Alkalinity regulation in calcium carbonate-buffered lakes

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Abstract

Biogenic calcite precipitation is the removal of calcite (CaCO₃) from the epilimnion to the sediments of hard-water lakes during summer stratification, caused by increased pH during algal blooms and by nucleation of calcite crystals on surfaces of micro-algae. Although this phenomenon has been studied for decades, details of the underlying mechanisms are still debated. Using results of approximately 70,000 alkalinity measurements from 13 hard-water Swiss lakes (each with approximately 30 yr to 50 yr of monitoring), we demonstrate that (i) calcium carbonate-buffered lakes act as alkalinity sinks during summer stratification but act as CO₂ sources during and immediately after spring overturn; (ii) as the alkalinity concentration ([Alk_mix]) and the total phosphorus concentration ([TP_mix]) at spring overturn increase, increasingly more alkalinity is lost from the epilimnion during summer stratification; (iii) [Alk_mix] is determined by the lake’s discharge-weighted average inflow concentration ([Alk_in]), flushing rate, mean depth and [TP_mix]; and (iv) [Alk_in] depends on the mineralogy and the land use affecting in-soil nitrification of ammonia and subsequent calcite dissolution in the catchment.

Biogeochemical processes involving calcium carbonate (calcite; CaCO₃) play important roles in lakes. Dissolution of calcite provides the major ions calcium (Ca²⁺) and bicarbonate (HCO₃⁻) that dominate the ionic composition of many hard-water lakes and to a large extent their ability to resist acidification (i.e., alkalinity buffers pH). Additionally, bicarbonate is an important source of CO₂ for aquatic photosynthesis. Bicarbonate and carbonate ions also decrease the bioavailability of toxic cationic metals (e.g., Ag, Cd, Cu, Ni, Pb, Zn) by forming inorganic complexes with the metals, and Ca²⁺ is an antagonist against cationic-metal toxicity (Meyer et al. 2007). At elevated pH values during summer due to photosynthesis, eutrophic lakes act as sinks for CO₂ and CaCO₃, partly counteracting accumulation of CO₂ in the atmosphere (Ridgewell and Zeebe 2005; Pacheco et al. 2013). This process of CO₂ uptake during summer also helps to decrease the annual net release of CO₂ to the atmosphere that is documented for the majority of lakes (McDonald et al. 2013; Raymond et al. 2013).

High loads of alkalinity are imported to lakes by tributaries that are mostly oversaturated with respect to calcite (Gruber et al. 2000). The calcite is dissolved in low-pH soils by groundwater that contains high partial pressures of CO₂ originating from decomposition of organic matter (Stumm and Morgan 1996). Even in similar neighboring catchments, alkalinity concentrations of tributaries can vary widely because alkalinity is influenced by a variety of other factors such as runoff (Raymond et al. 2008), acid deposition or decreased acid mine drainage (Kaushal et al. 2013), sewage effluents (Barnes and Raymond 2009) or excessive application of nitrogen fertilizers (Perrin et al. 2008).

Lakes loose alkalinity via their outflows and via the settling of newly formed CaCO₃ from the epilimnion to the sediments. Biogenically induced precipitation of calcite is the major process driving loss of alkalinity from the epilimnion in hard-water lakes (Brunskill 1969; Kelts and Hsu 1978). Although spectacular large-scale “whiting events” are observed from satellites (Strong and Eadie 1978), details of the underlying processes are still debated.

In the middle of the last century, Thomas (1953) postulated a positive coupling of epilimnetic calcite precipitation and total phosphorus concentration at lake overturn in spring ([TP_mix]) and suggested the involvement of phytoplankton production. Several authors (e.g., Rossnacht 1980; Murphy et al. 1983; Kleiner 1988; Hamilton et al. 2009) provided evidence for adsorption of phosphate to calcite surfaces or coprecipitation of phosphate with calcium carbonate, suggesting a negative feedback mechanism to eutrophication that simultaneously attenuates epilimnetic calcite precipitation and an increase in TP as the load to a lake increases. Therefore, epilimnetic alkalinity removal might be limited to a lake-specific maximum.

In laboratory experiments, Reddy (1977) reported that orthophosphate retarded CaCO₃ precipitation, and Giannimaras and Koutsoukos (1987) reported inhibition of calcite precipitation...
Table 1. Characteristics of the 13 hard-water Swiss lakes included in this study.

<table>
<thead>
<tr>
<th>Lake</th>
<th>Abbr.</th>
<th>Volume km³</th>
<th>Surface km²</th>
<th>Mean depth m</th>
<th>Flushing rate yr⁻¹</th>
<th>[Alkmix]*</th>
<th>[TPmix]**</th>
<th>Data range‡</th>
<th>Sampling interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Geneva</td>
<td>GE</td>
<td>89.1</td>
<td>582.2</td>
<td>153.1</td>
<td>0.089</td>
<td>1.80±0.03</td>
<td>20–94</td>
<td>1959–2012</td>
<td>biweekly</td>
</tr>
<tr>
<td>Lake Constance</td>
<td>CO</td>
<td>48.7</td>
<td>481.7</td>
<td>96.5</td>
<td>0.24</td>
<td>2.48±0.05</td>
<td>6–89</td>
<td>1963–2012</td>
<td>biweekly</td>
</tr>
<tr>
<td>Lake Neuchatel</td>
<td>NE</td>
<td>13.8</td>
<td>217.9</td>
<td>63.3</td>
<td>0.13</td>
<td>2.63±0.06</td>
<td>7–129</td>
<td>1967–2005</td>
<td>monthly</td>
</tr>
<tr>
<td>Lake Brienz</td>
<td>BR</td>
<td>5.0</td>
<td>29.8</td>
<td>168.5</td>
<td>0.39</td>
<td>1.52±0.05</td>
<td>3–28</td>
<td>1979–2010</td>
<td>biyearly</td>
</tr>
<tr>
<td>Lake Zürich</td>
<td>ZH</td>
<td>3.37</td>
<td>66.6</td>
<td>50.6</td>
<td>0.88</td>
<td>2.55±0.07</td>
<td>19–80</td>
<td>1984–2013</td>
<td>monthly</td>
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<tr>
<td>Walensee</td>
<td>WA</td>
<td>2.51</td>
<td>24.1</td>
<td>104.3</td>
<td>0.66</td>
<td>1.10±0.02</td>
<td>3–31</td>
<td>1976–2014</td>
<td>monthly</td>
</tr>
<tr>
<td>Sempachersee</td>
<td>SE</td>
<td>0.642</td>
<td>14.1</td>
<td>45.5</td>
<td>0.063</td>
<td>2.45±0.12</td>
<td>12–165</td>
<td>1976–2013</td>
<td>monthly</td>
</tr>
<tr>
<td>Aegerisee</td>
<td>AE</td>
<td>0.353</td>
<td>7.28</td>
<td>48.6</td>
<td>0.16</td>
<td>2.46±0.11</td>
<td>41–139</td>
<td>1980–2012</td>
<td>monthly</td>
</tr>
<tr>
<td>Hallwilersee</td>
<td>HA</td>
<td>0.295</td>
<td>9.95</td>
<td>29.7</td>
<td>0.26</td>
<td>2.86±0.11</td>
<td>17–235</td>
<td>1976–2012</td>
<td>bi-/monthly</td>
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<td>Baldeggsee</td>
<td>BA</td>
<td>0.174</td>
<td>5.22</td>
<td>33.4</td>
<td>0.23</td>
<td>3.43±0.17</td>
<td>23–520</td>
<td>1982–2013</td>
<td>monthly</td>
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<tr>
<td>Greifensee</td>
<td>GR</td>
<td>0.149</td>
<td>8.45</td>
<td>17.6</td>
<td>0.86</td>
<td>4.18±0.18</td>
<td>28–437</td>
<td>1977–2013</td>
<td>monthly</td>
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<tr>
<td>Pfäffikersee</td>
<td>PF</td>
<td>0.059</td>
<td>3.20</td>
<td>18.5</td>
<td>0.44</td>
<td>3.67±0.11</td>
<td>15–313</td>
<td>1972–2012</td>
<td>monthly</td>
</tr>
<tr>
<td>Türlensee</td>
<td>TU</td>
<td>0.0065</td>
<td>0.50</td>
<td>13.1</td>
<td>0.52</td>
<td>3.87±0.23</td>
<td>11–82</td>
<td>1988–2013</td>
<td>monthly</td>
</tr>
</tbody>
</table>

* [Alkmix] = alkalinity at lake overturn.
† [TPmix] = total phosphorus concentrations at spring overturn during the observation period.
‡ Only complete datasets including mean annual water discharge Q, [TPmix], [Alkmix], and epilimnetic alkalinity in spring and autumn were used for the mass-balance calculations and constitute the listed data range, even though longer data series existed for some parameters.
Alkalinity is generally determined by endpoint titration with HCl in unfiltered samples according to the European Norm EN ISO 9631-1 (GSM 2002), and [TP] is measured with the molybdenum blue method (EN ISO 6878) (GSM 2002) following an oxidative digestion (e.g., with K₂S₂O₈) of the unfiltered sample.

In the monitoring program of several lakes (GR, PF, and TU before 2000), alkalinity was analyzed only during a limited time period. We estimated the missing alkalinity values from conductivity measurements considering lake-specific linear relationships between alkalinity and conductivity. For Lake Geneva, alkalinity and conductivity data were not available for the period 1988–1992. Instead, we estimated alkalinity by calculating the difference in normality (as mEq L⁻¹) between the sum of the base cations (Ca²⁺, Mg²⁺, Na⁺, K⁺) and the sum of the strong-acid anions (Cl⁻, NO₃⁻, SO₄²⁻) (eq. 14 in Stumm and Morgan 1996: p. 165). The coefficient of variation (R²) for the regression of the estimated alkalinitities vs. the measured alkalinitities for the years 1992–2011 was 0.73, with a slope of 0.94.

Sediment-trap data were available for Baldeggersee (1994–1996; M. Sturm, unpubl. data) and Sempachersee (1988–1993; Gächter and Meyer 1990). In Baldeggersee, sequential traps were exposed at the 60-m depth (i.e., ~ 6 m above the lake bottom), allowing daily resolution of calcite deposition during the stratified season (Sturm et al. 1982). In Sempachersee, cylindrical traps deployed at the 20-m depth were sampled biweekly.

### Alkalinity mass-balance calculations

The annual alkalinity mass balance of seasonally mixing lakes is mainly affected by their annual external, riverine alkalinity load; their photosynthesis-related epilimnetic accumulation of alkalinity during summer stratification; their hypolimnetic accumulation of alkalinity during summer stratification; their alkalinity export via their effluent, as follows:

\[
\frac{\Delta[\text{Alk}_{\text{mix}}]}{\Delta t} = Q \times [\text{Alk}_{\text{in}}] - \Delta[\text{Alk}_{\text{epi}}] \times V_{\text{epi}} + \Delta[\text{Alk}_{\text{hypo}}] \times V_{\text{hypo}} + \beta \times [\text{Alk}_{\text{mix}}]
\]

where \([\text{Alk}_{\text{in}}]\) is the discharge-weighted average alkalinity of all inflows; \(\Delta[\text{Alk}_{\text{epi}}]\) and \(\Delta[\text{Alk}_{\text{hypo}}]\) are the difference between the volume-weighted alkalinity at spring overturn and at the end of summer stratification in the epilimnion and hypolimnion, respectively; \(Q\) is the total annual water discharge out of the lake; \(V_{\text{epi}}\) and \(V_{\text{hypo}}\) are the volumes of the total lake, the epilimnion (operationally assumed to be the layer between 0 m and 10 m depth), and the hypolimnion, respectively; and \(\beta\) equals \([\text{Alk}_0]/[\text{Alk}_{\text{mix}}]\) (where \([\text{Alk}_0]\) is the average alkalinity at the lake surface feeding the outlet). For the sake of simplification and lack of detailed data we assumed that evaporation equals precipitation. When \([\text{Alk}_{\text{mix}}]\) reaches an among-years steady state, Eq. 1 simplifies to:

\[
Q \times \beta \times [\text{Alk}_{\text{mix}}] = Q \times [\text{Alk}_{\text{in}}] - \Delta[\text{Alk}_{\text{epi}}] \times V_{\text{epi}} + \Delta[\text{Alk}_{\text{hypo}}] \times V_{\text{hypo}}
\]

Based on the data presented by Thomas (1953), Vollenweider (1970) suggested in his Fig. 12 that \(\Delta[\text{Alk}_{\text{epi}}]\) increases as \([\text{TP}_{\text{mix}}]\) increases and approaches a maximum \(\Delta[\text{Alk}_{\text{epi}}]_{\text{max}}\) at high \([\text{TP}_{\text{mix}}]\). That relationship can be numerically described by the following Monod-type function:

\[
\Delta[\text{Alk}_{\text{epi}}] = \Delta[\text{Alk}_{\text{epi}}]_{\text{max}} \times \frac{[\text{TP}_{\text{mix}}]}{K + [\text{TP}_{\text{mix}}]}
\]

where \(K\) is the half-saturation constant (i.e., the \([\text{TP}_{\text{mix}}]\) at which \(\Delta[\text{Alk}_{\text{epi}}] = 0.5 \times \Delta[\text{Alk}_{\text{epi}}]_{\text{max}}\).

The calcite saturation index (\(\Omega_{\text{CaCO}_3}\)) is:

\[
\Omega_{\text{CaCO}_3} = \frac{[\text{Ca}^{2+}] [\text{CO}_3^{2-}]}{K_{\text{sp}}}
\]

where \([\text{Ca}^{2+}]\) and \([\text{CO}_3^{2-}]\) represent the chemical activities of the calcium and carbonate ions, and \(K_{\text{sp}}\) is the solubility product of calcite at the ambient temperature.

### Calculation of CO₂ equilibria

In most lakes, the weak-acid anions are dominated by the bicarbonate/carbonate system (Stumm and Morgan 1996). In such systems, alkalinity usually is defined as:

\[
[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] + K_{\text{H}_2\text{CO}_3}\]

Using the mass action laws for the carbonate system (Supporting Information A), the concentration of solvated CO₂ in water ([CO₂(aq)]) can be calculated from the alkalinity, as follows:

\[
[\text{CO}_2(aq)] = \frac{[\text{Alk}] [\text{H}^+]}{1 + 2K_{\text{H}_2\text{CO}_3} [\text{H}^+] / [\text{H}_2\text{CO}_3]} \times K_{\text{H}_2\text{CO}_3} K_{\text{a}_1} K_{\text{a}_2}
\]

where \(K_{\text{a}_1}\) and \(K_{\text{a}_2}\) are the first and second dissociation constants of H₂CO₃, respectively, and \(K_{\text{H}_2\text{CO}_3}\) is the formation constant for H₂CO₃. Those thermodynamic constants (\(K_{\text{H}_2\text{CO}_3}, K_{\text{a}_1}, K_{\text{a}_2}\)) were estimated for the corresponding surface-water temperature according to Plummer and Busenberg (1982). The CO₂ saturation index \(\Omega_{\text{CO}_2}\) relates the partial pressure of CO₂(aq) observed in the surface water to the atmospheric partial pressure CO₂( atm) obtained from the Mauna Loa dataset for the corresponding year (annual mean, available at http://www.esrl.noaa.gov/gmd/ccgg/trends/co2/co2_annmean_mlo.txt):

\[
\Omega_{\text{CO}_2} = \frac{[\text{CO}_2(aq)]}{[\text{CO}_2(\text{atm})]}
\]

### Atmospheric acidic deposition

Acidic deposition from atmospheric precipitation was estimated from data of the Swiss National Air Pollution
Monitoring Network (NABEL) at the stations Rigi, Payerne, Dübendorf, and Chaumont as 57 mmol m$^{-2}$ yr$^{-1}$, considering that after deposition the oxidation of one equivalent of NH$_4^+$ releases two equivalents of H$^+$. Because direct deposition of this acidity (i) to lake surfaces would decrease epilimnetic alkalinity concentrations by only approximately 5.7 mmol L$^{-1}$ (i.e., less than approximately 1% of the generally observed losses), and (ii) to the surface of calcareous catchments would increase the alkalinity of the groundwater at most by approximately 28 mmol L$^{-1}$, atmospheric acid deposition did not significantly affect the alkalinity of the investigated hard-water lakes.

**Results and discussion**

**Seasonal alkalinity losses from the epilimnia of two eutrophic lakes**

Based on data from biweekly (Sempachersee) and daily (Baldeggersee) sediment-trap sampling, calcite precipitation is restricted to several distinctly separated periods during summer stratification (Fig. 1a,d), as previously reported for Lakes Constance (Stabel 1985) and Lucerne (Bloesch 1974). Unlike TP, epilimnetic alkalinity did not decrease immediately after spring overturn (March to April) in the top 10 m but instead continued to increase until May or even June or July, when calcite precipitation started. Thereafter, epilimnetic TP concentration and alkalinity decreased concurrently and rapidly, indicating a coupled transformation of bicarbonate/carbonate and phosphorus from the dissolved to the particulate phase and subsequent settling of calcite and phosphorus as described by Sturm et al. (1982). Epilimnetic alkalinity started to decrease when the surface saturation index $X_{CO_2}$ approached or decreased below unity (compare Fig. 1a with 1b and Fig. 1d with 1e). This behavior persisted despite a 23% decrease of [TP] in Sempachersee during the same time period (1988–1993; Fig. 2).

Epilimnetic alkalinity losses during summer stratification varied considerably among years in Baldeggersee and Sempachersee (Table 2; Supporting Information Fig. SI-B1). However, they compare well with results reported by Bloesch...
and (iv) one mole of CaCO₃ biased to a minor extent by settling allochthonous particles, (iii) sediment-trap measurements might occasionally be sedimentation but also to the continuous epilimnetic alkalinity loss during summer (1974) for the mesotrophic Bay of Horw in Lake Lucerne, where the average epilimnetic alkalinity loss during summer stratification was 11.6 mol m⁻². Taking into account that (i) the average epilimnion depth might have deviated from the assumed 10 m, (ii) Δ[Alk_epi] was subject not only to calcite sedimentation but also to the continuous epilimnetic alkalinity load via inflowing waters and the loss via the effluent, (iii) sediment-trap measurements might occasionally be biased to a minor extent by settling allochthonous particles, and (iv) one mole of CaCO₃ corresponds to two moles of alkalinity, the calcite collected in sediment traps during summer stratification agreed well with the observed epilimnetic alkalinity losses (Table 2). This result indicates calcite sedimentation was the dominant process causing the epilimnetic alkalinity losses.

In agreement with Sturm et al. (1982) and Stabel (1986), who reported no dissolution of calcite particles during settling, we did not observe a significant hypolimnetic alkalinity increase during summer stratification in any of the lakes. Instead, the peak loss of alkalinity from the epilimnion in summer was approximately matched by the peak flux of calcite measured in the sediment traps, while the peak gain of alkalinity in the epilimnion during fall/winter resulted in only a small corresponding signal in the hypolimnion (Fig. 1c,f). There was always a slight decrease of hypolimnetic alkalinity immediately before the epilimnetic alkalinity began to peak in fall/winter, suggesting that the epilimnetic gain was due to two separate processes: (i) post-stratification circulation that mixed the higher-alkalinity hypolimnetic water with the lower-alkalinity epilimnetic water, followed by (ii) higher-alkalinity riverine inflows mixing with the lower-alkalinity epilimnetic water. The post-stratification hypolimnetic alkalinity did not decrease much because the large volume of hypolimnetic water mixed with a relatively small volume of epilimnetic water, but the epilimnetic alkalinity increased considerably because of the large V_hypo: V_epi ratio. Therefore, we considered the hypolimnetic alkalinity increase was negligible for annual-budget calculations (Eqs. 1 and 2).

In concept, some calcite that reaches the sediment surface should be partly re-dissolved by the generally lower sediment porewater pH (relative to the hypolimnetic pH), resulting from aerobic decomposition of organic matter in the sediment. However, considerable dissolution of calcite does not appear to occur in these hard-water lakes; otherwise, bicarbonate would diffuse into the hypolimnion and increase [Alk_hypo]. Inhibition of calcite dissolution due to sorption of dissolved organic matter and phosphate onto calcite (Stumm and Morgan 1996, page 816) might be a plausible explanation for the lacking or negligible increase in [Alk_hypo] during summer stratification.

**CO₂ exchange between lake surface water and the atmosphere**

Lakes situated in calcareous catchments are sinks for calcite. Net CO₂ production by heterotrophic soil organisms results in elevated concentrations of carbonic acid in the water percolating through the soil, dissolving calcite and thus elevating concentrations of Ca²⁺, HCO₃⁻, and CO₃²⁻. Consequently, newly emerged groundwater is oversaturated with respect to CO₂ and calcite. Some of the Ca²⁺ and CO₃²⁻ combine to form calcite as the CO₂ concentration

### Table 2. Annual settling flux of calcite (CaCO₃) collected in sediment traps in two hard-water Swiss lakes [Sempachersee, Gächter and Meyer (1990); Baldeggersee (Sturm, unpublished data)] and annual maximum difference in epilimnetic alkalinity (Δ[Alk_epi], expressed as a loss from the top 10-m layer) and hypolimnetic alkalinity (Δ[Alk_hypo], expressed as a gain) from lake overturn in spring until the end of summer stratification, as calculated from monitoring data. One mole of settled CaCO₃ corresponds to two moles of alkalinity lost from the epilimnion.

<table>
<thead>
<tr>
<th>Lake</th>
<th>Year</th>
<th>CaCO₃ flux</th>
<th>Δ[Alk_epi]</th>
<th>Δ[Alk_hypo]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sempachersee</td>
<td>1988</td>
<td>5.3</td>
<td>10.9</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>1989</td>
<td>3.1</td>
<td>9.9</td>
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<td></td>
<td>1990</td>
<td>2.7</td>
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<td></td>
<td>1991</td>
<td>2.6</td>
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<tr>
<td></td>
<td>1992</td>
<td>3.2</td>
<td>7.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Baldeggersee</td>
<td>1994</td>
<td>6.0</td>
<td>11.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>1995</td>
<td>6.1</td>
<td>10.9</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>1996</td>
<td>7.3</td>
<td>15.0</td>
<td>0.0</td>
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</table>
equilibrates with the atmosphere (resulting in higher pH). The seasonal variation of the CO$_2$ saturation index ($\Omega_{\text{CO}_2}$) is depicted in Fig. 1b,d for Baldeggersee and Sempachersee, respectively. Both lakes were oversaturated with respect to atmospheric CO$_2$ during spring overturn but became undersaturated with respect to atmospheric CO$_2$ by the end of April, when the lakes started stratifying and epilimnetic primary production resulted in a net-removal of CO$_2$. Additionally, re-equilibration of formerly oversaturated hypolimnetic water with the atmosphere would have contributed in part to the decrease of the CO$_2$ oversaturation.

Although the CO$_2$ concentration of the surface water was up to sixfold to sevenfold oversaturated in Sempachersee and up to ninefold to nineteenfold oversaturated in Baldeggersee during spring overturn, those CO$_2$ concentrations decreased steeply usually in March (Fig. 1b,d). By the end of April, the lakes rapidly and reproducibly converted from being sources of CO$_2$ to being sinks (i.e., when calcite started precipitating from the epilimnion [Fig. 1a,c]).

An extensive analysis of factors controlling CO$_2$ emission from lakes is beyond the scope of this study. However, the excess CO$_2$ that vents to the atmosphere during and immediately after spring overturn must originate from (i) CO$_2$ that accumulated in the hypolimnion due to microbial decomposition of organic matter, (ii) direct infiltration of CO$_2$-oversaturated groundwater into the hypolimnion (Lewandowski et al. 2015), and (iii) tributaries importing water that had not equilibrated with the atmosphere before reaching the lakes (Gruber et al. 2000; Marcé et al. 2015). After spring overturn, at least some lakes become seasonal sinks for CO$_2$. For example, as soon as primary production started, Baldeggersee and Sempachersee were undersaturated with respect to CO$_2$ until the end of the stratification period. Both lakes were strongly eutrophic during the time periods shown in Fig. 1 and, thus, belonged to the class of lakes that are CO$_2$ sinks at least during summer stratification (Pacheco et al. 2013).

**Increasing CO$_2$ oversaturation with increasing [Alk$_{\text{mix}}$]**

Data from 13 hard-water lakes in Switzerland covering approximately 30 yr to 50 yr of monitoring (Fig. 3) demonstrate that during lake overturn (December–March), $\Omega_{\text{CO}_2}$ increased as [Alk$_{\text{mix}}$] increased. Hence, all of these lakes are sources of CO$_2$ to the atmosphere during that time. This amounts to a translocation of carbon from particulate calcite in soils to gaseous CO$_2$ in the atmosphere, via the intermediate of dissolved HCO$_3^-$ and CO$_3^{2-}$. Because (i) water in equilibrium with calcite and atmospheric pCO$_2$ (approximately 400 ppm atmospheric) results in an equilibrium alkalinity of approximately 1.24 mmol L$^{-1}$ (at 10°C, see Supporting Information B) (Stumm and Morgan 1996), and (ii) all 13 of the hard-water lakes have [Alk$_{\text{mix}}$] greater than or equal to 1.1 mmol L$^{-1}$ (Table 1), they were probably close to saturation or even oversaturated with respect to calcite during spring overturn even though no calcite precipitation was observed at spring overturn (Fig. 1a,c). The calculated equilibrium alkalinity concentration of 1.24 mmol L$^{-1}$ matches well with the value of 1.18 mmol L$^{-1}$ obtained from the linear regression of $\Omega_{\text{CO}_2}$ vs. [Alk$_{\text{mix}}$] at $\Omega_{\text{CO}_2} = 1$ in Fig. 3. Both results also support the conclusion of Marcé et al. (2015) that lakes with alkalinity exceeding approximately 1.2 mmol L$^{-1}$ are potential sources of CO$_2$ to the atmosphere during spring overturn, and dissolved inorganic carbon imported by inflows is their major source of the CO$_2$ (McDonald et al. 2013). However, in low-alkalinity waters, respiration of organic matter is the dominant CO$_2$ source (Lopez et al. 2011).

**Processes inducing precipitation of calcite from the epilimnion**

Starting with summer stratification, loss of CO$_2$ to the atmosphere and in-lake CO$_2$ removal by photosynthesis increases pH and further intensify the calcite oversaturation in the epilimnion. According to equilibrium calculations, the consumption of CO$_2$ (or HCO$_3^-$) in the productive zone causes precipitation of calcite in proportion to the consumed dissolved inorganic carbon (Supporting Information B). However, even lakes fed by tributaries that mainly drain crystalline catchments like Walensee (the Linth river, average alkalinity of 2.22 mmol L$^{-1}$) and Lake Constance (the Alpenrhein river, average alkalinity of 2.00 mmol L$^{-1}$) have up to 6- to 20-fold epilimnetic calcite oversaturation throughout the productive season, suggesting that in-lake alkalinity is not simply controlled by macroscale thermodynamic equilibria but by multiple processes discussed below.

Major calcite precipitation events are induced by algal primary production removing CO$_2$ or HCO$_3^-$, thus, locally increasing pH and providing crystallization sites within the DBL surrounding individual carbon-assimilating algal cells.
(Thompson et al. 1997; Dittrich and Obst 2004; Dittrich et al. 2004). This microscale view, considering pH and alkalinity gradients across the DBL, helps to understand why calcite can precipitate at the surface of plankton cells before it forms in the bulk water.

After the activation energy for the formation of a stable nucleus at an algal cell surface is exceeded, calcite crystals remain stable and additional calcite precipitates onto the new and growing surface (Morse et al. 2007). However, three processes inhibit unlimited crystal growth.

1. The growth rate of calcite crystals does not increase in proportion to the increased surface area (House and Totton 1982).
2. $\Omega_{\text{CaCO}_3}$ decreases within the diffusive boundary layer of the particle if the rate of calcite precipitation exceeds the rate of resupply of $\text{Ca}^{2+}$ and $\text{CO}_3^{2-}$ by diffusion.
3. The specific gravity of the particle continuously increases from an initial value of approximately 1 (the specific gravity of the algal cell) and approaches a value of 2.7 (the specific gravity of calcite).

Therefore, the growing calcite particle eventually sinks out of the productive zone into the hypolimnion, where respired $\text{CO}_2$ decreases the pH, thus, causing crystal growth to slow and eventually to halt as a result of the lower $\Omega_{\text{CaCO}_3}$.

As the rate of permanent burial of calcite in the sediment increases, the steady-state $[\text{Alk}_{\text{mix}}]$ decreases relative to the riverine and/or groundwater $[\text{Alk}_{\text{in}}]$. Therefore, the steady-state alkalinity of a lake depends to a large extent on (1) the mineral composition of its catchment and the production of carbonic and other acids in the catchment soil (which determine $[\text{Alk}_{\text{in}}]$) and (2) the rate of precipitation of calcite mainly induced by in-lake photosynthetic $\text{CO}_2$ removal.

**Calcite precipitation from the epilimnion is controlled by $[\text{Alk}_{\text{mix}}]$ and $[\text{TP}_{\text{mix}}]$**

Epilimnetic alkalinity losses, $\Delta[\text{Alk}_{\text{epi}}]$ in the 13 hard-water lakes increased approximately in proportion to $[\text{Alk}_{\text{mix}}]$ (Fig. 4a). However, the considerable scatter around this general trend suggests additional regulation of $\Delta[\text{Alk}_{\text{epi}}]$ by other factors. Consistent with Thomas (1953) and Vollenweider (1970), trophic state as indicated by $[\text{TP}_{\text{mix}}]$ appears to be another important regulator (Fig. 4b). Both relationships (Fig. 4a,b) indicate that epilimnetic alkalinity losses are simultaneously controlled by $[\text{Alk}_{\text{mix}}]$ and $[\text{TP}_{\text{mix}}]$. This finding is not surprising because (i) $[\text{Alk}_{\text{mix}}]$ defines the maximum possible amount of the $\text{CaCO}_3$ that can precipitate before re-establishing $\text{CaCO}_3$ saturation equilibrium, and (ii) in most temperate lakes in the northern hemisphere, $\text{CO}_2$ consumption by planktonic photosynthesis is controlled by bioavailable phosphorus (Vollenweider 1970).

We assume that incident solar radiation, light attenuation within the water column, temperature, and $[\text{Alk}_{\text{mix}}]$ define the maximum possible areal photosynthetic $\text{CO}_2$ assimilation and thus the maximum fraction $a$ of $[\text{Alk}_{\text{mix}}]$ that can precipitate during summer stratification. In concept, if $a$ is constant across all lakes, the maximum epilimnetic alkalinity loss ($\Delta[\text{Alk}_{\text{epi}}]_{\text{max}}$) is:

$$\Delta[\text{Alk}_{\text{epi}}]_{\text{max}} = a \times [\text{Alk}_{\text{mix}}]$$

(8)

Substitution of Eq. 8 into Eq. 3 results in:

$$\Delta[\text{Alk}_{\text{epi}}] = a \times [\text{Alk}_{\text{mix}}] \times \frac{[\text{TP}_{\text{mix}}]}{K + [\text{TP}_{\text{mix}}]}$$

(9)

From our database, we selected oligotrophic lakes with $[\text{TP}_{\text{mix}}] < 20 \mu g \text{P L}^{-1}$, mesotrophic lakes with $[\text{TP}_{\text{mix}}]$ ranging from 30 $\mu g \text{P L}^{-1}$ to 70 $\mu g \text{P L}^{-1}$, and eutrophic lakes with $[\text{TP}_{\text{mix}}] > 100 \mu g \text{P L}^{-1}$ (Fig. 5). A nonlinear regression fit of Eq. 9...
to the approximately 500 data points was highly significant ($R^2 = 0.624$; $F_{2, 479} = 2.475$; $p < 0.001$) and yielded values of $a = 0.295$ yr$^{-1}$ (95% C.I. = 0.281 to 0.308) and $K = 10.4$ µg P L$^{-1}$ (95% C.I. = 8.01 to 12.73). That is, on average, a maximum of 30% of the epilimnetic alkalinity is converted to calcite and settles into the hypolimnion during summer stratification in these hard-water lakes. Because the hypolimnetic alkalinity does not increase during summer stratification (Table 2), it appears that the particulate CaCO$_3$ descending through the hypolimnion does not dissolve but accumulates in the sediment. As Fig. 5 shows, Eq. 9 can successfully discriminate between [Alk$_{\text{epi}}$] of oligotrophic and eutrophic lakes. However, due to the remaining unexplained scatter, [Alk$_{\text{epi}}$] values of mesotrophic lakes partly overlap with the ranges predicted for both oligotrophic and eutrophic lakes. We attribute this scatter to the fact that, in addition to [Alk$_{\text{mix}}$] and [TP$_{\text{mix}}$], [Alk$_{\text{epi}}$] might be affected by other determinants that vary among lakes (e.g., temperature, water-column mixing, subsurface light attenuation, concentration of allochthonous particles, availability of other nutrients, algal species composition, and concentrations of humics and other calcium-complexing compounds).

Substituting Eq. 9 into Eq. 2 and assuming $\Delta[\text{Alk}_{\text{hyp}}]$ is negligible (as shown in Table 2) results in the following approximation for steady-state [Alk$_{\text{mix}}$]:

$$[\text{Alk}_{\text{mix}}] = [\text{Alk}_{\text{in}}] \times \frac{\rho z_{\text{epi}}}{\frac{\rho z_{\text{epi}}}{\frac{a}{K + [\text{TP}_{\text{mix}}]} \times \frac{[\text{TP}_{\text{mix}}]}{[\text{TP}_{\text{mix}}]} \times \frac{\rho}{K + [\text{TP}_{\text{mix}}]}}$$

where $\rho = Q/V$, $z_{\text{epi}}$ is the average depth of the epilimnion, and $z$ is the average depth of the lake. Equation 10 indicates that at steady state and a specified [Alk$_{\text{in}}$], [Alk$_{\text{mix}}$] decreases as [TP$_{\text{mix}}$] increases and as $\rho$ and $z$ decrease. For example, as expected from Eq. 10, annual average [Alk$_{\text{epi}}$] in Sempachse (ρ = 0.063 yr$^{-1}$, z = 45.5 m) increased significantly by 0.0128 mmol L$^{-1}$ yr$^{-1}$ (95% C.I. = 0.0093 to 0.0164; $R^2 = 0.66, p < 0.0001$) as [TP] decreased by approximately 88% during the 30-yr period 1984–2013 (Fig. 2a). In contrast, as also expected from Eq. 10, annual average [Alk$_{\text{epi}}$] in Baldeggersee increased by less and not significantly (only 0.0046 mmol L$^{-1}$ yr$^{-1}$ [95% C.I. = 0.0006 to 0.0098]; $R^2 = 0.11, p = 0.078$) as [TP] decreased by approximately the same percentage as in Sempachse during the same 30-yr period (Fig. 2b), because of the higher flushing rate and shallower average depth in Baldeggersee ($\rho = 0.23$ yr$^{-1}$, $z = 33.4$ m). In concept, [Alk$_{\text{mix}}$] asymptotically approaches a maximum value (Fig. 6) that theoretically should equal [Alk$_{\text{in}}$] as $\rho$ becomes large (see Eq. 10). Baldeggersee might have been approximately at its asymptotic maximum annual average [Alk$_{\text{epi}}$] during the past 30 yr; however, the gradual linear, statistically significant increase of annual average [Alk$_{\text{epi}}$] in Sempachse during the past 30 yr does not appear to be leveling off, suggesting that lake might attain a considerably higher epilimnetic alkalinity if [TP$_{\text{mix}}$] continues to decrease and all other factors (e.g., average annual flushing rate) remain approximately constant.

**Factors affecting [Alk$_{\text{in}}$]**

[Alk$_{\text{in}}$] depends on the climate, the types and quantities of minerals exposed to weathering, and anthropogenic activities (e.g., wastewater discharge, impacts of agriculture, and
air pollution) in lake catchments (Stets et al. 2014). To the south of a line reaching from the inflows of the Rivers Rhone and Rhine into Lakes Geneva and Constance, respectively, Swiss rivers drain catchments of mainly crystalline nature that are partly interspersed with calcareous sediments; whereas calcareous sediments dominate north of that line (Fig. 7). For example, major parts of the catchments of the tributaries to Walensee and to Lakes Brienz and Geneva are south of that line, and Lake Zürich is situated downstream of Walensee, thus, broadly explaining the low alkalinity concentrations in those four lakes (Table 1; Fig. 6).

Contrary to expectations, the alkalinity concentrations differ considerably among several mid-sized hard-water lakes in the sedimentary, calcareous Molasse Basin of the north-central Swiss plateau (NE, SE, AE, HA, BA, GR, PF, and TU; Table 1). These differences are in part attributed to the positive relationship between [Alk_{mix}] and lake flushing rate (Fig. 6). However, the differences in [Alk_{mix}] among lakes that have similar flushing rates (e.g., BA and HA) are probably also caused by differences in their [Alk_{in}]. In general, because of epilimnetic alkalinity losses during summer stratification, [Alk_{in}] to a downstream lake (e.g., HA) will be lower than to its upstream lake (e.g., BA) even if their tributaries drain catchments that contain similar bedrock and soils. Furthermore, differences in [Alk_{in}] can be partly attributed to differences in land use in the lakes’ drainage basins (e.g., with respect to the extent of fertilization, plowing, and soil draining).

Because leaching of municipal wastewater into groundwater is prohibited by law in Switzerland, and because atmospheric acid deposition is negligible, groundwater alkalinity that exceeds natural background values in upland soils can only be due to land use (i.e., application of ammonia-containing inorganic fertilizers or organic manure to fields, tilling practices, etc.). Unambiguously, the application of acid generating fertilizers increases rock weathering and thus increases concentrations of base cations (Ca^{2+}, Mg^{2+}, Na^+, K+) and NO_3^- (Aquilina et al. 2012; Kaushal et al. 2013). The behavior of alkalinity, however, is not as well understood. Johnson et al. (1997) documented increasing alkalinity concentrations with increasing intensive agricultural land use in streams draining clayey soils in the U.S. Midwest, and Raymond and Cole (2003) estimated that alkalinity load in the Mississippi River has increased twofold to threefold since pre-agricultural times. The liming of soils with low buffering capacity to counteract acidification increases alkalinity export (Oh and Raymond 2006; Barnes and Raymond 2009). In the calcareous catchment of the Garonne River (France), Semhi et al. (2000) reported up to 30% of the river’s alkalinity may be due to carbonate dissolution with acid induced by application of nitrogen-containing fertilizers. For the same catchment, Perrin et al. (2008) observed that intensive N fertilization caused a shift of the surface-water (Ca+Mg)/HCO_3 ratio and thus a relative loss of alkalinity while weathering rates increased in total.

Soil fertilization can affect [Alk_{in}]. For example, nitrification of 1 equivalent of NH_4^+ (Eq. 11) generates 2 equivalents of alkalinity (Eq. 13) due to the linked dissolution of calcite (Eq. 12).

\[
\text{NH}_4^+ + 2\text{O}_2 = \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O} \quad \text{(11)}
\]
Fig. 8. Hypolimnetic alkalinity ([Alk\textsubscript{hypo}]) in 68 Swiss lakes increases as total nitrogen (TN) concentration increases (data adapted from Müller et al. 1998). Because it is relatively constant throughout the year, hypolimnetic alkalinity is used here as a surrogate for whole-lake alkalinity. The data are fit to a Monod-type function in which \([\text{Alk}_{\text{hypo}}] = \frac{[\text{Alk}_{\text{hypo}}]_{\text{max}} \times \text{TN} / (\text{K} + \text{TN})}{\text{K}}\), where \([\text{Alk}_{\text{hypo}}]_{\text{max}} = 5.47\) (95% C.I. = 4.71-6.22; \(p < 0.0001\)) and \(K = 0.948\) (95% C.I. = 0.556-1.339; \(p < 0.0001\)) (\(R^2\) for regression = 0.58).

\[
2\text{CaCO}_3(s) + 2\text{H}^+ = 2\text{Ca}^{2+} + \text{HCO}_3^- \\
\text{NH}_4^+ + 2\text{O}_2 + 2\text{CaCO}_3(s) = \text{NO}_3^- + 2\text{Ca}^{2+} + 2\text{HCO}_3^- + \text{H}_2\text{O}
\]

This may explain why in groundwater, the highest alkalinity and \(\text{NO}_3^-\) concentrations occur concurrently in the northern Swiss lowlands, where the density of crop farms is highest (Fig. 7). The conclusion that nitrification affects alkalinity is further supported by a positive relationship between total nitrogen and alkalinity concentrations in 68 Swiss lakes (Fig. 8). However, other factors possibly contributing to an increased alkalinity export from soils cannot be ruled-out. For example, most fertile soils preferred for farming contain more-easily weathered minerals such as calcite. Therefore, the observed parallel increases of alkalinity and \(\text{NO}_3^-\) in waters draining agricultural soils may be partly coincidental. Moreover, frequent tilling and other mechanical working of soils may also increase the dissolution of minerals by increasing the contact of the interstitial water with freshly exposed surfaces.

**Summary and conclusions**

A lake’s alkalinity depends primarily on its riverine alkalinity load, the amount of calcite precipitation during summer stratification, its total phosphorus concentration, its average depth, and its flushing rate (Eq. 10). Although a lake’s alkalinity load is mainly controlled by the mineral composition of its catchment, other factors (e.g., soil fertilization, tilling, etc.) may also contribute to increased alkalinity concentrations in its tributaries.

During spring overturn, lakes discharge excess \(\text{CO}_2\) to the atmosphere, thus increasing the pH and preconditioning the lake water for photosynthesis-induced calcite precipitation during summer stratification. Lakes tend to maintain long-term steady-state alkalinity among years unless \(\text{TP}_{\text{mix}}\), \(\beta\), or \(\rho\) change.

The decrease of alkalinity in the epilimnion of hard-water lakes during summer stratification is related in part to \([\text{Alk}_{\text{mix}}]\) and \([\text{TP}_{\text{mix}}]\) (Fig. 4). However, the remaining scatter in this relationship suggests other factors also help control \(\Delta[\text{Alk}_{\text{ppl}}]\). For example, the concentration of orthophosphate inhibiting calcite precipitation, micro-algae species composition and population density, concentrations of other nutrients, temperature, and the concentration of allochthonous particles providing sites for calcite crystallization are involved in the regulation of lake alkalinity. Therefore, processes related to anthropogenic activity (e.g., climate change, temperature and hydrology, remediation of eutrophied lakes, soil fertilization) can alter a lake’s alkalinity and thus alter its ability to buffer acidic precipitation and control the bioavailability of metals.

**References**


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The regulation of alkalinity in calcium carbonate-buffered lakes

Supplemental Information

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Suppl. Information A - Derivation of eq. 6:

Alkalinity

\[
\text{Alk} = \left[ \text{HCO}_3^- \right] + 2\left[ \text{CO}_3^{2-} \right] + \left[ \text{OH}^- \right] - \left[ \text{H}^+ \right]
\]  (5)

1. Express \(\text{HCO}_3^-\) and \(\text{CO}_3^{2-}\) in Eq. 5 as functions of \(\text{CO}_2\) using Eq. 5a-5c:

\[
\text{CO}_2\text{(aq)} + \text{H}_2\text{O} = \text{H}_2\text{CO}_3
\]  (5a)

\[
\text{H}_2\text{CO}_3 = \text{HCO}_3^- + \text{H}^+
\]  (5b)

\[
\text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+
\]  (5c)

mass action equation from Eq. 5a:

\[
\frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2\text{(aq)}]} = K_{H,CO_3}
\]  (5d)

mass action equation from Eq. 5b:

\[
\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = K_a
\]  (5e)

mass action equation from Eq. 5c:

\[
\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = K_a
\]  (5f)

insert \(\text{H}_2\text{CO}_3\) from Eq. 5d in Eq. 5e and solve for \(\text{HCO}_3^-\):

\[
[\text{HCO}_3^-] = [\text{CO}_2\text{(aq)}] \frac{K_{H,CO_3}K_a}{[\text{H}^+]}.
\]  (5g)

insert \(\text{HCO}_3^-\) from Eq. 5g in Eq. 5f and solve for \(\text{CO}_3^{2-}\):

\[
[\text{CO}_3^{2-}] = [\text{CO}_2\text{(aq)}] \frac{K_{H,CO_3}K_aK_a}{[\text{H}^+]^2}.
\]  (5h)

2. Insertion of Eqs. 5g and 5h in Eq. 5, omission of [OH] and [H+], and rearrangement results in

\[
[\text{CO}_2\text{(aq)}] = \frac{[\text{Alk}] [\text{H}^+]}{1 + \frac{2K_a}{[\text{H}^+]}} K_{H,CO_3} K_a.
\]  (6)
**Suppl. Information B** - Proportionality of soluble calcite concentration when CO\(_2\) (aq) is consumed during assimilation (assuming thermodynamic equilibrium)

Reactions in Table S1 were considered for the modeling of the CO\(_2\)-calcite system. Calculations were performed using the application ChemEQL (http://www.eawag.ch/research_e/surf/Researchgroups/sensors_and_analytic/chemeql.html). The alkalinity calculated for 10\(^\circ\)C at the present pCO\(_2\) of 400 ppm is 1.24 mmol L\(^{-1}\).

**Table S1:**
Reactions considered for equilibrium calculations with ChemEQL. Thermodynamic equilibrium constants were estimated with the relationships from Plummer and Busenberg (1982) for 10\(^\circ\)C. The log \(K_{\text{CaOH}^+}\) value is from Stumm and Morgan (1996).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Constant</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3)</td>
<td>(\log K_{\text{H}_2\text{CO}_3})</td>
<td>-1.269</td>
</tr>
<tr>
<td>(\text{H}_2\text{CO}_3 = \text{HCO}_3^- + \text{H}^+)</td>
<td>(\log K_{a1})</td>
<td>-6.463</td>
</tr>
<tr>
<td>(\text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+)</td>
<td>(\log K_{a2})</td>
<td>-10.488</td>
</tr>
<tr>
<td>(\text{Ca}^{2+} + \text{HCO}_3^- = \text{CaHCO}_3^+)</td>
<td>(\log K_{\text{CaHCO}_3^+})</td>
<td>0.968</td>
</tr>
<tr>
<td>(\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3\text{(aq)})</td>
<td>(\log K_{\text{CaCO}_3\text{(aq)}})</td>
<td>3.134</td>
</tr>
<tr>
<td>(\text{Ca}^{2+} + \text{H}_2\text{O} = \text{CaOH}^- + \text{H}^+)</td>
<td>(\log K_{\text{CaOH}^-})</td>
<td>-12.78</td>
</tr>
<tr>
<td>(\text{CaCO}_3\text{(s)} = \text{Ca}^{2+} + \text{CO}_3^{2-})</td>
<td>(\log K_{s0})</td>
<td>-8.410</td>
</tr>
<tr>
<td>(\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-)</td>
<td>(\log K_w)</td>
<td>-14.380</td>
</tr>
</tbody>
</table>

**Figure SI-B1:** Calculation of the concentration of dissolved calcite when pure water establishes equilibrium with calcite and a constant partial pressure of atmospheric CO\(_2\) ([pCO\(_2\); 10\(^{-6}\) – 4x10\(^{-3}\) atm]) results in the red line. The blue line represents the total dissolved inorganic carbon, and the green line is the concentration of TIC that originates from CO\(_2\) dissolved from the atmosphere.
Figure SI-B2: Relation of dissolved calcite and DIC calculated for Figure SI-B1. The concentration of dissolved calcite decreases in proportion with decreasing dissolved inorganic carbon (e.g., CO₂ assimilation during photosynthesis). The relationship is best described with a second-order polynomial relationship.

\[
[Ca^{2+}] = 0.52[\text{DIC}] - 0.11[\text{DIC}]^2
\]