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Alkalinity Generation Constraints on Basalt Carbonation for Carbon Dioxide Removal at the Gigaton-per-year Scale

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seawater alkalinity (2.3 mmol HCO₃⁻/kg)

513x446mm (600 x 600 DPI)



123x91mm (600 x 600 DPI)



206x223mm (600 x 600 DPI)



152x101mm (600 x 600 DPI)

1	Alkalinity Generation Constraints on Basalt Carbonation for Carbon
2	Dioxide Removal at the Gigaton-per-year Scale
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14 **ABSTRACT**

15 The world adds about 51 gigatons of greenhouse gases to the atmosphere each year, which will 16 yield dire global consequences without aggressive action in the form of Carbon Dioxide Removal 17 (CDR) and other technologies. A suggested guideline requires that proposed CDR technologies be 18 capable of removing at least 1% of current annual emissions – about half a gigaton – from the 19 atmosphere each year once fully implemented for them to be worthy of pursuit. Basalt carbonation 20 coupled to Direct Air Capture (DAC) can exceed this baseline, but it is likely that implementation 21 at the gigaton-per-year scale will require increasing per-well CO₂ injection rates to a point where 22 CO_2 forms a persistent, free-phase CO_2 plume in the basaltic subsurface. Here, we use a series of 23 thermodynamic calculations and basalt dissolution simulations to show that the development of a 24 persistent plume will reduce carbonation efficiency (i.e., the amount of CO₂ mineralized per kg of 25 basalt dissolved) relative to existing field projects and experimental studies. We show that 26 variations in carbonation efficiency are directly related to carbonate mineral solubility, which is a 27 function of solution alkalinity and pH/CO₂ fugacity. The simulations demonstrate the sensitivity 28 of carbonation efficiency to solution alkalinity and caution against directly extrapolating 29 carbonation efficiencies inferred from laboratory studies and small-injection-rate field studies 30 conducted under elevated alkalinity and/or pH conditions to gigaton-per-year scale basalt 31 carbonation. Nevertheless, all simulations demonstrate significant carbonate mineralization, and 32 thus imply significant mineral carbonation can be expected even at the gigaton-per-year scale if 33 basalts are given time to react.

34

35 **Keywords:** basalt carbonation, alkalinity, carbon dioxide, direct air capture,

- geochemical modeling 36
- 37

38 **Synopsis:** This study highlights the differing carbonation efficiencies expected during

- 39 gigaton-per-year scale CO₂ injection into basalts versus those inferred from lab and pilot-scale studies.
- 40
- 41

INTRODUCTION 42

43 Atmospheric CO₂ concentrations are expected to double during the latter half of the twenty-44 first century unless aggressive action is taken to reduce anthropogenic emissions¹. The 2015 Paris 45 Agreement was set to curb greenhouse gas emissions and limit anthropogenic warming to 1.5-2°C, 46 which is the largely cited threshold above which many of the most severe consequences of global climate change would become inevitable^{2,3}. However, the International Panel on Climate Change 47 48 has noted that, even if emissions are kept to the levels prescribed by the Paris Agreement, global 49 temperature increases would still be expected to exceed 1.5°C4. Thus, restricting emissions alone 50 will likely be insufficient, and Carbon Dioxide Removal (CDR) techniques such as mineral carbonation coupled to Direct Air Capture $(DAC)^5$ of CO_2 will be required to prevent the most 51 52 dire consequences of global climate change².

53 Mineral carbonation mimics Earth's so-called silicate weathering "thermostat", in which 54 weathering of silicate rocks converts atmospheric CO_2 gas into carbonate minerals⁶. Mineral 55 carbonation is thus a method for "mineral trapping", which is the most stable CO₂ trapping 56 mechanism (in order of increasing stability, these are: structural/stratigraphic trapping; residual 57 trapping, solubility trapping, and mineral trapping^{5,7}). The carbonation process is heavily dependent on the presence of divalent cations (Mg²⁺, Ca²⁺, and Fe²⁺), such that ultramafic and 58

mafic rocks -i.e., peridotite and basalt, respectively - are ideal for mineral carbonation^{5,8,9}. Due to 59 60 their abundance at Earth's surface (they underly all of Earth's oceans, and are commonly exposed 61 in continental settings); high concentrations of cation-rich silicate minerals; and generally 62 favorable porosity, permeability, and injectivity, basaltic rocks have become ideal target lithologies for the rapid injection and mineralization of large volumes of CO₂⁵ When coupled with 63 64 DAC technologies, basalt carbonation holds promise for regulating global atmospheric CO₂ 65 concentrations, since CO₂ in the atmosphere can be accessed globally and a coupled DAC-basalt carbonation operation can be sited in any location where favorable basalt lithologies are available. 66

67 Pilot-scale basalt carbonation

The development of successful pilot-scale field experiments in Iceland (CarbFix^{8,10} and 68 CarbFix2¹¹, where CO₂ was injected as a dissolved phase,) and Wallula, Washington¹² (where CO₂ 69 was injected in supercritical form) has cemented the promise of basalt carbonation as a CO₂ 70 71 immobilization strategy. These projects have demonstrated significant, rapid mineralization of 72 injected carbon – over 95% of the injected CO₂ was mineralized within two years in the CarbFix 73 project⁸, >50% of the CO₂ was mineralized within the first three years at CarbFix2¹¹, and ~60% 74 of the CO₂ was mineralized at Wallula after two years¹³. A prominent characteristic of all three 75 field experiments is their limited amounts and rates of CO₂ injection, and the consequent, elevated 76 pH range of the formation fluids mediating the mineralization reactions. In the CarbFix 77 demonstration project, aquifer pH in monitoring wells never dropped much lower than about 6.5 78 from initial values of ~9.5⁸. Moreover, although the more recent CarbFix2 project saw injected 79 fluid pH as low as 4.7 during the most rapid CO_2 injection phase¹¹, pH rebounded quite quickly in 80 both CarbFix scenarios. In the Wallula demonstration, CO₂ was injected as a free (supercritical) phase into an aquifer with elevated (9.8) pH¹⁴. Although a monitoring well was not available to 81

82 monitor post-injection pH, models predict that pH briefly dropped as low as ~ 5.5 at the injection 83 point before swiftly rebounding¹⁵. Together, these field projects demonstrate that carbon 84 mineralization in basalts can be an effective means of permanently removing CO₂ from the 85 atmosphere or preventing it from ever entering it. Nonetheless, the fact that pH recovered, or was 86 predicted to recover, rapidly in these small-scale injection operations suggests that the quantity of injected CO_2 is small enough so as to not overwhelm the buffering capacity of the aquifer fluids. 87 88 Intuitively, injecting CO₂ at higher rates should stretch the limits of aquifer buffering and basalt 89 dissolution-driven pH maintenance beyond that explored in these field experiments, but this has 90 not yet been quantified.

91 Experimental studies of mineral carbonation

92 In addition to field demonstrations, numerous experimental studies have quantified primary silicate dissolution (e.g., Refs. ^{16–19} and works cited therein) and carbonation (e.g., Refs. 93 ^{20–22} and works cited therein) rates. Gadikota et al.²³ reviewed the sensitivity of mineral 94 95 carbonation – i.e., coupled primary silicate dissolution and carbonate precipitation – to various 96 parameters, and showed that, while changes in CO₂ partial pressure and salinity had limited impact, 97 increasing the reaction temperature and fluid alkalinity (in the form of NaHCO₃) notably increased 98 the extent of carbonation. Thus, although silicate dissolution rates tend to be slower at 99 circumneutral pH^{18,19}, the rates of carbonation tend to be more rapid in NaHCO₃-buffered systems, 100 likely, as discussed in more detail below, due to the decreasing solubility of carbonate minerals 101 with increasing pH. Overall, laboratory-based basalt carbonation studies have shown that, at 102 elevated alkalinity and pH conditions, mineral carbonation can be achieved in time periods as short as a few hours to a few $days^{23-26}$. 103

104	Importantly, many of these laboratory-based carbonation experiments have used solutions with
105	alkalinity (NaHCO ₃ or KHCO ₃) concentrations of $0.4 - 1.0$ M, and even as high as 8 M, to buffer
106	pH (at values of ~8), pCO ₂ , or both ^{21-23,27-29} . Concentrations this high would be semi-
107	representative of alkaline lakes – i.e., the highest-pH, naturally occurring solutions in equilibrium
108	with Earth's atmosphere ³⁰ – but several orders of magnitude above the maximum several
109	millimolar HCO ₃ ⁻ concentrations in seawater ³⁰ , peridotite-hosted hyperalkaline springs ³¹ , basaltic
110	groundwaters ³² , and sub-seafloor basaltic aquifers ³³ . Thus, when large amounts of NaHCO ₃ or
111	KHCO ₃ are used to buffer alkalinity and/or pCO ₂ in laboratory experiments, the alkalinity budget
112	of the experimental system is dramatically elevated in relation to high-injection-rate CO2
113	mineralization operations, where the process of dissolving CO ₂ (either gaseous or supercritical)
114	into solutions itself has no effect on fluid alkalinity ³⁴ . It is important to note that, even in
115	experiments where the initial NaHCO ₃ or KHCO ₃ charge is used to buffer pH, while an additional
116	free-phase CO ₂ source (e.g., a supercritical CO ₂ "bubble") is used to buffer pCO ₂ , the pH buffering
117	of the initial charge of NaHCO ₃ or KHCO ₃ is enough to make the experiments unrepresentative of
118	field-scale systems. The Na ⁺ or K ⁺ concentrations are unlikely to be depleted to any significant
119	degree under representative carbonation conditions, and thus the buffering effects of the initial
120	charge last throughout the experiment. Simply put, the addition of one mole of Na ⁺ for every one
121	mole of HCO ₃ ⁻ is effectively the equivalent of adding one mole of NaOH base alongside every
122	mole of CO ₂ , which would obviously be infeasible if not impossible at the field scale. This, in
123	turn, suggests that, although they provide valuable insight into the rates and mechanisms of mineral
124	carbonation reactions, many of the laboratory experiments that have been used as evidence to
125	support the efficiency of mineral carbonation for permanent CO ₂ storage are not directly

representative of carbonation conditions in basaltic or peridotite aquifers where fluid chemistryhas not been manipulated to dramatically increase alkalinity.

Interestingly, flow-through experiments performed at the opposite end of the alkalinity 128 spectrum – i.e., no initial alkalinity^{35,36} demonstrated no detectable carbonation over the examined 129 130 time scales of the fluid-basalt reaction. Although the 5-39 minute residence times in these 150°C, 150 bar, 0.65 molal CO₂ (f_{CO_2} = 92 bar) experiments were considerably lower than the expected 131 132 residence time of fluids in the basaltic oceanic crust (on the order of thousands or tens of thousands of years³⁷), they are on par with the shortest timescales of complete carbonation discussed above³⁸. 133 134 On the other hand, longer-duration, batch experiments reacting powdered basaltic glass with CO₂charged basaltic groundwaters^{39,40} and artificially fractured basalt cores with CO₂-charged 135 deionized water ^{41,42} demonstrated mineralization is possible over longer timescales (several 136 137 months), at least at fairly low water-to-rock ratios (≤ 5). It is important to note, however, that CO₂ 138 partial pressures were not maintained over the course of the powdered basaltic glass experiments, 139 and thus the partial pressure of CO_2 decreased as the mineralization reaction proceeded.

140 The contrasting behaviours observed in the various experiments discussed above reaffirms 141 the governing role of alkalinity and pCO₂ on basalt carbonation efficiency. Although neither 0 142 mmol/kg alkalinity nor >500 mmol/kg alkalinity are representative of carbonation fluids present 143 in real aquifers, the 2.3 mmol/kg alkalinity representative of seawater is much closer to the lower 144 end of this spectrum. In this regard, it is important to point out that, even over the relatively short 145 residence times of the zero initial alkalinity flow-through experiments, concentrations of Ca in 146 outlet fluids were all >10 µmol/kg, which would have enabled them to precipitate calcite at the temperature (260°C) and f_{CO_2} (~0.5 bar) conditions of the CarbFix2 project¹¹ (see calculations 147 148 below).

149 Meeting the scale of the climate problem with mineral carbonation

150 The world adds about 51 billion tons (1 Gigaton (Gt) = 1 billion tons) of greenhouse gases 151 to the atmosphere each year⁴³. Increasingly, funding organizations and investment groups are tying 152 their willingness to support proposed CDR technologies to this number for annual emissions. 153 Specifically, organizations such as Breakthrough Energy will only support technologies capable 154 of removing at least 1% of annual emissions – around half a gigaton – from the atmosphere each year once fully implemented⁴⁴. 155 The theoretical storage capacity of the basaltic oceanic crust is 156 100,000 - 250,000 Gt CO₂⁵, well in excess of this requirement, suggesting that carbon 157 mineralization in subseafloor basalts is a viable technology for meeting the scale of the climate 158 crisis. Importantly, however, global CO_2 capture and storage operations (including those which 159 are injecting into sedimentary formations) only currently amount to ~40 megatons of CO₂/year, 160 and the CarbFix project itself is currently injecting just ~12,000 tonnes/year captured from the 161 Hellisheiði power plant⁵.

162 Achieving gigaton-per-year levels of CO₂ mineralization in basalts – a $\sim 100 \times$ scaleup of 163 total current capture and storage and $\sim 10^5 \times$ scaleup of CarbFix – will likely require increased 164 implementation of DAC techniques in which CO_2 is directly removed from the atmosphere, in 165 addition to upscaling point source capture projects like CarbFix, and increased capacity for transporting CO_2 into, or capturing it directly in, offshore environments⁵. Siting CO_2 166 167 mineralization projects offshore would enable exploitation of the vast quantity of sub-seafloor 168 basalts^{5,45,46}, the largest aquifer system on the planet⁴⁷. Although abundant seawater would be 169 available for dissolved CO_2 injection (cf. CarbFix) in an offshore environment, it is likely that 170 many offshore CO₂ injection operations would inject free phase CO₂ in order to save on costs for 171 deep water drilling, since the per-well capacity of CO₂ injection as a dissolved phase is reduced by

the volume of water that accompanies the CO_2^5 . Similarly, many onshore CO_2 injection operations would inject free phase CO_2 in order to reduce the demand for water, which would be sizeable at the gigaton-per-year scale – typical water demand is on the order of 35 tonnes of H₂O per tonne of CO_2^5 .

176 This discussion leads to the paradox that, although the CarbFix projects have proven that 177 injecting dissolved CO₂ into basalts can yield rapid mineralization, meeting the scale of the climate 178 crisis with combined DAC and basalt carbonation is likely to require more rapid, free-phase CO₂ 179 injection, which, in turn, will shift the dynamics away from this high-carbonation-efficiency 180 regime. Thus, in order to quantify this technology's promise for meeting the challenge of the 181 climate crisis, we must ask the vital question: How efficient will basalt carbonation be at the 182 gigaton-per-year scale? To address this question in the context of previously published 183 experiments and pilot tests, we examine how the initial alkalinity and thus pH of carbonation fluids 184 affects mineral carbonation. We do this using a series of thermodynamic calculations and 185 numerical experiments with starting conditions representative of aquifer fluids in the Cascadia 186 Basin in the Northeastern Pacific Ocean, an area under active exploration for a basalt carbonation 187 demonstration project. The results suggest that, at conditions characteristic of free phase CO_2 188 injection into permeable basaltic aquifers, carbonation is significantly less efficient than in high-189 alkalinity laboratory experiments and low-volume (dissolved) CO₂ injection projects. Although 190 mineralization is predicted to be less efficient, the results confirm that CO₂ mineralization is 191 nevertheless viable at this scale.

192 **METHODS**

193 Calcite solubility calculations

194 To explore the effect of temperature, fugacity of $CO_2(f_{CO_2})$, and alkalinity on carbonate 195 mineral solubility during mineral carbonation, we performed a series of parameter space 196 exploration calculations using the Phase2 module of The Geochemist's Workbench software 197 package⁴⁸. For these calculations, we designate the temperatures and pressures relevant to subseafloor basaltic aquifers to be 0.01°C °C – 65 °C and f_{C0_2} < 100 bars, respectively. At 198 temperatures exceeding 250°C, Clark et al.¹¹ suggest that the thermodynamics of interactions 199 200 between basaltic mineral carbonation is no longer thermodynamically favorable (i.e., higher 201 temperatures can lead to decarbonation reactions). However, their conclusion is a consequence of 202 the low partial pressures of $CO_2(g)$ used in the CarbFix2 operation, and the limit of carbonation reactions should in fact be much higher than 250°C in situations where CO₂ is injected as a 203 204 supercritical phase (Fig. S1). Nevertheless, such high temperatures present unique challenges for 205 drilling and injection operations in oceanic settings, and much of the permeable basaltic oceanic 206 crust is present at temperatures much lower than this^{37,49,50}, and we therefore use 65°C as the upper 207 limit in our calculations. In calculations of the impact of a free (gaseous or supercritical) CO_2 208 phase on aqueous geochemical reactions in this paper, we use fugacity, rather than partial pressure, 209 to ensure compatibility with the Geochemist's Workbench thermodynamic formulation without 210 the added complexity of a temperature/pressure-dependent fugacity model. Fugacity coefficients 211 vary from ~ 0.2 to nearly 1 over the range studied here, with the highest pressures and lowest 212 temperatures, where the CO₂ is densest (i.e., the least gas-like) and hence the most non-ideal, 213 having the lowest fugacity coefficients (Fig. S2⁵¹). This translates to maximum fugacities that are a fraction of the partial pressure at these conditions. We use seawater chemistry⁵² as a 214 representative aquifer fluid for CO₂ storage in our calculations of the solubility limits of calcite 215 216 (Table S1). Although, as discussed below, differences should be expected for various aquifer fluids and/or other carbonate minerals, these calculations are sufficiently representative that conclusions based upon them are generally applicable. Indeed, as discussed above, most relevant fluids have alkalinity concentrations similar to or lower than that of seawater.

220 Simulating alkalinity generation and its effect on carbonation reactions

221 To test the effect of initial alkalinity, and alkalinity generation, on the efficiency of basalt 222 carbonation reactions, we performed a series of numerical experiments in which we reacted aquifer 223 fluids from the Cascadia Basin⁵³ with a typical basaltic protolith (Table S2) using the Geochemist's 224 Workbench React module⁴⁸. The starting aguifer fluid (Table S3) was sampled at International 225 Ocean Discovery Program Site 1301⁵³, which is representative of aquifer chemistry for CO₂ mineralization in the basaltic oceanic crust⁴⁶. Importantly, fluids derived from this basaltic aquifer 226 lack dissolved oxygen and nitrate^{33,53}, suggesting any Fe²⁺ released from basalt dissolution would 227 228 remain as Fe^{2+} rather than being oxidized to Fe^{3+} . We therefore do not simulate Fe redox in our 229 kinetic reaction path models. Simulations were performed at 60°C to represent conditions at 230 Cascadia⁵³ and 25°C to represent the often lower aquifer temperatures in other parts of the basaltic oceanic crust⁴⁷. CO₂ fugacity was fixed at 100 bars (representative of ~250 bars pCO₂ at 60°C, 231 232 Figs. 1 and S1) by swapping $CO_2(g)$ for H⁺ as a primary component in the initial solution. The 233 concentration of HCO₃⁻ was then adjusted automatically to facilitate charge balance. Initial basalt 234 composition was estimated based on x-ray diffraction analyses of basalts reported by Marieni et 235 al.⁵⁴. These analyses suggest that the remaining primary mineralogy of basalts recovered from 236 ocean drilling in the Juan de Fuca plate is ~55-68% plagioclase and ~41-44% augitic 237 clinopyroxene with trace amounts of olivine. Ignoring the contribution of "mesostasis," glass, and 238 opaques, we arrived at an estimated "primary" basalt composition consisting of 55% plagioclase 239 (70% anorthite/30% albite), 40% clinopyroxene (85% diopside/15% hedenbergite), and 5%

240 olivine (85% forsterite/15% fayalite) (Table S2). Because primary mineral dissolution is expected 241 to be the rate-limiting step during basalt carbonation, secondary minerals common to hydrothermal 242 alteration of basalt, including analcime, ankerite, annite, calcite, diaspore, dolomite, gibbsite, hematite, kaolinite, K-feldspar, magnesite, chalcedony (not guartz)⁵⁵, Fe/Mg-saponite⁵⁶, and 243 244 siderite, were allowed to precipitate if they became supersaturated (i.e., partial equilibrium with 245 respect to these phases was assumed). Kinetic effects requiring appreciable supersaturation for 246 carbonate precipitation would require more basalt dissolution to precipitate an equivalent amount of carbonate minerals⁵⁷ and thereby decrease carbonation efficiency. Total initial surface area of 247 all primary minerals was assumed to be 2500 cm²; thus, variations in reaction rates are attributable 248 249 only to variations in intrinsic, pH- and temperature-dependent rate constants rather than being 250 dependent upon highly uncertain estimates of mineral reactive surface areas in basalts. As such, 251 all basalt dissolution simulations are plotted as a function of normalized time (t/t_{max}) , which was 252 calculated by dividing time (t) by the total simulated time (t_{max}) required to dissolve 1 kg of basalt. 253 Although this modeling approach does not capture the important effects of chemical and pH gradients²⁸ that will accompany field-scale mineralization operations, it does provide a constant 254 255 reference frame for all simulated scenarios, which can then be used as a foundation for future 256 studies of these important reactive transport processes.

The sensitivity of carbonation reactions to the initial solution alkalinity was examined by repeating the simulations with 5% and 10% higher initial Na⁺ concentrations and hence alkalinity (Table S3), due to the charge balancing mechanism. As a base-case scenario, basalt dissolution simulations were run at a water-to-rock mass ratio of 100, which is a typical value inferred for water circulating through basaltic oceanic crust^{58,59}. The effect of water-to-rock ratio was also tested by re-running the simulations with water-to-rock ratios spanning the range of plausible values⁶⁰ for fluid circulation in basaltic aquifers (1, 10, 100, 1000, and 10000). The water-to-rock ratio was varied in these simulations by increasing the mass of solution with which the 1 kg of primary basaltic minerals was reacted. Results of all carbonation simulations are included as a multi-tab spreadsheet in the supporting information.

267 Thermodynamic and kinetic data

All geochemical calculations were performed using the Geochemist's Workbench⁴⁸ outfitted 268 269 with a custom 250 bar thermodynamic database created using the DBCreate software package⁶¹ and the extended Debye-Huckel formulation⁶² for calculating activity coefficients of charged 270 271 species. Equilibrium constants for plagioclase, clinopyroxene, and olivine dissolution were calculated using end-member thermodynamic data from Robie and Hemingway⁶³ and solid-272 273 solution interaction parameters from Stefánsson et al.⁶⁴ (Table S4). Thermodynamic properties for 274 most clay minerals were taken directly from Blanc et al.⁶⁵ or calculated using techniques detailed therein; thermodynamic properties for analcime were taken from Helgeson et al.⁶⁶. Aqueous 275 276 speciation data is consistent with Tutolo et al.⁶⁷, except for the properties of $SiO_2(aq)$, which were updated from $H_4SiO_4(aq)^{68}$ to $SiO_2(aq)^{69}$ to facilitate database creation and compatibility. Both 277 278 are consistent with the Rimstidt⁷⁰ paradigm for low-temperature thermodynamic properties of SiO₂(aq). All other thermodynamic data are consistent with the SUPCRT92⁷¹ data set and its 279 280 recent additions. Kinetic data used to simulate the dissolution of primary olivine, plagioclase, and pyroxene were taken from Palandri and Kharaka¹⁶ and are consistent with Pollyea et al.¹⁹ (Table 281 282 S2). These parameters were used with the following relationship:

283
$$k_{overall} = 10^{\left(\left[\log\left(k_{acid}\right) - \frac{E_a^{acid}}{R\ln(10)}\left(\frac{1}{r} - \frac{1}{298.15}\right) - n_{acid}\,pH\right] + \left[\log\left(k_{neutral}\right) - \frac{E_a^{neutral}}{R\ln(10)}\left(\frac{1}{r} - \frac{1}{298.15}\right)\right]\right)}, \qquad (1)$$

where *k* is the dissolution rate constant for the subscripted rate mechanism, *Ea* is the activation energy the superscripted dissolution mechanism, *T* is temperature in Kelvin, and n_{acid} accounts for the dependence of the rate on pH, in order to calculate the evolution of dissolution rate with increasing pH over the course of simulations at both 25 °C and 60 °C.

288 **RESULTS AND DISCUSSION**

289 Alkalinity controls on mineral carbonation

290 Simple calculations using seawater as a representative fluid can help to illustrate the 291 mechanisms for rapid carbonation in NaHCO₃-buffered solutions in spite of diminished rates of 292 primary silicate dissolution at circumneutral pH (Fig. 1). These calculations demonstrate the 293 fundamental role that alkalinity plays in controlling pH in CO₂-enriched fluids (Fig. 1a,c), which, 294 in turn, controls carbonate solubility (Fig. 1b,d) and hence plays an important role in CO₂ 295 mineralization efficiency - i.e. the amount of CO₂ mineralized per mass of basalt dissolved. In general, calcite solubility increases with increasing f_{CO_2} (i.e., decreasing pH) and decreasing 296 297 temperature at CO₂ mineralization conditions (Fig. 1b,d). The most significant increases in calcite solubility with increasing f_{CO_2} occur at temperatures less than ~60 °C, which are representative of 298 299 fluid circulation in the subseafloor basaltic aquifer system^{47,53}. At typical basaltic aquifer 300 temperatures and the range of CO₂ fugacities representative of supercritical CO₂ injection, calcite 301 solubility increases more than ten times, from ~10 mmol/kg in seawater to >110 mmol/kg, as pH is driven below ~5 with increasing f_{CO_2} over the plausible pCO₂ range for free-phase CO₂ injection 302 303 into seawater-filled aquifers (Fig. 1a,b). If, on the other hand, the initial alkalinity of the seawater 304 is increased to 500 mmol HCO₃/kg, which, although unrealistic, is representative of the lower end 305 of the alkalinity used in many published carbonation experiments reviewed above, the resulting

values of both pH and calcite solubility over the plausible range are dramatically transformed. Indeed, at the lowest f_{CO_2} , calcite is around three orders of magnitude less soluble than at similar temperature and pressure conditions in seawater without the alkalinity addition, while at the highest f_{CO_2} and lowest temperatures, Ca concentrations are just beginning to approach their levels in seawater (~10 mmol/kg)⁵².

311 It is important to note that these calculations are also in excellent agreement with the pH 312 (~7.3) and CO₂ fugacities (~0.3-0.9) measured on the ~260°C waters sampled from the CarbFix2 313 injection site¹¹, but that those conditions are unusual with respect to the range of possibilities for 314 sub-seafloor basaltic aquifers (Fig. 1), especially in scenarios where CO₂ injection rates are great 315 enough to permit the development of a free phase plume. As demonstrated in Fig. 1, calcite and 316 other carbonates play a governing role in carbonation efficiency via their thermodynamic solubility 317 - it simply takes more basalt dissolution to yield similar amounts of CO₂ mineralization in realistic 318 aquifer solutions than in strongly NaHCO₃-buffered solutions or low f_{CO_2} solutions. Thus, 319 although elevated pH and/or low- f_{CO_2} solutions highly favor carbonate mineralization due to the 320 insolubility of the carbonate minerals at these conditions, similar results are not guaranteed or even 321 likely elsewhere, especially if mineral carbonation is implemented at gigaton-per-year scales and CO₂ is injected as a plume-forming supercritical phase, a possibility which is explored in more 322 323 detail below.

Although calcite rather than Fe- or Mg-rich carbonate (e.g., ankerite, magnesite, or dolomite) solubility is plotted in Fig. 1 to illustrate the limits of carbonation reactions, similar results would be expected for these other carbonate minerals, whose general behavior as a function of f_{CO_2} , pH, and temperature is quite similar -i.e., all relevant carbonate minerals become more 328 soluble with increasing f_{CO_2} /decreasing pH and decreasing temperature over the relevant 329 conditions. Since the kinetics of calcite precipitation are generally rapid, equilibrium with respect to CaCO₃ is a reasonable guide to the limits of carbonate solubility⁷², although minerals such as 330 331 ankerite, magnesite and dolomite may be more kinetically limited in their precipitation. Of course, 332 pH is not just a simple function of f_{CO_2} , but also of the solution's alkalinity. The cations released 333 from the dissolution of primary plagioclase, clinopyroxene, and/or olivine that do not go towards 334 the production of carbonates and clays will tend to increase solution alkalinity and buffer pH to 335 higher values than would otherwise be possible, hence generating a positive feedback wherein 336 alkalinity generation increases carbonation efficiency. The intricacies of this process and this 337 feedback are discussed in the following section.

338 Alkalinity generation during mineral carbonation

Given the demonstration, in the previous section, that increased alkalinity can increase carbonation efficiency, it is worthwhile to place limits on the expected amounts of alkalinity that may be generated following CO_2 injection into sub-seafloor basalts. During CO_2 -basalt-water interactions, dissolved CO_2 will promote plagioclase (e.g., $Ca_{0.7}Na_{0.3}Al_{1.7}Si_{2.3}O_8$) and other primary mineral (e.g., clinopyroxene and olivine) dissolution through alkalinity-generating reactions such as:

However, after some amount of reaction, secondary clay minerals (e.g., cation-poor aluminosilicates such as kaolinite or cation- (e.g., Ca, Na, Mg, and/or Fe) bearing phyllosilicates such as analcime and saponite) and carbonates (e.g., calcite/aragonite (CaCO₃) and dolomite/ankerite/siderite ((Ca,Mg,Fe)(CO₃)₂) become supersaturated, begin to precipitate, and 350 curtail the alkalinity generation capacity of these reactions. Thus, the rate of alkalinity generation 351 ultimately depends not only on the rate of dissolution of the primary minerals, but also on the 352 solubility of secondary clays and carbonates and the rates at which they remove alkaline cations 353 from the solution. For example, a plagioclase carbonation reaction may be written:

354 plagioclase +
$$CO_2(aq)$$
 + 1.85 H₂O \rightarrow

$$0.85$$
 kaolinite + 0.3 Na⁺ + 0.7 calcite + 0.6 SiO₂(aq) + 0.3 HCO₃, (4)

356 where the right hand side has been generalized in the most simplistic way allowable (i.e., to avoid 357 the stoichiometric considerations accompanied by the formation of more complex clays and/or 358 carbonates), although more complex reactions are possible, as discussed below.

359 Aquifer fluids circulating at Cascadia and venting at the Baby Bare outcrop have notably 360 lower alkalinity (0.43 mmol/kg) than measurements of bottom seawater (2.4 mmol/kg)³³, 361 suggesting the basaltic aquifer system is in an alkalinity reducing, rather than generating, regime 362 (note that mmol alkalinity/kg = meq/kg alkalinity, provided that the alkalinity measurement 363 implies mmol HCO_3^{-1}/kg , which it does here). However, the perturbation supplied by the injection of large volumes of CO₂ will dramatically increase reactivity and thus impact the aquifer's 364 365 alkalinity generation and/or reduction regime. Simple, fully coupled kinetic simulations of CO₂-366 water-basalt reactions offer a useful guide for the magnitude of alkalinity generation at feasible 367 water-to-rock ratios (Fig. 2). As expected, these calculations show that basalt dissolution increases 368 alkalinity by 10s of meq/kg (~40-80 meq/kg), depending on the extent of reaction, but that even 369 after 1 kg of basalt is dissolved into 100 kg of aquifer fluid, the pH reaches a maximum of ~ 4.5 , 370 where carbonate minerals maintain their elevated solubility relative to higher-pH solutions. At 371 this pH, carbonate mineralization efficiency will remain much lower than in many NaHCO₃-

buffered experiments (Fig. 1 and associated discussion). In the following section, we present a series of simulations designed to explore the potential for mineral carbonation in representative Cascadia Basin aquifer fluids, and their contrast with otherwise identical fluids with increased alkalinity. In the interest of providing a realistic, quantitative perspective on basalt carbonation at gigaton-per-year scales, we do not consider the extreme (500 mmol/kg) levels of alkalinity discussed above any further.

378 Mineral carbonation efficiency as a function of aquifer alkalinity

379 Our simulations of alkalinity generation in Cascadia aquifer fluids at both 25 °C and 60 °C 380 demonstrate that alkalinity concentrations may increase by a maximum of several tens of meq/kg 381 at extreme extents of CO_2 -driven basalt dissolution (depending on temperature), with concomitant 382 increases in pH from initial, CO_2 -equibrated values below 3 up to ~4.5 (Fig. 2). To examine the 383 effect that this alkalinity generation may have on basalt carbonation efficiency and demonstrate 384 the significant sensitivity of carbonation reactions to initial alkalinity, we performed an additional 385 sequence of basalt dissolution simulations using Cascadia aquifer fluids with arbitrarily increased (by 5 and 10%) Na⁺ concentrations. Increasing Na⁺ while keeping f_{CO_2} and the concentrations of 386 387 all other major cations and anions (except HCO₃-) constant yields higher initial pH and higher 388 initial alkalinity (18 meg/kg for +5% Na⁺ and 39 meg/kg for +10% Na⁺ versus ~0.7 for the initial 389 solution at 60° C – Table S3), both of which, in turn, reduce carbonate solubility in the aquifer fluid 390 and increase carbonation efficiency.

Across all carbonation simulations, basalt dissolution yields the precipitation of kaolinite and chalcedony, as well as increasing quantities of dolomite and ankerite with increasing initial alkalinity (Fig. 3). The lower solubility of carbonate minerals at 60°C relative to 25°C also tends 394 to yield greater extents of carbonation and hence carbonation efficiency. Overall, the comparison 395 between the amount of carbonate formed in actual aquifer fluids versus that formed in the aquifer 396 fluids with artificially enhanced alkalinity demonstrates that these artificial increases in alkalinity 397 yield significant increases in carbonation. The sequence of depletion of primary minerals observed 398 in the simulation results is consistent with expectations based on field observations, where olivine 399 is often completely reacted out of recovered seafloor basalts⁵⁴. Interestingly, many of the other 400 secondary minerals common to hydrothermal alteration of basalt, such as saponite⁵³, did not 401 precipitate in these simulations. Activity diagram calculations show that, at this low pH, Al 402 released from plagioclase dissolution is preferentially incorporated into kaolinite, thereby 403 preventing precipitation of other Al-bearing minerals such as chlorite or saponite (Fig. S3) and 404 permitting Fe incorporation into ankerite and Mg incorporation into dolomite (Fig. 3).

405 Sensitivity of carbonation efficiency to water-rock ratios

406 All basalt dissolution simulations discussed to this point were conducted at a water-rock 407 mass ratio of 100, but the results of course depend upon the simulated water-to-rock mass ratio. 408 Although a water-to-rock ratio of 100 is a typical value inferred for water circulating through 409 basaltic oceanic crust^{58,59}, the plausible range inferred from geochemical and heat flow studies 410 suggests that higher values are possible⁶⁰. Nevertheless, these values are representative of the 411 natural system and significant changes in the hydrogeologic regime -i.e., the onset of two-phase 412 flow conditions and injection- induced pressure gradients – should be expected following the 413 injection of large quantities of CO₂. Intuitively, lower water-to-rock ratios will yield higher 414 carbonation efficiency because of the greater increases in solute concentration (and thus alkalinity) 415 per mass of basalt dissolved. On the other hand, changes in the initial alkalinity will have the most 416 pronounced effect at the highest water-to-rock ratios, not only in the field, but also in the lab, where

high water-to-rock ratio experiments are generally less difficult to conduct. The 5 and 10% increases in initial Na⁺ explored for a water-to-rock ratio of 100 above (Fig. 3) yield increases in carbonation efficiency at all water-to-rock ratios \geq 10, to the extent that, at the highest water-torock ratios (\geq 1000), the increased initial alkalinity means carbonates are precipitated in simulations where they otherwise would not have been (Fig. 4).

422 Overall, the calculations presented in Fig. 4 confirm that replicating aquifer alkalinity in 423 laboratory experiments and geochemical reaction path and reactive transport models is vital for 424 predicting the extent of carbonation in any proposed basalt carbonation operation, especially 425 during plume-forming CO₂ injection into sub-seafloor basaltic aquifers. Importantly, these 426 calculations should not be taken as a recommendation that increasing aquifer alkalinity is a strategy 427 by which carbonation efficiency may be increased. Rather, these calculations provide strong 428 evidence against directly extrapolating carbonation efficiencies inferred from laboratory studies 429 and small-injection-rate field studies conducted under elevated alkalinity and/or pH conditions to 430 gigaton-per-year scale basalt carbonation, since even our comparatively modest adjustments to 431 initial alkalinity have had such significant effects over the plausible range of water-to-rock ratios.

432 IMPLICATIONS FOR GIGATON-PER-YEAR SCALE BASALT 433 CARBONATION

If direct air capture (DAC) coupled to basalt carbonation is implemented at the gigaton-peryear scale, it is likely that many offshore CO_2 injection operations would inject free-phase CO_2 in order to maximize per-well capacity of CO_2 injection. In these situations, our thermodynamic and kinetic calculations show that carbon mineralization will be less efficient than suggested by many published experiments and field demonstration projects, due to the heightened solubility of

439 carbonate minerals at free phase CO₂-buffered conditions. Simply put, more basalt will need to 440 dissolve in order to yield comparable amounts of carbonation when free-phase CO₂ sets the pH 441 and solubility of carbonate minerals at representative values of solution alkalinity and water-to-442 rock ratio. Assuming similar rates of basalt dissolution, carbonation is likely to take longer in 443 these systems because it will take longer to dissolve enough basalt to generate enough alkalinity 444 to exceed the thermodynamic saturation of carbonate minerals. These results imply that serious 445 consideration should be given to alternating CO₂ injection with water injection (i.e., wateralternating-gas (WAG) injection), even if dissolved CO2 injection is not feasible, in order to 446 447 promote CO₂ dissolution and increase carbonation efficiency. Nevertheless, our simulations 448 demonstrate that, given time, and the ability of the impermeable sediments overlying sub-seafloor 449 basalts to prevent leakage as the free phase CO₂ dissolves and converts to carbonates, significant 450 mineral carbonation can be expected.

451 ASSOCIATED CONTENT

452 **Supporting Information**

The Supporting Information, which contains additional tables and figures to support the parameterization of the geochemical models, is available free of charge on the ACS Publications website at DOI: **XX/XX**.

456 **AUTHOR INFORMATION**

- 457 **Notes**
- 458 The authors declare no competing financial interest.

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465

466 **FIGURE CAPTIONS**

Figure 1 pH and calcite solubility in calcite-saturated seawater (a,b) and 500 mmol/kg alkalinity seawater analogue solution (c,d) as a function of temperature and fugacity of $CO_2(f_{CO_2})$. See Methods and Fig. S1 for a discussion and visualization, respectively of the relationship between f_{CO_2} and partial pressure of CO_2 .

Figure 2 Alkalinity and pH increases as a function of CO₂-driven basalt dissolution into Cascadia basin aquifer fluids at a water-to-rock mass ratio of 100. Calculations assume a constant $f_{CO_2} = 100$ bar.

474 Figure 3 Masses of mineral present in the system during CO₂-driven basalt dissolution into the 475 Site 1301 aquifer fluids (Na⁺= 463 mmol/kg), and into otherwise identical fluids with initial 476 alkalinity adjusted by increasing the initial Na⁺ by 5 and 10% and charge-balancing on HCO₃⁻. 477 Calculations assume a constant $f_{CO_2} = 100$ bar and a water-to-rock mass ratio of 100. Mineral 478 abundances plotted at 25 °C (a, c, d) and 60 °C (b, e, f) demonstrate that aquifer alkalinity and 479 temperature have a dramatic effect on the amount of carbonate (dolomite and ankerite) 480 precipitated, and thus the amount of CO₂ mineralized. Note the differing y-axis scales at 25 °C 481 versus 60 °C due to the larger amount of carbonate precipitation at 60°C.

Figure 4 Variation in carbonation efficiency at three different initial alkalinities as a function of water-to-rock mass ratio. Initial alkalinity was adjusted by increasing the concentration of Na⁺ in the Site 1301 aquifer fluids by 5 and 10% and charge-balancing on HCO_3^- . Typical values of water-to-rock ratio inferred for fluids circulating in the basaltic oceanic crust are >100.

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486 **REFERENCES**

- 487 (1) van Vuuren, D. P.; Edmonds, J.; Kainuma, M.; Riahi, K.; Thomson, A.; Hibbard, K.;
- 488 Hurtt, G. C.; Kram, T.; Krey, V.; Lamarque, J. F.; Masui, T.; Meinshausen, M.;
- 489 Nakicenovic, N.; Smith, S. J.; Rose, S. K. The Representative Concentration Pathways:
- 490 An Overview. *Clim. Change* **2011**, *109* (1), 5–31. https://doi.org/10.1007/s10584-011-
- 491 0148-z.
- 492 (2) Dong, C.; Dong, X.; Jiang, Q.; Dong, K.; Liu, G. What Is the Probability of Achieving the
- 493 Carbon Dioxide Emission Targets of the Paris Agreement? Evidence from the Top Ten
- 494 Emitters. *Sci. Total Environ.* **2018**, *622–623*, 1294–1303.
- 495 https://doi.org/10.1016/j.scitotenv.2017.12.093.
- 496 (3) Seo, S. N. Beyond the Paris Agreement: Climate Change Policy Negotiations and Future
- 497 Directions. *Reg. Sci. Policy Pract.* **2017**, *9* (2), 121–140.
- 498 https://doi.org/10.1111/rsp3.12090.
- 499 (4) IPCC. *Global Warming of* 1.5°C; 2018; Vol. 2.
- 500 (5) Snæbjörnsdóttir, S. Ó.; Sigfússon, B.; Marieni, C.; Goldberg, D.; Gislason, S. R.; Oelkers,
- 501 E. H. Carbon Dioxide Storage through Mineral Carbonation. *Nat. Rev. Earth Environ.*
- 502 **2020**, *1*, 90–102. https://doi.org/10.1038/s43017-019-0011-8.
- 503 (6) Walker, J. C. G.; Hays, P. B.; Kasting, J. F. A Negative Feedback Mechanism for the
- 504 Long-Term Stabilization of Earth's Surface Temperature. J. Geophys. Res. 1981, 86
- 505 (C10), 9776–9782. https://doi.org/10.1029/JC086iC10p09776.
- 506 (7) Benson, S. M.; Cole, D. R. CO2 Sequestration in Deep Sedimentary Formations. *Elements*

507		2008 , <i>4</i> (5), 325–331. https://doi.org/10.2113/gselements.4.5.325.
508	(8)	Matter, J. M.; Stute, M.; Snaebjornsdottir, S. O.; Oelkers, E. H.; Gislason, S. R.; Aradottir,
509		E. S.; Sigfusson, B.; Gunnarsson, I.; Sigurdardottir, H.; Gunnlaugsson, E.; Axelsson, G.;
510		Alfredsson, H. A.; Wolff-Boenisch, D.; Mesfin, K.; de la Reguera Taya, D. F.; Hall, J.;
511		Dideriksen, K.; Broecker, W. S. Rapid Carbon Mineralization for Permanent Disposal of
512		Anthropogenic Carbon Dioxide Emissions. Science 2016, 352 (6291), 1312–1314.
513		https://doi.org/10.1126/science.aad8132.
514	(9)	Kelemen, P. B.; Matter, J. In Situ Carbonation of Peridotite for CO ₂ Storage. Proc. Natl.
515		Acad. Sci. U. S. A. 2008, 105 (45), 17295–17300.
516		https://doi.org/10.1073/pnas.0805794105.
517	(10)	Gislason, S. R.; Wolff-Boenisch, D.; Stefansson, A.; Oelkers, E. H.; Gunnlaugsson, E.;
518		Sigurdardottir, H.; Sigfusson, B.; Broecker, W. S.; Matter, J. M.; Stute, M.; Axelsson, G.;
519		Fridriksson, T. Mineral Sequestration of Carbon Dioxide in Basalt: A Pre-Injection
520		Overview of the CarbFix Project. Int. J. Greenh. Gas Control 2010, 4 (3), 537-545.
521		https://doi.org/10.1016/j.ijggc.2009.11.013.
522	(11)	Clark, D. E.; Oelkers, E. H.; Gunnarsson, I.; Sigfússon, B.; Snæbjörnsdóttir, S.; Aradóttir,
523		E. S.; Gíslason, S. R. CarbFix2: CO ₂ and H ₂ S Mineralization during 3.5 Years of
524		Continuous Injection into Basaltic Rocks at More than 250 °C. Geochim. Cosmochim.
525		Acta 2020, 279, 45-66. https://doi.org/10.1016/j.gca.2020.03.039.
526	(12)	McGrail, B. P.; Schaef, H. T.; Spane, F. A.; Horner, J. A.; Owen, A. T.; Cliff, J. B.;
527		Qafoku, O.; Thompson, C. J.; Sullivan, E. C. Wallula Basalt Pilot Demonstration Project:
528		Post-Injection Results and Conclusions. In Energy Procedia; Elsevier Ltd, 2017; Vol. 114,

529	pp 5783–5790.	https://doi	.org/10.10	16/j.egypro.2	017.03.1716.
-----	---------------	-------------	------------	---------------	--------------

- 530 (13) White, S. K.; Spane, F. A.; Schaef, H. T.; Miller, Q. R. S.; White, M. D.; Horner, J. A.;
- 531 McGrail, B. P. Quantification of CO₂ Mineralization at the Wallula Basalt Pilot Project.
- 532 *Environ. Sci. Technol.* **2020**, *54* (22), 14609–14616.
- 533 https://doi.org/10.1021/acs.est.0c05142.
- 534 (14) McGrail, B. P.; Spane, F. A.; Sullivan, E. C.; Bacon, D. H.; Hund, G. The Wallula Basalt
- 535 Sequestration Pilot Project. *Energy Procedia* **2011**, *4*, 5653–5660.
- 536 https://doi.org/10.1016/j.egypro.2011.02.557.
- 537 (15) Schwartz, M. O. Can CO₂ Sequestration in Basalt Efficiently Reduce Greenhouse Gas
- 538 Emission? *Environ. Technol.* **2020**, 1–26.
- 539 https://doi.org/10.1080/09593330.2020.1815859.
- 540 (16) Palandri, J. L.; Kharaka, Y. K. A Compilation of Rate Parameters of Water-Mineral
- 541 Interaction Kinetics for Application to Geochemical Modeling. USGS Open File Rep.
- 542 **2004**, *2004–1068*, 71. https://doi.org/10.1098/rspb.2004.2754.
- 543 (17) Rimstidt, J. D.; Brantley, S. L.; Olsen, A. A. Systematic Review of Forsterite Dissolution

544 Rate Data. *Geochim. Cosmochim. Acta* **2012**, *99*, 159–178.

- 545 https://doi.org/10.1016/j.gca.2012.09.019.
- 546 (18) Gislason, S. R.; Oelkers, E. H. Mechanism, Rates, and Consequences of Basaltic Glass
- 547 Dissolution: II. An Experimental Study of the Dissolution Rates of Basaltic Glass as a
- 548 Function of PH and Temperature. *Geochim. Cosmochim. Acta* **2003**, *67* (20), 3817–3832.
- 549 https://doi.org/10.1016/S0016-7037(00)00176-5.

550	(19)	Pollyea, R. M.; Rimstidt, J. D. Rate Equations for Modeling Carbon Dioxide
551		Sequestration in Basalt. Appl. Geochemistry 2017, 81, 53-62.
552		https://doi.org/10.1016/j.apgeochem.2017.03.020.
553	(20)	Menefee, A. H.; Li, P.; Giammar, D. E.; Ellis, B. R. Roles of Transport Limitations and
554		Mineral Heterogeneity in Carbonation of Fractured Basalts. Environ. Sci. Technol. 2017,
555		51 (16), 9352–9362. https://doi.org/10.1021/acs.est.7b00326.
556	(21)	Peuble, S.; Andreani, M.; Gouze, P.; Pollet-Villard, M.; Reynard, B.; Van de Moortele, B.
557		Multi-Scale Characterization of the Incipient Carbonation of Peridotite. Chem. Geol.
558		2018 , 476 (November 2017), 150–160. https://doi.org/10.1016/j.chemgeo.2017.11.013.
559	(22)	Chizmeshya, A. V. G.; McKelvy, M. J.; Squires, K.; Carpenter, R. W.; Béarat, H. A Novel
560		Approach to Mineral Carbonation: Enhancing Carbonation While Avoiding Mineral
561		Pretreatment Process Cost. In U.S. Dep. Energy Final Rep. 924162,; 2006.
562	(23)	Gadikota, G.; Matter, J.; Kelemen, P.; Brady, P. V.; Park, A. H. A. Elucidating the
563		Differences in the Carbon Mineralization Behaviors of Calcium and Magnesium Bearing
564		Alumino-Silicates and Magnesium Silicates for CO ₂ Storage. Fuel 2020, 277 (April),
565		117900. https://doi.org/10.1016/j.fuel.2020.117900.
566	(24)	Schaef, H. T.; McGrail, B. P.; Owen, A. T.; Arey, B. W. Mineralization of Basalts in the
567		CO2-H2O-H2S System. Int. J. Greenh. Gas Control 2013, 16, 187–196.
568		https://doi.org/10.1016/j.ijggc.2013.03.020.
569	(25)	Schaef, H. T.; McGrail, B. P.; Owen, A. T. Basalt- CO ₂ -H ₂ O Interactions and Variability
570		in Carbonate Mineralization Rates. In Energy Procedia; 2009; Vol. 1, pp 4899–4906.
571		https://doi.org/10.1016/j.egypro.2009.02.320.

572 ((26)	Gysi, A. P.: Stefánsson.	A. Mineralogical As	pects of CO ₂ Sequestration during
	(-~)	<i>ojsiiiiiiiiiiiii</i>		

- 573 Hydrothermal Basalt Alteration An Experimental Study at 75 to 250°C and Elevated
- 574 PCO₂. Chem. Geol. **2012**, 306–307, 146–159.
- 575 https://doi.org/10.1016/j.chemgeo.2012.03.006.
- 576 (27) Andreani, M.; Luquot, L.; Gouze, P.; Godard, M.; Hoisé, E.; Gibert, B. Experimental
- 577 Study of Carbon Sequestration Reactions Controlled by the Percolation of CO₂-Rich Brine

578 through Peridotites. *Environ. Sci. Technol.* **2009**, *43* (4), 1226–1231.

- 579 https://doi.org/10.1021/es8018429.
- 580 (28) Menefee, A. H.; Giammar, D. E.; Ellis, B. R. Permanent CO₂ Trapping through Localized
- 581and Chemical Gradient-Driven Basalt Carbonation. Environ. Sci. Technol. 2018, 52 (15),

582 8954–8964. https://doi.org/10.1021/acs.est.8b01814.

- 583 (29) Kelemen, P. B.; Matter, J.; Streit, E. E.; Rudge, J. F.; Curry, W. B.; Blusztajn, J. Rates and
- 584 Mechanisms of Mineral Carbonation in Peridotite: Natural Processes and Recipes for
- 585 Enhanced, in Situ CO₂ Capture and Storage. Annu. Rev. Earth Planet. Sci. 2011, 39 (1),

586 545–576. https://doi.org/10.1146/annurev-earth-092010-152509.

587 (30) Edmonds, M.; Tutolo, B.; Iacovino, K.; Moussallam, Y. Magmatic Carbon Outgassing

and Uptake of CO_2 by Alkaline Waters. *Am. Mineral.* **2020**, *105* (1), 28–34.

- 589 https://doi.org/10.2138/am-2020-6986ccby.
- 590 (31) Chavagnac, V.; Monnin, C.; Ceuleneer, G.; Boulart, C.; Hoareau, G. Characterization of
- 591 Hyperalkaline Fluids Produced by Low-Temperature Serpentinization of Mantle
- 592 Peridotites in the Oman and Ligurian Ophiolites. *Geochemistry, Geophys. Geosystems*
- 593 **2013**, *14* (7), 2496–2522. https://doi.org/10.1002/ggge.20147.

- 594 (32) Arnorsson, S.; Gunnarsson, I.; Stefansson, A.; Andrsdottir, A.; Sveinbjrnsdottir, R. E.
- 595 Major Element Chemistry of Surface- and Ground Waters in Basaltic Terrain, N-Iceland.I.
- 596 Primary Mineral Saturation. *Geochim. Cosmochim. Acta* **2002**, *66* (23), 4015–4046.
- 597 https://doi.org/10.1016/S0016-7037(02)00991-2.
- 598 (33) Mottl, M. J.; Wheat, G.; Baker, E.; Becker, N.; Davis, E.; Feely, R.; Grehan, A.; Kadko,
- 599 D.; Lilley, M.; Massoth, G.; Moyer, C.; Sansone, F. Warm Springs Discovered on 3.5 Ma
- 600 Oceanic Crust, Eastern Flank of the Juan de Fuca Ridge. *Geology* **1998**, *26* (1), 51–54.

601 https://doi.org/10.1130/0091-7613(1998)026<0051:WSDOMO>2.3.CO;2.

- 602 (34) Stumm, W.; Morgan, J. J. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural*603 *Waters*; John Wiley & Sons: New York, NY, 1996.
- 604 (35) Luhmann, A. J.; Tutolo, B. M.; Bagley, B. C.; Mildner, D. F. R.; Seyfried, W. E.; Saar, M.
- 605 O. Permeability, Porosity, and Mineral Surface Area Changes in Basalt Cores Induced by
- 606 Reactive Transport of CO_2 -Rich Brine. *Water Resour. Res.* **2017**, *53* (3), 1908–1927.
- 607 https://doi.org/10.1002/2016WR019216.
- 608 (36) Luhmann, A. J.; Tutolo, B. M.; Tan, C.; Moskowitz, B. M.; Saar, M. O.; Seyfried, W. E.

609 Whole Rock Basalt Alteration from CO₂-Rich Brine during Flow-through Experiments at

- 610 150 °C and 150 Bar. Chem. Geol. 2017, 453, 92–110.
- 611 https://doi.org/10.1016/j.chemgeo.2017.02.002.
- 612 (37) Winslow, D. M.; Fisher, A. T.; Stauffer, P. H.; Gable, C. W.; Zyvoloski, G. A. Three-
- 613 Dimensional Modeling of Outcrop-to-Outcrop Hydrothermal Circulation on the Eastern
- 614 Flank of the Juan de Fuca Ridge. J. Geophys. Res. Solid Earth 2016, 121 (3), 1365–1382.
- 615 https://doi.org/10.1002/2015JB012606.

616	(38)	Gadikota.	G.:	Matter.	J.:	Kelemen.	P.:	Park.	A. E	[. A.	Chemical	and	Mor	phole	ogica	ıl
010	(20)	00000000000	$\sim \cdot ,$		•••						01101110001		1.101	p11010	/ D	••

- 617 Changes during Olivine Carbonation for CO₂ Storage in the Presence of NaCl and
- 618 NaHCO₃. Phys. Chem. Chem. Phys. **2014**, 16 (10), 4679–4693.
- 619 https://doi.org/10.1039/c3cp54903h.
- 620 (39) Gysi, A. P.; Stefánsson, A. Experiments and Geochemical Modeling of CO₂ Sequestration
- 621 during Hydrothermal Basalt Alteration. *Chem. Geol.* **2012**, *306–307*, 10–28.
- 622 https://doi.org/10.1016/j.chemgeo.2012.02.016.
- 623 (40) Gysi, A. P.; Stefánsson, A. CO₂-Water-Basalt Interaction. Low Temperature Experiments
- and Implications for CO₂ Sequestration into Basalts. *Geochim. Cosmochim. Acta* **2012**,
- 625 *81*, 129–152. https://doi.org/10.1016/j.gca.2011.12.012.
- 626 (41) Xiong, W.; Wells, R. K.; Menefee, A. H.; Skemer, P.; Ellis, B. R.; Giammar, D. E. CO2
- 627 Mineral Trapping in Fractured Basalt. Int. J. Greenh. Gas Control 2017, 66 (October),
- 628 204–217. https://doi.org/10.1016/j.ijggc.2017.10.003.
- 629 (42) Xiong, W.; Wells, R. K.; Horner, J. A.; Schaef, H. T.; Skemer, P. A.; Giammar, D. E. CO₂
- 630 Mineral Sequestration in Naturally Porous Basalt. *Environ. Sci. Technol. Lett.* **2018**, *5* (3),
- 631 142–147. https://doi.org/10.1021/acs.estlett.8b00047.
- 632 (43) Christiansen, L.; von Kursk, O.; Haselip, J. A. UN Environment Emissions Gap Report
 633 2018. 2018.
- 634 (44) Breakthrough Energy | Helping the world get to net-zero
- 635 https://www.breakthroughenergy.org/ (accessed 2021 -03 -12).
- 636 (45) Goldberg, D. S.; Lackner, K. S.; Han, P.; Slagle, A. L.; Wang, T. Co-Location of Air

637	Capture, Subseafloor	CO_2 Sequestration	on, and Energy	Production on the	he Kerguelen

- 638 Plateau. Environ. Sci. Technol. 2013, 47 (13), 7521–7529.
- 639 https://doi.org/10.1021/es401531y.
- 640 (46) Goldberg, D. S.; Takahashi, T.; Slagle, A. L. Carbon Dioxide Sequestration in Deep-Sea
- 641 Basalt. Proc. Natl. Acad. Sci. U. S. A. 2008, 105 (29), 9920–9925.
- 642 https://doi.org/10.1073/pnas.0804397105.
- 643 (47) Johnson, H. P.; Pruis, M. J. Fluxes of Fluid and Heat from the Oceanic Crustal Reservoir.
- 644 *Earth Planet. Sci. Lett.* **2003**, *216* (4), 565–574. https://doi.org/10.1016/S0012-
- 645 821X(03)00545-4.
- 646 (48) Bethke, C. M.; Farrell, B. *The Geochemist's Workbench® Release 15 Reference*647 *Manual*; 2021.
- 648 (49) Wheat, C. G.; Hulme, S. M.; Fisher, A. T.; Orcutt, B. N.; Becker, K. Seawater Recharge
- 649 into Oceanic Crust: IODP Exp 327 Site U1363 Grizzly Bare Outcrop. *Geochemistry*,
- 650 *Geophys. Geosystems* **2013**, *14* (6), 1957–1972. https://doi.org/10.1002/ggge.20131.
- (50) Fisher, A. T. Permeability within Basaltic Oceanic Crust. *Phys. Earth Planet. Inter.* 1998, *145* (97), 143–182.
- 653 (51) Duan, Z.; Møller, N.; Weare, J. H. An Equation of State for the CH₄-CO₂-H₂O System: I.
- 654 Pure Systems from 0 to 1000°C and 0 to 8000 Bar. *Geochim. Cosmochim. Acta* **1992**, *56*
- 655 (7), 2605–2617. https://doi.org/10.1016/0016-7037(92)90347-L.
- (52) Holland, H. D. *The Chemistry of the Atmosphere and Oceans*; John Wiley & Sons, Inc.,
 1978.

658	(53)	Hulme, S. M.; Wheat, C. G. Subseafloor Fluid and Chemical Fluxes Along a Buried-
659		Basement Ridge on the Eastern Flank of the Juan de Fuca Ridge. Geochemistry, Geophys.
660		Geosystems 2019, 20, 4922-4938. https://doi.org/10.1029/2019GC008408.
661	(54)	Marieni, C.; Matter, J. M.; Teagle, D. A. H. Experimental Study on Mafic Rock
662		Dissolution Rates within CO ₂ -Seawater-Rock Systems. Geochim. Cosmochim. Acta 2020,
663		272, 259–275. https://doi.org/10.1016/j.gca.2020.01.004.
664	(55)	Arnórsson, S.; Gunnlaugsson, E.; Svavarsson, H. The Chemistry of Geothermal Waters in
665		Iceland. III. Chemical Geothermometry in Geothermal Investigations. Geochim.
666		Cosmochim. Acta 1983, 47 (3), 567–577. https://doi.org/10.1016/0016-7037(83)90278-8.
667	(56)	Seyfried, W. E.; Bischoff, J. L. Low Temperature Basalt Alteration by Sea Water: An
668		Experimental Study at 70°C and 150°C. Geochim. Cosmochim. Acta 1979, 43 (12), 1937–
669		1947. https://doi.org/10.1016/0016-7037(79)90006-1.
670	(57)	Coogan, L. A.; Gillis, K. M. Evidence That Low-Temperature Oceanic Hydrothermal
671		Systems Play an Important Role in the Silicate-Carbonate Weathering Cycle and Long-
672		Term Climate Regulation. Geochemistry, Geophys. Geosystems 2013, 14 (6), 1771–1786.
673		https://doi.org/10.1002/ggge.20113.
674	(58)	Lawrence, J. R.; Drever, J. I. Evidence for Cold Water Circulation at DSDP Site 395:
675		Isotopes and Chemistry of Alteration Products. J. Geophys. Res. 1981, 86 (B6), 5125-
676		5133. https://doi.org/10.1029/JB086iB06p05125.
677	(59)	Alt, J. C.; Muehlenbachs, K.; Honnorez, J. An Oxygen Isotopic Profile through the Upper
678		Kilometer of the Oceanic Crust, DSDP Hole 504B. Earth Planet. Sci. Lett. 1986, 80 (3-4),
679		217-229. https://doi.org/10.1016/0012-821X(86)90106-8.

(60) Coogan, L. A.; Gillis, K. M. Low-Temperature Alteration of the Seafloor: Impacts on

680

681		Ocean Chemistry. Annu. Rev. Earth Planet. Sci. 2018, 46 (1), 21-45.
682		https://doi.org/10.1146/annurev-earth-082517-010027.
683	(61)	Kong, X. Z.; Tutolo, B. M.; Saar, M. O. DBCreate: A SUPCRT92-Based Program for
684		Producing EQ3/6, TOUGHREACT, and GWB Thermodynamic Databases at User-
685		Defined T and P. Comput. Geosci. 2013, 51, 415–417.
686		https://doi.org/10.1016/j.cageo.2012.08.004.
687	(62)	Helgeson, H. C. Thermodynamics of Hydrothermal Systems at Elevated Temperatures
688		and Pressures. American Journal of Science. 1969, pp 729-804.
689		https://doi.org/10.2475/ajs.267.7.729.
690	(63)	Robie, R. A.; Hemingway, B. S. Thermodynamic Properties of Minerals and Related
691		Substances at 298.15 K and 1 Bar (10 ⁵ Pascals) Pressure and at Higher Temperatures. US
692		Geol. Surv. Bull. 1995, 2131. https://doi.org/10.1016/0016-7037(79)90232-1.
693	(64)	Stefánsson, A.; Gíslason, S. R.; Arnórsson, S. Dissolution of Primary Minerals in Natural
694		Waters I. Calculation of Mineral Solubilities from 0°C to 350°C. Chem. Geol. 2001, 172
695		(3-4), 251-276. https://doi.org/10.1016/S0009-2541(00)00262-X.
696	(65)	Blanc, P.; Vieillard, P.; Gailhanou, H.; Gaboreau, S.; Gaucher, É.; Fialips, C. I.; Madé, B.;
697		Giffaut, E. A Generalized Model for Predicting the Thermodynamic Properties of Clay
698		Minerals. Am. J. Sci. 2015, 315 (8), 734–780. https://doi.org/10.2475/08.2015.02.
699	(66)	Helgeson, H. C.; Delany, J. M.; Nesbitt, H. W.; Bird, D. K. Summary and Critique of the
700		Thermodynamic Properties of the Rock-Forming Minerals. Am. J. Sci. 1978, 278A, 229.

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701	(67)	Tutolo, B. M.; Kong, X. Z.; Seyfried, W. E.; Saar, M. O. Internal Consistency in Aqueous
702		Geochemical Data Revisited: Applications to the Aluminum System. Geochim.
703		Cosmochim. Acta 2014, 133, 216–234. https://doi.org/10.1016/j.gca.2014.02.036.
704	(68)	Gunnarsson, I.; Arnórsson, S. Amorphous Silica Solubility and the Thermodynamic
705		Properties of H _{4SiO4° in the Range of 0°to 350°C at P(Sat). <i>Geochim. Cosmochim.</i>}
706		Acta 2000, 64 (13), 2295–2307. https://doi.org/10.1016/S0016-7037(99)00426-3.
707	(69)	Sverjensky, D. A.; Harrison, B.; Azzolini, D. Water in the Deep Earth: The Dielectric
708		Constant and the Solubilities of Quartz and Corundum to 60kb and 1200°C. Geochim.
709		Cosmochim. Acta 2014, 129, 125-145. https://doi.org/10.1016/j.gca.2013.12.019.
710	(70)	Rimstidt, J. D. Quartz Solubility at Low Temperatures. Geochim. Cosmochim. Acta 1997,
711		61 (13), 2553–2558. https://doi.org/10.1016/S0016-7037(97)00103-8.
712	(71)	Johnson, J. W.; Oelkers, E. H.; Helgeson, H. C. SUPCRT92: A Software Package for
713		Calculating the Standard Molal Thermodynamic Properties of Minerals, Gases, Aqueous
714		Species, and Reactions from 1 to 5000 Bar and 0 to 1000°C. Comput. Geosci. 1992, 18
715		(7), 899–947. https://doi.org/10.1016/0098-3004(92)90029-Q.
716	(72)	Hellevang, H.; Pham, V. T. H.; Aagaard, P. Kinetic Modelling of CO ₂ -Water-Rock
717		Interactions. Int. J. Greenh. Gas Control 2013, 15, 3–15.
718		https://doi.org/10.1016/j.ijggc.2013.01.027.

719