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2 **Ocean Alkalinity, Buffering and Biogeochemical Processes**

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10 **Key Points:**

- 11 • Titration and charge-balance alkalinity differ
- 12 • Ocean buffering is quantified using sensitivity factors
- 13 • The impact of biogeochemical processes on pH depends on environmental conditions
- 14 • Ocean alkalinity budget is balanced when the additional alkalinity input from riverine
15 particulate inorganic carbon and sedimentary sources is included
- 16

17 **Abstract**

18 Alkalinity, the excess of proton acceptors over donors, plays a major role in ocean chemistry, in
19 buffering and in calcium carbonate precipitation and dissolution. Understanding alkalinity
20 dynamics is pivotal to quantify ocean carbon dioxide uptake during times of global change. Here
21 we review ocean alkalinity and its role in ocean buffering as well as the biogeochemical
22 processes governing alkalinity and pH in the ocean. We show that it is important to distinguish
23 between measurable titration alkalinity and charge-balance alkalinity that is used to quantify
24 calcification and carbonate dissolution and needed to understand the impact of biogeochemical
25 processes on components of the carbon dioxide system. A general treatment of ocean buffering
26 and quantification via sensitivity factors is presented and used to link existing buffer and
27 sensitivity factors. The impact of individual biogeochemical processes on ocean alkalinity and
28 pH is discussed and quantified using these sensitivity factors. Processes governing ocean
29 alkalinity on longer time scales such as carbonate compensation, (reversed) silicate weathering
30 and anaerobic mineralization are discussed and used to derive a close-to-balance ocean alkalinity
31 budget for the modern ocean.

32

33 **Plain Language Summary**

34 The ocean plays a major role in the global carbon cycle and the storage of anthropogenic carbon
35 dioxide. This key function of the ocean is related to the reaction of dissolved carbon dioxide with
36 water to form bicarbonate (and minor quantities of carbonic acid and carbonate). Alkalinity, the
37 excess of bases, governs the efficiency at which this occurs and provides buffering capacity
38 towards acidification. Here we discuss ocean alkalinity, buffering and biogeochemical processes
39 and provide quantitative tools that may help to better understand the role of the ocean in carbon
40 cycling during times of global change.

41

42 **1 Introduction**

43 The ocean plays a major role in controlling atmospheric carbon dioxide and storage of
44 anthropogenic carbon (Gruber et al., 2019). For the last decade, ocean uptake of anthropogenic
45 carbon was $2.5 \pm 0.6 \text{ Pg C y}^{-1}$, i.e. about 23 % of annual anthropogenic carbon emissions due to
46 fossil fuels, cement production and land-use change (Friedlingstein et al., 2019). The cumulative
47 (1850-2019) total release of anthropogenic carbon was $655 \pm 65 \text{ Pg C}$, of which $160 \pm 20 \text{ Pg C}$
48 (about 24 %) has accumulated in the ocean (Friedlingstein et al., 2019). This crucial role of the
49 ocean in attenuating the increase in atmospheric carbon dioxide, and thus global warming, is
50 related to the large volume (and surface area) of the ocean and the reaction of dissolved carbon
51 dioxide with water to form carbonic acid, a weak acid that dissociates to protons and the
52 conjugated bases bicarbonate and carbonate which are not directly exchangeable with the
53 atmosphere (Butler, 1982). The redistributions among gaseous and dissolved carbon dioxide,
54 carbonic acid, bicarbonate and carbonate ions are governed by multiple co-occurring equilibria
55 with the result that approximately 19 out of the 20 molecules of carbon dioxide entering the
56 ocean are converted into bicarbonate and carbonate ions. The total amount of dissolved inorganic
57 carbon (DIC) in the ocean is typically about 200 times that of dissolved carbon dioxide (Zeebe
58 and Wolf-Gladrow, 2001; Middelburg, 2019).

59 This re-equilibration following the principles of le Chatelier (1884) provides resistance
60 to, but does not entirely eliminate, changes in ocean carbon chemistry. Oceanic uptake of
61 anthropogenic carbon dioxide has caused increases in dissolved carbon dioxide and total
62 inorganic carbon concentrations, and decreases in carbonate ions and ocean pH, i.e. ocean
63 acidification (Gattuso and Hanson, 2011). Ocean acidification has consequences for further
64 ocean carbon dioxide uptake, the precipitation and dissolution of carbonate minerals and for the
65 functioning and survival of marine organisms (Kroeker et al., 2013). It is therefore important that
66 we understand and are able to quantify the buffering, i.e. resistance, of the ocean in the changing
67 world of the Anthropocene. Detailed understanding and quantification of how biogeochemical
68 processes impact pH and marine carbon dioxide equilibria is pivotal to predicting the impact of
69 ocean acidification on marine organisms, carbonate mineral precipitation and dissolution,
70 (seasonal) variability in carbonate system parameters and the resilience of various ecosystem
71 functions (Orr et al., 2018). Understanding is also required to use pH observations to infer the
72 intensity and changes in biogeochemical processes and to evaluate the feasibility of ocean
73 engineering options (Soetaert et al., 2007; Renforth and Henderson, 2017; Gattuso et al., 2018).

74 Although acid-base equilibria of simple solutions are well understood (Butler, 1964,
75 1982; Stumm and Morgan, 1981; Morel and Hering, 1993), the carbon dioxide system in
76 seawater remains challenging because of the complexity of multiple equilibria (Zeebe and Wolf-
77 Gladrow, 2001). Alkalinity, the excess of bases (proton acceptors) over acids (proton donors) in
78 a solution (a complete definition is provided in section 2), is not only impacted by acid-base
79 additions, but also by redox reactions and mineral dissolution and precipitation. Oxidation
80 reactions involving oxygen generally consume alkalinity, while anaerobic processes usually
81 produce alkalinity. Dissolution of minerals is often accompanied by alkalinity generation.
82 Alkalinity is a central concept in our treatment of the oceanic carbon dioxide system, because it
83 is measurable, it remains unchanged with pressure and temperature (i.e. it is conservative), it is
84 governed by the net effect of multiple chemical equilibria and often needed to solve the
85 mathematical equilibrium problem (Butler, 1982; Stumm and Morgan, 1981). However, there are
86 multiple interpretations, and even definitions, of alkalinity that are not always used in a
87 consistent way. One of the goals of this review is to clarify inconsistencies or sources of
88 confusion, e.g. the distinction between titration alkalinity (that can be measured) and charge-
89 balance alkalinity (that should be used to interpret biogeochemical processes in nature). Another
90 goal is to discuss approaches to quantify the resistance (buffering) or its inverse, the sensitivity
91 of the ocean carbon dioxide system and pH to change. While many geochemical and
92 oceanographic studies mention ocean buffering there are few where buffer and/or sensitivity
93 factors are being used, except for the well-known Revelle factor expressing the sensitivity of
94 $p\text{CO}_2$ to changes in DIC (Revelle and Suess, 1957; Bolin and Eriksson, 1959; Sundquist et al.,
95 1979; Sarmiento and Gruber, 2006). This is surprising as rigorous treatments of buffering have
96 been published a century ago (Koppel and Spiro, 1914; Van Slyke, 1922).

97 Following a treatment of ocean alkalinity (section 2) and sensitivity and buffer factors
98 (section 3), we will discuss the impact of biogeochemical processes on pH and $p\text{CO}_2$ (section 4),
99 heterogeneous buffering, including carbonate compensation (section 5) and factors governing
100 ocean alkalinity, including an alkalinity budget of the ocean (section 6). Basic terminology is
101 explained in Box 1. The Supporting Information accompanying this article contains three
102 sections and the R script used to generate figures and results.

103

104

105 **2 Ocean alkalinity**

106 There is a long history from the 18th century observation that seawater is alkaline
 107 (Marsigli, 1725) to the modern concept of seawater alkalinity (Dickson, 1981; Zeebe and Wolf-
 108 Gladrow, 2001). The term alkalinity was already in use by chemists in the first half of the 19th
 109 century (e.g., Donovan, 1839) and utilized since in multiple disciplines, including medicine
 110 (Andral, 1850) and oceanography (Dittmar, 1884). Dickson (1992) provides an excellent
 111 historical account on the alkalinity concept in seawater and showed that it involved both
 112 advances in analytical procedures as well as the development of a chemical model for seawater.
 113 Rather than recapitulating the historical context, we believe it is instructive to formally
 114 distinguish between titration alkalinity, i.e. total alkalinity, as defined by Dickson (1981) and the
 115 charge balance alkalinity needed to quantify buffering and pH changes in natural environments.
 116 Observational and experimental studies in the ocean are normally based on titration alkalinity,
 117 but theoretical, modelling and geological studies sometimes employ the charge balance approach
 118 (e.g., Broecker, 1974; Boudreau, 1996; Turchyn and DePaolo, 2019) The charge balance
 119 alkalinity concept is often used in freshwater systems (with high concentrations of dissolved
 120 organic matter) and is also known as the excess negative charge (ENC; Soetaert et al., 2007) and
 121 linked to the explicit conservative expression of total alkalinity (Zeebe and Wolf-Gladrow, 2001;
 122 Wolf-Gladrow et al., 2007). This difference between titration alkalinity (TA) and charge balance
 123 alkalinity (CBA) is related to the equations used to solve the chemical equilibrium problem: the
 124 TA is based on a proton balance, while CBA is based on a charge balance closure (Supporting
 125 Information S1). Depending on the specific problem at hand and definition of the system, TA
 126 and CBA may differ or be identical. The lack of distinction between TA and CBA has caused
 127 confusion and discussion.

128

129 **2.1 Titration alkalinity**

130

131 In 1981 Dickson defined the alkalinity (TA) as follows: “*The total alkalinity of a natural*
 132 *water is thus defined as the number of moles of hydrogen ion equivalent to the excess of proton*
 133 *acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$ and zero ionic*
 134 *strength) over proton donors (acids with $K > 10^{-4.5}$) in one kilogram of sample”. The definition is
 135 stated in gravimetric units to remain independent of the temperature and pressure of the system.
 136 Furthermore, Dickson (1981) adopted a pK value of 4.5 as the reference level to distinguish
 137 between proton donors (acids with a dissociation constant pK < 4.5) and proton acceptors (pK ≥
 138 4.5) to continue the common practice to match the reference level with the carbonic acid
 139 equivalence point of a titration.*

140

141 Using this exact definition of alkalinity of Dickson (1981), it is straightforward to
 142 calculate the titration alkalinity for any system for which the contributing components are known
 143 and characterized in terms of dissociation constants. Figure 1A shows the distribution diagram
 144 of acid-base pairs (Bjerrum plot) for the carbonate system in seawater. For the CO₂-H₂O system,
 145 at pH=4.5, carbonic acid is by far the dominant species and used as reference. Referenced to this
 146 point, we then arrive at the proton balance, a mass balance for protons (see Supporting
 147 Information S1):



148 with proton donors on the left-hand side and proton acceptors on the right-hand side. The
 149 carbonate ion is counted twice because it is two protons below the reference level H_2CO_3 .
 150 The titration alkalinity, i.e. excess of proton acceptors over donors with respect to carbonic acid,
 151 the reference level, is then defined as:

$$152 \text{TA} = \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{OH}^- - \text{H}^+ \quad (\text{eq. 2}).$$

153 Other acid-base systems can be included in the alkalinity expression. To this end, all chemical
 154 species in the solution have to be classified either as proton donor or acceptor relative to the zero
 155 level of protons for each acid-base system (Fig. 1B). Dickson (1981) included fluoride, sulphate,
 156 borate, phosphate, silicate, ammonia and hydrogen sulphide to eventually arrive at:

$$157 \text{TA} = \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{OH}^- + \text{B}(\text{OH})_4^- + \text{HPO}_4^{2-} + 2\text{PO}_4^{3-} + \text{H}_3\text{SiO}_4^- + \text{NH}_3 + \text{HS}^- + 2\text{S}^{2-} \\ 158 - \text{H}^+ - \text{HF} - \text{HSO}_4^- - \text{H}_3\text{PO}_4 \quad (\text{eq.3}).$$

159 This proton balance approach towards alkalinity allows an exact definition of alkalinity. Dickson
 160 (1981) focused on the quantification of alkalinity in seawater from titration data and therefore
 161 did not include the strong acids H_2SO_4 and HNO_3 , nor HNO_2 and $\text{H}_2\text{SiO}_4^{2-}$. However, these can
 162 easily be included using the same approach (Soetaert et al., 2007; Wolf-Gladrow et al., 2007)
 163 and results in:

$$164 \text{TA} = \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{OH}^- + \text{B}(\text{OH})_4^- + \text{HPO}_4^{2-} + 2\text{PO}_4^{3-} + \text{H}_3\text{SiO}_4^- + 2\text{H}_2\text{SiO}_4^{2-} + \text{NH}_3 + \text{HS}^- \\ 165 + 2\text{S}^{2-} - \text{H}^+ - \text{HF} - \text{HSO}_4^- - 2\text{H}_2\text{SO}_4 - \text{H}_3\text{PO}_4 - \text{HNO}_2 - \text{HNO}_3 \quad (\text{eq. 4}),$$

166 where H_2SO_4 and HNO_3 are zero for the pH values > 0 .

167 The titration alkalinity definition of Dickson (1981) is fully consistent with the conservation
 168 equation for hydrogen ions (TOT) of Morel and Hering (1993), which is also based on a proton
 169 (mass) balance (Supporting Information S1). Specifically, $\text{TA} = -\text{TOT}$ when the components
 170 chosen are the reference level species at $\text{pH}=4.5$.

171

172 2.2. Charge balance alkalinity

173

174 Electrolyte solutions, including seawater, obey the electroneutrality condition: i.e. the
 175 sum of negative and positive charges balances at the macroscale (Boudreau et al., 2004; Wolf-
 176 Gladrow et al., 2007; Soetaert et al., 2007). For seawater, we thus have to balance the sum of
 177 cation concentrations:

$$178 \text{Na}^+ + 2\text{Mg}^{2+} + 2\text{Ca}^{2+} + \text{K}^+ + 2\text{Sr}^{2+} + (\dots) + \text{NH}_4^+ + \text{H}^+ \quad (\text{eq. 5a}),$$

179 with the sum of anion concentrations:

$$180 \text{Cl}^- + \text{Br}^- + (\dots) + \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{OH}^- + \text{B}(\text{OH})_4^- + \text{H}_2\text{PO}_4^- + 2\text{HPO}_4^{2-} + 3\text{PO}_4^{3-} + \text{H}_3\text{SiO}_4^- + \\ 181 2\text{H}_2\text{SiO}_4^{2-} + \text{HS}^- + 2\text{S}^{2-} + \text{F}^- + \text{HSO}_4^- + 2\text{SO}_4^{2-} + \text{NO}_2^- + \text{NO}_3^- \quad (\text{eq. 5b}),$$

182 where the ellipses (...) stand for additional ions in solution. In charge conservation equations,
 183 ions are multiplied with their charge. This equation can be re-arranged into a part that is
 184 conservative and a part that is not and involves species exchanging protons. Accordingly, when
 185 ignoring minor conservative species (...), the sum of strong base cations minus the sum of strong
 186 acid anions (i.e. excess positive charge of conservative ions):

$$187 \text{EPC} = \text{Na}^+ + 2\text{Mg}^{2+} + 2\text{Ca}^{2+} + \text{K}^+ + 2\text{Sr}^{2+} - \text{Cl}^- - \text{Br}^- \quad (\text{eq. 6a})$$

188 should balance the excess negative charge (ENC) of non-conservative ions that are involved in
 189 proton exchange reactions:

$$190 \text{ENC} = \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{OH}^- + \text{B}(\text{OH})_4^- + \text{H}_2\text{PO}_4^- + 2\text{HPO}_4^{2-} + 3\text{PO}_4^{3-} + \text{H}_3\text{SiO}_4^- + \\ 191 2\text{H}_2\text{SiO}_4^{2-} + \text{HS}^- + 2\text{S}^{2-} + \text{F}^- + \text{HSO}_4^- + 2\text{SO}_4^{2-} + \text{NO}_2^- + \text{NO}_3^- - \text{NH}_4^+ - \text{H}^+ \quad (\text{eq. 6b}).$$

192 This excess negative charge (Soetaert et al., 2007) is also known as charge balance alkalinity
 193 (CBA). Hence, CBA is defined as the sum of non-conservative ions involved in proton exchange
 194 reactions that account for the difference between the sum of conservative cations and anions.

195 Charge balance alkalinity (CBA; eq. 6b) and titration alkalinity (TA; eq. 4) are linked via:

$$196 \text{TA} = \text{CBA} + \sum \text{NH}_3 - \sum \text{NO}_3 - \sum \text{NO}_2 - \sum \text{PO}_4 - 2\sum \text{SO}_4 - \sum \text{F} \quad (\text{eq. 7}),$$

197

198 where $\sum \text{NH}_3 = \text{NH}_3 + \text{NH}_4^+$, $\sum \text{NO}_3 = \text{NO}_3^- + \text{HNO}_3$, $\sum \text{NO}_2 = \text{NO}_2^- + \text{HNO}_2$, $\sum \text{PO}_4 = \text{H}_3\text{PO}_4 +$
 199 $\text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-} + \text{PO}_4^{3-}$, $\sum \text{SO}_4 = \text{H}_2\text{SO}_4 + \text{HSO}_4^- + \text{SO}_4^{2-}$ and $\sum \text{F} = \text{HF} + \text{F}^-$ are the total
 200 concentrations of ammonia, nitrate, nitrite, phosphate, sulphate and fluoride, respectively. This
 201 difference between titration and charge-balance alkalinity is due to the charge of components at
 202 the reference pH level of 4.5. At pH 4.5, ammonia is present as ammonium (+1), while nitrate,
 203 nitrite, fluoride and phosphate have an overall charge of -1 and sulphate is present as SO_4^{2-} with
 204 charge -2 (Fig. 1C). Accordingly, dissolved inorganic carbon does not appear in eq. 7 because it
 205 is present as the uncharged carbon dioxide at pH 4.5. In other words, the difference between
 206 CBA and TA is caused by components for which the species used as zero proton level are
 207 charged (e.g. H_2PO_4^- is the zero-proton level for phosphate, Dickson, 1981).

208 Wolf-Gladrow et al. (2007) introduced the explicitly conservative expression of total
 209 alkalinity (TA_{ec}) that relates the sum of conservative cations and anions (i.e. excess positive
 210 charge, eq. 6a) and total concentrations of ammonia, nitrate, nitrite, phosphate, sulphate and
 211 fluoride with titration alkalinity (TA):

$$212 \text{TA}_{\text{ec}} = \text{Na}^+ + 2 \text{Mg}^{2+} + 2 \text{Ca}^{2+} + \text{K}^+ + 2 \text{Sr}^{2+} - \text{Cl}^- - \text{Br}^- + (\dots)$$

$$213 + \sum \text{NH}_3 - \sum \text{NO}_3 - \sum \text{NO}_2 - \sum \text{PO}_4 - 2\sum \text{SO}_4 - \sum \text{F} \quad (\text{eq. 8}),$$

214 or alternatively formulated: $\text{TA}_{\text{ec}} = \text{EPC} + \text{TA} - \text{CBA}$.

215 This explicitly conservative form of alkalinity is equivalent to Dickson's expression (as $\text{EPC} -$
 216 $\text{CBA} = 0$) for titration alkalinity (eq.4), but each single term is conservative to proton exchange
 217 and pressure and temperature changes (Wolf-Gladrow et al., 2007). Since charge balance
 218 alkalinity is directly related to the difference between conservative cations and anions, it is
 219 evident that CBA and thus also TA co-vary with salinity. Alkalinity and salinity are both affected
 220 to the same degree by processes that dilute or concentrate seawater, such as precipitation,
 221 evaporation and melting or formation of ice.

222

223 2.3 Alternative alkalinity and related expressions

224

225 The titration and charge balance alkalinity expressions (eq. 4 and 6b) are well defined
 226 and traceable to the use of a proton or charge balance (Supporting Information S1), but
 227 alternative expressions are often used. There are a number of reasons for this. One, alkalinity and
 228 related concepts are used in multiple disciplines (e.g., chemistry, medicine, environmental
 229 engineering, ecology, geology, hydrology, limnology, oceanography) with their own specific
 230 scientific traditions and terminology. Two, although many species are included in the formal
 231 definition of alkalinity in seawater, a few of these dominate by far and most others can be
 232 ignored as a first-order approximation. Carbonate alkalinity ($\text{CA} = \text{HCO}_3^- + 2\text{CO}_3^{2-}$) typically
 233 accounts for >95% of the total alkalinity in the ocean. Many studies (e.g., Broecker and Peng,
 234 1982) use a simple form of alkalinity including only water and carbonate alkalinity terms (eq. 2).
 235 In seawater, a slightly more accurate expression is obtained when borate alkalinity is included as
 236 well. Zeebe and Wolf-Gladrow (2001) termed this alkalinity for most practical purposes ($\text{PA}_{\text{ZW-}}$
 237 G):

238 $PA_{ZW-G} = HCO_3^- + 2CO_3^{2-} + B(OH)_4^- + OH^- - H^+ = CA + \text{borate alkalinity} + \text{water alkalinity}$
 239 (eq. 9).

240 PA_{ZW-G} is often used interchangeably with TA because it typically represents > 99% of total
 241 alkalinity in oxygenated ocean surface waters. In anoxic waters and pore-waters of marine
 242 sediments in which metabolites (ammonia, phosphate, sulphide and silicate) have accumulated,
 243 some of these are then included in the operational definition of alkalinity for that system (Ben-
 244 Yaakov, 1973; Boudreau and Canfield, 1993; Hiscock and Millero, 2006). Finally, a major
 245 reason for alternative alkalinity expressions relates to application of the measurable property TA
 246 to biogeochemical processes that impact CBA because of electroneutrality constraints.

247 248 2.3.1 Use of titration alkalinity as proxy for charge balance alkalinity

249
250 Charge balance and titration alkalinity differ by the total amounts of nitrite, nitrate,
 251 ammonia, phosphate, sulphate and fluoride (eq. 7; Soetaert et al., 2007; Wolf-Gladrow et al.,
 252 2007). Processes such as primary production, organic matter degradation and nitrification
 253 involve these components and thus potentially impact alkalinity. Brewer and Goldman (1976)
 254 and Goldman and Brewer (1980) documented increases in alkalinity due to nitrate and phosphate
 255 uptake and a decrease in alkalinity due to ammonium uptake (see section 4). These alkalinity
 256 changes (ΔTA) due to biological consumption or production processes have to be taken into
 257 account when using measured TA values for quantification of calcium carbonate precipitation or
 258 dissolution. Specifically, Brewer et al. (1975) introduced the potential alkalinity change ($\Delta P.A.$)
 259 as a measure of calcite formation/dissolution:

$$260 \Delta P.A. = \Delta TA + \Delta \sum NO_3 + \Delta \sum PO_4 \quad (\text{eq. 10}).$$

261 By comparing eq. 10 and 7, it is clear that potential alkalinity change is a proxy for CBA change
 262 based on measured nitrate, phosphate and TA. However, only changes in nitrate and phosphate
 263 due to biological processes should be considered, not those due to physical mixing (Huang et al.,
 264 2015). Similarly, Kanamori and Ikegami (1982) identified the need to include nitrate, phosphate
 265 and sulphate when using measured TA for calculating alkalinity changes due to calcium
 266 carbonate dynamics. Including nitrate, phosphate and sulphate contributions in Redfield
 267 proportions would result in the following expression for potential alkalinity (P.A.):

$$268 P.A. = TA + a * \sum NO_3 \quad (\text{eq. 11})$$

269 where a varies from 1.06 (Chen, 1978), 1.26 (Kanamori and Ikegami, 1982) to 1.36 (Wolf-
 270 Gladrow et al., 2007), depending on the Redfield ratios considered.

271 The Alk^* tracer (Carter et al., 2014) combines the potential alkalinity (eq. 11 with
 272 $a=1.26$) with salinity normalization to single out the effect of calcium carbonate dynamics on
 273 alkalinity. Similarly, Feely et al. (2002) introduced the TA^* tracer which expresses the change in
 274 TA due to calcium carbonate dynamics: $TA^* = 0.5 (TA_s - TA_s^0) + 0.63 * (0.0941 \text{ AOU})$, where
 275 TA_s and TA_s^0 are the measured and preformed salinity-normalized TA, respectively, and AOU is
 276 the apparent oxygen utilization, introduced to correct for charges generated during organic
 277 matter dynamics. Finally, ecologists studying calcification by benthic communities (coral reefs,
 278 bivalves) often employ the alkalinity anomaly technique (Kinsey, 1978; Chisholm and Gattuso,
 279 1991; Gazeau et al., 2015) which involves measurement of TA and correcting it with
 280 ammonium, nitrate and phosphate for obtaining calcium carbonate dynamics.

281 282 2.3.2 Organic alkalinity

283

284 While oceanographers usually measure TA and introduce empirical corrections to arrive
 285 at the CBA needed for quantitative applications (eq. 10, 11), freshwater scientists studying soft
 286 natural waters have to use a charge balance of the major conservative ions because of an
 287 important contribution of organic acids (Hemond, 1990). Contrary to the inorganic acid-base
 288 species discussed before, dissolved organic compounds comprise a complex, heterogeneous
 289 group, which poses a challenge on classifying its acid-base properties and quantifying their
 290 contribution to TA (Hu, 2020). The composition and thus acid-base properties of dissolved
 291 organic compounds depend on whether these compounds are derived from locally produced
 292 organic matter or transported from adjacent terrestrial ecosystems (Leenheer and Croue, 2003).
 293 Phytoplankton-derived dissolved organic compounds are found to have two distinct proton
 294 binding sites with pK values of 4.4-4.9 and 6.1-6.9, respectively (Ko et al., 2016). In contrast,
 295 terrestrially-derived organic matter is dominated by humic substances. These comprise a much
 296 wider range of proton binding sites, often described by carboxyl and phenolic groups having
 297 average pK values of about 3.7 ± 2.4 and about 12.5 ± 1.8 , respectively (Perdue et al., 1984). This
 298 wide range in pK values implies that at least part of the dissolved organic compounds, either of
 299 autochthonous or allochthonous origin, acts as proton acceptor at pK 4.5, thus contributing to TA
 300 despite being absent in eq. 4.

301 Substantial contributions of organic alkalinity to TA have been found in laboratory
 302 incubations (Ko et al., 2016), estuaries (Cai et al., 1998), sediment pore waters (Łukawska-
 303 Matuszewska, 2016; Łukawska-Matuszewska et al. 2018), coastal waters receiving high
 304 terrestrial inputs, like the Baltic Sea (Kulínski et al., 2014; Hammer et al., 2017) or salt marsh-
 305 influenced coastal waters (Song et al., 2020), and ocean waters (Fong & Dickson, 2019). Organic
 306 alkalinity is normally assessed by difference: that is, carbonate alkalinity is derived from two out
 307 of three other measurable parameters in the $\text{CO}_2\text{-H}_2\text{O}$ system (pH, DIC or pCO_2), and organic
 308 alkalinity is calculated as the difference between TA measured and calculated from the
 309 contributions of the inorganic species following eq. 3. This method relies on at least one
 310 parameter (pH or pCO_2) which value is affected by the presence of organic compounds, and
 311 therefore does not allow for an exact value of organic alkalinity. Back-titration methods to
 312 directly quantify organic alkalinity are used by others (Cai et al., 1998; Hernández-Ayon et al.,
 313 2007; Muller and Bleie, 2008; Yang et al, 2015), showing no clear correlation with organic
 314 alkalinity estimated by difference (Song et al, 2020). Alternatively, chemical equilibrium models
 315 describing proton binding to humic substances, which are well-known in the freshwater
 316 community (Kinniburgh et al., 1999), can be coupled to inorganic carbonate system calculations
 317 (Ulfsbo et al., 2015).

318 319 2.3.3 Acid neutralizing capacity

321 Although not often used in oceanography, the term acid neutralizing capacity (ANC), is
 322 closely linked to titration alkalinity (TA). The ANC of a solution to the carbonic acid equivalent
 323 point of a titration is fully consistent with the Dickson (1981) definition of TA (Weber and
 324 Stumm, 1963; Stumm and Morgan, 1981). Other equivalence points are termed p- alkalinity
 325 (phenolphthalein endpoint of titration, corresponding to the proton balance of eq. 1.13 in
 326 Supporting Information S1) and caustic alkalinity, the reverse of acidity, with the proton balance:
 327 $\text{TOT} = \text{OH}^- - \text{H}^+ - 2 \text{H}_2\text{CO}_3 - \text{HCO}_3^-$ (Stumm and Morgan, 1981). Theoretically, one can use
 328 any expression for alkalinity to solve the $\text{CO}_2\text{-H}_2\text{O}$ system as long it is properly defined.

329 Some researchers distinguish between TA and ANC whether water samples are filtered or
330 not, respectively (Asuero and Michalowski, 2011; Michalowski and Asuero, 2012). The
331 chemical model underlying Dickson's TA only includes homogeneous reactions in solution and
332 ignores proton exchange with particles and organisms. This implies that water samples for
333 alkalinity should be filtered before titration because of potential proton exchange with the
334 surface of phytoplankton, bacteria and inorganic particles and the dissolution of suspended
335 particulate inorganic carbon (Kim et al., 2006), and dedicated filtration methods have been
336 developed (Bockman and Dickson, 2014). However, differences between filtered and unfiltered
337 samples are often negligible (open ocean: Chanson and Millero, 2007; coastal systems: Hagens
338 et al., 2015), but might be substantial in experimental systems with high densities of organisms
339 or particles.

340

341 **Section 3. Buffering and sensitivity factors**

342

343 Seawater is a solution with multiple weak acids and bases in contact with both the
344 atmosphere and sediments containing minerals that have the potential to react when solution
345 composition or physical conditions change. Seawater is consequently well buffered, i.e. able to
346 resist changes by transferring protons. The response of a chemical equilibrium system to a
347 perturbation follows the principle of le Chatelier. The original statement of Henry Louis le
348 Chatelier (1884) "*Tout système en équilibre chimique stable soumis à l'influence d'une cause*
349 *extérieure qui tend à faire varier soit sa température, soit sa condensation (pression,*
350 *concentration, nombre de molécules dans l'unité de volume) dans sa totalité ou seulement dans*
351 *quelques-unes de ses parties, ne peut éprouver que des modifications intérieures, qui, si elles se*
352 *produisaient seules, amèneraient un changement de température ou de condensation de signe*
353 *contraire à celui résultant de la cause extérieure.*" is often re-phrased as: whenever a system in
354 equilibrium is disturbed by changing the conditions, the positions of the equilibria shift in such a
355 way that the effect of the change will be moderated.

356 In this section, we discuss the sensitivity and resistance of ocean chemistry to changes. It
357 is instructive to distinguish between homogeneous reactions in solution and heterogeneous
358 buffering involving interactions with particles (e.g. dissolution or precipitation of carbonate
359 minerals modifying alkalinity). Homogeneous buffering takes place nearly instantaneously and is
360 most relevant for quantifying and understanding the impact of biogeochemical processes on pH
361 on short (hour-days) timescales (Frankignoulle, 1994; Soetaert et al., 2007; Egleston et al.,
362 2010). Heterogeneous buffering reactions may involve very long time scales (months to millions
363 of years) and will be discussed in section 5.

364

365 3.1. Buffer capacity systematics

366

367 Although the buffer capacity of seawater and its role in earth system science has been
368 recognized in the first part of the 20th century (Thompson and Bonnar, 1931; Mitchell and
369 Rakestraw, 1933) and mathematical tools to quantify buffer efficiency have been developed a
370 century ago (Koppel and Spiro, 1914; van Slyke, 1922), quantitative treatments of seawater
371 buffering have historically received little attention, except for the homogeneous Revelle factor
372 (Revelle and Suess, 1957) and the acid-base buffer capacity (van Slyke, 1922; Weber and
373 Stumm, 1963). The acid-base buffer value β was originally defined for biological fluids by
374 Koppel and Spiro (1914) but is commonly attributed to van Slyke (1922):

$$375 \quad \beta = \frac{-dC_a}{dpH} \quad (\text{eq.12})$$

376 where C_a is the quantity of acid added to a solution. For seawater, TA is substituted for C_a and
377 partial derivatives are used to indicate that other properties are kept constant during the titration:

$$378 \quad \beta = \frac{\partial TA}{\partial pH} \quad (\text{eq.13})$$

379 The buffer value β is always positive because every solution resists pH change according to the
380 principle of le Chatelier. It is based on pH rather than proton concentrations because of historical
381 reasons and laboratory procedures.

382 The Revelle factor (R ; Revelle and Suess, 1957; Bolin and Eriksson, 1959; Sundquist et al.,
383 1979) expresses the sensitivity of $p\text{CO}_2$ to changes in DIC:

$$384 \quad R = \frac{\partial \ln p\text{CO}_2}{\partial \ln \text{DIC}} = \frac{\text{DIC}}{p\text{CO}_2} \left(\frac{\partial p\text{CO}_2}{\partial \text{DIC}} \right) \quad (\text{eq. 14})$$

385 where use is made of the property $\partial \ln x = \frac{1}{x} \partial x$. This Revelle factor is limited to homogeneous
386 systems, because the partial derivatives indicate that other variables such as alkalinity are kept
387 constant. Sundquist and Plummer (1981) extended the homogeneous Revelle factor to allow for
388 changes in alkalinity (e.g. due to calcification/dissolution):

$$389 \quad R_{tot} = \frac{\text{DIC}}{p\text{CO}_2} \left(\frac{dp\text{CO}_2}{d\text{DIC}} \right) = \frac{\text{DIC}}{p\text{CO}_2} \left[\left(\frac{\partial p\text{CO}_2}{\partial \text{DIC}} \right)_{TA} + \left(\frac{\partial p\text{CO}_2}{\partial TA} \right)_{\text{DIC}} \cdot \frac{dTA}{d\text{DIC}} \right] \quad (\text{eq. 15}).$$

390 In seawater, the term $\left(\frac{\partial p\text{CO}_2}{\partial TA} \right)_{\text{DIC}}$ is negative, while $\frac{dTA}{d\text{DIC}}$ varies from zero (no TA change) to 2
391 when all changes in DIC are due to calcium carbonate dissolution; heterogeneous buffering thus
392 lowers the Revelle factor (i.e. ocean buffering is larger when carbonate minerals are involved).

393 The Revelle and acid-base buffer factors are just two out of many ways to quantify the
394 response of seawater to changes and some additional (chemical) buffer factors have been
395 proposed (e.g., Frankignoulle, 1994; Frankignoulle et al., 1994; Egleston et al., 2010; Hagens
396 and Middelburg, 2016a; Table 1). However, there are multiple inconsistencies in terminology
397 and their relationships are not clear (Table 1). To clarify matters and link the various buffer
398 capacities and factors in the literature, we present a systematic treatment involving partial
399 derivatives as sensitivities. While the application of Le Chatelier's principle is straightforward
400 for simple systems, it becomes difficult to predict the response of individual reactions when
401 multiple reactions sharing ions are involved (Fishtik et al., 1995) and a sensitivity analysis is
402 then useful. Sensitivities are also known as chemical buffer factors (Frankignoulle, 1994;
403 Soetaert et al., 2007; Egleston et al., 2010). Sensitivities express the rate of change of output
404 quantities (Y) in terms of input quantities (X), i.e. their partial derivatives (Morel et al., 1976;
405 Smith and Missen, 2003). The (first-order) sensitivity coefficient (Smith and Missen, 2003) or
406 interaction capacity (Morel et al., 1976) is defined as:

$$407 \quad S_{Y,X} = \frac{\partial Y}{\partial X} \quad (\text{eq.16})$$

408 which can be normalized using logarithms so that the % change in output can be directly linked
409 to % change in input (interaction intensity values (Morel et al., 1976) or normalized first-order
410 sensitivities, (Smith and Missen, 2003)):

$$411 \quad S_{Y,X}^{nor} = \frac{\partial \ln Y}{\partial \ln X} \quad (\text{eq. 17})$$

412 In the case of pH during an acid titration of TA, the sensitivity is the inverse of the well-known
413 acid-base buffer capacity (β , eq. 13)

$$414 \quad S_{pH,TA} = \frac{\partial pH}{\partial TA} = \beta^{-1} \quad (\text{eq. 18}).$$

415 The use of both sensitivities (=tendency to change), in which the cause of change is in the
 416 denominator and the resulting change is in the numerator (e.g., $\frac{\partial pH}{\partial TA}$), and buffering capacities
 417 (=resistance to change), which are just the inverse (e.g., $\frac{\partial TA}{\partial pH}$) is one of the reasons for confusion
 418 in the literature. Buffer capacity β expresses the ability to resist changes and is normally
 419 presented as

$$420 \beta_{pH} = \left(\frac{\partial pH}{\partial TA}\right)^{-1} \quad (\text{eq. 19})$$

421 (Stumm and Morgan, 1981; Morel and Hering, 1993; Middelburg, 2019). The Revelle factor (R,
 422 eq. 14) is a (normalized) sensitivity factor.

423 Another cause of inconsistencies among studies relates to the use of pH, $\ln[H^+]$ or $[H^+]$.
 424 The original buffer factor β is based on pH (eq. 13, 19), but Egleston et al. (2010) and Hofmann
 425 et al. (2010) presented definitions based on the natural logarithm of proton concentrations and
 426 proton concentrations, respectively:

$$427 \beta_{TA} = \left(\frac{\partial \ln H}{\partial TA}\right)^{-1} \quad \text{and} \quad \beta_H = \left(\frac{\partial H}{\partial TA}\right)^{-1} \quad (\text{eq. 20, 21}).$$

428 While β_{pH} values are always positive, β_H and β_{TA} are negative. Note that these buffer factors
 429 have been defined as inverse of sensitivity factors. The interchangeable and inconsistent use of
 430 the terms buffer capacity, intensity, and index for β is another cause of confusion. Analytical
 431 chemists favour the term buffer capacity, geochemists prefer buffer intensity and engineers use
 432 the term buffer index (Urbansky and Schock, 2000). Others distinguish between buffer intensity
 433 for the actual value at a certain pH (the differential) and buffer capacity for the integral over a
 434 distinct range (Chiriac and Balea, 1997).

435 Using a first-order sensitivity approach the response in Y due to changes in the drivers
 436 TA, DIC, T, S and any other property X can be described as:

$$438 dY = \left(\frac{\partial Y}{\partial TA}\right) dTA + \left(\frac{\partial Y}{\partial DIC}\right) dDIC + \left(\frac{\partial Y}{\partial T}\right) dT + \left(\frac{\partial Y}{\partial S}\right) dS + \left(\frac{\partial Y}{\partial X}\right) dX \quad (\text{eq. 22})$$

439 where the partial derivatives imply that the other factors are constant. These and other
 440 sensitivities have been used and named in the literature, either in this particular, a normalized or
 441 similar form (Table 1). Sometimes a different name is used for the same sensitivity or the same
 442 name is used for different sensitivities. For instance, Sarmiento and Gruber (2006) define their
 443 alkalinity factor (γ_{TA}) as

$$445 \gamma_{TA} = \left(\frac{\partial pCO_2}{\partial TA}\right) \frac{TA}{pCO_2} = \left(\frac{\partial \ln pCO_2}{\partial \ln TA}\right) \quad (\text{eq. 23})$$

446 while Egleston et al. (2010) use the same symbol for a different sensitivity:

$$447 \gamma_{TA} = \left(\frac{\partial TA}{\partial \ln CO_2}\right) \quad (\text{eq. 24}).$$

448 Similarly, the Revelle factor (R, eq. 14) is also known as homogeneous buffer factor B_{hom}
 449 (Sundquist et al., 1979), β_D (Frankignoulle, 1994) and γ_{DIC} (Sarmiento and Gruber, 2006).
 450 Moreover, it relates to DIC/γ_{DIC} using the γ_{DIC} definition of Egleston et al. (2010), which is
 451 again different from that of Sarmiento and Gruber (2006). Most of the sensitivities in Table 1 can
 452 be explicitly linked (Frankignoulle, 2004; Hagens and Middelburg, 2016a) as documented in
 453 Supporting Information S2. *To prevent further confusion and propagation of inconsistencies, we*
 454 *propose to explicitly add the term sensitivity to factors such as the Revelle sensitivity factor and*
 455 *restrict the use of buffer for its inverse, i.e. the resistance to change. Consequently, we*
 456 *discourage the common use of the term buffer or chemical buffer factor for sensitivities.*

457 3.2 Sensitivity of seawater

458

459 Most of the sensitivities presented above depend non-linearly on the solution
 460 composition. Figure 2 shows the sensitivities of pH towards changes in CBA and DIC and of
 461 pCO₂ towards a change in DIC (Revelle sensitivity factor) as a function of pH for average
 462 seawater. The carbonic acid system dominates the buffering capacity of seawater and these
 463 sensitivities thus show extrema related to the pK₁ (≈5.9) and pK₂ (≈9) values of carbonic acid in
 464 seawater. The sensitivity $\left(\frac{\partial pH}{\partial CBA}\right)$ shows maxima at pH values of about 4.5 and 7.5. The former is
 465 the proton reference level chosen at the well-known inflection point of the alkalinity titration
 466 (Dickson, 1981) and the latter is consistent with the minor species theorem that it should be half
 467 way between pK₁ and pK₂ (Morel and Hering, 1993; Egleston et al., 2010). These sensitivities
 468 show minima close to the pK₁ and pK₂ values of carbonic acid in seawater, consistent with the
 469 well-established concept that buffers are most efficient close to their pK value (Butler, 1964;
 470 Stumm and Morgan, 1981). At pH values of about 7.5, sensitivity towards addition of dissolved
 471 inorganic carbon $\left(\frac{\partial pH}{\partial DIC}\right)$, a weak acid, is similar to that of $\left(\frac{\partial pH}{\partial CBA}\right)$, addition of proton acceptors,
 472 but for the sign. However, seawater is more sensitive to CBA than to DIC changes below the pK₁
 473 of the carbonic acid system (pH≈5.9). Conversely, the sensitivity towards DIC changes is larger
 474 than that due to CBA changes at pH > 7.5. This can be attributed to the number of protons
 475 released (Egleston et al, 2010). The Revelle sensitivity factor is very low at pH values below 6
 476 and above 12, and shows maxima at pH values of about 7.5 and 10 and a minimum around the
 477 pK₂ of the carbonic acid system (pH≈9) because of the prominent role of the carbonate ion in
 478 buffering the carbon dioxide added (Gattuso and Hanson, 2011):



480 These and other seawater sensitivities have many applications, ranging from propagating
 481 uncertainties in the carbonic acid system (Orr et al., 2018), attributing changes in pCO₂ to
 482 temperature, salinity and other factors (Takahashi et al., 1993; 2014; Sarmiento and Gruber,
 483 2006; Middelburg, 2019), understanding factors governing pH seasonality (Hagens and
 484 Middelburg, 2016b) and how these factors will change because of global warming and ocean
 485 acidification (Hagens and Middelburg, 2016a). For instance, Richier et al. (2018) showed that
 486 the CO₂ sensitivity of phytoplankton correlates with the sensitivity $\left(\frac{\partial pH}{\partial DIC}\right)$ of seawater. This
 487 quantification of sensitivities is pivotal to understanding earth system functioning and the
 488 magnitude of climate feedbacks during times of global change. For instance, Frankignoulle et al.
 489 (1994) showed how the stoichiometry of carbon dioxide release during calcite precipitation
 490 would change with increasing atmospheric carbon dioxide levels. Multiple authors have shown
 491 that the seasonality of pH and pCO₂ will increase due to elevated sensitivities induced by ocean
 492 acidification (Riebesell et al., 2009; Schulz and Riebesell, 2013; Hagens and Middelburg, 2016a;
 493 Kwiatkowski and Orr, 2018; Gallego et al., 2019). Seawater sensitivity analysis has also
 494 contributed to elucidating interactions among various factors perturbing seawater pH and pCO₂
 495 such as hypoxia (Cai et al., 2011; 2017; Hagens et al., 2015; Hagens and Middelburg, 2016a) and
 496 atmospheric deposition (Hagens et al., 2014). Finally, explicit quantification of sensitivities
 497 allows estimation of simple projections or retrodictions. For instance, the present-day value for
 498 $\left(\frac{\partial pH}{\partial pCO_2}\right)$ is about -0.0011 (ppmv⁻¹; Hagens and Middelburg, 2016a). Combining this sensitivity
 499 with global annual increases in pCO₂ of 1.1 to 2.1 ppmv yr⁻¹ for the periods 1964-1975 and
 500 2005-2014 generates annual ocean pH declines of about 0.0012 to 0.0023 units, similar to that

501 observed (Dore et al., 2009). Similarly, using the sensitivity $\left(\frac{\partial DIC}{\partial pCO_2}\right)$ of about 0.51 ($\mu\text{M kg}^{-1}/$
 502 ppmv), one would retrodict that the global ocean surface DIC would have increased by about 1
 503 $\mu\text{M kg}^{-1} \text{ yr}^{-1}$ from 1994 to 2007, consistent with observations by Gruber et al. (2019).
 504

505 **4. Biogeochemical processes and inorganic carbon dynamics**

506
 507 The marine carbon dioxide system is impacted by many biogeochemical processes:
 508 mineral dissolution and precipitation, organic matter production and respiration and transfers of
 509 electrons, i.e. redox processes (Soetaert et al., 2007; Wolf-Gladrow et al., 2007; Middelburg,
 510 2019). The impact of biogeochemical processes on pH and pCO_2 is often analysed graphically in
 511 the form of TA versus DIC plots with isolines for pH and pCO_2 (Fig. 3). The impact of
 512 biogeochemical processes on DIC, TA or any of its constituents can be represented as a vector
 513 (Deffeyes, 1965). For instance, calcium carbonate dissolution results in the release of one unit
 514 DIC and two units of TA and the resulting vector on Figure 3 shows that it will cause an increase
 515 in pH and decrease in pCO_2 . However, for the very same process intensity (vector length and
 516 direction), the resulting change in pH and pCO_2 is different because it depends on the initial
 517 conditions (i.e. the sensitivity of the system, section 3.2). Changes in pH and pCO_2 are smaller in
 518 well buffered water with a high TA: DIC ratio, i.e. low sensitivity (Fig. 3).

519 Although this graphical approach is instructive, there is a need to quantify these changes
 520 to improve our predictive capabilities. Ben-Yaakov (1973) recognized that a given reaction can
 521 change the pH of a solution by changing the total charge or by adding (or removing) an acid or
 522 base. Soetaert et al. (2007) elaborated this approach and showed that the effect of a single
 523 biogeochemical process on pH can be calculated from the product of the net charge exchanged
 524 during a biogeochemical process (Δcharge) and the sensitivity factor of seawater $\left(\frac{\partial pH}{\partial CBA}\right)$.
 525 Specifically, the instantaneous effect of a single process with intensity I_{process} ($\text{mol m}^{-3} \text{ s}^{-1}$) on pH
 526 can be calculated as:

$$527 \quad dpH = \Delta\text{charge} \cdot \left(\frac{\partial pH}{\partial CBA}\right) \cdot I_{\text{process}} \quad (\text{eq. 26})$$

528 where Δcharge is the sum of the pH independent ΔCBA (Table 2) and the pH dependent charge
 529 (i.e. proton transfer) calculated from reaction stoichiometry and charge of acid-base systems (see
 530 Soetaert et al., 2007). Since both the sensitivity of seawater $\left(\frac{\partial pH}{\partial CBA}\right)$ and Δcharge depend on the
 531 pH, this equation shows that the effect of a specific biogeochemical process on pH also depends
 532 on pH. Hofmann et al. (2010a) and Middelburg (2019) presented similar approaches, but
 533 focused on proton rather than charge transfers and used the sensitivity factors $\left(\frac{\partial H}{\partial TA}\right)$ and $\left(\frac{\partial pH}{\partial TA}\right)$,
 534 respectively.

535 Figure 4 shows the impact of denitrification with Redfield organic matter (R2 in Table 2)
 536 on the Δcharge and pH. The process involves the production of DIC, $\sum\text{NH}_3$ and $\sum\text{PO}_4$, and the
 537 consumption of $\sum\text{NO}_3$. Denitrification does not impact charge balance alkalinity ($\Delta CBA = 0$). At
 538 $\text{pH} < 4$, nitrate is charged negatively, ammonium positively while DIC and $\sum\text{PO}_4$ are present as
 539 uncharged carbonic and phosphoric acids, the Δcharge of the reaction is about +0.95 At $\text{pH} > 10$,
 540 nitrate is still charged negatively, while carbonate and phosphate ions dominate the DIC and
 541 $\sum\text{PO}_4$ with the consequence that the Δcharge of the reaction is about -1.08 (Fig. 4). At a pH of
 542 about 7 the Δcharge is zero because the positive charge due to nitrate consumption and
 543 ammonium production is compensated by the production of bicarbonate, the major species in the

544 DIC pool at this pH, with contributions from carbonate, dihydrogenphosphate and
545 hydrogenphosphate. The overall effect of denitrification on pH is obtained by multiplying the
546 Δ charge and sensitivity at a specific pH value (eq. 26; Fig. 4). Consequently, the pH increases at
547 pH values below about 7 (Δ charge > 0), while it decreases pH at higher pH because the
548 production of bicarbonate, carbonate and phosphate ions outcompetes the consumption of nitrate
549 and production of ammonium (Δ charge < 0). Thus, Δ charge defines the direction of the pH
550 change (i.e. increase or decrease), while the sensitivity determines the magnitude of the response.

551 Soetaert et al (2007) presented a full list of processes and how they impact pH over the
552 full pH range, here we focus on aerobic and anaerobic mineralization, primary production and
553 calcium carbonate production and dissolution (Table 2). Figure 5 shows that the overall impact
554 of a biogeochemical process on pH is a highly non-linear function with multiple processes
555 crossing the zero-pH-change line, implying that the direction (sign of Δ charge) and magnitude
556 (sensitivity times Δ charge) of pH change depend on the initial conditions. For instance, calcium
557 carbonate dissolution always increases the pH but the response depends on the sensitivity factor,
558 i.e. on the initial conditions, consistent with the graphical approaches presented above (Fig. 3).
559 Aerobic respiration (R1) and methanogenesis (R6) increase pH at pH < 5.2 and 5.6 , respectively
560 (Soetaert et al., 2007), because the production of ammonium is not compensated by sufficient
561 production of anions (bicarbonate and phosphate anions). At higher pH, aerobic respiration and
562 methanogenesis decrease pH because of bicarbonate, carbonate and phosphate ion production
563 (Fig. 5). Aerobic respiration accompanied by nitrification (oxidation of ammonium to nitrate, R
564 7) always results in a pH decrease (Fig. 5) because there is no positive charge produced (Soetaert
565 et al., 2007). Similarly, primary production based on nitrate always results in pH increase, while
566 regenerated production based on ammonium results in pH decrease at low pH (ammonium
567 uptake is compensated by proton release for electroneutrality; Soetaert et al., 2007; Wolf-
568 Gladrow et al., 2007). Sulphate reduction (R5) causes a stronger pH increase at low pH values
569 because of sulphate ion consumption and switches to proton production (pH decrease) at a higher
570 pH value. In other words, the impact of sulphate reduction in sediments on pH depends on the
571 initial conditions: i.e. whether the sediment has experienced extensive denitrification and metal-
572 oxide reduction before initiation of sulphate reductions (Boudreau and Canfield, 1993; Soetaert
573 et al, 2007; Meister, 2013).

574

575 **5. Heterogeneous buffering**

576

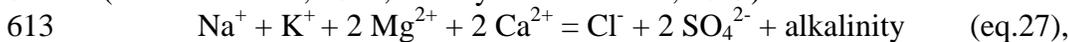
577 While homogeneous buffering due to equilibria in solution is nearly instantaneous and
578 can be quantified using seawater sensitivities discussed in section 3, heterogeneous buffering
579 mechanisms involving particles occur over multiple time scales (Archer et al., 1998; Sarmiento
580 and Gruber, 2006; Boudreau et al., 2018). For instance, proton sorption to surfaces occurs almost
581 instantaneously, while mineral dissolution and precipitation are kinetically controlled (Lasaga,
582 1998). Moreover, homogeneous buffering is spatially rather uniform in the ocean because of the
583 limited range and relative uniform distribution of salinity, dissolved inorganic carbon and
584 alkalinity. Heterogeneous buffering involves particles suspended in the water column, sediments
585 deposited at the seafloor and benthic and pelagic calcifying organisms. Calcification is
586 dominated by pelagic organisms in the open ocean, while benthic organisms dominate in the
587 coastal domain (Milliman, 1993; Morse and Mackenzie, 1990; Morse et al., 2007). Sediments
588 dominate heterogeneous buffering because of the large size of this reservoir: i.e. there are orders
589 of magnitude more particles at the seafloor than suspended in the water column.

590 Particles suspended in the water column and deposited on the seafloor may contribute to
 591 buffering of seawater via dissolution, precipitation and mineral surface reactions. Sorption of
 592 protons to surfaces increases alkalinity (Table 2). Reactions at the surfaces of organic, biogenic
 593 carbonate and detrital silicate particles contribute to instantaneous buffering; alkalinity titrations
 594 of unfiltered samples containing phytoplankton and bacteria have shown that particulate matter
 595 surfaces neutralize some of the protons added (Kim et al., 2006). However, this heterogeneous
 596 buffer capacity is very limited for typical marine suspended matter concentrations. The role of
 597 surface reactions in buffering pore-water chemistry is largely unknown although Jahnke and
 598 Jahnke (2004) identified the need to consider mineral surface reactions to properly understand
 599 sediment pH dynamics.

600 Dissolution, precipitation and transformation reactions of sedimentary silicates and
 601 biogenic carbonates govern heterogeneous buffering in the ocean. Heterogeneous buffering in
 602 the ocean is dominated by carbonate compensation (Pytkowicz, 1967; Berner, 2004; Ridgwell
 603 and Zeebe, 2005) and we will focus on this as well (section 5.2), realizing that processes
 604 involving silicate minerals, such as reverse weathering and submarine weathering contribute as
 605 well, in particular on very long times scales (section 5.1; Sillen, 1967; Mackenzie and Garrels,
 606 1966; Wallmann et al., 2008; Isson and Planavsky, 2018).

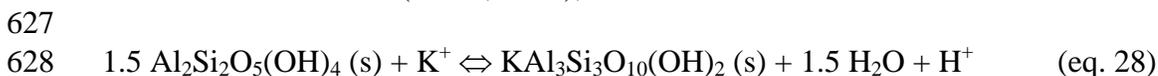
607 608 5.1 Silicate reactions

609
610 The impact of seawater-rock interactions on alkalinity is often quantified via a charge
 611 balance of major cations on the one hand and chloride, sulphate and alkalinity on the other hand
 612 (Antonelli et al., 2017; Turchyn and dePaolo, 2019):

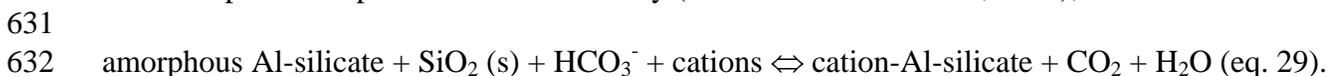


614 where exchanges between the univalent and divalent cations or between magnesium and calcium
 615 are considered of less importance for the balance. High-temperature hydrothermal vents result in
 616 the removal of Ca^{2+} and SO_4^{2-} via anhydrite precipitation and of Mg^{2+} via hydroxy-silicate
 617 formation (Antonelli et al., 2017). The latter process generates acidity that enhances release of
 618 Ca^{2+} from basalt so that charge remains balanced. Most of the calcium released is eventually
 619 precipitated as calcium carbonate in the oceanic crust. Overall, submarine weathering results in
 620 carbon dioxide consumption and bicarbonate and calcium release (Staudigel et al., 1989;
 621 Caldeira, 1995; Berner, 2004).

622 Reverse weathering refers to the consumption of alkalinity and generation of protons
 623 during marine authigenic clay formation. Weathering on the continents results in the formation
 624 of cation-depleted clay minerals which after transport and deposition at the seafloor react with
 625 major elements in seawater. Reverse weathering can be written in multiple forms: e.g. kaolinite
 626 to mica transformation (Sillen, 1967),



629
630 or cation-poor amorphous Al-silicate to clay (Mackenzie and Garrels, 1966),



632
633
634 The latter reaction involves the transformation of bicarbonate to carbon dioxide via reaction with
 635 cation-depleted, acidic Al-silicates. Reverse weathering can be written in multiple forms, but

636 they all lower marine pH and alkalinity, and increase carbon dioxide concentrations (Isson and
637 Planavsky, 2018).

638 Another submarine weathering process is induced by organic matter degradation in
639 anoxic sediments. This degradation results in the release of carbon dioxide and dissolved organic
640 matter (fulvic and humic acids) and these may cause dissolution of primary silicate minerals and
641 generate high alkalinity levels (Wallmann et al., 2008). Marine weathering contributes to carbon
642 dioxide consumption and alkalinity release and thus counteracts reverse weathering processes.
643 Although seafloor weathering and in particular reverse weathering processes may have played a
644 prominent role during past periods with warm, silica-rich ocean waters (e.g. Precambrian), these
645 heterogeneous buffering reactions involving silicates are considered of less importance for the
646 present ocean than those involving carbonate minerals (Pytkowicz, 1967; Berner, 2004; Isson
647 and Planavsky, 2018; see section 6).

648

649 5.2 Carbonate compensation dynamics

650

651 Carbonate compensation refers to the reactions between carbonate minerals and seawater
652 and it is instructive to distinguish between chemical and biological carbonate compensation.
653 Chemical compensation focuses on the dissolution or preservation of carbonates at the seafloor,
654 while biological compensation centres on the role of precipitation and its dependence on solution
655 chemistry (Boudreau et al. 2018).

656 Surface oceans waters are supersaturated with respect to most carbonate minerals (Morse
657 and Mackenzie, 1990). Supersaturation must be reduced to undersaturation, at least in the local
658 microenvironment, before carbonate minerals will dissolve and contribute to buffering (but for
659 surface reactions). Carbonate particles settling to the ocean floor will experience pressure
660 increases and temperature decreases that increase solubility of carbonate minerals (Morse and
661 Mackenzie, 1990; Millero, 2007). Moreover, subsurface ocean waters are usually richer in
662 carbon dioxide and lower in carbonate ions because of organic matter degradation (Sarmiento
663 and Gruber, 2006). As a consequence, seawater becomes undersaturated with respect to
664 carbonate minerals at a certain depth and below this saturation depth mineral dissolution rates
665 increase with depth (Ridgwell and Zeebe, 2005). At the carbonate compensation depth, the flux
666 of carbonate particles downwards is exactly balanced by the rate of carbonate dissolution (at the
667 seafloor) with the consequence that no carbonate minerals accumulate at steady state (Boudreau
668 et al., 2010a). The lysocline refers to the depth range between the carbonate saturation and
669 compensation depths (Boudreau et al., 2018). Ocean buffering dynamics is reflected in changes
670 in the depth distribution of the saturation and compensation depths (Sigman et al., 1998;
671 Ridgwell and Zeebe, 2005; Boudreau et al., 2010b). During periods of ocean acidification,
672 saturation and carbonate compensation depths will shallow, causing increases in carbonate
673 mineral dissolution and alkalinity release, counteracting the acidification. Conversely, during
674 ocean alkalization, saturation and compensation depths will deepen, with the result that
675 carbonate dissolution and alkalinity release diminish (Sigman et al., 1998; Ridgwell and Zeebe,
676 2005; Boudreau et al., 2018).

677 Almost all marine carbonate minerals are of biological origin: e.g. coccoliths, pteropods
678 and foraminifera in the open ocean and corals and mollusks in the coastal domain (Morse and
679 Mackenzie, 1990; Milliman, 1993). Calcifying organisms consume alkalinity and any change in
680 their activity due to alteration in environmental conditions (e.g. temperature, ocean acidification)
681 or food web structure (e.g. food resources, predators or viruses) consequently impacts their role

682 in ocean buffering. This role of calcifiers in carbonate compensation has impact on buffering at
 683 multiple timescales (Caldeira and Rampino, 1993; Boudreau et al., 2018). Lower calcification
 684 rates because of ocean acidification (Gazeau et al., 2007; Kroeker et al., 2013) or global warming
 685 (Hoegh-Guldberg et al., 2007) directly impact alkalinity removal and thus represent a rapidly
 686 operating negative feedback mechanism, that will be detectable within decades (Schlunegger et
 687 al., 2019). Less calcification in the surface layer also implies less export of biogenic calcite and
 688 thus less calcite dissolution in the subsurface. Boudreau et al. (2010a, 2018) provided an
 689 equation to approximate carbonate compensation depth (z_{CCD}):.

$$690 \quad z_{CCD} \approx z_{ref} \ln \left(\frac{F_{car} [Ca^{2+}]}{K_{sp} A \beta_{mt}} + \frac{[Ca^{2+}] [CO_3^{2-}]}{K_{sp}} \right) \quad (\text{eq. 30})$$

691 where F_{car} is the export flux of calcium carbonate, A is the surface area of the seafloor, β_{mt} is the
 692 mass transfer of solutes across the diffusive boundary layer at the seafloor, K_{sp} is the
 693 temperature, salinity and pressure dependent stoichiometric solubility product, $[Ca^{2+}]$ and $[CO_3^{2-}]$
 694 are the concentrations of dissolved calcium and carbonate ions and z_{ref} is a scaling parameter.
 695 Lower calcification and export of calcium carbonate F_{car} will thus lead to a shallowing of the
 696 carbonate compensation depth on shorter time scales (years), but would cause additional
 697 deepening on longer timescales (10^4 years), because of alkalinity accumulation during periods of
 698 lower calcification (Boudreau et al., 2018). This additional deepening due to biological carbonate
 699 compensation is an alternative to CO_2 -enhanced continental weathering (Ridgwell, 2007; Zeebe
 700 et al., 2009) for $CaCO_3$ overshooting in the geological record (Luo et al., 2016).

701

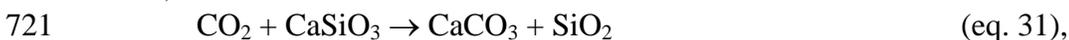
702 **6 Processes governing alkalinity in the ocean**

703

704 The distribution of alkalinity often co-varies with salinity. This is logical because
 705 oceanographic processes impacting salinity by freshwater addition (such as precipitation, river
 706 and groundwater discharge and ice melting) or removal (e.g. evaporation and ice formation) also
 707 impact alkalinity. These processes are most intense in surface waters that are exposed to the
 708 atmosphere, cryosphere and riverine inputs. It is for this reason that alkalinity can be predicted
 709 quite well in ocean surface water using salinity and temperature (Millero et al., 1998; Lee et al.,
 710 2006). Alkalinity is often normalized to salinity to infer the other processes affecting alkalinity
 711 such as calcite production and dissolution (Feely et al., 2004; Sarmiento and Gruber, 2006;
 712 Carter et al., 2014). However, salinity normalization might induce biases, because of regional
 713 differences in salinity-alkalinity relationships (Friis et al., 2003; Jiang et al., 2014).

714

715 Whole ocean alkalinity is largely governed by the balance between ions generated by
 716 weathering and removal of ions via the formation of calcium carbonate. Continental weathering
 717 on land generates cations that are charge balanced by alkalinity (Mackenzie and Garrels, 1966;
 718 Berner and Berner, 2012; Turchyn and DePaolo, 2019). Rivers and groundwater deliver cations
 719 and alkalinity to the ocean where calcifiers produce skeletons and remove alkalinity. On million-
 720 year timescales this is usually represented by the Urey-Ebelman reaction (Urey, 1952; Berner,
 2004):



722 which illustrates the net transfer of carbon from the atmosphere to the sedimentary record.

723 Accordingly, over geological timescales one would expect that riverine delivery of alkalinity to
 724 the ocean is balanced by burial of carbonate in marine sediments (Fig. 6A).

725 Estimates of riverine alkalinity delivery range from 26 to 36 Tmol y^{-1} (Supporting
 726 Information S3, Table 3) and have been derived either from river DIC export or global estimates

727 of CO₂ consumption by chemical weathering of silicate and carbonate rocks (Berner et al., 1983;
 728 Meybeck, 1987; Ludwig et al., 1996; 1998; Gaillardet et al., 1999; Suchet et al., 2003; Hartmann
 729 et al., 2014; Li et al., 2017). River biogeochemists normally assume that bicarbonate equals the
 730 alkalinity and dissolved inorganic carbon (Suchet et al., 2003; Raymond and Hamilton, 2018).
 731 Consequently, global estimates of DIC delivery to the ocean can be used as a proxy for alkalinity
 732 transfer from weathering to the ocean. Carbonate burial estimates range from 18 to 34 Tmol C y⁻¹
 733 ¹ (Supporting Information S3), with clear consensus about carbonate burial in the deep sea of
 734 11-12 Tmol C y⁻¹, while ocean margin contributions vary from 6 to 23 Tmol C y⁻¹ (Morse and
 735 Mackenzie, 1990; Milliman, 1993; Wollast, 1994; Milliman and Droxler, 1996; Iglesias-
 736 Rodrigues et al., 2002; Smith, 2013; Smith and Mackenzie, 2016; O'Mare and Dunne, 2019).
 737 Calcium carbonate formation involves the consumption of two moles of alkalinity per mole of
 738 carbon (Table 2), indicating an imbalance between alkalinity inputs from chemical weathering
 739 (26-36 Tmol y⁻¹) and alkalinity outputs by carbonate burial (54-62 Tmol y⁻¹), the latter based on
 740 carbonate (carbon) burial equal to 27-31 Tmol C y⁻¹ (Fig. 6 and Supporting Information S3).
 741 This imbalance has been identified before based on Ca and HCO₃⁻ budgets of the ocean (Berner
 742 and Berner, 2012).

743 This imbalance of 18 to 36 Tmol y⁻¹ can be explained in three ways. One, the present-day
 744 ocean may not be at steady-state regarding alkalinity (Milliman, 1993). The inventory of
 745 alkalinity in the ocean is about 3.15 10¹⁸ mol, based on a total ocean volume of 1.34 10¹⁸ m³ and
 746 a mean ocean alkalinity of about 2.35 mol m⁻³ (Sarmiento and Gruber, 2006). Accordingly, the
 747 residence time of alkalinity is about 88-121 ky with respect to a riverine input of 26-36 Tmol y⁻¹.
 748 Consequently, the modern ocean alkalinity budget may still be recovering from last glacial sea
 749 level drop and related shifts in carbonate burial/exposure on continental shelves. Two, carbonate
 750 burial in ocean margin sediments may be lower than consensus values (16-20 Tmol C y⁻¹:
 751 Milliman and Droxler, 1996; Iglesias-Rodrigues et al., 2002; Smith, 2013; Smith and Mackenzie,
 752 2015; O'Mare and Dunne, 2019). Morse and Mackenzie (1990; their Fig. 5.1) reported a long-
 753 term carbonate burial of about 6 Tmol C y⁻¹ in ocean margin sediments. Total alkalinity removal
 754 by carbonate burial would then be about 34 Tmol y⁻¹ (2*(6+11)) and result in a balanced budget.
 755 van der Ploeg et al. (2019) reported an alkalinity removal via Cenozoic marginal carbonate burial
 756 of 14.3 Tmol y⁻¹ by balancing riverine and anaerobic mineralization inputs with marginal and
 757 deep-sea carbonate burial. However, there is consensus that modern carbonate burial in ocean
 758 margins is about 16-20 Tmol C y⁻¹ (Supporting Information S3), hence an alkalinity removal of
 759 32-40 Tmol y⁻¹. Three, this simple depiction of riverine alkalinity balancing calcium carbonate
 760 burial in marine sediment (Fig. 6A) requires revision because of additional alkalinity inputs from
 761 land (e.g., riverine particulate inorganic carbon and groundwater alkalinity) or from marine
 762 sediments (Fig. 6B).

763 Rivers deliver elements to the ocean not only in dissolved form, but also in particulate
 764 form (Martin and Meybeck, 1979). If riverine particulate carbonates are unreactive they will
 765 eventually be buried in marine sediments and are then implicitly included in the marine
 766 carbonate burial term. Similarly, if riverine particulate carbonates are reactive and dissolve, they
 767 represent an alkalinity source and should be added to the input. Irrespective of their fate, transfer
 768 of particulate inorganic carbon from rivers to the ocean would reduce the imbalance. There are
 769 very few data on the global particulate inorganic carbon input to the ocean. On the basis of a
 770 very small dataset, Meybeck (1987) reported a PIC flux of 14.2 Tmol C y⁻¹ and this is still used
 771 in global carbon assessments (Li et al., 2017). This PIC flux implies an additional alkalinity
 772 source of 28.4 Tmol y⁻¹. This is not only of similar magnitude as the alkalinity delivered in

773 dissolved form, but it would also close the modern ocean alkalinity budget (Table 3). This large,
774 so far overlooked, alkalinity input to the ocean is however poorly constrained. Using the global
775 sediment delivery estimate (19 Pg y^{-1} ; range $11\text{-}27 \text{ Pg y}^{-1}$) of Beusen et al. (2005) and the
776 average of PIC content of US rivers (0.47 wt% C) from Canfield (1997), a lower riverine PIC
777 delivery is estimated ($7.4 \text{ Tmol C y}^{-1}$, range $4.3\text{-}10.6 \text{ Tmol C y}^{-1}$). However, this would still
778 correspond to an alkalinity flux of almost 15 Tmol y^{-1} . This difference is primarily due to
779 difference in PIC content of suspended particles (0.9 wt% for Meybeck (1982) versus 0.47 wt%
780 in US river data base (Canfield, 1997)). The average of these two uncertain numbers is used for
781 the alkalinity budget (Fig. 6B, Table 3).

782 Part of the freshwater return flow to the ocean occurs via groundwater discharge rather
783 than via rivers (Slomp and van Cappellen, 2005) and this is an additional alkalinity input. Zhou
784 et al. (2019) reported a global freshwater submarine discharge flux of $489 \text{ km}^3 \text{ y}^{-1}$, which
785 corresponds to about 1.3% of the global river discharge and is significantly lower than the 5%
786 adopted by Slomp and van Cappellen (2005). Combining these fractions with assumptions about
787 the alkalinity of groundwater (one to three times that of river water, Zhang & Planavasky, 2019),
788 we estimate a global fresh groundwater alkalinity input of about 1 Tmol y^{-1} , range $0.4\text{-}4.7 \text{ Tmol}$
789 y^{-1} ; Supporting Information S3).

790 Besides these additional alkalinity inputs from riverine PIC and submarine groundwater
791 discharge, there is also alkalinity production and consumption in marine sediments due to
792 anaerobic degradation of organic matter, organic matter burial and reactions involving silicates
793 (Berner et al. 1970; Ben-Yaakov, 1973; Boudreau and Canfield, 1993; Soetaert et al., 2007;
794 Wallmann et al., 2008; Hu and Cai, 2011). Although we understand the impact of individual
795 processes on TA quite well (see sections 4 and 5), the overall effect of these processes on ocean
796 TA is more difficult to assess because of the tight coupling between alkalinity generating and
797 consuming processes within a sediment column. For instance, dissimilatory sulphate reduction
798 and sulphate reduction coupled to anaerobic methane oxidation generate TA (Table 2), but most
799 of the sulphide and ammonium generated during these processes are re-oxidized, resulting in
800 alkalinity consumption (Table 2). Consequently, net overall impact of sedimentary sulphate
801 reduction on ocean alkalinity is limited to the small fraction of reduced sulphur that is eventually
802 buried (Wallmann et al., 2008; Hu and Cai, 2011; Krumins et al., 2013; Gustafsson et al., 2019).
803 Moreover, alkalinity released from the sediment in the form of reduced substances (e.g.
804 ammonium, sulphide) that are subsequently oxidized (e.g. nitrification, sulphide oxidation) in the
805 water column does not contribute to the whole ocean alkalinity balance either (Hu and Cai,
806 2011).

807 In the context of the global ocean alkalinity balance, anaerobic alkalinity production can
808 conceptually be considered as an anion charge transfer process, as discussed in section 4 (Ben-
809 Yaakov, 1973; Hu and Cai, 2011). During denitrification (reduction of nitrate to dinitrogen gas),
810 the charge of nitrate is transferred to bicarbonate and thus increases alkalinity. Similarly, the
811 reduced sulphur buried in marine sediments initially entered the ocean as a sulphate ion; this
812 implies a charge transfer to bicarbonate. In contrast, solid phase oxidants such as iron and
813 manganese oxides enter the ocean uncharged and leave the ocean in an uncharged solid form
814 (e.g. FeS_2), with no impact on global ocean alkalinity. Accordingly, it is only the charge transfer
815 from land-derived nitrate and sulphate to bicarbonate produced by anaerobic respiration that
816 matters for the whole ocean alkalinity balance (Hu and Cai, 2011).

817 Net alkalinity production due to denitrification/anammox is thus about 1.5 Tmol y^{-1} (Hu
818 and Cai, 2011) based on a river nitrate input of 21 Tg N y^{-1} (Seitzinger et al., 2006). The net

819 alkalinity production due to sulphate reduction is derived from the burial of sulphur in marine
820 sediments because most of the sulphate produced is re-oxidized (Jorgensen, 1977, 1982).
821 Estimates of sulphur burial are based on organic carbon burial and vary from 1.2 (Berner, 1982)
822 to 3.4 Tmol S y⁻¹ (Supporting Information S3), implying a potential alkalinity source of 2.4 to
823 6.9 Tmol y⁻¹ to the ocean. These are upper estimates because part of the net alkalinity generated
824 within sediments results in authigenic carbonate formation and does not contribute to ocean
825 alkalinity. Accordingly, the total contribution of anaerobic biogeochemical processes to the
826 ocean alkalinity balance varies between 3.9 and 8.4 Tmol y⁻¹.

827 Primary production based on new nitrogen (e.g. nitrate) is an alkalinity source, while
828 aerobic respiration accompanied by nitrification represent an alkalinity sink (Table 2). If all
829 organic matter produced were respired there would be no impact on alkalinity, but a small part of
830 the organic matter produced in the photic zone is eventually buried in marine sediments. Based
831 on organic carbon burial estimates of Berner (1982) and Burdige (2007) we estimate a net
832 alkalinity production of 3 Tmol y⁻¹ (see Supporting Information S3).

833 Quantifying the contribution of sediment silicate reactions to ocean alkalinity is also
834 complicated by multiple alkalinity production and consumption processes: reverse weathering in
835 surface sediments, marine weathering at depth, in particular in the methanogenic zone
836 (Wallmann et al., 2008) and ocean crust weathering (Staudigel et al., 1989; Caldeira, 1995;
837 Berner, 2004). Moreover, the alkalinity generated at depth by mineral weathering result in
838 authigenic carbonate formation. Although alteration of oceanic crust is likely on the order of 2
839 Tmol y⁻¹, most bicarbonate generated is precipitated as calcite and does not contribute to ocean
840 alkalinity. Reverse weathering is a sink of alkalinity (e.g. equations 28 and 29) on the order of
841 about 0.5-1.5 Tmol y⁻¹ (Isson and Planavsky, 2018), but varies locally depending on the supply
842 of materials (Michalopoulos and Aller, 1995, 2004 Rahman et al., 2016). Wallmann et al. (2008)
843 reported high rates of submarine weathering of 3.3 to 13.3 Tmol y⁻¹. Their estimate is based on
844 the assumption that all carbon dioxide produced during methanogenesis is converted to
845 bicarbonate and that one third is removed by authigenic carbonate formation and two-third is
846 released as alkalinity to the ocean. These numbers are likely too high given that these are based
847 on global methane production rates of 5 Tmol C y⁻¹ (Reeburgh et al., 1993) and 20 Tmol C y⁻¹
848 (Hinrichs and Boetius, 2002). More recent estimates for marine methane formation are 2.8 Tmol
849 y⁻¹ (Egger et al., 2018) and 0.3 to 2.1 Tmol C y⁻¹ (Wallmann et al., 2012). This would lower
850 submarine weathering alkalinity input to 2-3 Tmol y⁻¹ (Supporting Information S3).

851 Figure 6A and Table 3 clearly show that the ocean alkalinity budget based on the balance
852 between riverine alkalinity inputs and carbonate burial at the ocean floor is imbalanced by about
853 27 Tmol y⁻¹ and provides only part of the story. Additional alkalinity from riverine PIC delivery
854 (about 21 Tmol y⁻¹), anaerobic mineralization (about 6.2 Tmol y⁻¹) provides the majority of the
855 alkalinity to balance the budget with minor additional inputs from submarine groundwater
856 discharge (about 1 Tmol y⁻¹), organic matter burial (about 3 Tmol y⁻¹) and silicate interactions
857 (about 1 Tmol y⁻¹: submarine weathering minus reversed weathering).

858

859 7. Conclusions

860

861 Alkalinity is a central concept in ocean buffering and it is of the utmost importance to
862 understand and quantify its role in carbon dioxide uptake, carbonate mineral formation and ocean
863 buffering during times of global change. In section 2 we have shown that it is instructive to
864 distinguish between measurable titration alkalinity (TA) that is based on a proton balance and

865 charge-balance alkalinity (CBA). This distinction is needed to understand and quantify the
866 impact of biogeochemical processes such as calcification or primary production on alkalinity.

867 Although much progress has been made in accurate and reproducible measurements of
868 titration alkalinity, quantification of ocean buffering through the use of buffer or sensitivity
869 factors is underexplored, except for the Revelle sensitivity factor (Sundquist et al., 1979) and the
870 acid-base buffer capacity (Weber and Stumm, 1963). This is unfortunate because such a
871 sensitivity analysis is critical to attribute changes in $p\text{CO}_2$ and/or pH to physical (temperature,
872 salinity) and chemical/biological changes (alkalinity, dissolved inorganic carbon). In section 3
873 we have provided a systematic treatment of these sensitivity factors and identified and resolved
874 inconsistent terminology. Together with the availability of public domain packages such as
875 *seacarb* (Gattuso et al., 2019) and *AquaEnv* (Hofmann et al., 2010b) that facilitate their
876 calculation, this provides researchers with the tools to understand and predict changes in ocean
877 chemistry. This can be retrodiction of past or prediction of future pH changes due to ocean
878 acidification, or prediction of future pH, $p\text{CO}_2$ or carbonate saturation values upon alkalinity
879 manipulation during geo-engineering (Renforth and Henderson, 2017).

880 While these sensitivity factors provide a powerful approach to deal with equilibrium
881 reactions, they are less useful when buffering is provided by interactions with slowly reacting
882 solids or by changes in biological processes (e.g. calcification). These heterogeneous buffering
883 reactions are dominated by calcium carbonate formation and dissolution, and normally discussed
884 in terms of ocean carbonate compensation dynamics (Boudreau et al., 2018). Traditionally the
885 focus has been on the role of carbonate mineral dissolution in the water column and sediments,
886 i.e. chemical dissolution, which provides long-term buffering (Archer et al., 1998; 2009; Sigman
887 et al., 1998; Ridgwell and Zeebe, 2005). However, ocean acidification or warming also impact
888 calcification (e.g. coral bleaching). This biological carbonate compensation mechanism has
889 implications on the short-term (months) for the carbonate compensation depth and on the longer
890 term (kyr) for alkalinity accumulation in the ocean (Boudreau et al., 2018). Homogeneous
891 buffering, chemical and biological carbonate compensation and weathering feedbacks together
892 govern the long-term fate of anthropogenic carbon dioxide (Archer et al., 1998; 2009; Boudreau
893 et al., 2010a). The very same processes have also been involved in the recovery of ocean
894 chemistry to carbon perturbations in the past (Ridgwell and Zeebe, 2005; Boudreau et al., 2018).

895 Ocean alkalinity is controlled by multiple processes operating over multiple time scales
896 complicating the elucidation of the present-day budget (Table 3) as well as reconstructions of
897 alkalinity, carbon and pH of the past ocean. Nevertheless, some studies (Tyrell and Zeebe, 2004;
898 Caves et al., 2016; Boudreau et al., 2019; Zeebe and Tyrell, 2019;) have reported alkalinity
899 reconstructions for the last 50-60 million years indicating relatively minor fluctuations: e.g.
900 between 1.5 and 3 mM. The Urey-Ebelmen concept implies that riverine alkalinity delivery
901 should be balanced by carbonate burial in the ocean on geological timescales (Fig. 6A). The
902 imbalance of the present-day ocean alkalinity budget between riverine DIC input and marine
903 carbonate burial cannot be resolved by including alkalinity delivery by submarine groundwater
904 or within ocean alkalinity production by anaerobic mineralization or submarine weathering.
905 However, the alkalinity budget can readily be balanced by including alkalinity input to the ocean
906 through riverine particulate inorganic carbon delivery (Table 3, Fig. 6B). The global riverine flux
907 of PIC is poorly known but reasonable estimates (7.5 to 15 Tmol C y^{-1} ; corresponding to an
908 alkalinity flux of 15-30 Tmol y^{-1}) indicate that it is similarly sized as the global riverine DIC flux
909 (26-36 Tmol y^{-1}). This not only urges detailed research to better constrain this flux, but also

910 implies a reconsideration of past and present ocean alkalinity budgets that ignore physical
 911 weathering products delivered to the ocean.

912

913 **Box 1. Terminology**

914

- 915 • *Acid*: substance donating a proton
- 916 • *Base*: substance accepting a proton
- 917 • *Conjugated acids/bases*: substances that only differ by one proton
- 918 • *strong acid*: acid that donates all protons in natural water
- 919 • *weak acid*: acid that partly dissociates to conjugate base and proton in water
- 920 • *pH*: $-\log_{10}$ of proton concentration (H^+)
- 921 • *pK*: $-\log_{10}$ of equilibrium constant (K)
- 922 • *Bjerrum plot*: graph showing the distribution of acids and their conjugated bases as a
 923 function of pH
- 924 • *alkalinity*: the excess of proton acceptors (over proton donors) in a solution
- 925 • *titration alkalinity (TA)*: measurable alkalinity based on a proton balance
- 926 • *charge balance alkalinity (CBA)*: alkalinity based on excess of proton exchanging anions
 927 over cations, also known as excess negative charge (ENC)
- 928 • *buffer*: solution with a mixture of weak acids and conjugated bases that resist changes by
 929 transferring protons
- 930 • *homogeneous buffer*: solution resisting drastic changes by re-arrangement of protons in
 931 solution phase only
- 932 • *heterogeneous buffer*: a buffer system comprising both a solution and particles
- 933 • *buffer capacity*: ability of a solution to resist changes, also known as buffer index or
 934 intensity.
- 935 • *sensitivity factor*: change in output due to change in input, also known as chemical buffer
 936 factor, and the inverse of buffer capacity
- 937 • *carbonate compensation*: response of carbonate production and dissolution processes in
 938 the ocean upon changes
- 939 • *proton balance*: mass balance of protons
- 940 • *proton acceptor level*: the number of protons that can be accepted for an acid-base system
 941 at a specific pH, the reverse is known as the proton level
- 942 • *reference level species*: the major species of an acid-base system present at the reference
 943 level (e.g. pH=4.5)
- 944 • *Revelle factor*: a sensitivity factor expressing the change in carbon dioxide to the change
 945 in dissolved inorganic carbon

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953 **Author contributions**

954 JJM designed research and wrote the manuscript with contributions from KS and MH, in
955 particular for sections 2, 3 and 4. KS and MH performed the calculations presented in Figures 1-
956 5.

957

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1468 **Table 1.** Overview of sensitivities of the ocean carbon system ($\frac{\partial response}{\partial driver}$) and their relations to
 1469 buffering quantities in the literature. Based on the Hagens & Middelburg (2016a) approach,
 1470 Supporting Information S2 explicitly links the various sensitivities.
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Driver	Response	Sensitivity factor	Symbol	Name	Reference
TA	pH	$\left(\frac{\partial pH}{\partial TA}\right)$	$-\Phi_H$ β_{pH}^{-1}	Chemical buffer factor Inverse of Buffer capacity	Frankignoulle (1994) Van Slyke (1922)
	lnH	$\left(\frac{\partial \ln H}{\partial TA}\right)$	β_{TA}^{-1}		Egleston et al. (2010)
	H	$\left(\frac{\partial H}{\partial TA}\right)$	$-\beta_H^{-1}$	Negative inverse of Proton concentration buffer factor	Hofmann et al. (2010)
	pCO ₂	$\left(\frac{\partial pCO_2}{\partial TA}\right)$	$-\Pi_H$	Buffer factor	Frankignoulle (1994)
	lnpCO ₂	$\left(\frac{\partial pCO_2}{\partial TA}\right) \frac{TA}{pCO_2}$ or $\left(\frac{\partial \ln pCO_2}{\partial \ln TA}\right)$	γ_{TA}	Alkalinity factor	Sarmiento & Gruber (2006)
	lnCO ₂	$\left(\frac{\partial \ln CO_2}{\partial TA}\right)$	γ_{TA}^{-1}		Egleston et al. (2010)
	CO ₂	$\frac{1}{K_0} \left(\frac{\partial CO_2}{\partial TA}\right)$	$-\Pi_H$		Frankignoulle (1994)
	lnCO ₃ ²⁻	$\left(\frac{\partial \ln CO_3^{2-}}{\partial TA}\right)$	ω_{TA}^{-1}		Egleston et al. (2010)
DIC	pH	$\left(\frac{\partial pH}{\partial DIC}\right)$	Φ $\beta_{CO_2}^{-1}$		Frankignoulle (1994) Weber and Stumm, 1963
	lnH	$\left(\frac{\partial \ln H}{\partial DIC}\right)$	β_{DIC}^{-1}		Egleston et al. (2010)
	pCO ₂	$\left(\frac{\partial pCO_2}{\partial DIC}\right)$	Π_D		Frankignoulle (1994)
	lnpCO ₂	$\left(\frac{\partial pCO_2}{\partial DIC}\right) \frac{DIC}{pCO_2}$ or	R B_{hom}	Homogeneous buffer factor or Revelle factor	Bolin and Eriksson (1959) Sundquist et al. (1979)

		$\left(\frac{\partial \ln pCO_2}{\partial \ln DIC}\right)$	β_D γ_{DIC}		Frankignoulle (1994) Sarmiento & Gruber (2006)
	$\ln CO_2$	$\left(\frac{\partial \ln CO_2}{\partial DIC}\right)$	γ_{DIC}^{-1}		Egleston et al. (2010)
	TA	$\left(\frac{\partial TA}{\partial DIC}\right)$	Q	Isocapnic quotient	Humphreys et al. (2018)
	$\ln CO_3^{2-}$	$\left(\frac{\partial \ln CO_3^{2-}}{\partial DIC}\right)$	ω_{DIC}^{-1}		Egleston et al. (2010)
pCO_2	pH	$\left(\frac{\partial pH}{\partial pCO_2}\right)$	Φ_D		Frankignoulle (1994)
	$\ln H$	$\left(\frac{\partial \ln H}{\partial \ln pCO_2}\right)$	H^{-1}		Omta et al. (2010)
	$\ln CO_3^{2-}$	$\left(\frac{\partial CO_3^{2-}}{\partial pCO_2}\right) \frac{pCO_2}{CO_3^{2-}}$ or $\left(\frac{\partial \ln CO_3^{2-}}{\partial \ln pCO_2}\right)$	β_C^{-1} O^{-1}		Frankignoulle (1994) Omta et al. (2010)

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1475 **Table 2** Biogeochemical processes and their impact on charge balance alkalinity (ΔCBA) and
 1476 titration alkalinity (ΔTA) (after Soetaert et al., 2007).

Process	Reaction	ΔCBA	ΔTA
(R1) Aerobic mineralization	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + \text{O}_2 \rightarrow \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + \text{H}_2\text{O}$	0	n-p
(R2) Denitrification	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + 0.8 \text{HNO}_3 \rightarrow \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + 0.4 \text{N}_2 + 1.4 \text{H}_2\text{O}$	0	0.8+n-p
(R3) Mn-oxide reduction	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + 2 \text{MnO}_2 + 4\text{H}^+ \rightarrow \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + 2 \text{Mn}^{2+} + 3\text{H}_2\text{O}$	4	n-p+4
(R4) Fe-oxide reduction	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + 2 \text{Fe}_2\text{O}_3 + 8\text{H}^+ \rightarrow \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + 4 \text{Fe}^{2+} + 5\text{H}_2\text{O}$	8	n-p+8
(R5) Sulphate reduction	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + 0.5 \text{H}_2\text{SO}_4 \rightarrow \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + 0.5 \text{H}_2\text{S} + \text{H}_2\text{O}$	0	n-p+1
(R6) Methanogenesis	$(\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p \rightarrow 0.5 \text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + 0.5 \text{CH}_4 + \text{H}_2\text{O}$	0	n-p
(R7) Nitrification	$\text{NH}_3 + 2 \text{O}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O}$	0	-2
(R8) Annamox	$\text{NH}_3 + \text{HNO}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$	0	0
(R9) Aerobic oxidation of methane	$\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$	0	0
(R10) Anaerobic oxidation of methane	$\text{CH}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{CO}_2 + \text{H}_2\text{S} + 2 \text{H}_2\text{O}$	0	2
(R11) Calcite precipitation	$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3$	-2	-2
(R12) Primary production (nitrate)	$\text{CO}_2 + n \text{HNO}_3 + p \text{H}_3\text{PO}_4 + (1+n) \text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + (1+2n) \text{O}_2$	0	p+n
(R13) Primary production (ammonium)	$\text{CO}_2 + n \text{NH}_3 + p \text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O})(\text{NH}_3)_n(\text{H}_3\text{PO}_4)_p + \text{O}_2$	0	p-n
(R14) CO_2 emission to air	$\text{CO}_2 \rightarrow \text{CO}_2(\text{g})$	0	0
(R15) Proton sorption	$\text{H}^+ \rightarrow \text{H}^+\text{-surface}$	1	1
(R15) Ammonium sorption	$\text{NH}_4^+ \rightarrow \text{NH}_4^+\text{-surface}$	1	0

1477 n = N/C ratio of organic matter and p = P/C ratio of organic matter

1478 **Table 3** Global alkalinity balance of the ocean (Tmol y^{-1}). Supporting Information S3 provides a
 1479 detailed documentation for the various terms, including the range.

1480

Alkalinity sources/sinks	Riverine DIC and carbonate burial balance	Complete Alkalinity balance
Riverine DIC	32	32
Riverine PIC		21
Submarine groundwater		1
Submarine silicate		2.8
Sulphur burial		4.7
Denitrification		1.5
Organic matter burial		3
Total Sources	32	66
Open ocean carbonate burial	23	23
Ocean margin carbonate burial	36	36
Reverse weathering		1
Total sinks	59	60
Imbalance	27	-6

1481

1482

1483 Figure captions.

1484

1485 **Figure 1.** Speciation, proton acceptor levels and charge as a function of pH. (A) Bjerrum plot
 1486 showing the distribution of carbonic acid, bicarbonate and carbonate as a function of pH and the
 1487 corresponding proton acceptor level (solid black line) and charge (red dashed line); (B) The
 1488 proton acceptor level for selected acid-base pairs; (C) The charge for selected acid-base pairs.
 1489 Details of the calculations are presented in the supporting information.

1490

1491 **Figure 2** The sensitivities $dpH/dCBA$ (A), $dpH/dDIC$ (B), and the Revelle sensitivity factor (C)
 1492 as function of pH. Left column over the entire pH range; right column focuses on the changes
 1493 from pH 6 to 9. Vertical grey lines indicate maxima/minima. Details of the calculations are
 1494 presented in the supporting information.

1495

1496 **Figure 3.** TA versus DIC plots (i.e. Deffeyes diagrams) showing the equilibrium pH at free scale
 1497 (A) and pCO_2 in μatm (B) as contours. Both graphs show vectors for the addition of protons
 1498 (vertically downward) and dissolution of calcium carbonate (slope 2:1). Notice that the resulting
 1499 change in pH and pCO_2 for the same amount of calcite dissolved or acid added (same vector)
 1500 differs because of differences in sensitivity (buffering). For instance, the ΔpH and ΔpCO_2 for
 1501 proton additions are -0.074 and +136 μatm , respectively, at low buffering (high DIC/TA ratio),
 1502 and -0.037 and +20.9 μatm at high buffering (low DIC/TA ratio). Similarly, for the calcite
 1503 dissolution vector, the ΔpH values are 0.022 and 0.013 and the ΔpCO_2 values are -33.9 and -5.9
 1504 μatm for low and high buffering, respectively.

1505

1506 **Figure 4** The response in pH due to denitrification as a function of pH. (A) The sensitivity factor
 1507 $dpH/dCBA$ of seawater, (B) The change in charge due to denitrification, (C) The resulting
 1508 change in pH as calculated by eq. 26. Details of the calculations are presented in the supporting
 1509 information.

1510

1511 **Figure 5** The impact of biogeochemical processes on pH. (A) The change in pH for aerobic
 1512 mineralization with and without nitrification. (B) The change in pH due to sulphate reduction
 1513 and methanogenesis. (C) The change in pH due to primary production based on ammonium or
 1514 nitrate. (D) The change in pH due to calcification and calcium carbonate dissolution. Note the
 1515 break at the pH corresponding to calcium carbonate equilibrium (modified from Soetaert et al.,
 1516 2007). Details of the calculations are presented in the supporting information.

1517

1518 **Figure 6** Alkalinity balance of the ocean (Fluxes are in $Tmol y^{-1}$). (A) Traditional alkalinity
 1519 balance considering river input of DIC and calcium carbonate burial. (B) Revised oceanic
 1520 alkalinity balance considering additional sources and sinks based on Table 3.

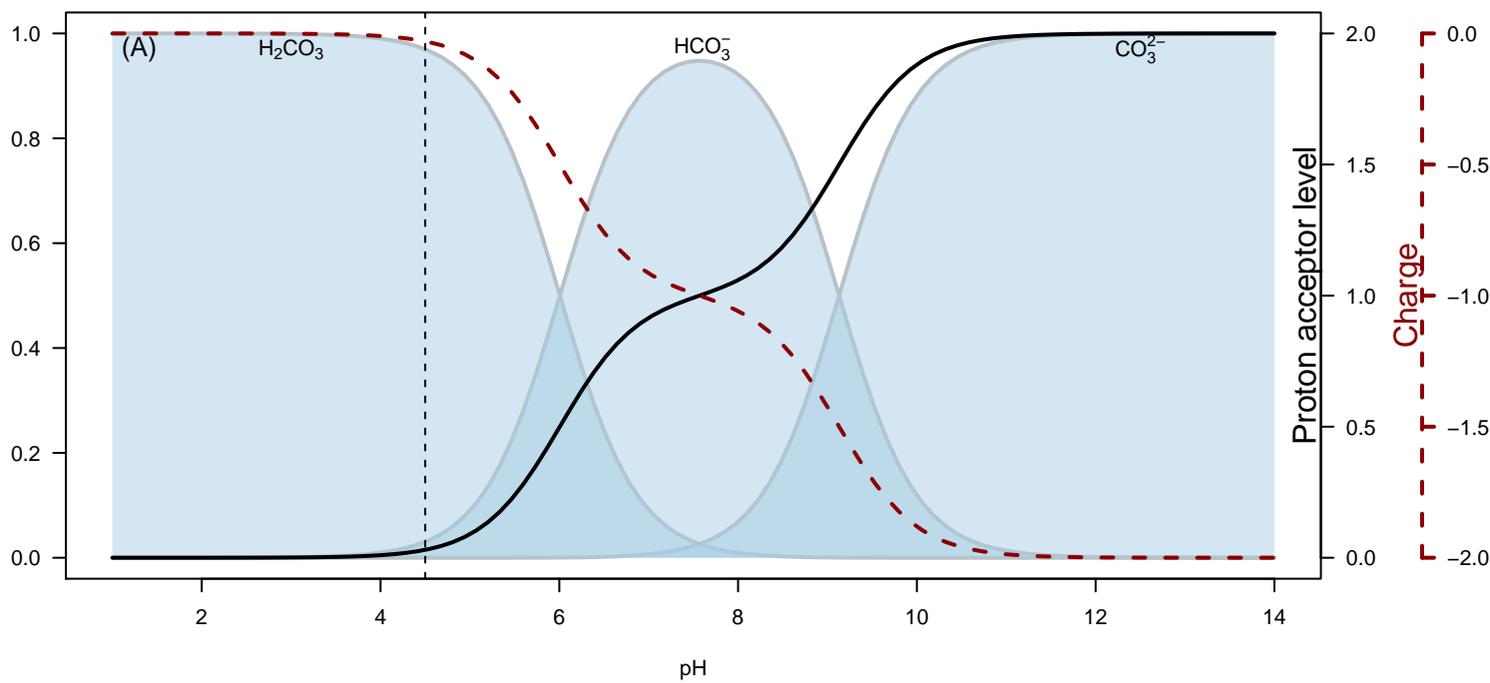
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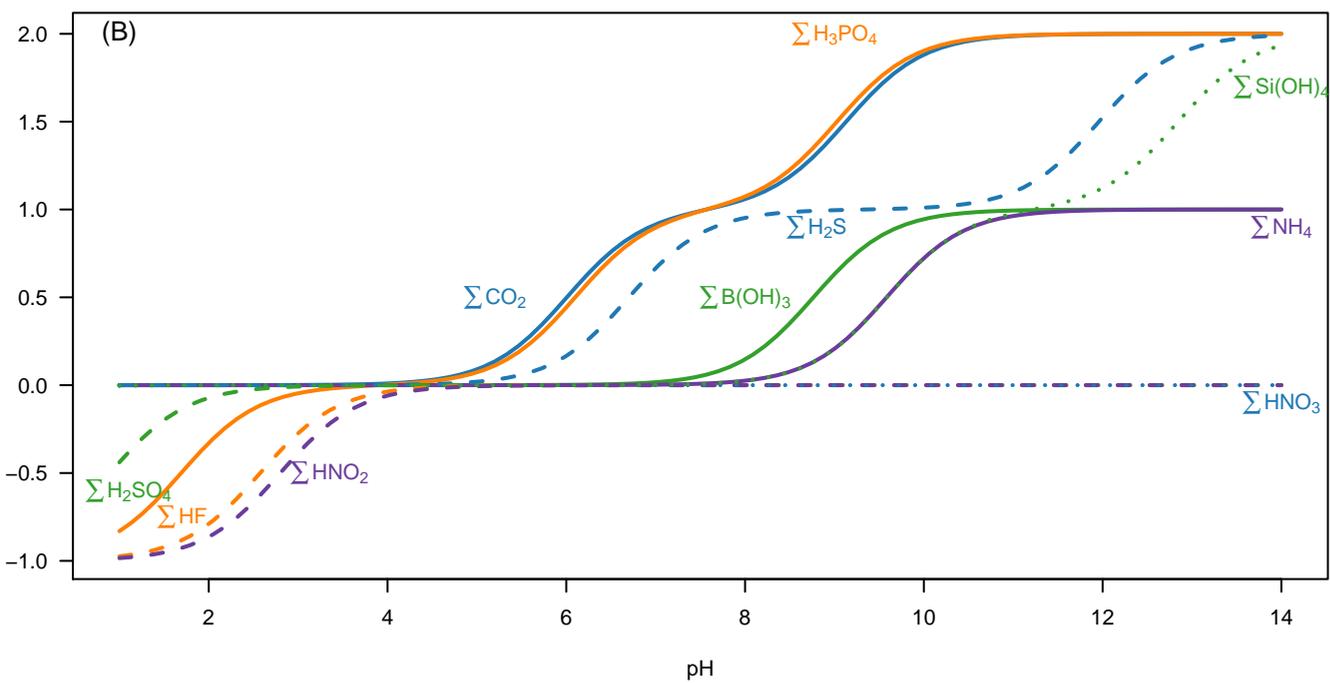
1523

Figure 1.

DIC speciation



Proton acceptor level



Charge

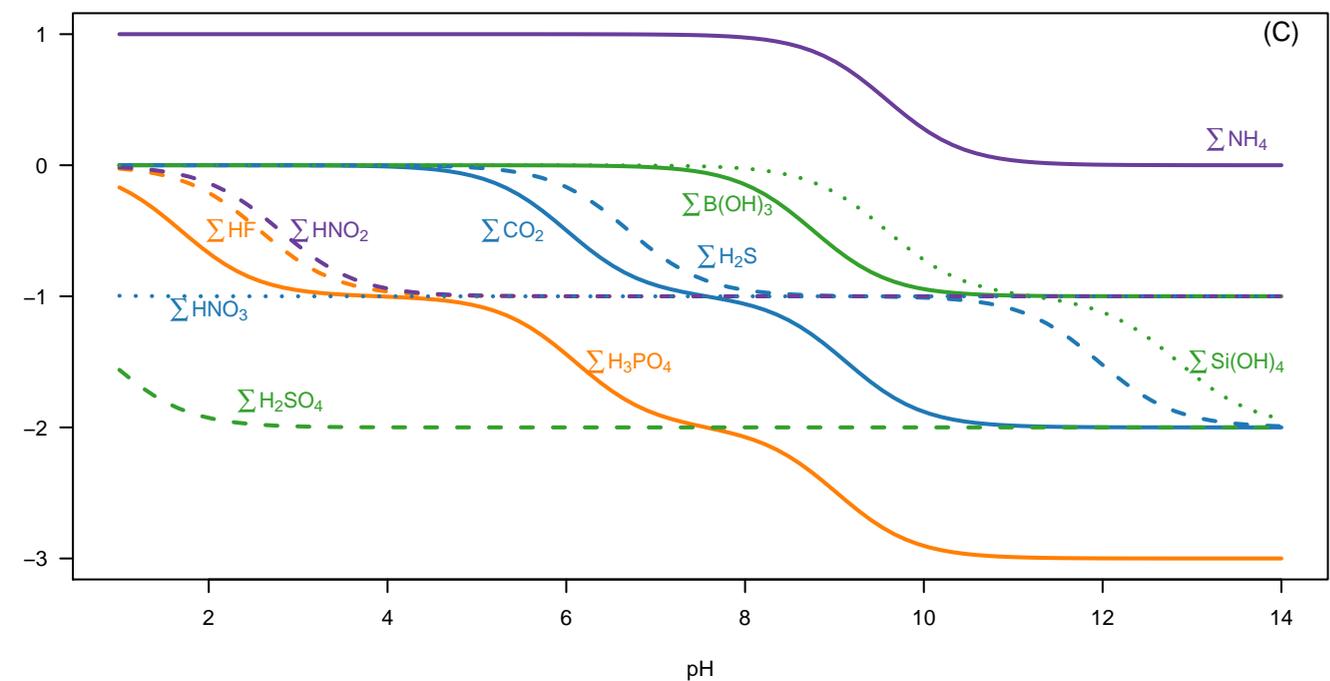


Figure 2.

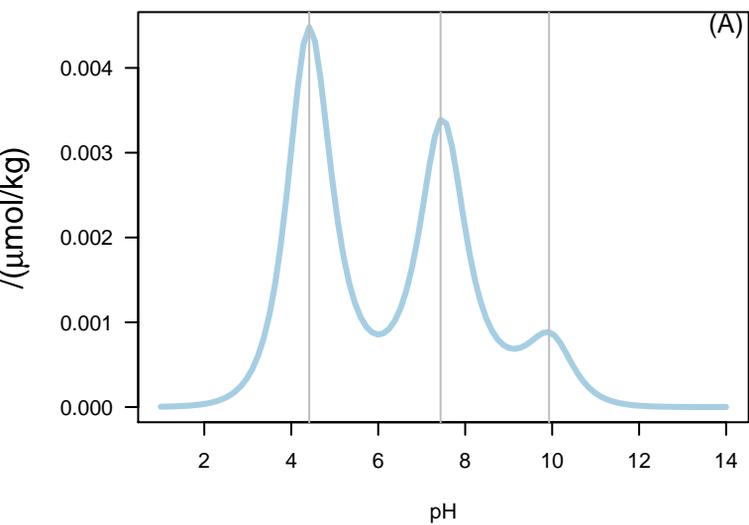
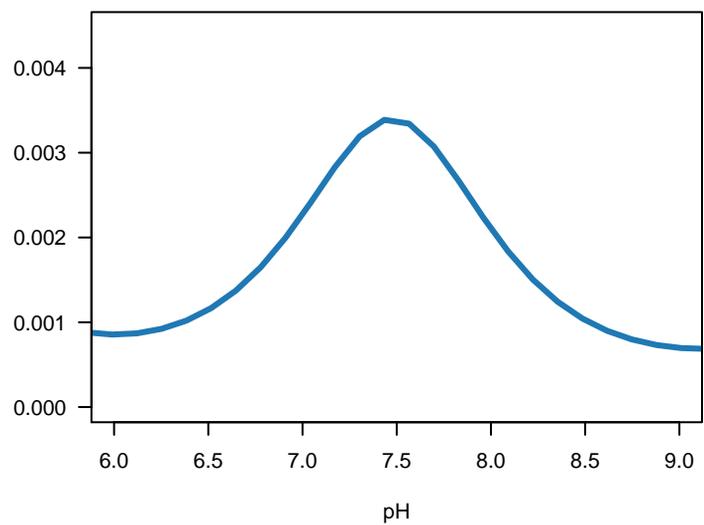
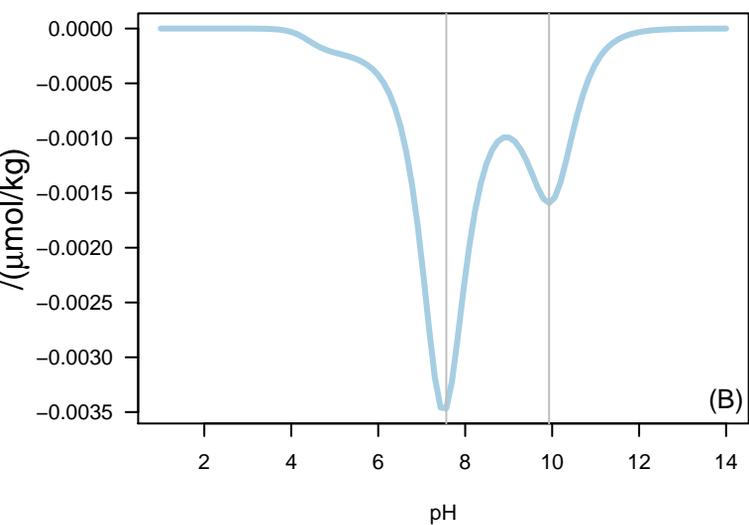
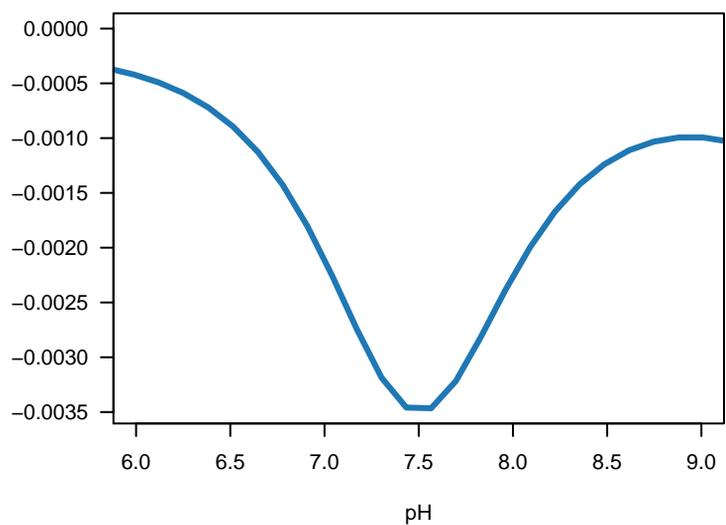
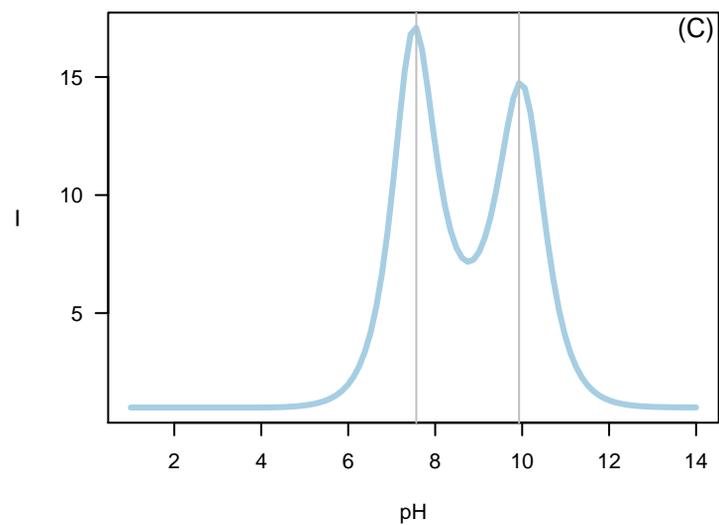
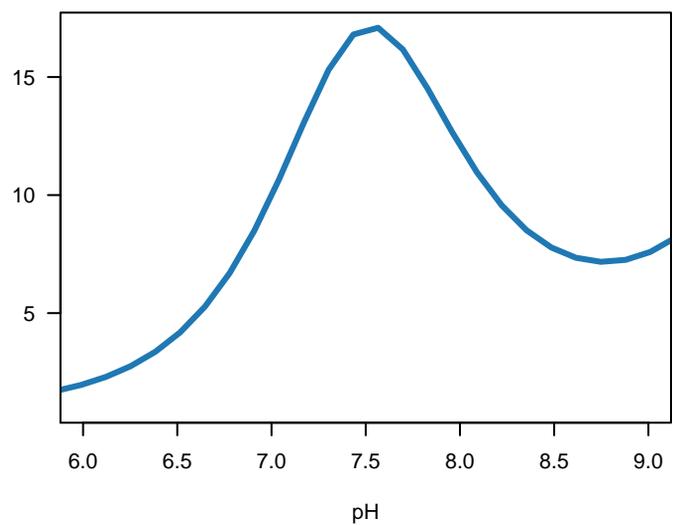
dpH/dCBA**dpH/dCBA****dpH/dDIC****dpH/dDIC****Revelle sensitivity factor****Revelle sensitivity factor**

Figure 3.

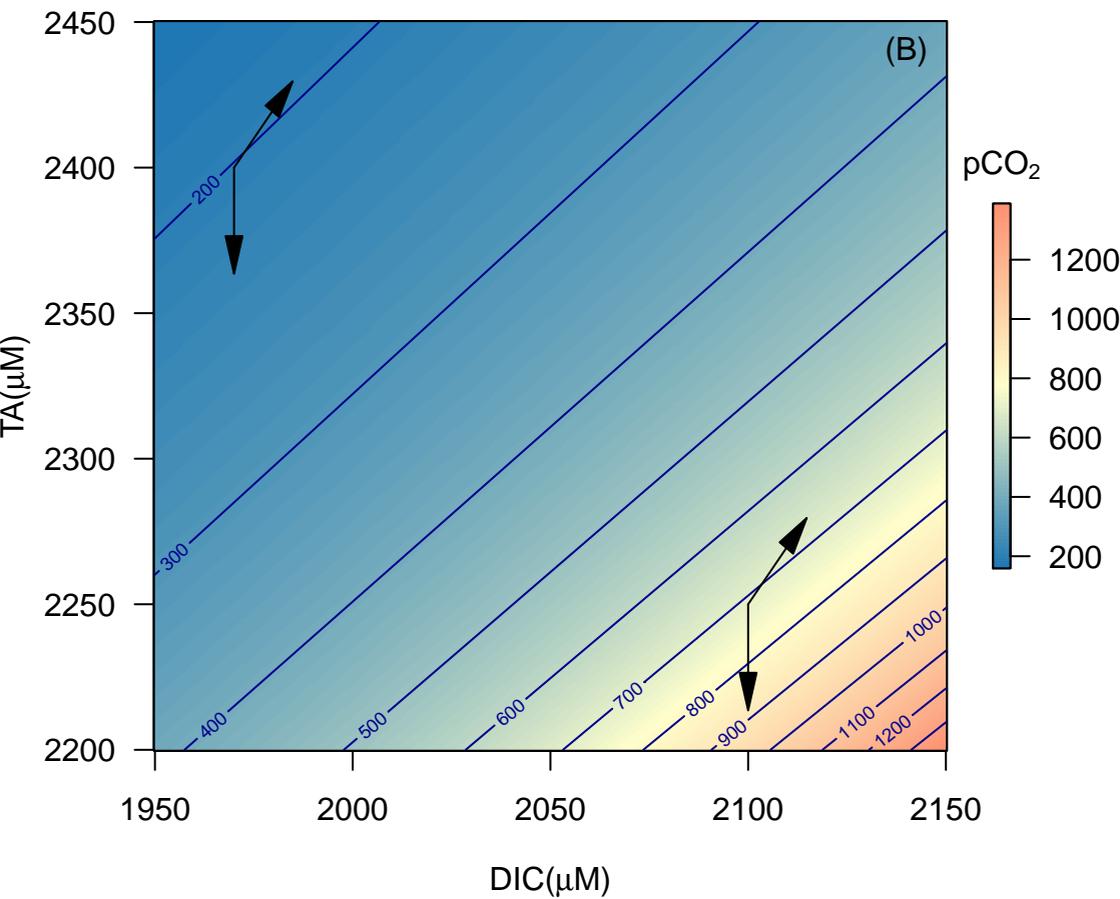
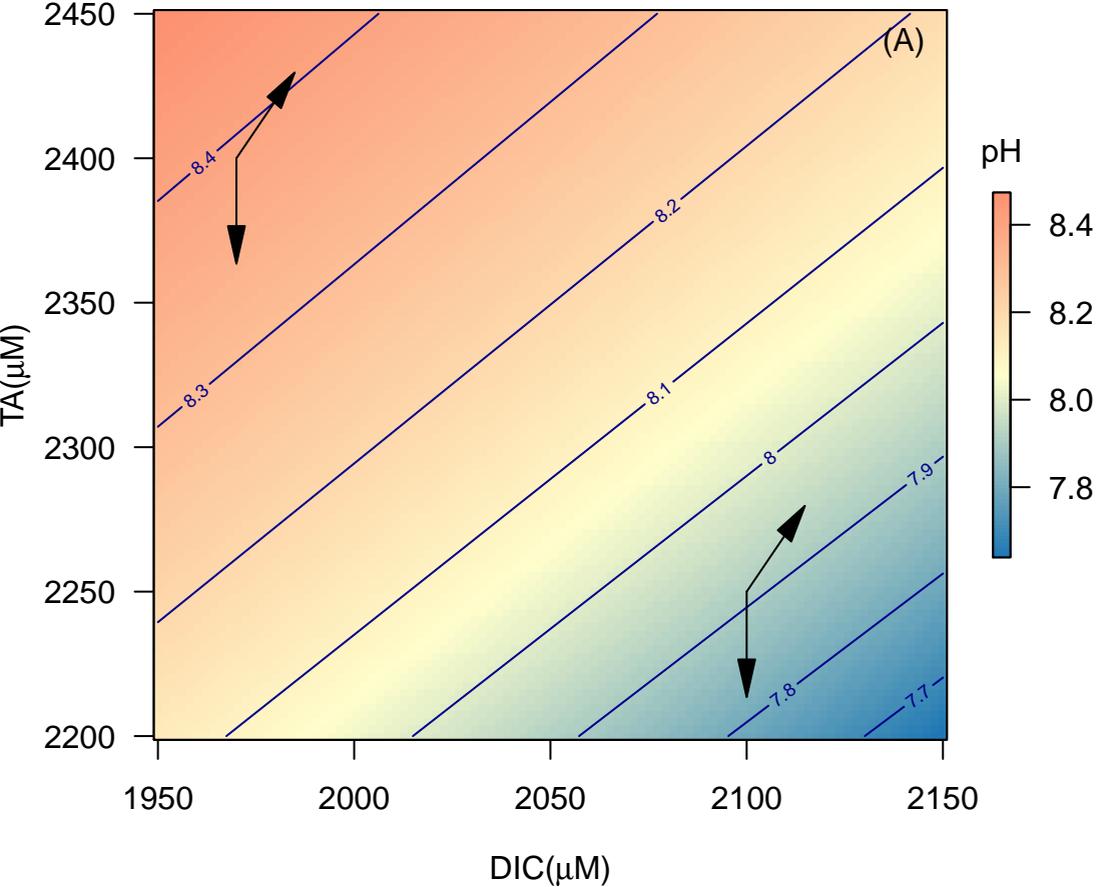


Figure 4.

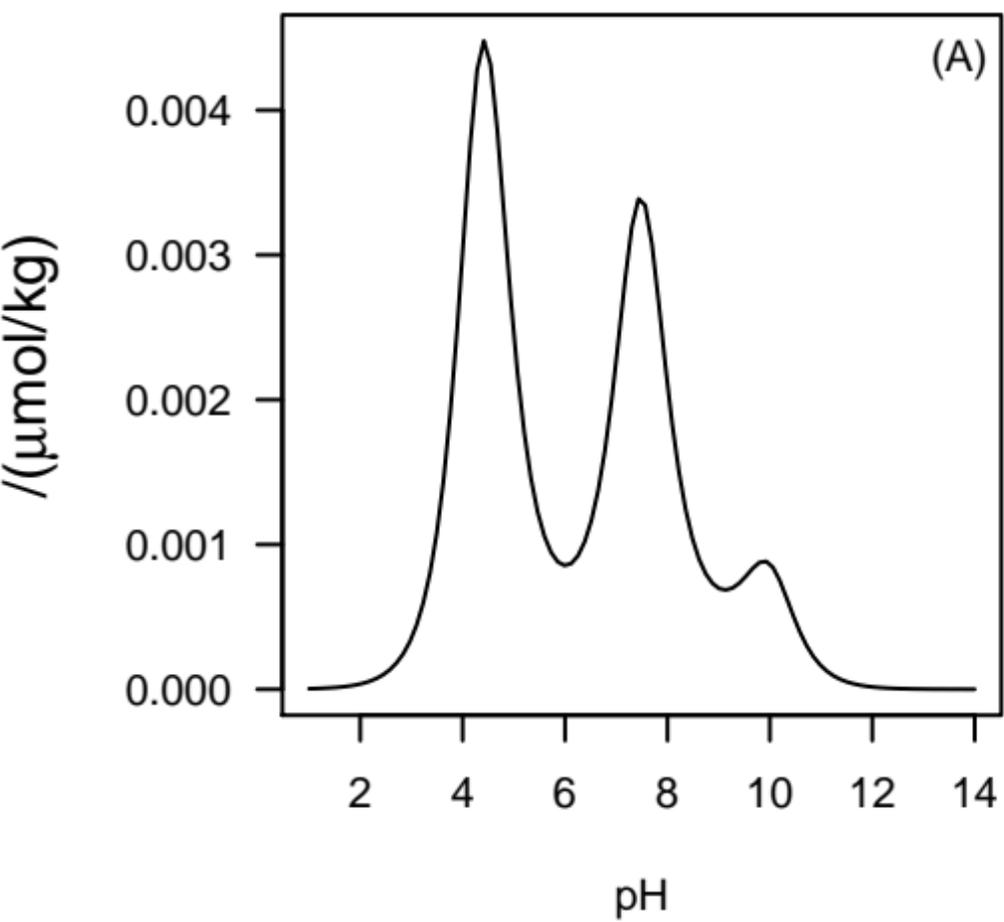
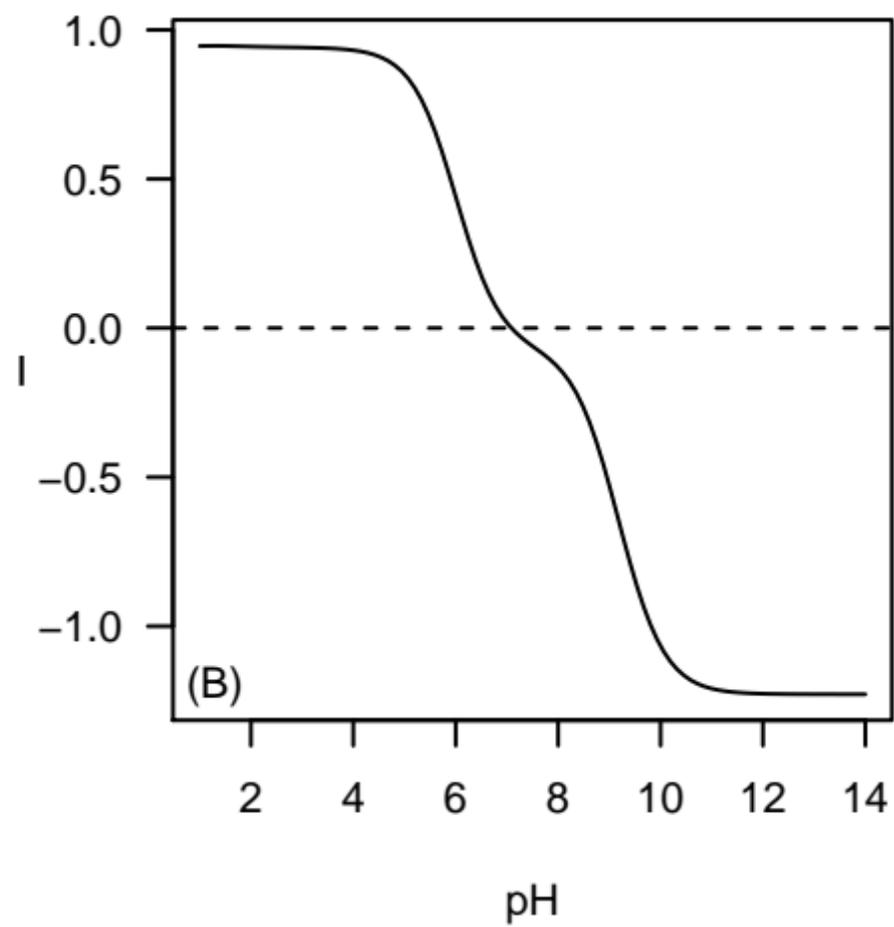
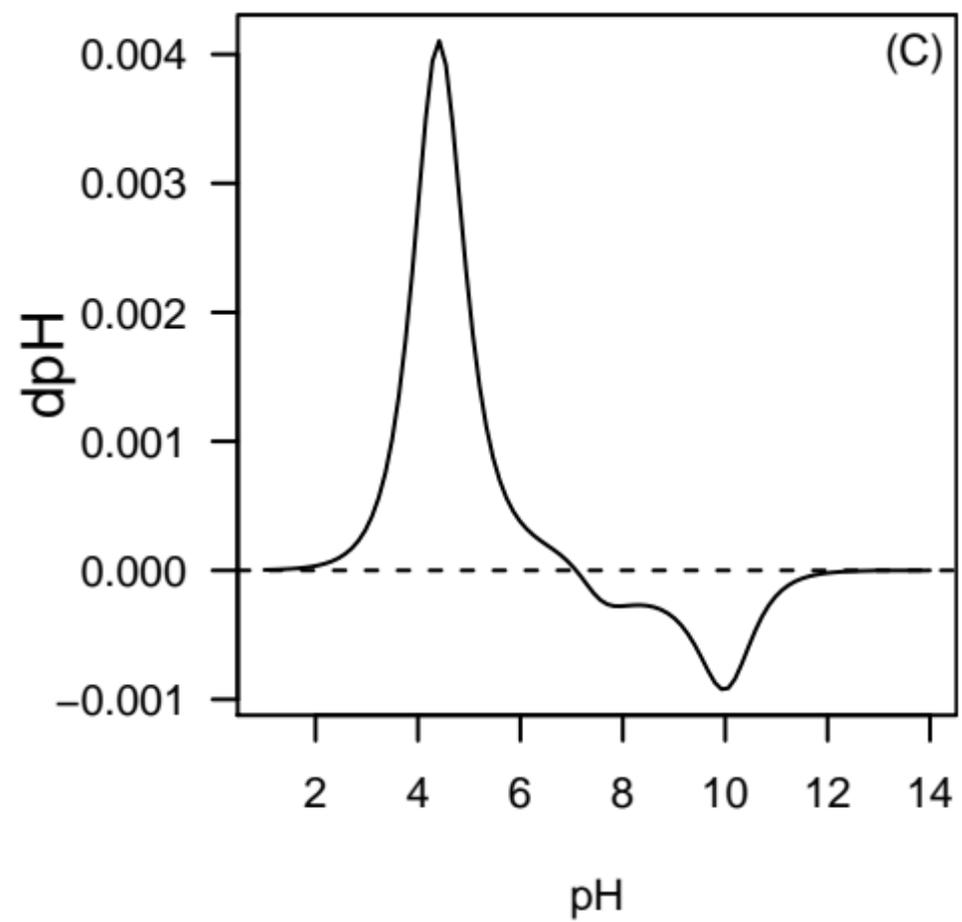
sensitivity **Δcharge** **response**

Figure 5.

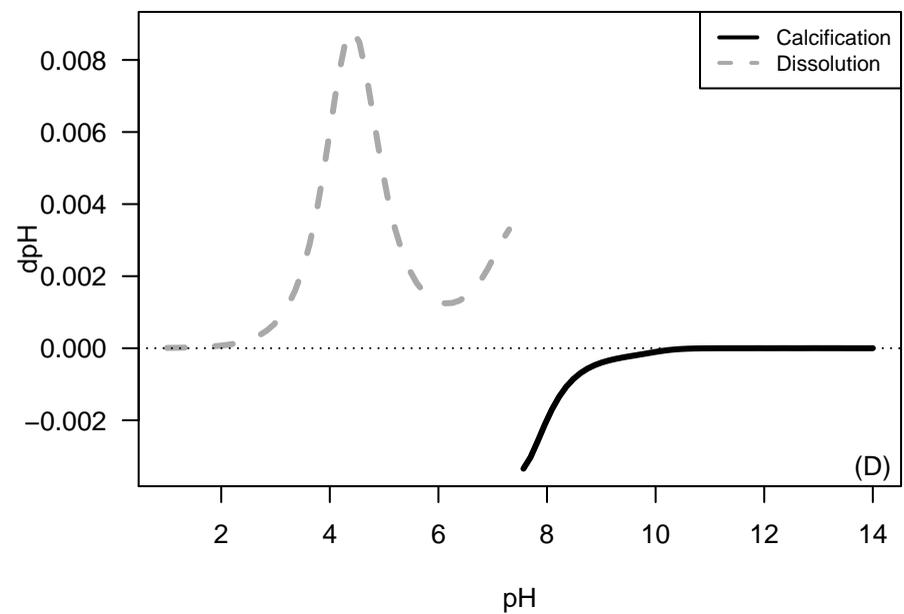
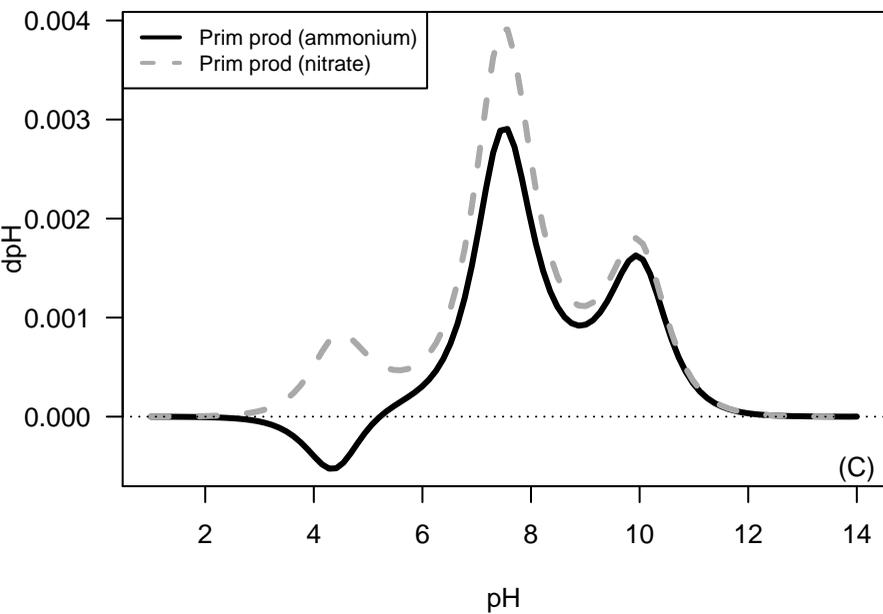
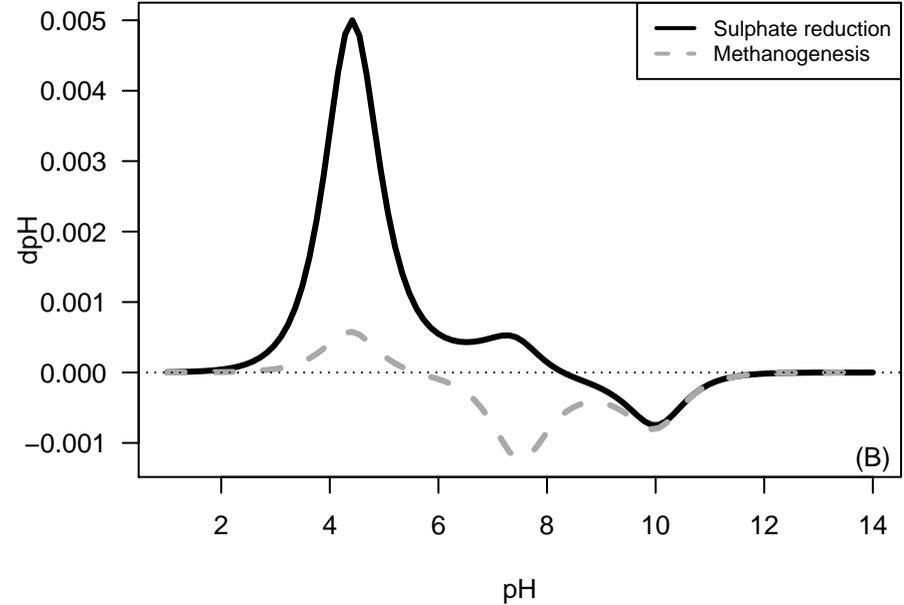
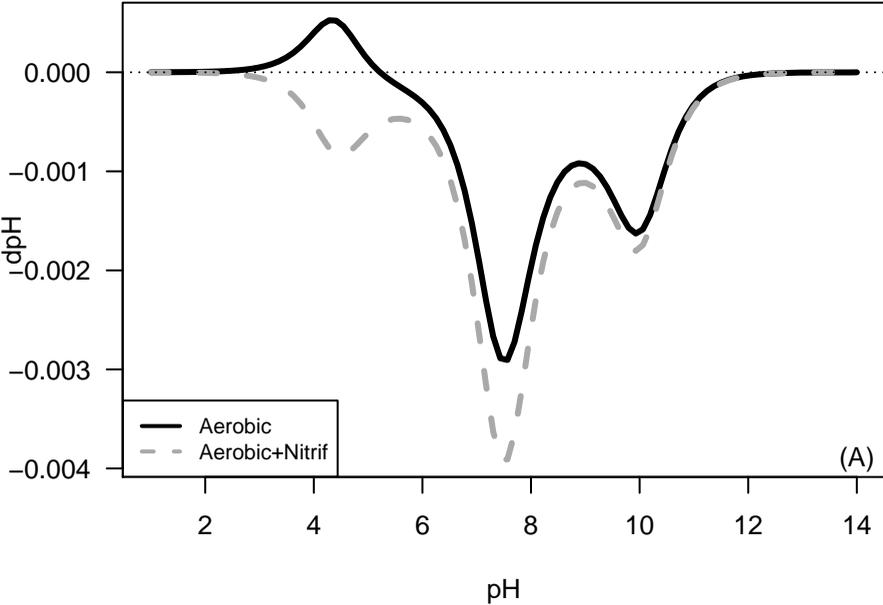


Figure 6.

A

Input = 32 vs. Output = 59

DIC: 32 (26-36)

River DIC

Continental Margin

Open Ocean

36 (32-46)

CaCO₃ burial

23 (22-24)

CaCO₃ burial

DIC: 32 (26-36)

PIC: 21 (15-28)

Input = 66 vs. Output = 60

B

River

Continental Margin

Open Ocean

Submarine
groundwater
discharge, 1

Submarine weathering, 2.8

Anaerobic processes, 6.2 (3.9-8.4)

Organic matter burial, 3.0

Reverse weathering

1

36 (32-46)

CaCO₃ burial

23 (22-24)

CaCO₃ burial