóttir,
819 E.S., Gíslason, S.R., 2020. CarbFix2: CO₂ and H₂S mineralization during 3.5 years of
820 continuous injection into basaltic rocks at more than 250 °C. *Geochimica et Cosmochimica*
821 *Acta* 279, 45-66.
- 822 Coggon, R.M., Teagle, D.A.H., Cooper, M.J., Vanko, D.A., 2004. Linking basement
823 carbonate vein compositions to porewater geochemistry across the eastern flank of the Juan
824 de Fuca Ridge, ODP Leg 168. *Earth and Planetary Science Letters* 219, 111-128.
- 825 Coogan, L.A., Gillis, K.M., 2013. Evidence that low-temperature oceanic hydrothermal
826 systems play an important role in the silicate-carbonate weathering cycle and long-term
827 climate regulation. *Geochemistry, Geophysics, Geosystems* 14, 1771-1786.
- 828 Dai, Z., Kan, A.T., Shi, W., Zhang, N., Zhang, F., Yan, F., Bhandari, N., Zhang, Z., Liu, Y.,
829 Ruan, G., 2017. Solubility measurements and predictions of gypsum, anhydrite, and calcite
830 over wide ranges of temperature, pressure, and ionic strength with mixed electrolytes. *Rock*
831 *Mechanics and Rock Engineering* 50, 327-339.

- 832 Daval, D., 2018. Carbon dioxide sequestration through silicate degradation and carbon
833 mineralisation: promises and uncertainties. *npj Materials Degradation* 2, 11.
- 834 Davis, E.E., Mottl, M.J., Fisher, A.T., Firth, J.V., 1997. Proc. ODP, Init. Repts., 168, 470 pp.,
835 Ocean Drilling Program, College Station, TX.
- 836 Fisher, A.T., Tsuji, T., Petronotis, K., the Expedition 327 Scientists, 2011. *Proc. IODP*, 327:
837 Tokyo (Integrated Ocean Drilling Program Management International, Inc.).
- 838 Franzson, H., Zierenberg, R., Schiffman, P., 2008. Chemical transport in geothermal systems
839 in Iceland. *Journal of Volcanology and Geothermal Research* 173, 217-229.
- 840 Freedman, A.J.E., Bird, D.K., Arnórsson, S., Fridriksson, T., Elders, W.A., Fridleifsson, G.Ó.,
841 2009. Hydrothermal minerals record CO₂ partial pressures in the Reykjanes geothermal
842 system, Iceland. *American Journal of Science* 309, 788-833.
- 843 Galeczka, I., Wolff-Boenisch, D., Oelkers, E.H., Gislason, S.R., 2014. An experimental study
844 of basaltic glass–H₂O–CO₂ interaction at 22 and 50°C: Implications for subsurface storage of
845 CO₂. *Geochimica et Cosmochimica Acta* 126, 123-145.
- 846 Gillis, K.M., Coogan, L.A., 2011. Secular variation in carbon uptake into the ocean crust.
847 *Earth and Planetary Science Letters* 302, 385-392.
- 848 Gislason, S.R., Oelkers, E.H., 2003. Mechanism, rates, and consequences of basaltic glass
849 dissolution: II. An experimental study of the dissolution rates of basaltic glass as a function of
850 pH and temperature. *Geochimica et Cosmochimica Acta* 67, 3817-3832.
- 851 Gislason, S.R., Oelkers, E.H., 2014. Carbon storage in basalt. *Science* 344, 373-374.
- 852 Goldberg, D.S., Takahashi, T., Slagle, A.L., 2008. Carbon dioxide sequestration in deep-sea
853 basalt. *Proceedings of the National Academy of Sciences* 105, 9920.
- 854 Gudbrandsson, S., Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H., 2011. An experimental
855 study of crystalline basalt dissolution from 2 ≤ pH ≤ 11 and temperatures from 5 to 75 °C.
856 *Geochimica et Cosmochimica Acta* 75, 5496-5509.
- 857 Gunnarsson, I., Aradóttir, E.S., Oelkers, E.H., Clark, D.E., Arnarson, M.P., Sigfússon, B.,
858 Snæbjörnsdóttir, S.Ó., Matter, J.M., Stute, M., Júlíusson, B.M., Gíslason, S.R., 2018. The
859 rapid and cost-effective capture and subsurface mineral storage of carbon and sulfur at the
860 CarbFix2 site. *International Journal of Greenhouse Gas Control* 79, 117-126.
- 861 Gysi, A.P., Stefánsson, A., 2008. Numerical modelling of CO₂-water-basalt interaction.
862 *Mineralogical Magazine* 72, 55-59.
- 863 Gysi, A.P., Stefánsson, A., 2011. CO₂-water-basalt interaction. Numerical simulation of low
864 temperature CO₂ sequestration into basalts. *Geochimica et Cosmochimica Acta* 75, 4728-
865 4751.
- 866 Gysi, A.P., Stefánsson, A., 2012a. CO₂-water-basalt interaction. Low temperature
867 experiments and implications for CO₂ sequestration into basalts. *Geochimica et*
868 *Cosmochimica Acta* 81, 129-152.
- 869 Gysi, A.P., Stefánsson, A., 2012b. Experiments and geochemical modeling of CO₂
870 sequestration during hydrothermal basalt alteration. *Chemical Geology* 306-307, 10-28.

- 871 Gysi, A.P., Stefánsson, A., 2012c. Mineralogical aspects of CO₂ sequestration during
872 hydrothermal basalt alteration — An experimental study at 75 to 250°C and elevated pCO₂.
873 *Chemical Geology* 306-307, 146-159.
- 874 Helgadóttir, H.M., 2011. The Gráuhnúkar geothermal system, Helliheiði: Geology and
875 hydrothermal alteration. University of Iceland, p. 186.
- 876 Kagel, A., Gawell, K., 2005. Promoting geothermal energy: air emissions comparison and
877 externality analysis. *The Electricity Journal* 18, 90-99.
- 878 Kanakiya, S., Adam, L., Esteban, L., Rowe, M.C., Shane, P., 2017. Dissolution and
879 secondary mineral precipitation in basalts due to reactions with carbonic acid. *Journal of*
880 *Geophysical Research: Solid Earth* 122, 4312-4327.
- 881 Kelemen, P.B., Matter, J.M., 2008. In situ carbonation of peridotite for CO₂ storage.
882 *Proceedings of the National Academy of Sciences* 105, 17295-17300.
- 883 Kristmannsdóttir, H., 1979. Alteration of basaltic rocks by hydrothermal activity at 100-300
884 °C. *Developments in sedimentology* 27, 359-367.
- 885 Kristmannsdóttir, H., Tomasson, J., 1978. Zeolite zones in geothermal areas in Iceland, in:
886 Sand, L.B., Mumpton, F.M. (Eds.), *Natural Zeolite Occurrence, Properties and Use*.
887 Pergamon Press, Oxford, pp. 277-284.
- 888 Langmuir, D., 1997. *Aqueous Environmental Geochemistry*. Prentice Hall, Upper Saddle
889 River, NJ.
- 890 Larsson, D., Grönvold, K., Oskarsson, N., Gunnlaugsson, E., 2002. Hydrothermal alteration
891 of plagioclase and growth of secondary feldspar in the Hengill Volcanic Centre, SW Iceland.
892 *Journal of Volcanology and Geothermal Research* 114, 275-290.
- 893 Luhmann, A.J., Tutolo, B.M., Tan, C., Moskowitz, B.M., Saar, M.O., Seyfried, W.E., 2017.
894 Whole rock basalt alteration from CO₂-rich brine during flow-through experiments at 150 °C
895 and 150 bar. *Chemical Geology* 453, 92-110.
- 896 Marieni, C., Henstock, T.J., Teagle, D.A.H., 2013. Geological storage of CO₂ within the
897 oceanic crust by gravitational trapping. *Geophysical Research Letters* 40, 6219-6224.
- 898 Marieni, C., Prikryl, J., Aradóttir, E.S., Gunnarsson, I., Stefánsson, A., 2018. Towards 'green'
899 geothermal energy: Co-mineralization of carbon and sulfur in geothermal reservoirs.
900 *International Journal of Greenhouse Gas Control* 77, 96-105.
- 901 Matter, J.M., Stute, M., Snæbjörnsdóttir, S.Ó., Oelkers, E.H., Gislason, S.R., Aradóttir, E.S.,
902 Sigfusson, B., Gunnarsson, I., Sigurdardóttir, H., Gunnlaugsson, E., Axelsson, G.,
903 Alfredsson, H.A., Wolff-Boenisch, D., Mesfin, K., Taya, D.F.d.I.R., Hall, J., Dideriksen, K.,
904 Broecker, W.S., 2016. Rapid carbon mineralization for permanent disposal of anthropogenic
905 carbon dioxide emissions. *Science* 352, 1312.
- 906 McGrail, B.P., Schaef, H.T., Spang, F.A., Cliff, J.B., Qafoku, O., Horner, J.A., Thompson,
907 C.J., Owen, A.T., Sullivan, C.E., 2016. Field validation of supercritical CO₂ reactivity with
908 basalts. *Environmental Science & Technology Letters*.
- 909 Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L., 2005. *IPCC Special Report on*
910 *Carbon Dioxide Capture and Storage*, Cambridge University Press, UK.

- 911 Millero, F.J., Feistel, R., Wright, D.G., McDougall, T.J., 2008. The composition of standard
912 seawater and the definition of the reference-composition salinity scale. *Deep Sea Research*
913 *Part I: Oceanographic Research Papers* 55, 50-72.
- 914 Nakamura, K., Kato, Y., 2004. Carbonatization of oceanic crust by the seafloor hydrothermal
915 activity and its significance as a CO₂ sink in the Early Archean. *Geochimica et Cosmochimica*
916 *Acta* 68, 4595-4618.
- 917 Neuhoﬀ, P.S., Fridriksson, T., Arnorsson, S., Bird, D.K., 1999. Porosity evolution and mineral
918 paragenesis during low-grade metamorphism of basaltic lavas at Teigarhorn, eastern
919 Iceland. *American Journal of Science* 299, 467-501.
- 920 Neveu, M., Desch, S.J., Castillo-Rogez, J.C., 2017. Aqueous geochemistry in icy world
921 interiors: Equilibrium fluid, rock, and gas compositions, and fate of antifreezes and
922 radionuclides. *Geochimica et Cosmochimica Acta* 212, 324-371.
- 923 Oelkers, E.H., Gislason, S.R., 2001. The mechanism, rates and consequences of basaltic
924 glass dissolution: I. An experimental study of the dissolution rates of basaltic glass as a
925 function of aqueous Al, Si and oxalic acid concentration at 25 C and pH= 3 and 11.
926 *Geochimica et Cosmochimica Acta* 65, 3671-3681.
- 927 Oelkers, E.H., Gislason, S.R., Matter, J., 2008. Mineral carbonation of CO₂. *Elements* 4, 333-
928 337.
- 929 Ohmoto, H., Lasaga, A.C., 1982. Kinetics of reactions between aqueous sulfates and
930 sulfides in hydrothermal systems. *Geochimica et Cosmochimica Acta* 46, 1727-1745.
- 931 Pacala, S., Socolow, R., 2004. Stabilization wedges: Solving the climate problem for the next
932 50 years with current technologies. *Science* 305, 968-972.
- 933 Parkhurst, D.L., Appelo, C.A.J., 2013. Description of input and examples for PHREEQC
934 version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and
935 inverse geochemical calculations. US Geological Survey.
- 936 Peng, D.-Y., Robinson, D.B., 1976. Two and three phase equilibrium calculations for systems
937 containing water. *The Canadian Journal of Chemical Engineering* 54, 595-599.
- 938 Peuble, S., Godard, M., Luquot, L., Andreani, M., Martinez, I., Gouze, P., 2015. CO₂
939 geological storage in olivine rich basaltic aquifers: new insights from reactive-percolation
940 experiments. *Applied Geochemistry* 52, 174-190.
- 941 Power, I.M., Harrison, A.L., Dipple, G.M., Wilson, S.A., Kelemen, P.B., Hitch, M., Southam,
942 G., 2013. Carbon mineralization: from natural analogues to engineered systems. *Reviews in*
943 *Mineralogy and Geochemistry* 77, 305-360.
- 944 Rausch, S., 2012. Carbonate veins as recorders of seawater evolution, CO₂ uptake by the
945 ocean crust, and seawater-crust interaction during low-temperature alteration. Bremen,
946 Universität Bremen.
- 947 Rausch, S., Böhm, F., Bach, W., Klügel, A., Eisenhauer, A., 2013. Calcium carbonate veins
948 in ocean crust record a threefold increase of seawater Mg/Ca in the past 30 million years.
949 *Earth and Planetary Science Letters* 362, 215-224.
- 950 Rogelj, J., Shindell, D., Jiang, K., Fifita, S., Forster, P., Ginzburg, V., Handa, C., Kheshgi, H.,
951 Kobayashi, S., Krieglner, E., Mundaca, L., Séférian, R., Vilariño, M.V., 2018. Mitigation
952 Pathways Compatible with 1.5°C in the Context of Sustainable Development, in: Masson-

- 953 Delmotte, V., P. Zhai, H.-O. Pörtner, D. Roberts, J. Skea, P.R. Shukla, A. Pirani, W.
954 Moufouma-Okia, C. Péan, R. Pidcock, S. Connors, J.B.R. Matthews, Y. Chen, X. Zhou, M.I.
955 Gomis, E. Lonnoy, T. Maycock, M. Tignor, and T. Waterfield (Ed.), In: *Global Warming of*
956 *1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-*
957 *industrial levels and related global greenhouse gas emission pathways, in the context of*
958 *strengthening the global response to the threat of climate change, sustainable development,*
959 *and efforts to eradicate poverty, In Press.*
- 960 Rogers, K.L., Neuhoﬀ, P.S., Pedersen, A.K., Bird, D.K., 2006. CO₂ metasomatism in a
961 basalt-hosted petroleum reservoir, Nuussuaq, West Greenland. *Lithos* 92, 55-82.
- 962 Rose, N.M., 1991. Dissolution rates of prehnite, epidote, and albite. *Geochimica et*
963 *Cosmochimica Acta* 55, 3273-3286.
- 964 Rosenbauer, R.J., Thomas, B., Bischoﬀ, J.L., Palandri, J., 2012. Carbon sequestration via
965 reaction with basaltic rocks: Geochemical modeling and experimental results. *Geochimica et*
966 *Cosmochimica Acta* 89, 116-133.
- 967 Sanna, A., Uibu, M., Caramanna, G., Kuusik, R., Maroto-Valer, M., 2014. A review of mineral
968 carbonation technologies to sequester CO₂. *Chemical Society Reviews* 43, 8049-8080.
- 969 Schaef, H.T., McGrail, B.P., 2009. Dissolution of Columbia River Basalt under mildly acidic
970 conditions as a function of temperature: Experimental results relevant to the geological
971 sequestration of carbon dioxide. *Applied Geochemistry* 24, 980-987.
- 972 Schaef, H.T., McGrail, B.P., Owen, A.T., 2009. Basalt- CO₂-H₂O interactions and variability
973 in carbonate mineralization rates. *Energy Procedia* 1, 4899-4906.
- 974 Schaef, H.T., McGrail, B.P., Owen, A.T., 2010. Carbonate mineralization of volcanic province
975 basalts. *International Journal of Greenhouse Gas Control* 4, 249-261.
- 976 Schiffman, P., Fridleifsson, G.O., 1991. The smectite-chlorite transition in drillhole NJ-15,
977 Nesjavellir geothermal field, Iceland: XRD, BSE and electron microprobe investigations.
978 *Journal of Metamorphic Geology* 9, 679-696.
- 979 Seyfried, W., Bischoﬀ, J.L., 1977. Hydrothermal transport of heavy metals by seawater: the
980 role of seawater/basalt ratio. *Earth and Planetary Science Letters* 34, 71-77.
- 981 Seyfried, W.E., Bischoﬀ, J.L., 1979. Low temperature basalt alteration by sea water: an
982 experimental study at 70°C and 150°C. *Geochimica et Cosmochimica Acta* 43, 1937-1947.
- 983 Seyfried, W.E., Bischoﬀ, J.L., 1981. Experimental seawater-basalt interaction at 300°C, 500
984 bars, chemical exchange, secondary mineral formation and implications for the transport of
985 heavy metals. *Geochimica et Cosmochimica Acta* 45, 135-147.
- 986 Shanks, W.C., Bischoﬀ, J.L., Rosenbauer, R.J., 1981. Seawater sulfate reduction and sulfur
987 isotope fractionation in basaltic systems: interaction of seawater with fayalite and magnetite
988 at 200–350 °C. *Geochimica et Cosmochimica Acta* 45, 1977-1995.
- 989 Shibuya, T., Tahata, M., Kitajima, K., Ueno, Y., Komiya, T., Yamamoto, S., Igisu, M.,
990 Terabayashi, M., Sawaki, Y., Takai, K., Yoshida, N., Maruyama, S., 2012. Depth variation of
991 carbon and oxygen isotopes of calcites in Archean altered upperoceanic crust: Implications
992 for the CO₂ flux from ocean to oceanic crust in the Archean. *Earth and Planetary Science*
993 *Letters* 321-322, 64-73.

- 994 Shibuya, T., Yoshizaki, M., Masaki, Y., Suzuki, K., Takai, K., Russell, M.J., 2013. Reactions
995 between basalt and CO₂-rich seawater at 250 and 350 °C, 500 bars: Implications for the CO₂
996 sequestration into the modern oceanic crust and the composition of hydrothermal vent fluid in
997 the CO₂-rich early ocean. *Chemical Geology* 359, 1-9.
- 998 Sissmann, O., Brunet, F., Martinez, I., Guyot, F., Verlaguet, A., Piquier, Y., Daval, D., 2014.
999 Enhanced Olivine Carbonation within a Basalt as Compared to Single-Phase Experiments:
1000 Reevaluating the Potential of CO₂ Mineral Sequestration. *Environmental Science &*
1001 *Technology* 48, 5512-5519.
- 1002 Snæbjörnsdóttir, S.Ó., Gislason, S.R., 2016. CO₂ Storage potential of basaltic rocks offshore
1003 Iceland. *Energy Procedia* 86, 371-380.
- 1004 Snæbjörnsdóttir, S.Ó., Gislason, S.R., Galeczka, I.M., Oelkers, E.H., 2018a. Reaction path
1005 modelling of in-situ mineralisation of CO₂ at the CarbFix site at Hellisheidi, SW-Iceland.
1006 *Geochimica et Cosmochimica Acta* 220, 348-366.
- 1007 Snæbjörnsdóttir, S.Ó., Sigfússon, B., Marieni, C., Goldberg, D., Gislason, S.R., Oelkers,
1008 E.H., 2020. Carbon dioxide storage through mineral carbonation. *Nature Reviews Earth &*
1009 *Environment* 1, 90-102.
- 1010 Snæbjörnsdóttir, S.Ó., Tómasdóttir, S., Sigfússon, B., Aradóttir, E.S., Gunnarsson, G., Niemi,
1011 A., Basirat, F., Dessirier, B., Gislason, S.R., Oelkers, E.H., Franzson, H., 2018b. The geology
1012 and hydrology of the CarbFix2 site, SW-Iceland. *Energy Procedia* 146, 146-157.
- 1013 Snæbjörnsdóttir, S.Ó., Tómasdóttir, S., Sigfússon, B., Aradóttir, E.S., Gunnarsson, G., Niemi,
1014 A., Basirat, F., Dessirier, B., Gislason, S.R., Oelkers, E.H., Franzson, H., 2018c. The geology
1015 and hydrology of the CarbFix2 site, SW-Iceland. *Energy Procedia* 146, 146-157.
- 1016 Staudigel, H., Hart, S.R., Schmincke, H.-U., Smith, B.M., 1989. Cretaceous ocean crust at
1017 DSDP Sites 417 and 418: Carbon uptake from weathering versus loss by magmatic
1018 outgassing. *Geochimica et Cosmochimica Acta* 53, 3091-3094.
- 1019 Stefánsson, A., Arnórsson, S., Gunnarsson, I., Kaasalainen, H., Gunnlaugsson, E., 2011.
1020 The geochemistry and sequestration of H₂S into the geothermal system at Hellisheidi,
1021 Iceland. *Journal of Volcanology and Geothermal Research* 202, 179-188.
- 1022 Sturmer, D.M., Tempel, R.N., Soltanian, M.R., 2020. Geological carbon sequestration:
1023 Modeling mafic rock carbonation using point-source flue gases. *International Journal of*
1024 *Greenhouse Gas Control* 99, 103106.
- 1025 Thien, B.M.J., Kosakowski, G., Kulik, D.A., 2015. Differential alteration of basaltic lava flows
1026 and hyaloclastites in Icelandic hydrothermal systems. *Geothermal Energy* 3, 11.
- 1027 Trias, R., Ménez, B., le Campion, P., Zivanovic, Y., Lecourt, L., Lecoivre, A., Schmitt-
1028 Kopplin, P., Uhl, J., Gislason, S.R., Alfreðsson, H.A., Mesfin, K.G., Snæbjörnsdóttir, S.Ó.,
1029 Aradóttir, E.S., Gunnarsson, I., Matter, J.M., Stute, M., Oelkers, E.H., Gérard, E., 2017. High
1030 reactivity of deep biota under anthropogenic CO₂ injection into basalt. *Nature*
1031 *Communications* 8, 1063.
- 1032 U.S. Environmental Protection Agency, 2010. Available and emerging technologies for
1033 reducing greenhouse gas emissions from the petroleum refining industry. Office of Air and
1034 Radiation. Office of Atmospheric Programs, Research Triangle Park, North Carolina, October
1035 2010.

- 1036 Voigt, M., Marieni, C., Clark, D.E., Gíslason, S.R., Oelkers, E.H., 2018a. Evaluation and
1037 refinement of thermodynamic databases for mineral carbonation. *Energy Procedia* 146, 81-
1038 91.
- 1039 Voigt, M., Pearce, C.R., Baldermann, A., Oelkers, E.H., 2018b. Stable and radiogenic
1040 strontium isotope fractionation during hydrothermal seawater-basalt interaction. *Geochimica
1041 et Cosmochimica Acta*.
- 1042 Wiese, F., Fridriksson, T., Ármannsson, H., 2008. CO₂ fixation by calcite in high-temperature
1043 geothermal systems in Iceland. ÍSOR, Iceland Geosurvey, Reykjavík.
- 1044 Wolff-Boenisch, D., Galeczka, I.M., 2018. Flow-through reactor experiments on basalt-(sea)
1045 water-CO₂ reactions at 90 °C and neutral pH. What happens to the basalt pore space under
1046 post-injection conditions? *International Journal of Greenhouse Gas Control* 68, 176-190.
- 1047 Wolff-Boenisch, D., Gíslason, S.R., Oelkers, E.H., 2004a. The effect of fluoride on the
1048 dissolution rates of natural glasses at pH 4 and 25°C. *Geochimica et Cosmochimica Acta* 68,
1049 4571-4582.
- 1050 Wolff-Boenisch, D., Gíslason, S.R., Oelkers, E.H., 2006. The effect of crystallinity on
1051 dissolution rates and CO₂ consumption capacity of silicates. *Geochimica et Cosmochimica
1052 Acta* 70, 858-870.
- 1053 Wolff-Boenisch, D., Gíslason, S.R., Oelkers, E.H., Putnis, C.V., 2004b. The dissolution rates
1054 of natural glasses as a function of their composition at pH 4 and 10.6, and temperatures from
1055 25 to 74°C. *Geochimica et Cosmochimica Acta* 68, 4843-4858.
- 1056 Wolff-Boenisch, D., Wenau, S., Gíslason, S.R., Oelkers, E.H., 2011. Dissolution of basalts
1057 and peridotite in seawater, in the presence of ligands, and CO₂: implications for mineral
1058 sequestration of carbon dioxide. *Geochimica et Cosmochimica Acta* 75, 5510-5525.
- 1059 Xu, T., Apps, J.A., Pruess, K., Yamamoto, H., 2007. Numerical modeling of injection and
1060 mineral trapping of CO₂ with H₂S and SO₂ in a sandstone formation. *Chemical Geology* 242,
1061 319-346.
- 1062 Xu, X., Song, C., Wincek, R., Andresen, J.M., Miller, B.G., Scaroni, A.W., 2003. Separation
1063 of CO₂ from power plant flue gas using a novel CO₂ "molecular basket" adsorbent. *Fuel
1064 Chem. Div. Prepr* 48, 162-163.
- 1065

1066 **TABLES**

1067 **Table 1.** Physical and chemical properties of Stapafell basaltic glass (BG).

BG stoichiometry	$\text{SiTi}_{0.024}\text{Al}_{0.358}\text{Fe}_{0.188}\text{Mg}_{0.281}\text{Ca}_{0.264}\text{Na}_{0.079}\text{K}_{0.008}\text{O}_{3.370}$
Molecular weight	123 g/mol
Molar mass	$43.158 \text{ cm}^3/\text{mol}$

1068

1069 **Table 2.** Freshwater (Gunnarsson et al., 2018), seawater (Millero et al., 2008), and averaged
1070 formation water (Clark et al., 2020) compositions used in the reactive path calculations.
1071 Values are given in mmol/kgw; TA stands for total alkalinity, given in meq/kgw, and DIC for
1072 dissolved inorganic carbon.

	Freshwater	Seawater	Formation water
T, °C	25	25	263
pH	8.99	8.10	7.17
TA	1.88	2.30	2.34
DIC	0.35	2.04	8.15
Al	0.05	-	0.07
Si	8.45	-	8.84
Na	6.36	486	5.83
Mg	-	54.74	-
Ca	0.01	10.66	0.02
K	0.64	10.58	0.57
H ₂ S	0.49	-	1.05
SO ₄	0.24	29.26	0.27
Cl	3.58	566	2.89
F	0.05	0.07	0.10

1073

1074 **Table 3.** Initial fluid compositions of carbon and sulfur used for the gas-charged and CO₂-rich
1075 reaction path calculations. Total DIC and DS are the water concentrations that include
1076 injected CO₂ and H₂S, and carbon and sulfur already present in natural freshwater or
1077 seawater.

	Gas-charged freshwater	Gas-charged seawater	CO₂-rich freshwater	CO₂-rich seawater
Injected CO ₂ (mmol/kgw)	30.6	30.6	127.0	114.4
Injected H ₂ S (mmol/kgw)	21.9	21.9	21.9	21.9
Total DIC (mmol/kgw)	30.8	32.0	127.2	115.8
Total DS (mmol/kgw)	22.4	42.4	22.4	42.4

1078

1079 **Table 4.** Compositions, formulas, molar volumes and thermal stability field of the secondary
 1080 phases allowed to precipitate during the reaction path calculations presented in the present
 1081 study.

Phase	Formula	Molar volume (cm ³ /mol)	Thermal stability	Reference
Carbonates				
Ankerite	CaFe(CO ₃) ₂	66.060		
Aragonite	CaCO ₃	34.15		
Calcite	CaCO ₃	36.934		
Magnesite	MgCO ₃	28.018		
Siderite	FeCO ₃	29.378		
S-minerals				
Anhydrite	CaSO ₄	45.94	≥100 °C	[1]
Pyrite	FeS ₂	23.94		
Pyrrhotite	FeS	18.2		
Fe oxy-hydroxides				
Goethite	FeOOH	20.82		
Hematite	Fe ₂ O ₃	30.274		
Ilmenite	FeTiO ₃	32.15		
Magnetite	Fe ₃ O ₄	44.524		
Titanite	CaTiSiO ₅	55.65		
Feldspars				
Albite	NaAlSi ₃ O ₈	100.25	≥250 °C	[2]
K-feldspar	KAlSi ₃ O ₈	108.87	≥250 °C	[2]
Clay minerals (Smectites)				
Saponite-Fe-Fe	Fe _{3.175} Al _{0.35} Si _{3.65} O ₁₀ (OH) ₂	142.672	<200 °C	[3, 4, 5, 6]
Saponite-Fe-K	K _{0.35} Fe ₃ Al _{0.35} Si _{3.65} O ₁₀ (OH) ₂	147.639	<200 °C	[3, 4, 5, 6]
Saponite-Mg-Mg	Mg _{3.175} Al _{0.35} Si _{3.65} O ₁₀ (OH) ₂	140.285	<200 °C	[3, 4, 5, 6]
Saponite-Mg-K	K _{0.35} Mg ₃ Al _{0.35} Si _{3.65} O ₁₀ (OH) ₂	145.383	<200 °C	[3, 4, 5, 6]
Saponite-Mg-Fe	Fe _{0.175} Mg ₃ Al _{0.35} Si _{3.65} O ₁₀ (OH) ₂	140.416	<200 °C	[3, 4, 5, 6]
Beidellite-Ca	Ca _{0.175} Al _{2.35} Si _{3.65} O ₁₀ (OH) ₂	133.081	<200 °C	[3, 4, 5, 6]
Beidellite-Fe	Fe _{0.175} Al _{2.35} Si _{3.65} O ₁₀ (OH) ₂	134.293	<200 °C	[3, 4, 5, 6]
Beidellite-K	K _{0.35} Al _{2.35} Si _{3.65} O ₁₀ (OH) ₂	137.214	<200 °C	[3, 4, 5, 6]
Beidellite-Mg	Mg _{0.175} Al _{2.35} Si _{3.65} O ₁₀ (OH) ₂	132.116	<200 °C	[3, 4, 5, 6]
Beidellite-Na	Na _{0.35} Al _{2.35} Si _{3.65} O ₁₀ (OH) ₂	134.522	<200 °C	[3, 4, 5, 6]
Mica				
Celadonite	KMgAlSi ₄ O ₁₀ (OH) ₂	157.1	≤100 °C	[3]
Chlorites				
Clinochlore	Mg ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	207.11	>200 °C	[3, 5, 6]
Zeolites				
Analcime	Na _{0.96} Al _{0.96} Si _{2.04} O ₆ ·H ₂ O	97.43	<200 °C	[2]
Chabazite-Ca	CaAl ₂ Si ₄ O ₁₂ ·6H ₂ O	247.45	≤100 °C	[4]
Chabazite-Na	Na ₂ Al ₂ Si ₄ O ₁₂ ·6H ₂ O	247.45	≤100 °C	[4]
Laumontite	CaAl ₂ Si ₄ O ₁₂ ·4.5H ₂ O	209.68	100-200 °C	[4]
Mordenite-Ca	Ca _{0.5} AlSi ₅ O ₁₂ ·4H ₂ O	208.74	80-230 °C	[7]
Stilbite-Ca	CaAl ₂ Si ₇ O ₁₈ ·7H ₂ O	333.48	70-150 °C	[7]
Thomsonite	Ca ₂ NaAl ₅ Si ₅ O ₂₀ ·6H ₂ O	338.10	≤100 °C	[4]
Wairakite	CaAl ₂ Si ₄ O ₁₂ ·2H ₂ O	190.35	>180 °C	[2, 4]
Other silicates				
Epidote	Ca ₂ FeAl ₂ Si ₃ O ₁₂ OH	139.2	>200 °C	[2, 8]
Kaolinite *	Al ₂ Si ₂ O ₅ (OH) ₄	99.52		
Quartz	SiO ₂	22.68	>180 °C	[5]
Amorphous silica **	SiO ₂	29.00	75-150 °C	[9]
Prehnite	Ca ₂ Al ₂ Si ₃ O ₁₀ (OH) ₂	140.33	>200 °C	[8]

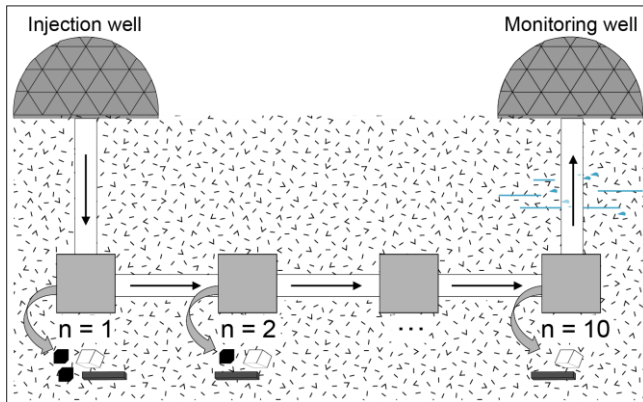
1082 [1] Blounot and Dickson (1969), [2] Larsson et al. (2002), [3] Alt (1995), [4] Kristmannsdóttir (1979), [5] Snæbjörnsdóttir et al.
 1083 (2018b), [6] Schiffman and Fridleifsson (1991), [7] Kristmannsdóttir and Tomasson (1978), [8] Rose (1991), [9] Gysi and
 1084 Stefánsson (2012c)

1085 * Only in seawater system without gases at 170 °C

1086 ** Only in systems with more concentrated CO₂ fluids

1087 **FIGURES**

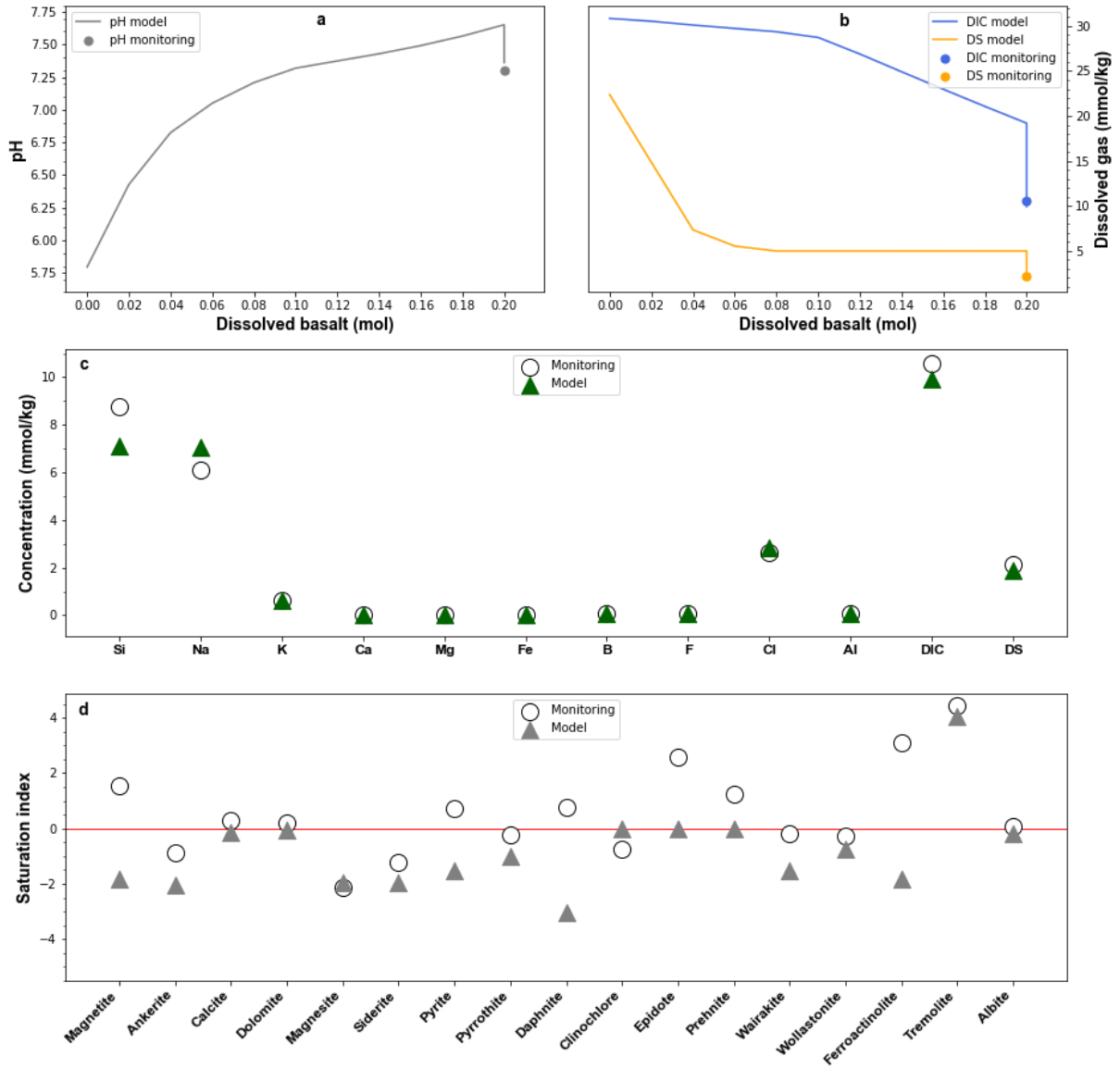
1088 **Figure 1.** Conceptual illustration of the reaction path model structure used in PHREEQC (v3)
1089 to simulate the injection front moving away from the injection well. In total, ten reactive rock
1090 'boxes' of porous basaltic glass were allowed to interact with the injected fluid consecutively.



1091

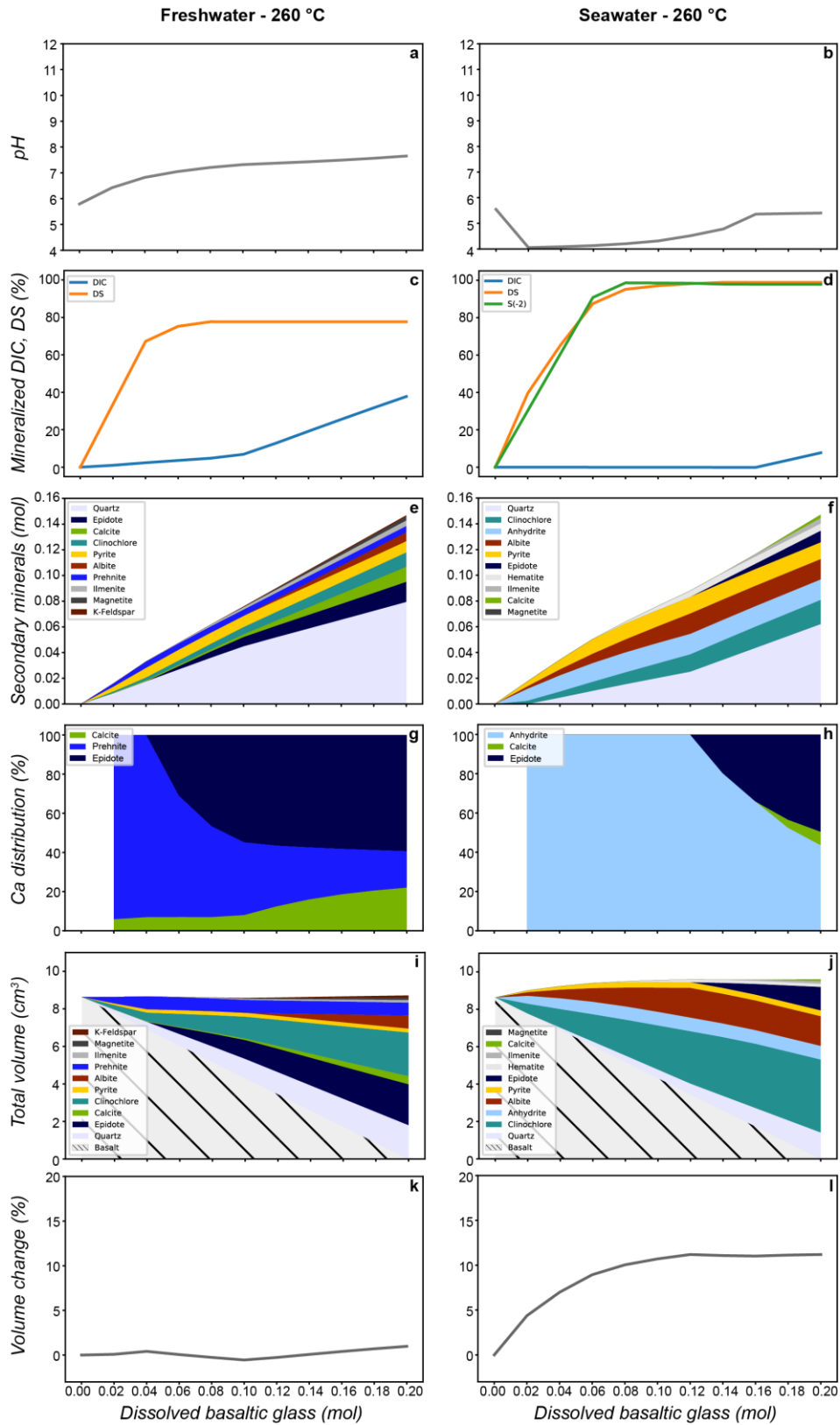
1092

1093 **Figure 2.** Comparison of selected results from the reaction path calculations at 260 °C
 1094 performed to simulate the CarbFix2 system (samples collected on the 3rd of November 2015).
 1095 From top to bottom: (a) pH and (b) aqueous DIC and DS shown as a function of dissolved
 1096 basaltic glass mass, (c) aqueous element concentrations, and (d) saturation indices of
 1097 secondary minerals.

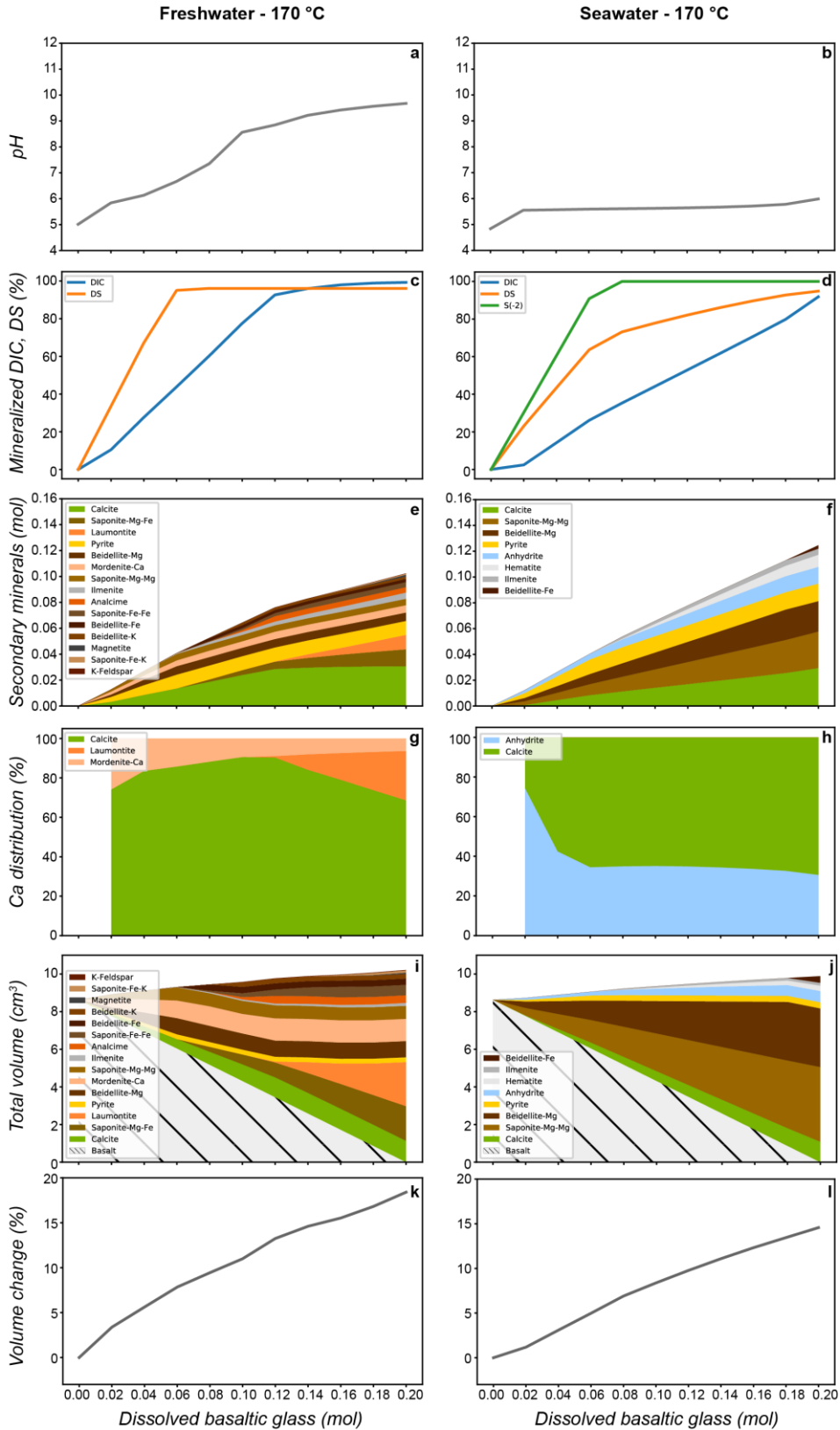


1098

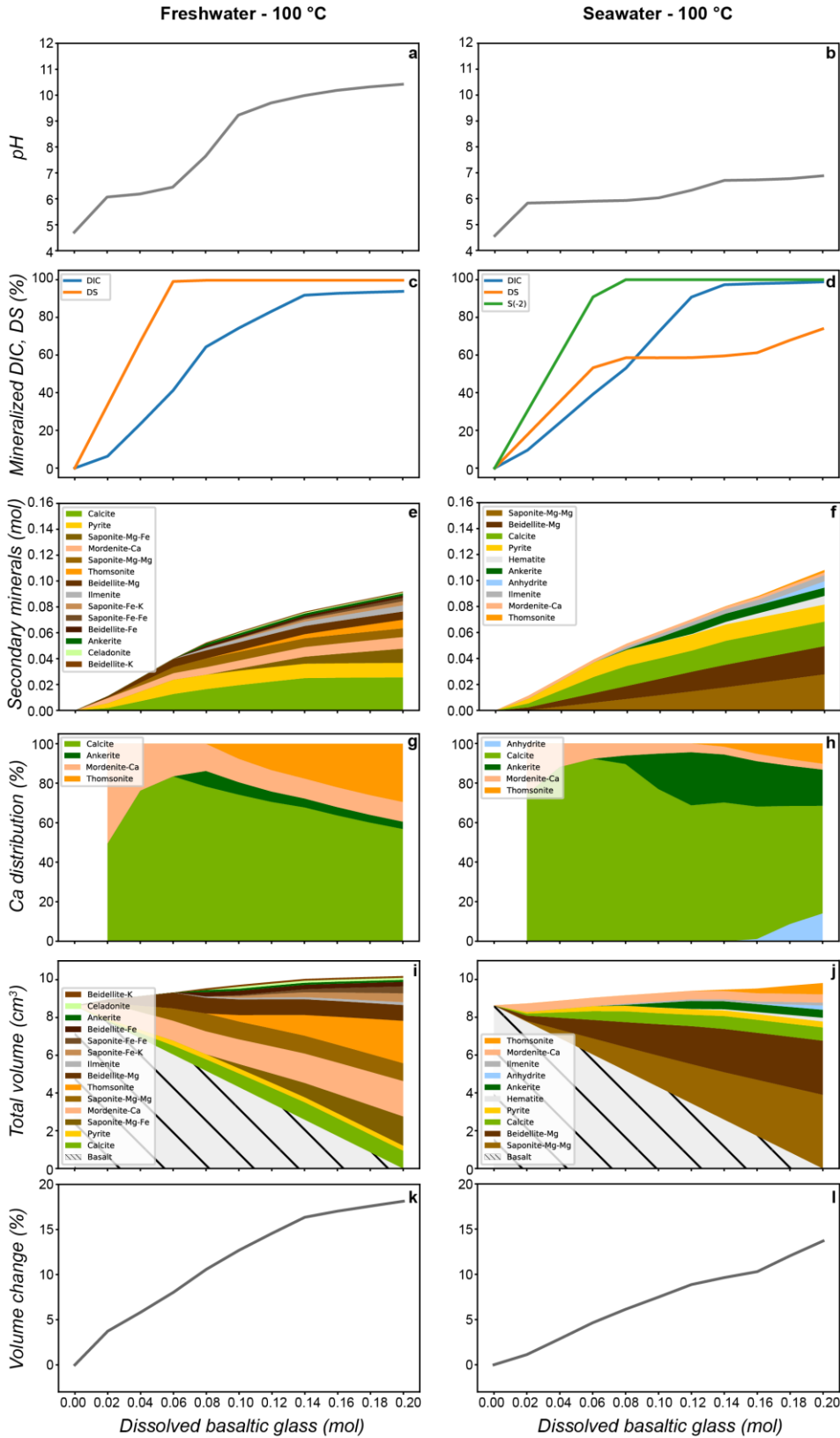
1099 **Figure 3.** Reaction path calculations results of gas-charged waters at 260 °C of (a, b) pH, (c,
 1100 d) mineralized proportion of DIC and DS, (e, f) cumulative secondary mineral abundance per
 1101 kg of injected fluid, (g, h) Ca distribution in the precipitated secondary minerals, (i, j)
 1102 cumulative total volume of minerals dissolved or precipitated per kg of injected fluid, and (k, l)
 1103 their volume change for freshwater (left) and seawater (right) injections.



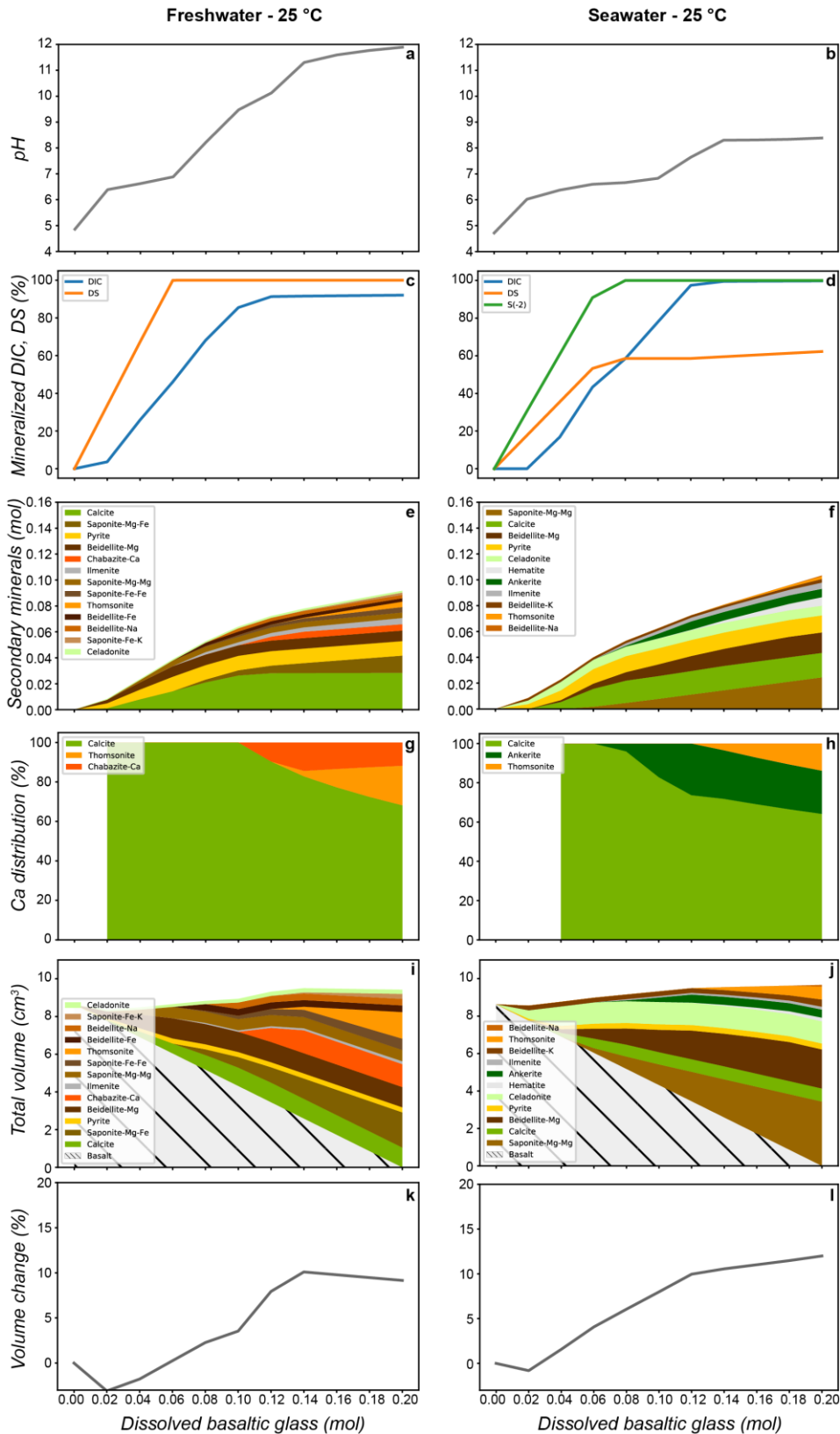
1105 **Figure 4.** Reaction path calculations results of gas-charged waters at 170 °C of (a, b) pH, (c, d)
 1106 mineralized proportion of DIC and DS, (e, f) cumulative secondary mineral abundance per
 1107 kg of injected fluid, (g, h) Ca distribution in the precipitated secondary minerals, (i, j)
 1108 cumulative total volume of minerals per kg of injected fluid and (k, l) their volume change for
 1109 freshwater (left) and seawater (right) injections.



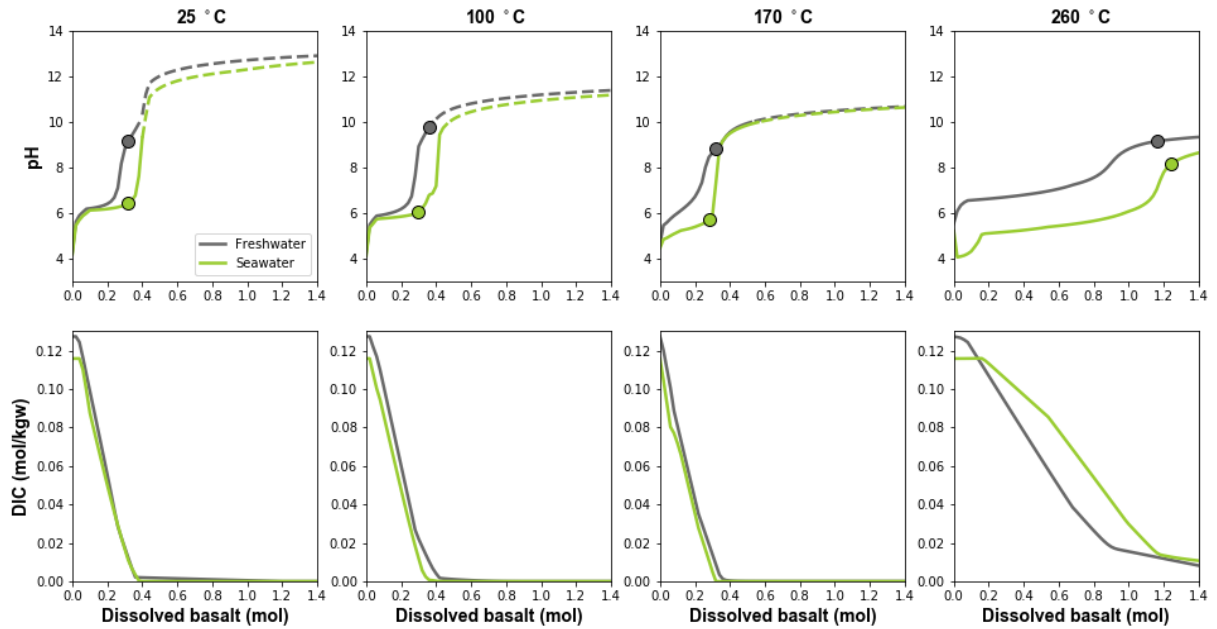
1111 **Figure 5.** Reaction path calculations results of gas-charged waters at 100 °C of (a, b) pH, (c, d)
 1112 mineralized proportion of DIC and DS, (e, f) cumulative secondary mineral abundance per
 1113 kg of injected fluid, (g, h) Ca distribution in the precipitated secondary minerals, (i, j)
 1114 cumulative total volume of minerals per kg of injected fluid and (k, l) their volume change for
 1115 freshwater (left) and seawater (right).



1117 **Figure 6.** Reaction path calculations results of gas-charged waters at 25 °C of (a, b) pH, (c, d)
 1118 mineralized proportion of DIC and DS, (e, f) cumulative secondary mineral abundance per
 1119 kg of injected fluid, (g, h) Ca distribution in the precipitated secondary minerals, (i, l)
 1120 cumulative total volume of minerals per kg of injected fluid and (k, l) their volume change for
 1121 freshwater (left) and seawater (right).

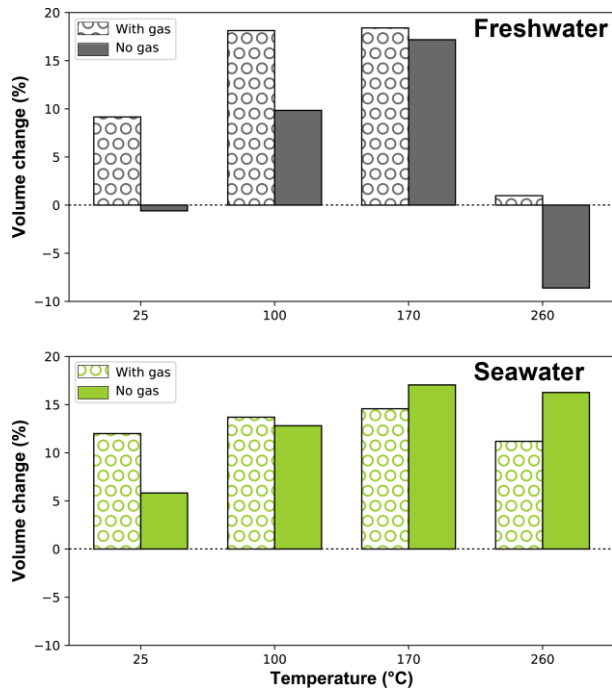


1123 **Figure 7.** Results of reaction path calculations with CO₂-rich waters at temperatures from 25
 1124 to 260 °C of pH (top) and aqueous DIC (bottom) as a function of dissolved basalt mass.
 1125 Results of CO₂-rich freshwater injections are shown in grey, whereas those of seawater are
 1126 shown in green. Circles represent the mass of basaltic glass dissolution required to
 1127 mineralize ~90% of the injected CO₂ (DIC concentration <0.012 mol/kgw). Dashed lines
 1128 indicate the continuation of reaction paths once pH increased beyond 10 (see text for
 1129 explanation).



1130

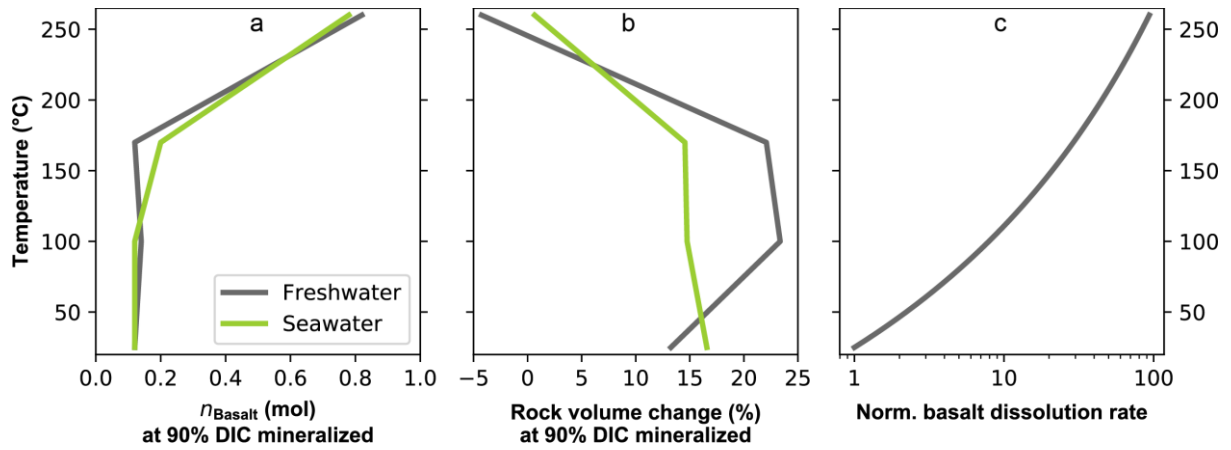
1131 **Figure 8.** Calculated rock volume change in response to the dissolution and interaction of
1132 0.2 mol of basaltic glass with freshwater and seawater as a function of temperature and gas
1133 content. The “with gas” bars represent results obtained using a gas-charged injection fluid
1134 with lower DIC concentrations, whereas the “no gas” bars show results of corresponding
1135 calculations performed using gas-free injection waters.



1136

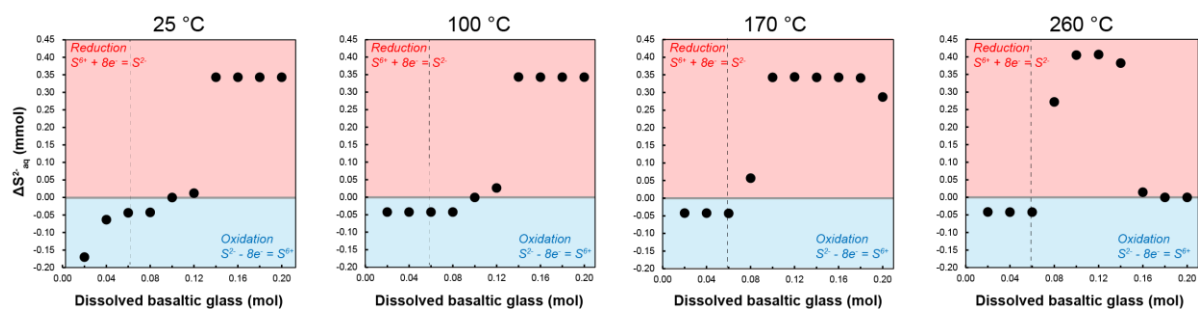
1137

1138 **Figure 9.** Plots summarizing the differences between freshwater and seawater reaction path
1139 model results in the gas-charged systems with lower DIC concentrations as a function of
1140 temperature in terms of a) mass of basaltic glass dissolution required to mineralize 90% of
1141 the injected DIC; b) rock volume change when 90% of the injected DIC is mineralized; and c)
1142 reaction rates of basaltic glass as predicted by the Arrhenius equation (Arrhenius, 1889), with
1143 an activation energy of 25.5 kJ/mol (Gislason and Oelkers, 2003) normalized to rates at 25
1144 °C.



1145

1146 **Figure 10.** Extent of sulfur oxidation-reduction (redox) reactions determined as the
 1147 concentration difference between sulfide (S^{2-}) precipitated as pyrite and aqueous sulfide from
 1148 the injected H_2S in seawater, as a function of dissolved basaltic glass. Note the pyrite
 1149 reaction in the *carbfix.dat* thermodynamic database: $FeS_2 + H_2O = 0.25H^+ + 0.25SO_4^{2-} +$
 1150 $Fe^{2+} + 1.75HS^-$. Positive values of ΔS^{2-} indicate sulfate reduction reaction, negative ΔS^{2-}
 1151 sulfide oxidation reaction, and $\Delta S^{2-}=0$ no detectable redox reactions. The dashed line
 1152 represents the quantity of dissolved basaltic glass above which the S^{2-} concentrations are <1
 1153 mmol/kgw (see text for explanation).



1154