

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

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Revision 1

Magmatic carbon outgassing and uptake of CO₂ 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 CO₂ 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 CO₂.

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

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36 1. Introduction

37

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 CO₂ in our atmosphere must rank high on the
42 list. The concentration of CO₂ 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 CO₂ 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 (Berner 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 CO₂ 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 10¹² 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 CO₂ 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

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

67 (which is also included in the ‘volcanic’ estimate above), is hundreds of Tg/year of CO₂
68 (Tamburello et al., 2018).

69

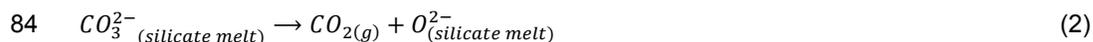
70 The majority of the volcanic flux is derived from the degassing of carbon from silicate melts
71 generated in the mantle, linked to mantle plumes or plate boundary processes, which ascend
72 towards the surface of the Earth. The melts contain dissolved carbon at the point of generation
73 in the mantle. 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 CO₂ and dissolved carbonate respectively (where O²⁻ is a non-bridging
87 oxygen) (Guillot and Sator, 2011). Both species are present in silicate melts, with molecular CO₂
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 CO₂ 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 CO₂ into the atmosphere (**figure 1**), triggering
99 a systematic response in the surface reservoir (Berner, 1999). An equilibrium exists between

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

100 the CO₂ in the atmosphere and in the oceans. On short timescales, the atmosphere-ocean
101 system responds to an increase in atmospheric CO₂ by allowing more carbon to dissolve in the
102 ocean:

103



105

106 Aqueous CO₂ dissociates to carbonate and bicarbonate, with the relative proportions dependent
107 on the pH of the ocean water:

108



110

111 Adding more CO₂ to the ocean increases acidity (at the expense of carbonate); increasing the
112 alkalinity of the ocean will tend to draw down CO₂. 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 CO₂-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 CO₂ between gas and water and silicate melts therefore plays an outsized role in
125 connecting its various 'spheres'. Metamorphic and magmatic CO₂ 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

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

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 CO₂ 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 CO₂ release and ocean drawdown of
147 CO₂.

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 CO₂-rich fluid may migrate
167 semi-independently of the magma through the crust, leading to large areas of so-called 'diffuse'

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

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 CO₂ 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 CO₂ solubility in silicate melts*

179 CO₂ exists as both dissolved carbonate and as molecular CO₂ 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 CO₂ 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⁺, Ca²⁺, and Mg²⁺ (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 CO₂
191 + O²⁻ = CO₃²⁻ equilibrium in the melt shifts towards CO₂ with increasing temperature and that in
192 the melt, molecular CO₂ is present even in basaltic and carbonated melt compositions.

193

194 CO₂ solubility in silicate melts is controlled by the melt composition via the attractive-repulsive
195 behaviour of each component with CO₂ (Papale et al., 2006). Of these, Si and Al are by far the
196 dominant factors, with CO₂ 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 CO₂
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.

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

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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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ solubility is illustrated in **Figure 2b**, where as the coexisting
221 vapor phase becomes more H₂O-rich, the concentration (solubility) of CO₂ 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 CO₂ 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 CO₂ may 'flush' overlying stored magmas (Blundy et al., 2010; Caricchi et al., 2018; Cashman,
230 2004). In this case, the addition of CO₂ raises the concentration of CO₂ in the co-existing vapor
231 phase, thereby enhancing CO₂ solubility in the silicate melt. This process of CO₂ flushing has
232 been invoked to explain anomalously high CO₂ concentrations in olivine-hosted melt inclusions
233 from Etna, for example (Métrich and Wallace, 2008).

234

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

235 The volcanic and tectonic flux of CO₂ 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 CO₂-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 CO₂ 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 CO₂ released in extensional
242 regions are trapped by aquifer systems, which, in turn, allow quantification of the CO₂ 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 CO₂ 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 CO₂ 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 CO₂ and the alkalinity and pH of the solution, is speciated into carbonic acid (CO_{2(aq)}),
262 bicarbonate (HCO₃⁻), and carbonate (CO₃²⁻). Examination of Eqn. (5) shows that
263 dissolving/exsolving CO_{2(g)}, 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 HCO₃⁻, CO₃²⁻, H⁺,

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

269 and OH⁻, 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 CO₂.
271 Atmospheric CO₂ 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⁻
282 and SO₄⁻, 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 CO₂ 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 CO₂ degassing from the system is rapidly absorbed by
290 the overlying seawater due to its high solubility at seafloor depths. For example, although CO₂
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 CO₂ in the vicinity of submarine hydrothermal systems.

294

295 It is now clear that continental rifts are important sites of magmatic CO₂ release (Hunt et al.,
296 2017): the eastern branch of the East African Rift, for example, may be emitting more CO₂
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 CO₂ held in storage both

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

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 CO₂ emitted from the East African Rift may vary along-rift (Hunt et al., 2017).
306 The CO₂ 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⁺, Ca²⁺, HCO₃⁻ and relatively little Cl⁻ and SO₄⁻ 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 CO₂ release and ocean response**

332

333 We have shown that the flux of carbon from Earth's interior, and the potential for uptake of CO₂
334 by alkaline surface waters, are first order controls on the concentration of CO₂ 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

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

337 processes that we discuss here are also relevant to a pressing predicament facing humankind
338 in the 21st century. Namely, is anthropogenic CO₂ generation a stronger driver of climate than
339 CO₂ injected into the atmosphere by natural processes? And how is the atmosphere-ocean
340 system responding?

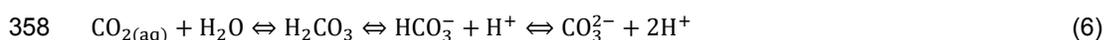
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342 The answer to the first is unequivocally yes. Numerous estimates of CO₂ delivered into the
343 atmosphere by volcanism lead to an inescapable conclusion: anthropogenic sources of CO₂ far
344 exceed the volcanic and tectonic flux of CO₂ into the atmosphere. The burning of fossil fuel and
345 manufacture of cement released 31,000 ± 1845 Tg CO₂ into the atmosphere in 2009
346 (Friedlingstein et al., 2010). Volcanoes and volcanic regions annually supply 240 – 350 Tg CO₂
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 CO₂ produced anthropogenically since the mid-
355 20th century (Sabine et al., 2004) through Eqn. 3. Uptake of CO₂ in ocean water decreases the
356 pH by:

357



359

360 thereby increasing CO₂ 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⁺ 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 CO₂ 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

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

371 end of the Permian has been linked to the outpouring of 7-15 million km³ 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 10⁵
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). CO₂ 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 CO₂ from the surface
387 reservoir however, takes much longer: weathering processes and deposition of carbonate in
388 oceanic crust occurs on timescales of 10⁵-10⁶ years (Archer et al., 2009; Lenton and Britton,
389 2006).

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398 **References**

399

- 400 Ague, J.J., and Nicolescu, S. (2014) Carbon dioxide released from subduction zones by fluid-
401 mediated reactions. *Nature Geoscience*, 7(5), 355-360.
402 Allard, P., Carbonnelle, J., Dajlevic, D., Le Bronec, J., Morel, P., Robe, M., Maurenas, J.,
403 Faivre-Pierret, R., Martin, D., and Sabroux, J. (1991) Eruptive and diffuse emissions of
404 CO₂ from Mount Etna. *Nature*, 351(6325), 387-391.

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

- 405 Archer, D., Eby, M., Brovkin, V., Ridgwell, A., Cao, L., Mikolajewicz, U., Caldeira, K.,
406 Matsumoto, K., Munhoven, G., and Montenegro, A. (2009) Atmospheric lifetime of fossil
407 fuel carbon dioxide. *Annual review of earth and planetary sciences*, 37, 117-134.
- 408 Behrens, H., Tamic, N., and Holtz, F. (2004) Determination of the molar absorption coefficient
409 for the infrared absorption band of CO₂ in rhyolitic glasses. *American Mineralogist*, 89(2-
410 3), 301-306.
- 411 Berner, R.A. (1994) GEOCARB II: A revised model of atmospheric CO [sub 2] over phanerozoic
412 time. *American Journal of Science;(United States)*, 294(1).
- 413 -. (1999) A new look at the long-term carbon cycle. *Gsa Today*, 9(11), 1-6.
- 414 Berner, R.A., and Caldeira, K. (1997) The need for mass balance and feedback in the
415 geochemical carbon cycle. *Geology*, 25(10), 955-956.
- 416 Bethke C. M., Farrell B. and Yeakel S. (2018) The Geochemist's Workbench® Release 12.0 -
417 Reaction Modeling Guide. *Aqueous Solutions, LLC, Champaign, Illinois*.
- 418 Black, B.A., Elkins-Tanton, L.T., Rowe, M.C., and Peate, I.U. (2012) Magnitude and
419 consequences of volatile release from the Siberian Traps. *Earth and Planetary Science*
420 *Letters*, 317, 363-373.
- 421 Black, B.A., and Gibson, S.A. (2019) Deep carbon and the life cycle of Large Igneous
422 Provinces. *Elements*.
- 423 Black, B.A., Neely, R.R., Lamarque, J.-F., Elkins-Tanton, L.T., Kiehl, J.T., Shields, C.A., Mills,
424 M.J., and Bardeen, C. (2018) Systemic swings in end-Permian climate from Siberian
425 Traps carbon and sulfur outgassing. *Nature Geoscience*, 11(12), 949.
- 426 Blank, J.G., and Brooker, R.A. (1994) Experimental studies of carbon dioxide in silicate melts;
427 solubility, speciation, and stable carbon isotope behavior. *Reviews in Mineralogy and*
428 *Geochemistry*, 30(1), 157-186.
- 429 Blundy, J., Cashman, K.V., Rust, A., and Witham, F. (2010) A case for CO₂-rich arc magmas.
430 *Earth and Planetary Science Letters*, 290(3), 289-301.
- 431 Boulard, E., Pan, D., Galli, G., Liu, Z., and Mao, W.L. (2015) Tetrahedrally coordinated
432 carbonates in Earth's lower mantle. *Nature communications*, 6, 6311.
- 433 Bowen, G.J., Maibauer, B.J., Kraus, M.J., Röhl, U., Westerhold, T., Steimke, A., Gingerich,
434 P.D., Wing, S.L., and Clyde, W.C. (2015) Two massive, rapid releases of carbon during
435 the onset of the Palaeocene–Eocene thermal maximum. *Nature Geoscience*, 8(1), 44.
- 436 Brune, S., Williams, S.E., and Müller, R.D. (2017) Potential links between continental rifting, CO
437 2 degassing and climate change through time. *Nature Geoscience*, 10(12), 941.
- 438 Burton, M.R., Sawyer, G.M., and Granieri, D. (2013) Deep carbon emissions from volcanoes.
439 *Rev. Mineral. Geochem*, 75(1), 323-354.
- 440 Caldeira, K., and Wickett, M.E. (2003) Oceanography: anthropogenic carbon and ocean pH.
441 *Nature*, 425(6956), 365.
- 442 Candela, P.A. (1997) A review of shallow, ore-related granites: textures, volatiles, and ore
443 metals. *Journal of petrology*, 38(12), 1619-1633.
- 444 Caricchi, L., Sheldrake, T.E., and Blundy, J. (2018) Modulation of magmatic processes by CO₂
445 flushing. *Earth and Planetary Science Letters*, 491, 160-171.
- 446 Carter, L.B., and Dasgupta, R. (2015) Hydrous basalt–limestone interaction at crustal
447 conditions: Implications for generation of ultracalcic melts and outflux of CO₂ at volcanic
448 arcs. *Earth and Planetary Science Letters*, 427, 202-214.
- 449 Cashman, K.V. (2004) Volatile controls on magma ascent and eruption. *The State of the Planet:*
450 *Frontiers and Challenges in Geophysics*, 109-124.
- 451 Cerling, T. (1994) Chemistry of closed basin lake waters: a comparison between African Rift
452 Valley and some central North American rivers and lakes. *The Global Geological Record*
453 *of Lake Basins*, 1, 29-30.
- 454 Cerling, T.E. (1979) Paleochemistry of plio-pleistocene lake Turkana, Kenya. *Palaeogeography,*
455 *Palaeoclimatology, Palaeoecology*, 27, 247-285.

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

- 456 Chiodini, G., Cardellini, C., Amato, A., Boschi, E., Caliro, S., Frondini, F., and Ventura, G.
457 (2004) Carbon dioxide Earth degassing and seismogenesis in central and southern Italy.
458 Geophysical Research Letters, 31(7).
- 459 Chiodini, G., Frondini, F., Cardellini, C., Parello, F., and Peruzzi, L. (2000) Rate of diffuse
460 carbon dioxide Earth degassing estimated from carbon balance of regional aquifers: the
461 case of central Apennine, Italy. Journal of Geophysical Research: Solid Earth, 105(B4),
462 8423-8434.
- 463 Chiodini, G., Frondini, F., and Ponziani, F. (1995) Deep structures and carbon dioxide
464 degassing in central Italy. Geothermics, 24(1), 81-94.
- 465 Chiodini, G., Granieri, D., Avino, R., Caliro, S., Costa, A., Minopoli, C., and Vilardo, G. (2010)
466 Non-volcanic CO₂ Earth degassing: Case of Mefite d'Ansanto (southern Apennines),
467 Italy. Geophysical Research Letters, 37(11).
- 468 Dasgupta, R. (2013) Ingassing, storage, and outgassing of terrestrial carbon through geologic
469 time. Rev Mineral Geochem, 75(1), 183-229.
- 470 Dasgupta, R., Chi, H., Shimizu, N., Buono, A.S., and Walker, D. (2013) Carbon solution and
471 partitioning between metallic and silicate melts in a shallow magma ocean: Implications
472 for the origin and distribution of terrestrial carbon. Geochimica et Cosmochimica Acta,
473 102, 191-212.
- 474 Dasgupta, R., and Hirschmann, M.M. (2010a) The deep carbon cycle and melting in Earth's
475 interior. Earth and Planetary Science Letters, 298(1-2), 1-13.
- 476 -. (2010b) The deep carbon cycle and melting in Earth's interior. Earth and Planetary Science
477 Letters, 298(1), 1-13.
- 478 Deffeyes, K.S. (1965) Carbonate equilibria: A graphic and algebraic approach 1. Limnology and
479 Oceanography, 10(3), 412-426.
- 480 DePaolo, D.J. (2015) Sustainable carbon emissions: The geologic perspective. MRS Energy &
481 Sustainability, 2.
- 482 Dixon, J.E., Clague, D.A., Wallace, P., and Poreda, R. (1997) Volatiles in alkalic basalts form
483 the North Arch Volcanic Field, Hawaii: extensive degassing of deep submarine-erupted
484 alkalic series lavas. Journal of Petrology, 38(7), 911-939.
- 485 Dixon, J.E., and Stolper, E.M. (1995) An experimental study of water and carbon dioxide
486 solubilities in mid-ocean ridge basaltic liquids. Part II: applications to degassing. Journal
487 of Petrology, 36(6), 1633-1646.
- 488 Dixon, J.E., Stolper, E.M., and Holloway, J.R. (1995) An experimental study of water and carbon
489 dioxide solubilities in mid-ocean ridge basaltic liquids. Part I: calibration and solubility
490 models. Journal of Petrology, 36(6), 1607-1631.
- 491 Doney, S.C., Fabry, V.J., Feely, R.A., and Kleypas, J.A. (2009) Ocean acidification: the other
492 CO₂ problem.
- 493 Dutkiewicz, A., Müller, R.D., Cannon, J., Vaughan, S., and Zahirovic, S. (2018) Sequestration
494 and subduction of deep-sea carbonate in the global ocean since the Early Cretaceous.
495 Geology, 47(1), 91-94.
- 496 Evans, M.J., Derry, L.A., and France-Lanord, C. (2008) Degassing of metamorphic carbon
497 dioxide from the Nepal Himalaya. Geochemistry, Geophysics, Geosystems, 9(4).
- 498 Facq, S., Daniel, I., Montagnac, G., Cardon, H., and Sverjensky, D.A. (2014) In situ Raman
499 study and thermodynamic model of aqueous carbonate speciation in equilibrium with
500 aragonite under subduction zone conditions. Geochimica et Cosmochimica Acta, 132,
501 375-390.
- 502 Farrar, C., Sorey, M., Evans, W., Howle, J., Kerr, B., Kennedy, B.M., King, C.-Y., and Southon,
503 J. (1995) Forest-killing diffuse CO₂ emission at Mammoth Mountain as a sign of
504 magmatic unrest. Nature, 376(6542), 675-678.
- 505 Fine, G., and Stolper, E. (1985) The speciation of carbon dioxide in sodium aluminosilicate
506 glasses. Contributions to Mineralogy and Petrology, 91(2), 105-121.

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

- 507 -. (1986) Dissolved carbon dioxide in basaltic glasses: concentrations and speciation. *Earth and*
508 *Planetary Science Letters*, 76(3), 263-278.
- 509 Fogel, R.A., and Rutherford, M.J. (1990) The solubility of carbon dioxide in rhyolitic melts; a
510 quantitative FTIR study. *American Mineralogist*, 75(11-12), 1311-1326.
- 511 Foley, S.F., and Fischer, T.P. (2017) An essential role for continental rifts and lithosphere in the
512 deep carbon cycle. *Nature Geoscience*, 10(12), 897.
- 513 Friedlingstein, P., Houghton, R., Marland, G., Hackler, J., Boden, T., Conway, T., Canadell, J.,
514 Raupach, M., Ciais, P., and Le Quéré, C. (2010) Update on CO₂ emissions, *Nat.*
515 *Geosci.*, 3, 811–812.
- 516 Garrels, R., and MacKenzie, F. (1967) Origin of the chemical compositions of some springs and
517 lakes: equilibrium concepts in natural waters systems. *Am. Chem. Soc. Adv. Chem*, 222-
518 242.
- 519 Garrels, R.M. (1983) The carbonate-silicate geochemical cycle and its effect on atmospheric
520 carbon dioxide over the past 100 million years. *Am J Sci*, 283, 641-683.
- 521 Gerlach, T. (2011) Volcanic versus anthropogenic carbon dioxide. *Eos, Transactions American*
522 *Geophysical Union*, 92(24), 201-202.
- 523 Ghiorso, M.S., and Gualda, G.A. (2015) An H₂O–CO₂ mixed fluid saturation model compatible
524 with rhyolite-MELTS. *Contributions to Mineralogy and Petrology*, 169(6), 1-30.
- 525 Gorman, P.J., Kerrick, D., and Connolly, J. (2006) Modeling open system metamorphic
526 decarbonation of subducting slabs. *Geochemistry, Geophysics, Geosystems*, 7(4).
- 527 Guillot, B., and Sator, N. (2011) Carbon dioxide in silicate melts: A molecular dynamics
528 simulation study. *Geochimica et Cosmochimica Acta*, 75(7), 1829-1857.
- 529 Hauri, E.H., Cottrell, E., Kelley, K.A., Tucker, J.M., Shimizu, K., Le Voyer, M., Marske, J., and
530 Saal, A.E. (2019) Carbon in the Convecting Mantle. *Earth's Deep Carbon: past to*
531 *present*. Cambridge University Press.
- 532 Hauri, E.H., MacLennan, J., McKenzie, D., Gronvold, K., Oskarsson, N., and Shimizu, N. (2018)
533 CO₂ content beneath northern Iceland and the variability of mantle carbon. *Geology*,
534 46(1), 55-58.
- 535 Hirschmann, M.M. (2018) Comparative deep Earth volatile cycles: The case for C recycling from
536 exosphere/mantle fractionation of major (H₂O, C, N) volatiles and from H₂O/Ce,
537 CO₂/Ba, and CO₂/Nb exosphere ratios. *Earth and Planetary Science Letters*, 502, 262-
538 273.
- 539 Hirschmann, M.M., and Dasgupta, R. (2009) The H/C ratios of Earth's near-surface and deep
540 reservoirs, and consequences for deep Earth volatile cycles. *Chemical Geology*, 262(1-
541 2), 4-16.
- 542 Hunt, J.A., Zafu, A., Mather, T.A., Pyle, D.M., and Barry, P.H. (2017) Spatially Variable CO₂
543 Degassing in the Main Ethiopian Rift: Implications for Magma Storage, Volatile
544 Transport, and Rift-Related Emissions. *Geochemistry, Geophysics, Geosystems*, 18(10),
545 3714-3737.
- 546 Hutchison, W., Mather, T.A., Pyle, D.M., Biggs, J., and Yirgu, G. (2015) Structural controls on
547 fluid pathways in an active rift system: A case study of the Aluto volcanic complex.
548 *Geosphere*, 11(3), 542-562.
- 549 Kelemen, P.B., and Manning, C.E. (2015) Reevaluating carbon fluxes in subduction zones, what
550 goes down, mostly comes up. *Proceedings of the National Academy of Sciences*,
551 112(30), E3997-E4006.
- 552 Kerrick, D., and Connolly, J. (2001) Metamorphic devolatilization of subducted marine
553 sediments and the transport of volatiles into the Earth's mantle. *Nature*, 411(6835), 293-
554 296.
- 555 Kerrick, D.M., and Caldeira, K. (1998) Metamorphic CO₂ degassing from orogenic belts.
556 *Chemical Geology*, 145(3-4), 213-232.

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

- 557 Korschak, A., and Keppler, H. (2014) The speciation of carbon dioxide in silicate melts.
558 Contributions to Mineralogy and Petrology, 167(5), 998.
- 559 Lee, C.-T.A., Jiang, H., Dasgupta, R., and Torres, M. (2019) A framework for understanding
560 whole Earth carbon cycling. In B. Orcutt, I. Daniel, and R. Dasgupta, Eds. Earth's Deep
561 Carbon: Past to Present. Cambridge University Press.
- 562 Lee, C.-T.A., Shen, B., Slotnick, B.S., Liao, K., Dickens, G.R., Yokoyama, Y., Lenardic, A.,
563 Dasgupta, R., Jellinek, M., and Lackey, J.S. (2013) Continental arc–island arc
564 fluctuations, growth of crustal carbonates, and long-term climate change. Geosphere,
565 9(1), 21-36.
- 566 Lee, H., Muirhead, J.D., Fischer, T.P., Ebinger, C.J., Kattenhorn, S.A., Sharp, Z.D., and Kianji,
567 G. (2016) Massive and prolonged deep carbon emissions associated with continental
568 rifting. Nature Geoscience.
- 569 Lenton, T.M., and Britton, C. (2006) Enhanced carbonate and silicate weathering accelerates
570 recovery from fossil fuel CO₂ perturbations. Global Biogeochemical Cycles, 20(3).
- 571 Li, J., Chen, B., Mookherjee, M., and Morard, G. (2019) Carbon versus other light elements in
572 Earth's core. Deep Carbon: past to present, p. xx-xx. Cambridge University Press.
- 573 Li, J., and Fei, Y. (2003) Experimental constraints on core composition. Treatise on
574 geochemistry, 2, 568.
- 575 Lilley, M.D., Butterfield, D.A., Lupton, J.E., and Olson, E.J. (2003) Magmatic events can
576 produce rapid changes in hydrothermal vent chemistry. Nature, 422(6934), 878.
- 577 Lupton, J., Lilley, M., Butterfield, D., Evans, L., Embley, R., Massoth, G., Christenson, B.,
578 Nakamura, K.i., and Schmidt, M. (2008) Venting of a separate CO₂-rich gas phase from
579 submarine arc volcanoes: Examples from the Mariana and Tonga-Kermadec arcs.
580 Journal of Geophysical Research: Solid Earth, 113(B8).
- 581 Mason, E., Edmonds, M., and Turchyn, A.V. (2017) Remobilization of crustal carbon may
582 dominate volcanic arc emissions. Science, 357(6348), 290-294.
- 583 Métrich, N., and Wallace, P.J. (2008) Volatile Abundances in Basaltic Magmas and Their
584 Degassing Paths Tracked by Melt Inclusions. Reviews in Mineralogy and Geochemistry,
585 69(1), 363-402.
- 586 Moore, G. (2008) Interpreting H₂O and CO₂ contents in melt inclusions: constraints from
587 solubility experiments and modeling. Reviews in Mineralogy and Geochemistry, 69(1),
588 333-362.
- 589 Moore, G., Vennemann, T., and Carmichael, I.S.E. (1998) An empirical model for the solubility
590 of H₂O in magmas to 3 kilobars. American Mineralogist, 83(1-2), 36-42.
- 591 Morizet, Y., Kohn, S., and Brooker, R. (2001) Annealing experiments on CO₂-bearing jadeite
592 glass: an insight into the true temperature dependence of CO₂ speciation in silicate
593 melts. Mineralogical Magazine, 65(6), 701-707.
- 594 Morizet, Y., Vuilleumier, R., and Paris, M. (2015) A NMR and molecular dynamics study of CO₂-
595 bearing basaltic melts and glasses. Chemical Geology, 418, 89-103.
- 596 Mörner, N.-A., and Etiope, G. (2002) Carbon degassing from the lithosphere. Global and
597 Planetary Change, 33(1), 185-203.
- 598 Moussallam, Y., Florian, P., Corradini, D., Morizet, Y., Sator, N., Vuilleumier, R., Guillot, B.,
599 Iacono-Marziano, G., Schmidt, B.C., and Gaillard, F. (2016) The molecular structure of
600 melts along the carbonatite–kimberlite–basalt compositional joint: CO₂ and
601 polymerisation. Earth and Planetary Science Letters, 434, 129-140.
- 602 Moussallam, Y., Morizet, Y., Massuyeau, M., Laumonier, M., and Gaillard, F. (2015) CO₂
603 solubility in kimberlite melts. Chemical Geology, 418, 198-205.
- 604 Mysen, B.O., Arculus, R., and Egger, D.H. (1975) Solubility of carbon dioxide in melts of
605 andesite, tholeiite, and olivine nephelinite composition to 30 kbar pressure. Contributions
606 to Mineralogy and Petrology, 53(4), 227-239.

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

- 607 Newman, S., and Lowenstern, J.B. (2002) VolatileCalc: a silicate melt–H₂O–CO₂ solution
608 model written in Visual Basic for excel. *Computers & Geosciences*, 28(5), 597-604.
- 609 Nowak, M., Porbatzki, D., Spickenbom, K., and Diedrich, O. (2003) Carbon dioxide speciation in
610 silicate melts: a restart. *Earth and Planetary Science Letters*, 207(1-4), 131-139.
- 611 Ogden, D.E., and Sleep, N.H. (2012) Explosive eruption of coal and basalt and the end-Permian
612 mass extinction. *Proceedings of the National Academy of Sciences*, 109(1), 59-62.
- 613 Orr, J.C., Fabry, V.J., Aumont, O., Bopp, L., Doney, S.C., Feely, R.A., Gnanadesikan, A.,
614 Gruber, N., Ishida, A., and Joos, F. (2005) Anthropogenic ocean acidification over the
615 twenty-first century and its impact on calcifying organisms. *Nature*, 437(7059), 681.
- 616 Pan, D., and Galli, G. (2016) The fate of carbon dioxide in water-rich fluids under extreme
617 conditions. *Science advances*, 2(10), e1601278.
- 618 Papale, P., Moretti, R., and Barbato, D. (2006) The compositional dependence of the saturation
619 surface of H₂O+ CO₂ fluids in silicate melts. *Chemical Geology*, 229(1-3), 78-95.
- 620 Reichow, M.K., Pringle, M., Al'Mukhamedov, A., Allen, M., Andreichev, V., Buslov, M., Davies,
621 C., Fedoseev, G., Fitton, J., and Inger, S. (2009) The timing and extent of the eruption of
622 the Siberian Traps large igneous province: Implications for the end-Permian
623 environmental crisis. *Earth and Planetary Science Letters*, 277(1), 9-20.
- 624 Saal, A.E., Hauri, E.H., Langmuir, C.H., and Perfit, M.R. (2002) Vapour undersaturation in
625 primitive mid-ocean-ridge basalt and the volatile content of Earth's upper mantle. *Nature*,
626 419(6906), 451-455.
- 627 Sabine, C.L., Feely, R.A., Gruber, N., Key, R.M., Lee, K., Bullister, J.L., Wanninkhof, R., Wong,
628 C., Wallace, D.W., and Tilbrook, B. (2004) The oceanic sink for anthropogenic CO₂.
629 *science*, 305(5682), 367-371.
- 630 Saunders, A.D. (2005) Large igneous provinces: origin and environmental consequences.
631 *Elements*, 1(5), 259-263.
- 632 Shirey, S.B., Cartigny, P., Frost, D.J., Keshav, S., Nestola, F., Nimis, P., Pearson, D.G.,
633 Sobolev, N.V., and Walter, M.J. (2013) Diamonds and the geology of mantle carbon.
634 *Rev Mineral Geochem*, 75(1), 355-421.
- 635 Shishkina, T.A., Botcharnikov, R.E., Holtz, F., Almeev, R.R., Jazwa, A.M., and Jakubiak, A.A.
636 (2014) Compositional and pressure effects on the solubility of H₂O and CO₂ in mafic
637 melts. *Chemical Geology*, 388, 112-129.
- 638 Sleep, N.H., and Zahnle, K. (2001) Carbon dioxide cycling and implications for climate on
639 ancient Earth. *Journal of Geophysical Research: Planets*, 106(E1), 1373-1399.
- 640 Stocker, T.F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y.,
641 Bex, V., and Midgley, P.M. (2013) Climate change 2013: The physical science basis.
642 Intergovernmental Panel on Climate Change, Working Group I Contribution to the IPCC
643 Fifth Assessment Report (AR5)(Cambridge Univ Press, New York), 25.
- 644 Stolper, E., and Holloway, J.R. (1988) Experimental determination of the solubility of carbon
645 dioxide in molten basalt at low pressure. *Earth and Planetary Science Letters*, 87(4),
646 397-408.
- 647 Stumm, W., and Morgan, J.J. (2012) Aquatic chemistry: chemical equilibria and rates in natural
648 waters. John Wiley & Sons.
- 649 Sundquist, E.T. (1993) The global carbon dioxide budget. *Science*, 934-941.
- 650 Svensen, H., Planke, S., Polozov, A.G., Schmidbauer, N., Corfu, F., Podladchikov, Y.Y., and
651 Jamtveit, B. (2009) Siberian gas venting and the end-Permian environmental crisis.
652 *Earth and Planetary Science Letters*, 277(3), 490-500.
- 653 Sverjensky, D.A., and Huang, F. (2015) Diamond formation due to a pH drop during fluid-rock
654 interactions. *Nature communications*, 6.
- 655 Tamburello, G., Pondrelli, S., Chiodini, G., and Rouwet, D. (2018) Global-scale control of
656 extensional tectonics on CO₂ earth degassing. *Nature communications*, 9(1), 4608.

Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

- 657 Tutolo, B.M., and Tosca, N.J. (2018) Experimental examination of the Mg-silicate-carbonate
658 system at ambient temperature: Implications for alkaline chemical sedimentation and
659 lacustrine carbonate formation. *Geochimica et Cosmochimica Acta*, 225, 80-101.
- 660 Wallace, P.J., Anderson, A.T., and Davis, A.M. (1999) Gradients in H₂O, CO₂, and exsolved
661 gas in a large-volume silicic magma system: Interpreting the record preserved in melt
662 inclusions from the Bishop Tuff. *Journal of Geophysical Research: Solid Earth*, 104(B9),
663 20097-20122.
- 664 Werner, C., and Brantley, S. (2003) CO₂ emissions from the Yellowstone volcanic system.
665 *Geochemistry, Geophysics, Geosystems*, 4(7).
- 666 Werner, C., Fischer, T.P., Aiuppa, A., Edmonds, M., Cardellini, C., Carn, S., Chiodini, G.,
667 Cottrell, E., Burton, M., Shinohara, H., and Allard, P. (2019) Carbon Dioxide Emissions
668 from Subaerial Volcanic Regions: Two decades in review. In B. Orcutt, I. Daniel, and R.
669 Dasgupta, Eds. *Earth's Deep Carbon, Past to Present*. Cambridge University Press.
- 670 Winguth, A.M., Thomas, E., and Winguth, C. (2012) Global decline in ocean ventilation,
671 oxygenation, and productivity during the Paleocene-Eocene Thermal Maximum:
672 Implications for the benthic extinction. *Geology*, 40(3), 263-266.
- 673 Wood, B.J. (1993) Carbon in the core. *Earth and Planetary Science Letters*, 117(3-4), 593-607.
- 674 Wood, B.J., Li, J., and Shahar, A. (2013) Carbon in the core: its influence on the properties of
675 core and mantle. *Reviews in Mineralogy and Geochemistry*, 75(1), 231-250.
- 676 Wright, V.P. (2012) Lacustrine carbonates in rift settings: the interaction of volcanic and
677 microbial processes on carbonate deposition. Geological Society, London, Special
678 Publications, 370, SP370. 2.
- 679 Zachos, J.C., Röhl, U., Schellenberg, S.A., Sluijs, A., Hodell, D.A., Kelly, D.C., Thomas, E.,
680 Nicolo, M., Raffi, I., and Lourens, L.J. (2005) Rapid acidification of the ocean during the
681 Paleocene-Eocene thermal maximum. *Science*, 308(5728), 1611-1615.
- 682 Zeebe, R.E., Ridgwell, A., and Zachos, J.C. (2016) Anthropogenic carbon release rate
683 unprecedented during the past 66 million years. *Nature Geoscience*, 9(4), 325.
- 684 Zeebe, R.E., Zachos, J.C., Caldeira, K., and Tyrrell, T. (2008) Carbon emissions and
685 acidification. *Science*, 321(5885), 51-52.
- 686
- 687
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Earth in Five Reactions: CO₂ outgassing and uptake by alkaline waters: Edmonds, Tutolo, Iacovino, Moussallam

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

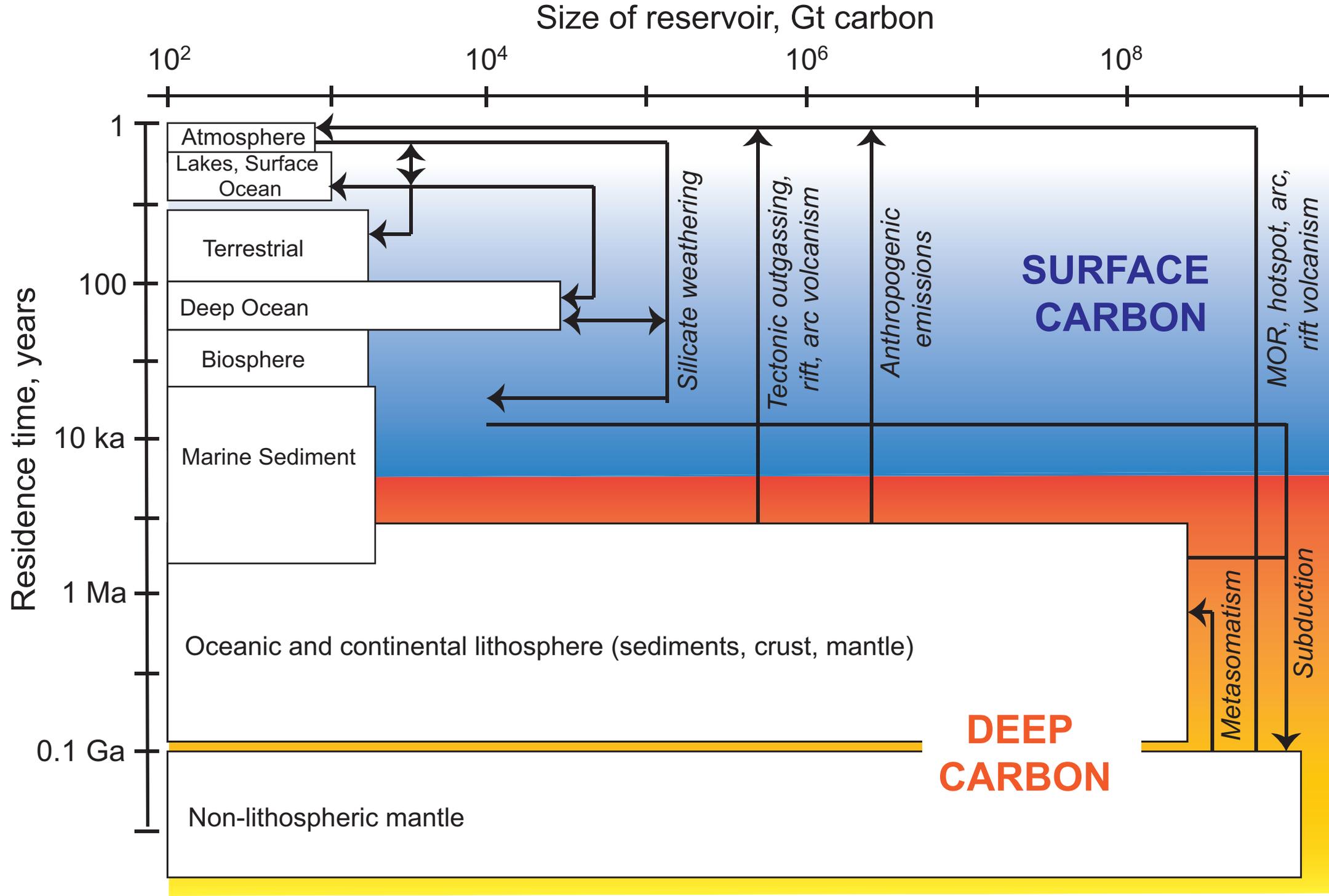
698 **FIGURE 2:** Summary diagram to illustrate the major controls (melt composition and pressure)
699 on CO₂ solubility in silicate melts. a) Compositionally dependent Pi parameter and melt CO₂
700 content at saturation for 50 synthetic basalt to alkali basalt melt compositions (colored symbols).
701 CO₂ 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 CO₂ solubility. b) Natural
704 basalt melt CO₂ and H₂O 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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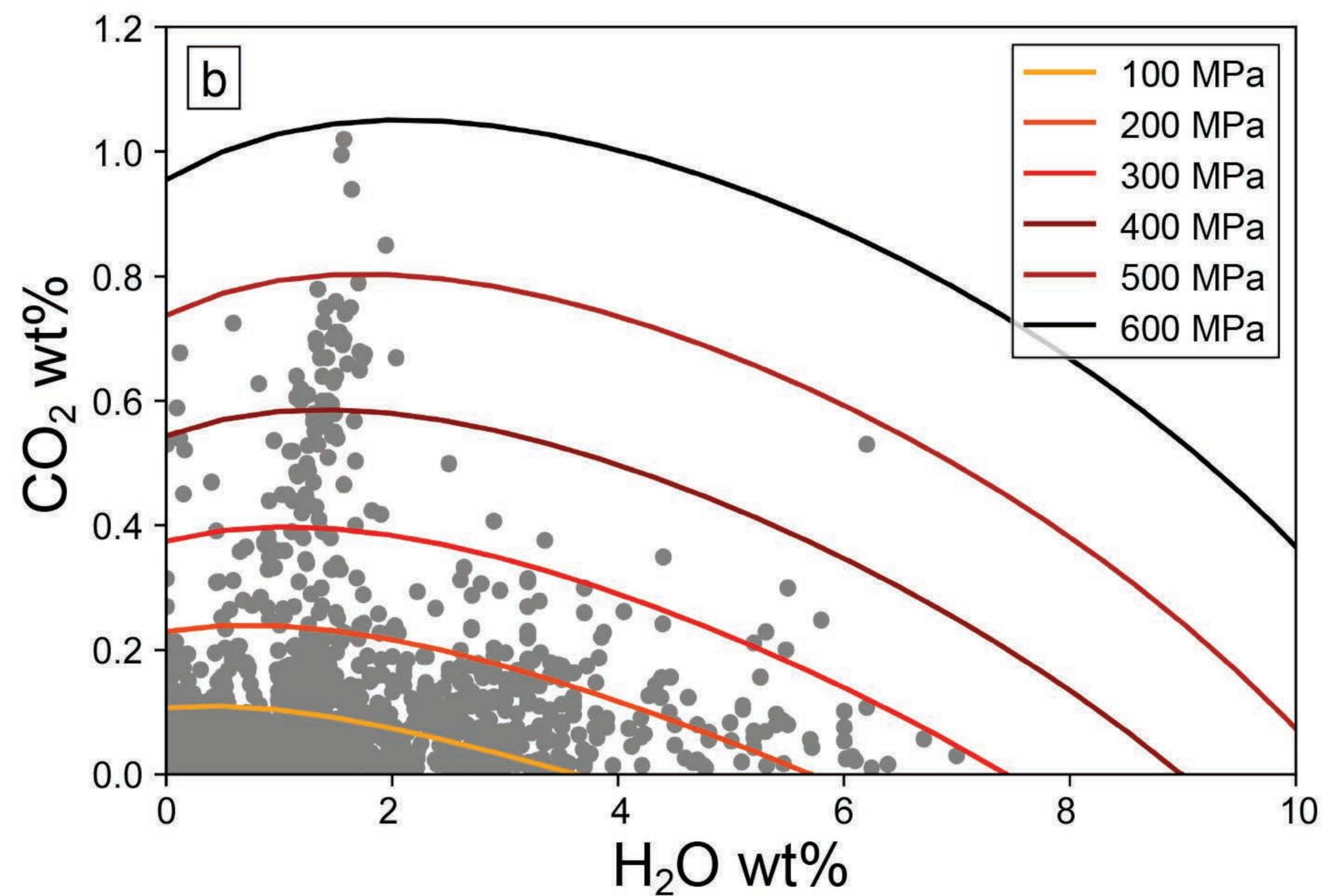
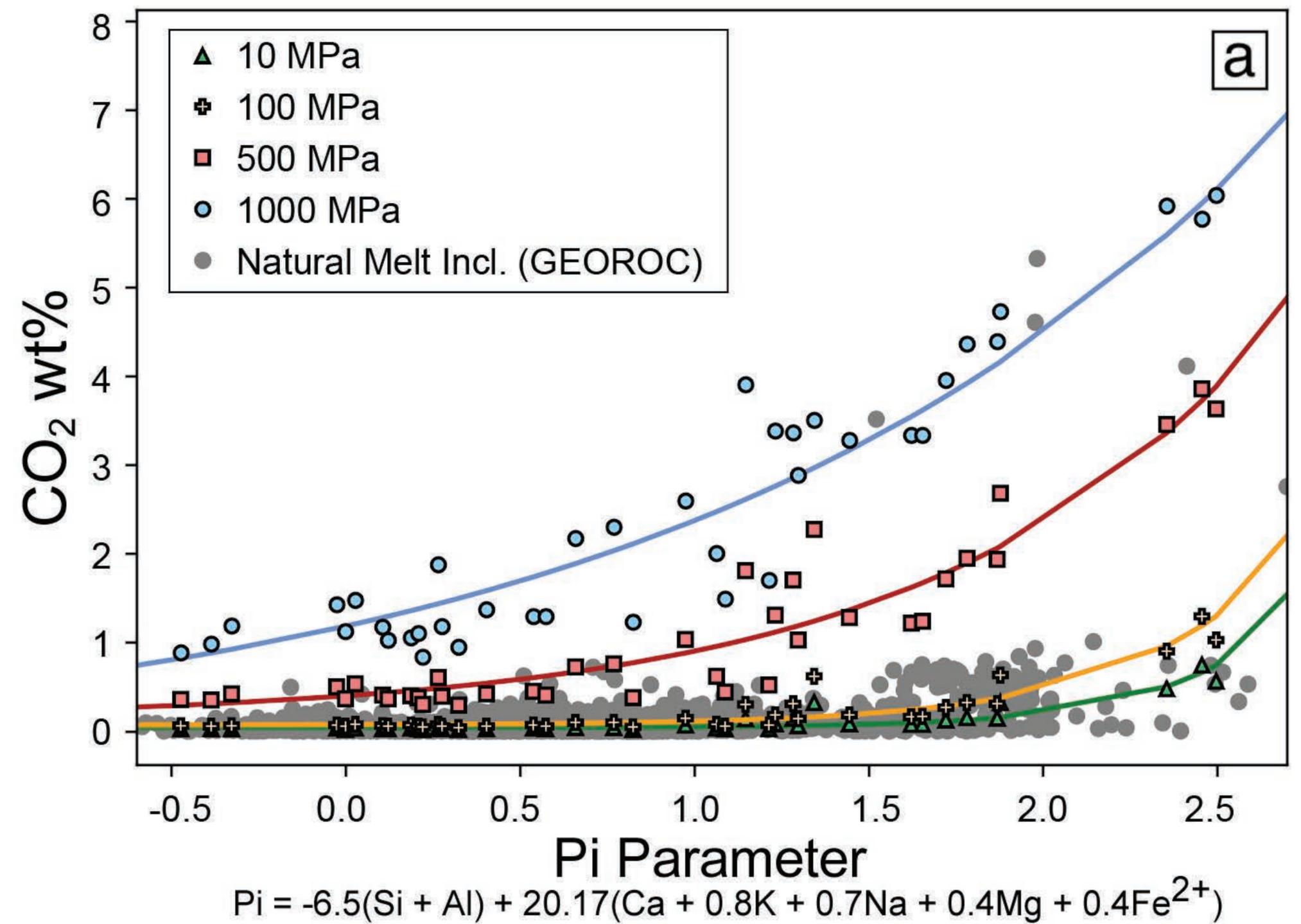


Figure 2

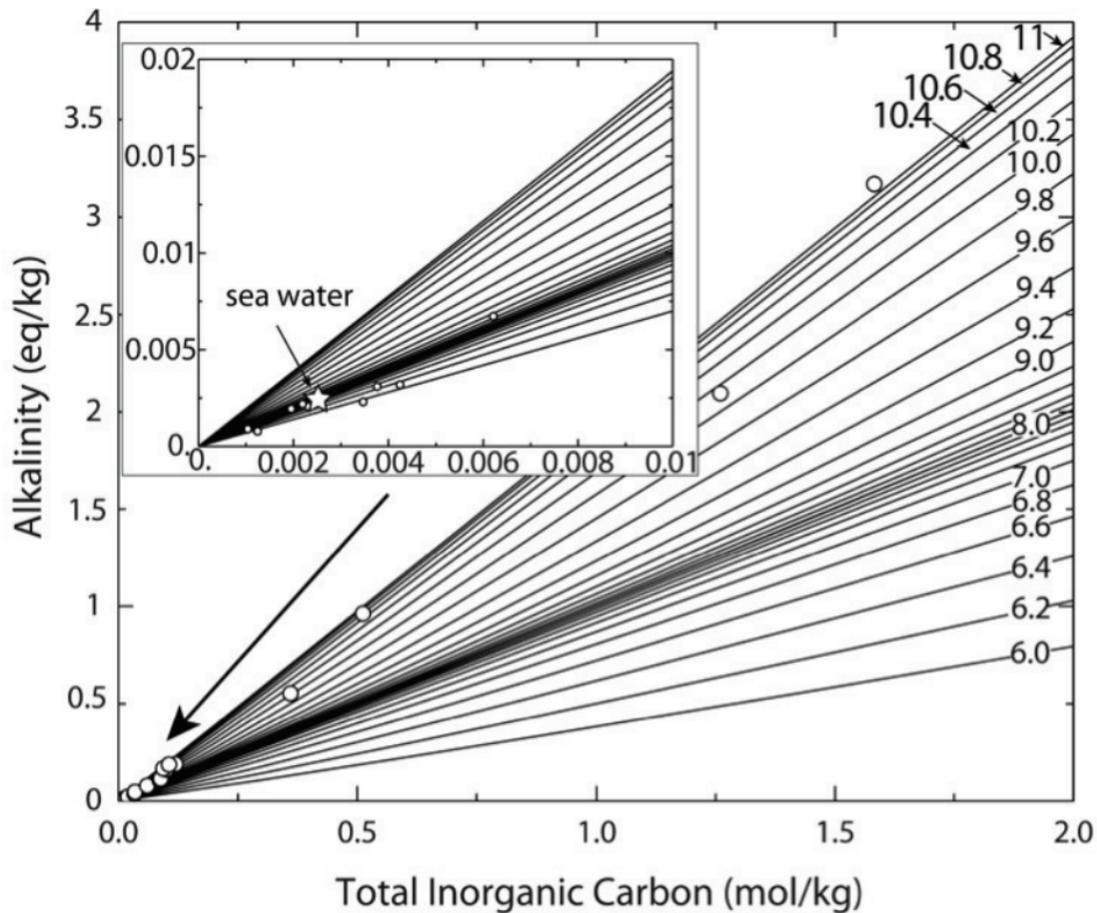


Figure 3