

*Earth in Five Reactions: CO<sub>2</sub> outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam*

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## Revision 1

### Magmatic carbon outgassing and uptake of CO<sub>2</sub> by alkaline waters

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#### Abstract

Much of Earth's carbon resides in the 'deep' realms of our planet: sediments, crust, mantle and core. The interaction of these deep reservoirs of carbon with the surface reservoir (atmosphere and oceans) leads to a habitable surface environment, with an equitable atmospheric composition and comfortable range in temperature that together have allowed life to proliferate. The *Earth in Five Reactions* project (part of the Deep Carbon Observatory program) identified the most important carbon-bearing reactions of our planet, defined as those which perhaps make our planet unique among those in our solar system, to highlight and review how the deep and surface carbon cycles connect. Here we review the important reactions which control the concentration of carbon dioxide in our atmosphere: outgassing from magmas during volcanic eruptions and during magmatic activity; and uptake of CO<sub>2</sub> by alkaline surface waters. We describe the state of our knowledge about these reactions and their controls, the extent to which we understand the mass budgets of carbon that are mediated by these reactions, and finally, the implications of these reactions for understanding present-day climate change that is driven by anthropogenic emission of CO<sub>2</sub>.

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## 36 **1. Introduction**

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38 We present this paper as part of the *Earth in Five Reactions* series, which identifies the most  
39 important carbon-bearing reactions in Earth from the perspective of the 'deep' carbon cycle.  
40 When considering the most important carbon-bearing reactions, it seems clear that those  
41 reactions that directly control the concentration of CO<sub>2</sub> in our atmosphere must rank high on the  
42 list. The concentration of CO<sub>2</sub> in our atmosphere controls the habitability of our planet via our  
43 equitable climate and the existence of photosynthesizing organisms. How does the deep carbon  
44 cycle impact the concentration of CO<sub>2</sub> in our atmosphere?

45

46 The Earth's 'surface reservoir' i.e. the atmosphere, oceans and sediments combined, of carbon  
47 makes up only a small fraction of the Earth's total carbon budget, with most of the carbon  
48 inventory of the planet (estimates vary from 75 to 99%) residing in the Earth's core (Dasgupta et  
49 al., 2013; Dasgupta and Hirschmann, 2010a; DePaolo, 2015; Li et al., 2019; Wood, 1993). Over  
50 long geological timescales, fluxes of carbon from the mantle to the atmosphere and oceans via  
51 magmatism, volcanism and metamorphic decarbonation, modulate the composition of Earth's  
52 atmosphere and climate (Dasgupta, 2013; Sleep and Zahnle, 2001) (**figure 1**). The delicate  
53 carbon balance of the surface reservoir is largely maintained (Bernier and Caldeira, 1997),  
54 despite the immense size of Earth's internal reservoirs and fluxes, which requires equally  
55 important fluxes of carbon back into the mantle, through subduction (Dasgupta, 2013;  
56 Hirschmann, 2018; Kelemen and Manning, 2015). This return flux replenishes the carbon lost  
57 from the mantle via melting and degassing (Dasgupta, 2013; Hirschmann, 2018).

58

59 The volcanic, tectonic and metamorphic flux of CO<sub>2</sub> from Earth's interior is large. For the  
60 volcanic portion, current estimates range from 280 to 360 Tg C per year (equivalent to 6.4 to 8.2  
61 x 10<sup>12</sup> moles C per year) (Burton et al., 2013; Gerlach, 2011; Werner et al., 2019). Volcanic C is  
62 derived from the outgassing of silicate melts at low pressure. The tectonic flux includes direct  
63 outgassing of mantle-derived CO<sub>2</sub> fluids (Chiodini et al., 2010; Mörner and Etiope, 2002), as well  
64 as metamorphic decarbonation in orogenic belts (Kerrick and Caldeira, 1998). Degassing of  
65 crustal- and mantle-derived fluids associated with extensional tectonic regimes (e.g. outgassing  
66 from continental rifts) constitutes a large fraction of the total outgassing flux; a recent estimate

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67 (which is also included in the ‘volcanic’ estimate above), is hundreds of Tg/year of CO<sub>2</sub>  
68 (Tamburello et al., 2018).

69

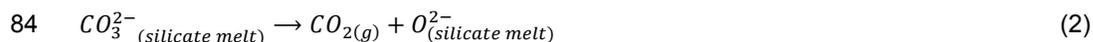
70 The majority of the volcanic flux is derived from the degassing of carbon from silicate melts  
71 generated in the mantle, linked to mantle plumes or plate boundary processes, which ascend  
72 towards the surface of the Earth. The melts contain dissolved carbon at the point of generation  
73 in the mantle. It has been shown that the mantle is heterogeneous with respect to carbon (Hauri  
74 et al., 2019; Hauri et al., 2018; Hirschmann and Dasgupta, 2009; Saal et al., 2002), which leads  
75 to melts produced in different settings containing different amounts of carbon. Mid-ocean ridge  
76 melts are largely carbon-depleted relative to those formed in arcs and hotspot settings (Blundy  
77 et al., 2010; Hauri et al., 2019). Carbon solubility in silicate melts plummets with decreasing  
78 pressure, which causes melts to outgas their carbon almost entirely once they reach the shallow  
79 crust. This reaction might be represented by:

80



82 and

83



85

86 for dissolved molecular CO<sub>2</sub> and dissolved carbonate respectively (where O<sup>2-</sup> is a non-bridging  
87 oxygen) (Guillot and Sator, 2011). Both species are present in silicate melts, with molecular CO<sub>2</sub>  
88 becoming more important as the silica content of the melt increases (and temperature  
89 decreases) (Stolper and Holloway, 1988). The controls on silicate melt degassing (reactions 1  
90 and 2) are explored further in section 2. Melts may also assimilate carbon from the mantle  
91 lithosphere, or from the crust (Carter and Dasgupta, 2015; Lee et al., 2013; Mason et al., 2017),  
92 where carbon resides as carbonate and organic carbon, and transfer this carbon to the  
93 atmosphere. Because of the low solubility of carbon in silicate melts, intrusive magmatism  
94 contributes to the outgassing flux of carbon, leading to diffuse emissions of CO<sub>2</sub> around the  
95 flanks of volcanoes and in volcanic regions, often mediated by large scale faults and fractures  
96 (Allard et al., 1991; Chiodini et al., 1995; Farrar et al., 1995; Hunt et al., 2017).

97

98 Volcanoes and extensional tectonic regions pump CO<sub>2</sub> into the atmosphere (**figure 1**), triggering  
99 a systematic response in the surface reservoir (Berner, 1999). An equilibrium exists between

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100 the CO<sub>2</sub> in the atmosphere and in the oceans. On short timescales, the atmosphere-ocean  
101 system responds to an increase in atmospheric CO<sub>2</sub> by allowing more carbon to dissolve in the  
102 ocean:

103



105

106 Aqueous CO<sub>2</sub> dissociates to carbonate and bicarbonate, with the relative proportions dependent  
107 on the pH of the ocean water:

108



110

111 Adding more CO<sub>2</sub> to the ocean increases acidity (at the expense of carbonate); increasing the  
112 alkalinity of the ocean will tend to draw down CO<sub>2</sub>. The residence time of carbon in the  
113 atmosphere-ocean-sediment system is relatively short; only ~100 ka (Berner, 1994). Carbon is  
114 removed from the surface reservoir through weathering and removal of bicarbonate through  
115 rivers into the ocean. Then, carbon is precipitated from the ocean water as carbonate above the  
116 carbonate compensation depth (CCD), forming both limestones on the ocean floor and  
117 carbonate precipitated in oceanic crust, which may eventually be returned to the mantle via  
118 subduction. A fraction of this carbon may be removed from the slab during subduction, via  
119 dissolution or metamorphic decarbonation (Agué and Nicolescu, 2014; Facq et al., 2014;  
120 Gorman et al., 2006; Kerrick and Connolly, 2001), migrating back to the surface in the forearc or  
121 subarc in the form of CO<sub>2</sub>-rich fluids and by dissolution within primary arc melts and transport to  
122 the surface through volcanism (Dutkiewicz et al., 2018).

123

124 The transfer of CO<sub>2</sub> between gas and water and silicate melts therefore plays an outsized role in  
125 connecting its various 'spheres'. Metamorphic and magmatic CO<sub>2</sub> inputs from Earth's interior  
126 enter the atmosphere through the forward expression of reactions 1 and 2, dissolve into its  
127 hydrosphere through the forward expression of reaction 3, and ultimately interact with cations  
128 derived from lithospheric weathering to form carbonate minerals, often through biosphere-  
129 mediated processes (Garrels, 1983). Indeed, this silicate weathering feedback is the primary  
130 reason that the surface of our planet is clement (Agué et al., this issue). Moreover, much of the  
131 carbon available to biological metabolisms such as photosynthesis (see Schrenk et al., this  
132 issue) ultimately originates through a coupling of reactions (1+2) and 3. Due to their  
133 significance in connecting earth's spheres, Reactions 1 (and 2) and 3 together were chosen as

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134 one of the five most important reactions that make Earth unique in the solar system by  
135 delegates of the Deep Carbon Observatory's Earth in Five Reactions workshop.

136

137 **In this paper**, we review the current state of understanding of both reactions in detail, with  
138 application to the case of alkaline melts and fluids generated in continental rifts, which have had  
139 considerable importance for supplying CO<sub>2</sub> fluxes to the surface reservoir through  
140 supercontinent cycles of the past (Brune et al., 2017) and in the modern day (Hunt et al., 2017;  
141 Lee et al., 2016; Werner et al., 2019). We discuss the dependence of these reactions on other  
142 parameters in the geological system, and we consider their importance for the Earth's deep  
143 carbon cycle, tracking carbon reactions from the mantle to the surface. Finally, we draw  
144 attention to the relevance of both of these naturally occurring reactions, which have played such  
145 an important role in shaping Earth's climate and surface environment over its long history, to our  
146 present-day societal challenges related to anthropogenic CO<sub>2</sub> release and ocean drawdown of  
147 CO<sub>2</sub>.

148

## 149 **2. Carbon degassing from silicate melts**

150

151 Carbon exists in many forms in the Earth's mantle: as fluids, dissolved as oxidized carbonate  
152 species (Pan and Galli, 2016) or as reduced hydrocarbons (Sverjensky and Huang, 2015) or as  
153 solid carbonate (Boulard et al., 2015)(Cerantola et al., this issue); as elemental carbon (graphite  
154 and diamond, (Shirey et al., 2013)) in the deep mantle; and as Fe-metal carbide in the mantle  
155 (McCammon et al., this issue) core (Li and Fei, 2003; Wood et al., 2013). Carbonated silicate  
156 melts may be ubiquitous in the mantle, and may be the precursor to mid-ocean ridge basalts,  
157 kimberlites, and melts derived from subducting slabs (Dasgupta and Hirschmann, 2010a;  
158 Moussallam et al., 2015). As silicate melts generated in the mantle ascend into the crust, they  
159 transport their dissolved carbon load toward to the surface of the Earth. As they decompress,  
160 carbon dioxide exsolves and forms a separated supercritical fluid, transforming to a gas phase  
161 close to the surface. In this way, carbon may be transferred from the interior of the Earth (the  
162 mantle) to the surface (atmosphere and ocean); this is a critical flux of the deep carbon cycle  
163 (**figure 1**).

164

165 Because of the relatively high pressures in the crust and upper mantle (at depths of perhaps up  
166 to 40-50 km) under which silicate melt degassing occurs, generated CO<sub>2</sub>-rich fluid may migrate  
167 semi-independently of the magma through the crust, leading to large areas of so-called 'diffuse'

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168 degassing at the surface (Chiodini et al., 2004), with the fluid making use of fractures and  
169 tectonic structures in the crust to reach the atmosphere. Diffuse degassing takes place in a  
170 range of tectonic settings, e.g. at mid-ocean ridges, volcanic arcs over subduction zones and  
171 submarine arc vents, in continental rifts (Hunt et al., 2017), and in large silicic calderas (Werner  
172 and Brantley, 2003). In this way, the carbon content of unerupted magmas may yet reach the  
173 atmosphere, despite the source magma stalling in the crust. In the case of volcanic eruptions,  
174 the CO<sub>2</sub> is carried directly to the surface in ascending magmas (in both dissolved and exsolved  
175 forms), and it is outgassed to the atmosphere either prior to or during eruption. In this section  
176 we review our state of understanding of carbon degassing from silicate melts.

177

#### 178 *2.1 Controls on CO<sub>2</sub> solubility in silicate melts*

179 CO<sub>2</sub> exists as both dissolved carbonate and as molecular CO<sub>2</sub> in silicate glasses (Fine and  
180 Stolper, 1985; Fine and Stolper, 1986; Mysen et al., 1975). In basalts, basanites, and other  
181 silica-undersaturated magmas, carbon exists solely as carbonate (Blank and Brooker, 1994;  
182 Moussallam et al., 2016), whereas in rhyolitic glasses, only molecular CO<sub>2</sub> is found (Fogel and  
183 Rutherford, 1990). Intermediate magmas and evolved, silica-undersaturated glasses such as  
184 phonolites, have both species present (Behrens et al., 2004). Carbon speciation in silicate melts  
185 is a strong function not only of melt silica content but also of melt structure and availability of  
186 cations such as Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> (Fine and Stolper, 1985). The speciation of carbon dioxide  
187 in glasses (i.e., at surface P-T conditions) however is not necessarily that of the melt (i.e., at  
188 depth). Evidence from annealing experiments (Morizet et al., 2001; Nowak et al., 2003),  
189 molecular dynamic simulation studies (Guillot and Sator, 2011; Morizet et al., 2015; Moussallam  
190 et al., 2016) and in-situ spectroscopy studies (Konschak and Keppler, 2014) show that the CO<sub>2</sub>  
191 + O<sup>2-</sup> = CO<sub>3</sub><sup>2-</sup> equilibrium in the melt shifts towards CO<sub>2</sub> with increasing temperature and that in  
192 the melt, molecular CO<sub>2</sub> is present even in basaltic and carbonated melt compositions.

193

194 CO<sub>2</sub> solubility in silicate melts is controlled by the melt composition via the attractive-repulsive  
195 behaviour of each component with CO<sub>2</sub> (Papale et al., 2006). Of these, Si and Al are by far the  
196 dominant factors, with CO<sub>2</sub> solubility decreasing drastically with increasing Si and Al and  
197 increasing with increasing Ca, K, and Na content (plus more minor effect with increasing Mg  
198 and Fe; **Figure 2a**) (Blank and Brooker, 1994; Dixon et al., 1997; Moussallam et al., 2015;  
199 Shishkina et al., 2014). This is well illustrated by the empirical relationship between CO<sub>2</sub>  
200 solubility and the compositional “Pi parameter” (Dixon et al., 1997), which incorporates negative  
201 Si and Al terms and positive Ca, K, Na, Mg, and Fe terms.

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202

203 The relatively dry and shallow melting regime beneath rift margins relative to other plate  
204 boundaries results in the generation very low-degree (<3%) partial mantle melts. Such melts are  
205 characteristically low in Si and rich in Ca, K, Na, and Mg, resulting in a stronger propensity to  
206 dissolve available carbon (as carbonate). At mantle pressures, primary melts may dissolve  
207 several wt. % of carbon (up to 6 wt. % at mantle pressures; **Figure 2a**).

208

209 The solubility of CO<sub>2</sub> increases with pressure for all silicate melt compositions (**Figure 2b**). At  
210 300 MPa in the crust, for example, basalts may hold 3000-4000 ppm in solution, depending on  
211 the amount of other volatile species present (see below), decreasing to only a couple of  
212 hundred ppm at 50 MPa. Much of the CO<sub>2</sub> load of a basaltic melt, which may reach 0.5 or even  
213 1 wt. % in the crust, therefore resides in the exsolved magmatic volatile phase in the mid- and  
214 upper crust.

215

216 The presence of other volatiles affects the solubility of CO<sub>2</sub> in silicate melts. Henry's Law applies  
217 to volatile solubility certainly at pressures pertaining to the mid- and upper-crust. For a vapor-  
218 saturated melt, where more than one volatile species is present, the concentration, or activity, of  
219 a particular species is diluted, thereby reducing its solubility in the melt (Moore, 2008). The  
220 magnitude of this effect on melt CO<sub>2</sub> solubility is illustrated in **Figure 2b**, where as the coexisting  
221 vapor phase becomes more H<sub>2</sub>O-rich, the concentration (solubility) of CO<sub>2</sub> in the melt is reduced  
222 (Dixon and Stolper, 1995; Dixon et al., 1995; Moore, 2008; Moore et al., 1998; Newman and  
223 Lowenstern, 2002). This occurs in nature during a process known as second boiling, where  
224 magmas crystallize at a fixed pressure in the crust (Candela, 1997). During crystallization, the  
225 melt volume reduces, and volatiles are forced out of solution and outgassed. Over time, the  
226 vapor phase thus produced gets progressively more water-rich, thereby reducing the solubility  
227 of CO<sub>2</sub> in the remaining melt, as observed in quartz melt inclusions erupted in the Bishop Tuff,  
228 for example (Wallace et al., 1999). Conversely, underplating mafic magmas producing exsolved  
229 CO<sub>2</sub> may 'flush' overlying stored magmas (Blundy et al., 2010; Caricchi et al., 2018; Cashman,  
230 2004). In this case, the addition of CO<sub>2</sub> raises the concentration of CO<sub>2</sub> in the co-existing vapor  
231 phase, thereby enhancing CO<sub>2</sub> solubility in the silicate melt. This process of CO<sub>2</sub> flushing has  
232 been invoked to explain anomalously high CO<sub>2</sub> concentrations in olivine-hosted melt inclusions  
233 from Etna, for example (Métrich and Wallace, 2008).

234

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235 The volcanic and tectonic flux of CO<sub>2</sub> to the surface environment encompasses contributions  
236 from mid-ocean ridges (which is released dominantly into the oceans), from continental rifts,  
237 volcanic arcs, hotspots, extensional regions where the Earth's mantle supplies CO<sub>2</sub>-rich fluids  
238 direct to the surface, and orogenic belts where limestones are heated and devolatilized (Sleep  
239 and Zahnle, 2001). The fraction of this CO<sub>2</sub> that is released directly into the atmosphere, and  
240 that which is absorbed into water bodies such as oceans, lakes, and groundwater aquifers, is  
241 unknown. It has been well documented that a large fraction of the CO<sub>2</sub> released in extensional  
242 regions are trapped by aquifer systems, which, in turn, allow quantification of the CO<sub>2</sub> produced  
243 over large areas, e.g. in the eastern Himalayas (Evans et al., 2008) and in the Apennines region  
244 of Italy (Chiodini et al., 2000).

245

### 246 **3. Uptake of magmatic CO<sub>2</sub> by surface water bodies**

247

#### 248 *3.1 Alkalinity and carbon storage in surface water bodies*

249 Earth's surface water bodies can play a vital role in controlling the ultimate fate of carbon  
250 degassed from silicate melts. The amount of inorganic carbon in a solution in equilibrium with  
251 gaseous CO<sub>2</sub> is a function of the solution's alkalinity and its pH (**Figure 3**). In essence, alkalinity  
252 is a charge balance equation defined in relation to the speciation of dissolved inorganic carbon.  
253 Formally, carbonate alkalinity is defined (Stumm and Morgan, 2012) as:

254

$$255 \text{ [Alkalinity]} = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (5)$$

256

257 where the brackets indicate concentrations of the bracketed species in mole-based units (e.g.,  
258 molal).

259

260 Inorganic carbon enters solution through reaction (3), and, depending on the partial pressure of  
261 CO<sub>2</sub> and the alkalinity and pH of the solution, is speciated into carbonic acid (CO<sub>2(aq)</sub>),  
262 bicarbonate (HCO<sub>3</sub><sup>-</sup>), and carbonate (CO<sub>3</sub><sup>2-</sup>). Examination of Eqn. (5) shows that  
263 dissolving/exsolving CO<sub>2(g)</sub>, an electrically neutral molecule, into/out of solution cannot directly  
264 impact alkalinity, although it may have the side effect of making minerals more or less soluble,  
265 which will, in turn, impact the solution alkalinity. Additionally, Eqn. (5) shows that the total  
266 inorganic carbon in solution can be directly related to pH and alkalinity (**Figure 3**). Nonetheless,  
267 meaningful use of Eqn. (4) in the study of dynamic aqueous environments begs the question  
268 "What else is there?" - i.e., what are the concentrations of cations other than HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, H<sup>+</sup>,

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269 and OH<sup>-</sup>, and how might they contribute to the overall behaviour (i.e, pH, carbon storage  
270 capacity) of the solution and/or reflect its history? Basalt have an excess of cations over CO<sub>2</sub>.  
271 Atmospheric CO<sub>2</sub> binds with the cations once the rock eventually weathers, making the  
272 weathering of basalt a carbon sink. For this purpose, an “alternative definition” of alkalinity  
273 reflecting the non-carbonate carbon portion of the charge balance (Stumm and Morgan 1996) is:  
274

$$275 \text{ [Alkalinity]} = [\text{Na}^+] + [\text{K}^+] + 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] - [\text{Cl}^-] - 2[\text{SO}_4^{2-}] - 2[\text{NO}_3^{2-}] \quad (6)$$

276

277 In equation (6), the impact of water chemistry on alkalinity and hence carbon storage and pH  
278 (**Figure 3**) can be more readily discerned. Notably this is a functional version of the equation  
279 that includes the “major” cationic and anionic species representative of most natural waters; it  
280 would need to be expanded for waters where other ions may be important. An important aspect  
281 of Eqn. (6) is that it shows that the alkalinity is reduced by concentrations of anions such as Cl<sup>-</sup>  
282 and SO<sub>4</sub><sup>-</sup>, two of the dominant anions in seawater.

283

### 284 *3.2 Aqueous carbon storage at rifted margins*

285 At the same time as our understanding of carbon fluxes from continental rifts has increased  
286 through the efforts of DCO members and others (Brune et al., 2017; Hunt et al., 2017; Lee et al.,  
287 2016), attention has also been refocused on the fluxes of CO<sub>2</sub> from mid-ocean ridges (e.g.,  
288 Lund et al., 2016) and their variability in relation to long-term geologic variations. In the case of  
289 mid-ocean ridge systems, much of the CO<sub>2</sub> degassing from the system is rapidly absorbed by  
290 the overlying seawater due to its high solubility at seafloor depths. For example, although CO<sub>2</sub>  
291 concentrations of continuously venting hydrothermal fluids are commonly in the tens to  
292 hundreds of millimolal e.g., (Lilley et al., 2003), it is rare, although not unheard of (Lupton et al.,  
293 2008) to observe free-phase CO<sub>2</sub> in the vicinity of submarine hydrothermal systems.

294

295 It is now clear that continental rifts are important sites of magmatic CO<sub>2</sub> release (Hunt et al.,  
296 2017): the eastern branch of the East African Rift, for example, may be emitting more CO<sub>2</sub>  
297 (~3.9–32.7 Mt/year) than all of the world’s mid-ocean ridges combined (Hauri et al., 2019; Hunt  
298 et al., 2017; Lee et al., 2016), although there are large uncertainties attached to these  
299 estimates. Sites of continental breakup tap directly the vast volatile storage region in the sub-  
300 continental lithosphere, where small fraction, volatile-rich melts freeze as they cross their  
301 solidus as they ascend from the convecting mantle (Foley and Fischer, 2017). Over geological  
302 time, supercontinent breakup may have released enormous fluxes of CO<sub>2</sub> held in storage both

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303 in the sub-continental lithosphere but also in the form of sediments on the continents, which  
304 may have played an important role in shaping Earth's climate (Brune et al., 2017; Lee et al.,  
305 2013). Today, the CO<sub>2</sub> emitted from the East African Rift may vary along-rift (Hunt et al., 2017).  
306 The CO<sub>2</sub> migrates to the surface along faults at the rift margins (Hutchison et al., 2015), where it  
307 may be intercepted by surface water in the form of rift lakes.

308

309 The geology of the watersheds feeding rift lakes exerts an important control on the aqueous  
310 geochemistry of the lake waters (Cerling, 1994; Cerling, 1979; Wright, 2012). Analyses  
311 presented by (Cerling, 1994) demonstrates that weathering of the volcanic rocks feeding East  
312 African Rift-hosted lakes provides mainly Na<sup>+</sup>, Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup> and relatively little Cl<sup>-</sup> and SO<sub>4</sub><sup>-</sup> to  
313 the lake waters. When examined in the alkalinity framework represented by Eqn. 5, one can see  
314 the alkalinity of these lakes tends to be quite high (**figure 3**). If the lakes are in a closed basin,  
315 evaporation-dominated setting, then the alkalinity, and hence pH, tends to increase during  
316 evaporation (Garrels and MacKenzie, 1967; Tutolo and Tosca, 2018). As both pH and alkalinity  
317 increase, the amount of inorganic carbon stored in the lake also increases (**Figure 3**), such that  
318 evaporation-dominated rift basin lake waters can contain concentrations of inorganic carbon  
319 significantly greater than seawater. This inorganic carbon can be deposited as carbonate  
320 minerals or converted to biomass and stored in lake sediments, often through interactions with  
321 cyanobacterial or algal communities (Wright, 2012). Hence, a significant amount of carbon  
322 emitted from silicate melts in continental rifts may not go much further than the sediments  
323 deposited in the overlying lakes. Because the rift environment is dynamic, with lakes changing  
324 in size and alkalinity over time, intimately linked to the tectonics of rifting, the system does not  
325 necessarily reach a steady state equilibrium; and the total carbon sequestered by lakes in rift  
326 environments remains unquantified. In this way, rifted margins are locations where the  
327 lithosphere, in the form of magmatic degassing, the hydrosphere, in the form of rift-basin lakes  
328 or seawater, and the biosphere, in the form of cyanobacteria, algae, and higher-order  
329 organisms, all interact with one another.

330

#### 331 **4. Implications for present-day anthropogenic CO<sub>2</sub> release and ocean response**

332

333 We have shown that the flux of carbon from Earth's interior, and the potential for uptake of CO<sub>2</sub>  
334 by alkaline surface waters, are first order controls on the concentration of CO<sub>2</sub> in our  
335 atmosphere. Up to now, we have confined our discussion to the natural cycles of magmatism  
336 and tectonics that have characterized our planet for the past two billion years. However, the

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337 processes that we discuss here are also relevant to a pressing predicament facing humankind  
338 in the 21st century. Namely, is anthropogenic CO<sub>2</sub> generation a stronger driver of climate than  
339 CO<sub>2</sub> injected into the atmosphere by natural processes? And how is the atmosphere-ocean  
340 system responding?

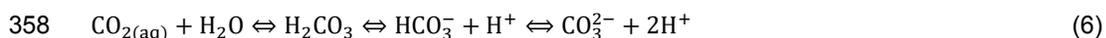
341

342 The answer to the first is unequivocally yes. Numerous estimates of CO<sub>2</sub> delivered into the  
343 atmosphere by volcanism lead to an inescapable conclusion: anthropogenic sources of CO<sub>2</sub> far  
344 exceed the volcanic and tectonic flux of CO<sub>2</sub> into the atmosphere. The burning of fossil fuel and  
345 manufacture of cement released 31,000 ± 1845 Tg CO<sub>2</sub> into the atmosphere in 2009  
346 (Friedlingstein et al., 2010). Volcanoes and volcanic regions annually supply 240 – 350 Tg CO<sub>2</sub>  
347 per year to the atmosphere and ocean system (Burton et al., 2013; Gerlach, 2011; Werner et  
348 al., 2019), that is 83 to 137 times less than the anthropogenic sources named above. The  
349 massive fluxes of carbon into the surface reservoir caused by anthropogenic activities,  
350 principally the burning of fossil fuels (buried organic carbon from the deep reservoir; **Figure 1**),  
351 has exceeded the Earth system's ability to compensate, upsetting the delicate balance in the  
352 geologic carbon cycle (Berner and Caldeira, 1997).

353

354 The ocean has absorbed around a third of the CO<sub>2</sub> produced anthropogenically since the mid-  
355 20th century (Sabine et al., 2004) through Eqn. 3. Uptake of CO<sub>2</sub> in ocean water decreases the  
356 pH by:

357



359

360 thereby increasing CO<sub>2</sub> and bicarbonate at the expense of carbonate. Since the mid-20th  
361 century, it is estimated that ocean pH has dropped by 0.1 log units, which represents an almost  
362 30% increase in H<sup>+</sup> ions (Caldeira and Wickett, 2003). The increase in acidity lowers the  
363 saturation state of calcite and aragonite in the oceans and is slowing or shutting down  
364 calcification in many marine organisms, including those that inhabit coral reefs (Doney et al.,  
365 2009; Orr et al., 2005; Zeebe et al., 2008).

366

367 Recent work has attempted to compare the recent rates of anthropogenic CO<sub>2</sub> release to  
368 periods of dramatic carbon release from deep reservoirs to the atmosphere-ocean system in  
369 Earth's history, which are recorded as light carbon isotope excursions in sedimentary records  
370 (Zeebe et al., 2016). A large carbon isotopic excursion and associated mass extinction at the

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371 end of the Permian has been linked to the outpouring of 7-15 million km<sup>3</sup> basalt (Black et al.,  
372 2012; Black and Gibson, 2019; Reichow et al., 2009; Saunders, 2005) as well as the  
373 metamorphic devolatilization (Svensen et al., 2009) and combustion (Ogden and Sleep, 2012)  
374 of buried coal by sills. This event may have released 20,000 to 30,000 Pg C over as long as 10<sup>5</sup>  
375 years, but probably in discrete pulses over much shorter timescales (Black et al., 2018). The  
376 fastest large carbon release of the Cenozoic (past 66 Myr) occurred at the onset of the  
377 Palaeocene–Eocene Thermal Maximum (~56 Myr ago) (Zachos et al., 2005), when 2,500 to  
378 4,500 Pg carbon was emitted to the ocean-atmosphere system over up to 4000 years  
379 (Bowen et al., 2015; Zeebe et al., 2016). These estimates yield annual carbon emissions  
380 during the PETM perhaps as little as 1 Pg carbon per year (Stocker et al., 2013; Zeebe et al.,  
381 2016) or as much as ~9.5 Pg carbon/year, which is similar to present day anthropogenic  
382 fluxes (Bowen et al., 2015). The PETM was associated with massive extinction of benthic  
383 foraminifera, synchronous with a large decline in oceanic productivity and oxygenation  
384 (Winguth et al., 2012). CO<sub>2</sub> released from combustion of fossil fuels in our atmosphere  
385 equilibrates, as discussed above, among the carbon reservoirs of the ocean, atmosphere and  
386 biosphere over centuries-timescales. Geological sequestration of the CO<sub>2</sub> from the surface  
387 reservoir however, takes much longer: weathering processes and deposition of carbonate in  
388 oceanic crust occurs on timescales of 10<sup>5</sup>-10<sup>6</sup> years (Archer et al., 2009; Lenton and Britton,  
389 2006).

390  
391

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397

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689 **Figure captions**

690

691 **FIGURE 1:** Simplified box model to show the carbon reservoirs and fluxes of Earth (excluding  
692 the core). The size of each reservoir is approximately indicated by the horizontal dimension of  
693 the box; the approximate residence time for carbon in each reservoir by the vertical dimension  
694 (Burton et al., 2013; Dasgupta and Hirschmann, 2010b; DePaolo, 2015; Friedlingstein et al.,  
695 2010; Lee et al., 2019; Sundquist, 1993; Werner et al., 2019). The types of fluxes between each  
696 reservoir are shown against the arrows; the size of these fluxes is not indicated.

697

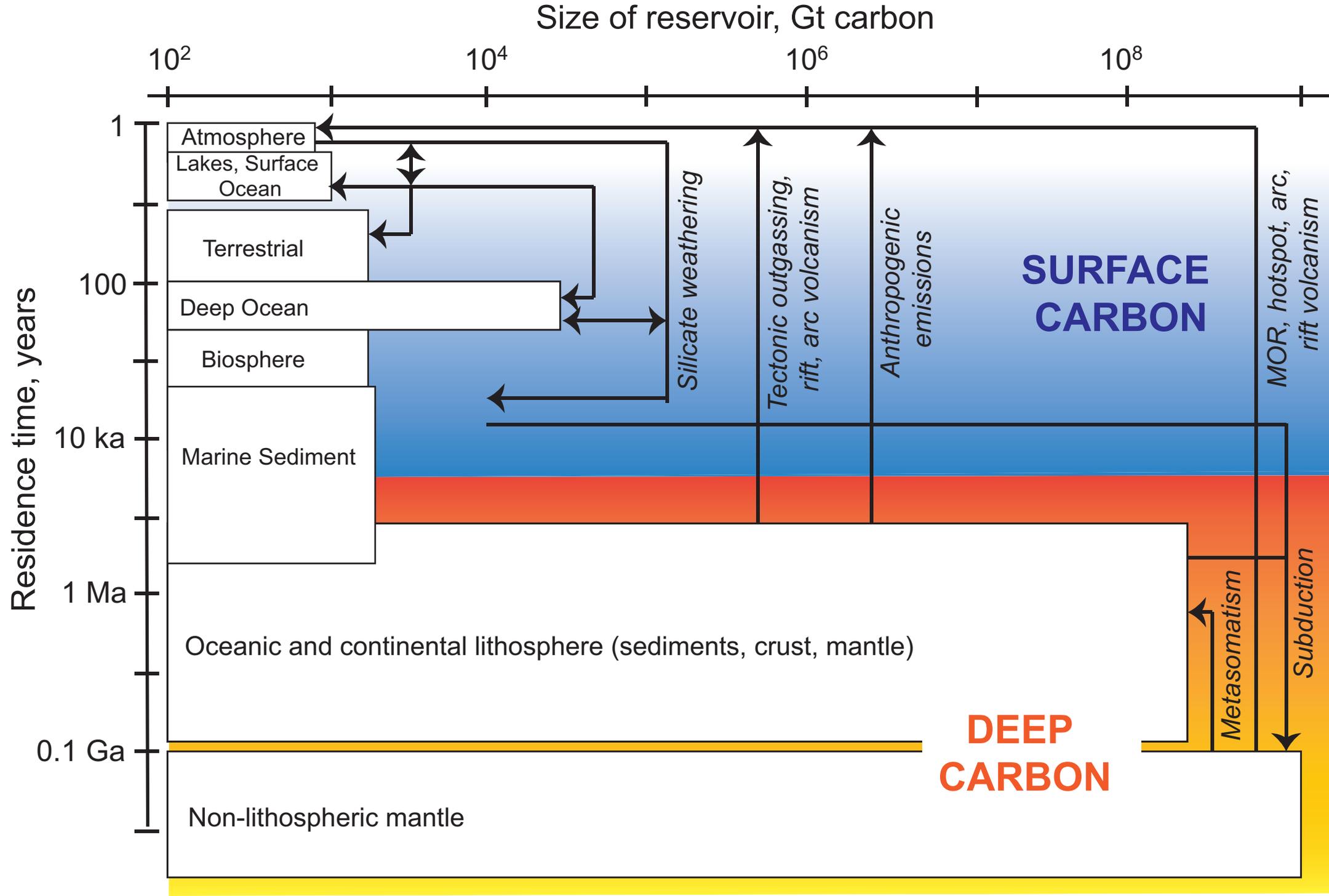
698 **FIGURE 2:** Summary diagram to illustrate the major controls (melt composition and pressure)  
699 on CO<sub>2</sub> solubility in silicate melts. a) Compositionally dependent Pi parameter and melt CO<sub>2</sub>  
700 content at saturation for 50 synthetic basalt to alkali basalt melt compositions (colored symbols).  
701 CO<sub>2</sub> concentrations calculated at 4 saturation pressures using MagmaSat (Ghiorso and Gualda,  
702 2015) in the ENKI framework (<http://enki-portal.org/>). Colored curves are best-fit to the data at  
703 each pressure and illustrate the Pi parameter as a good predictor of CO<sub>2</sub> solubility. b) Natural  
704 basalt melt CO<sub>2</sub> and H<sub>2</sub>O contents (gray dots, data from GEOROC) plotted with isobars (colored  
705 curves; calculated for an alkali basalt using MagmaSat in the ENKI framework), which represent  
706 the saturation surface at given pressures.

707

708 **FIGURE 3:** Diagram showing the relationship between pH, alkalinity, and total carbonate carbon  
709 concentration (after (Deffeyes, 1965); calculated by speciating solutions along axes using the  
710 Geochemist's Workbench (Bethke and Yeakel, 2018). Labels on lines indicate the pH of the  
711 solution, and circles are analyses of East African Rift lakes collected by (Cerling, 1979). Inset is  
712 plotted to emphasize the magnitude of the difference in carbon and alkalinity concentrations  
713 between seawater and alkaline rift lakes.

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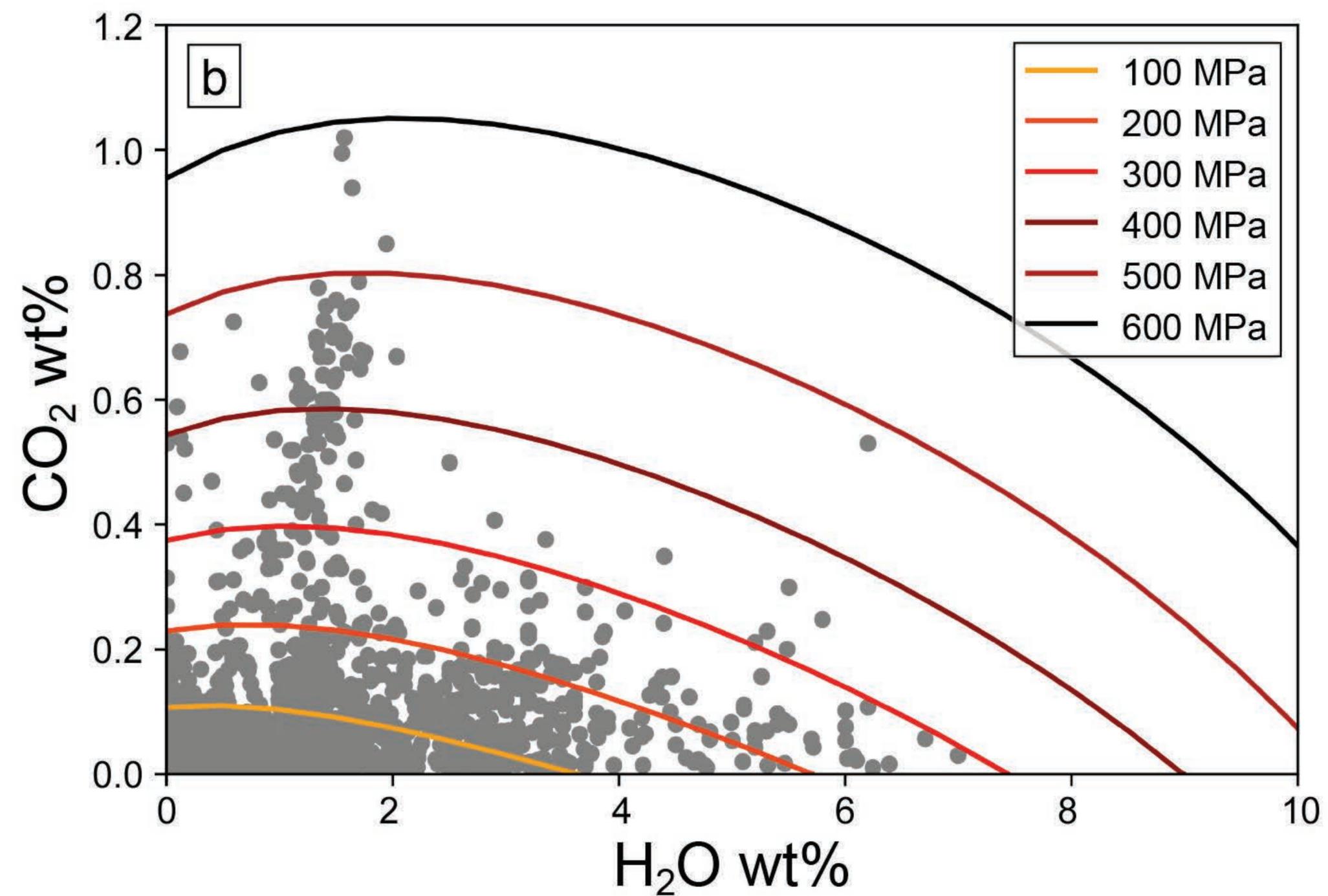
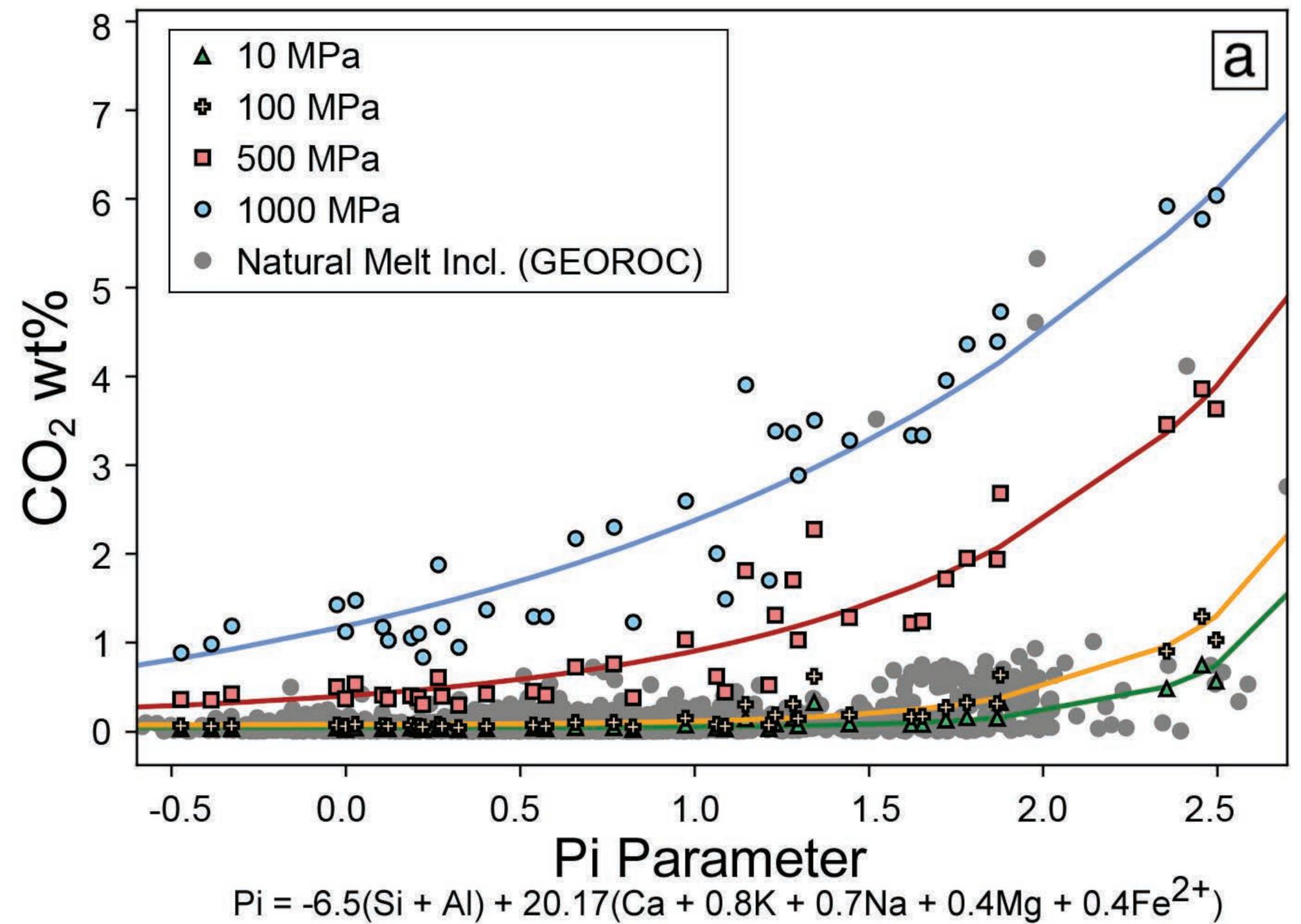


Figure 2

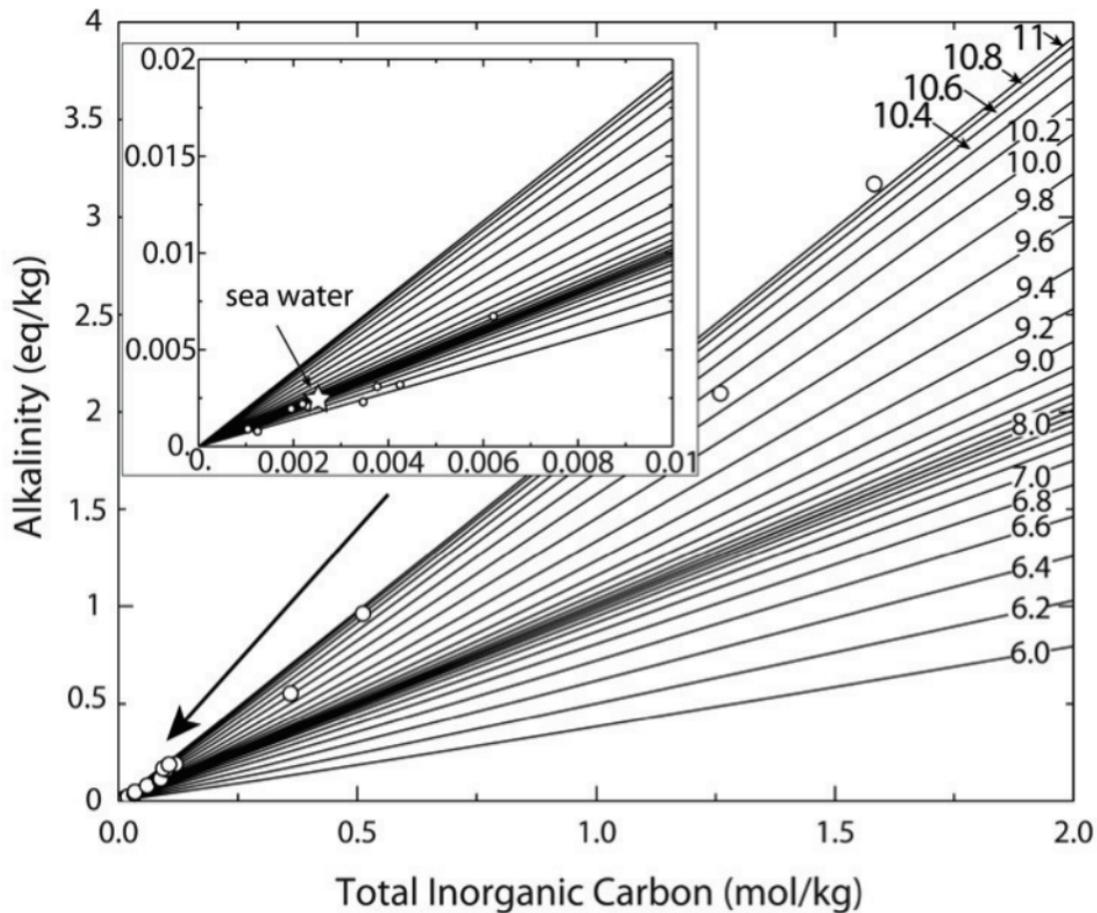


Figure 3