Processes determining the marine alkalinity and calcium carbonate saturation state distributions

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Received: 1 July 2014 – Published in Biogeosciences Discuss.: 21 July 2014
Revised: 21 November 2014 – Accepted: 21 November 2014 – Published: 19 December 2014

Abstract. We introduce a composite tracer for the marine system, Alk*, that has a global distribution primarily determined by CaCO₃ precipitation and dissolution. Alk* is also affected by riverine alkalinity from dissolved terrestrial carbonate minerals. We estimate that the Arctic receives approximately twice the riverine alkalinity per unit area as the Atlantic, and 8 times that of the other oceans. Riverine inputs broadly elevate Alk* in the Arctic surface and particularly near river mouths. Strong net carbonate precipitation results in low Alk* in subtropical gyres, especially in the Indian and Atlantic oceans. Upwelling of dissolved CaCO₃-rich deep water elevates North Pacific and Southern Ocean Alk*. We use the Alk* distribution to estimate the variability of the calcite saturation state resulting from CaCO₃ cycling and other processes. We show that regional differences in surface calcite saturation state are due primarily to the effect of temperature differences on CO₂ solubility and, to a lesser extent, differences in freshwater content and air–sea disequilibria. The variations in net calcium carbonate cycling revealed by Alk* play a comparatively minor role in determining the calcium carbonate saturation state.

1 Introduction

Our goal is to use high-quality total alkalinity (AT) observations to examine the effects of calcium carbonate cycling on marine AT and calcium carbonate saturation states. This study is motivated in part by ocean acidification. With marine calcite saturation states decreasing due to anthropogenic carbon uptake (Orr et al., 2005), it is important to understand the degree to which carbonate cycling impacts the calcium carbonate saturation state.

Carbonate saturation state is a measure of how supersaturated seawater is with respect to a given mineral form of calcium carbonate. It is expressed for calcite as the ratio \(\Omega_{C}\) between the product of Ca\(^{2+}\) and CO\(_2\)\(^{-}\) ion concentrations and the calcite thermodynamic equilibrium solubility product. Values of \(\Omega_{C}\) greater than 1 indicate calcite precipitation is favored thermodynamically over calcite dissolution, and the reverse is true for values less than 1.

Marine calcium carbonate cycling includes both internal and external calcium carbonate sources and sinks. Internal cycling refers to the formation of 67–300 T mol AT yr\(^{-1}\) worth of calcium carbonate in the surface ocean (Berelson et al., 2007) and net dissolution of most of this calcium carbonate at depth. External marine carbonate cycling refers to inputs of carbonate minerals dissolved in rivers, sediment pore waters, hydrothermal vent fluids, and submarine groundwater discharge, as well as to loss due to biogenic carbonate mineral burial and authigenic mineralization in sediments. Rivers add 33 T mol AT yr\(^{-1}\) worth of dissolved bicarbonate to the ocean (Cai et al., 2008). Wolery and Sleep (1988) estimate that hydrothermal vents add an additional 6.6 T mol AT yr\(^{-1}\), though deVilliers (1998) argues the hydrothermal contribution may be as high as 30 T mol AT yr\(^{-1}\). Submarine groundwater discharge is poorly constrained, but it is thought to exceed riverine inputs in some areas (Moore, 2010).

We investigate calcium carbonate cycling using the global AT distribution in a dataset we created by merging the Global Data Analysis Project (GLODAP), Carbon in the North Atlantic (CARINA), and Pacific Ocean Interior...
Carbon (PACIFIC) discrete data products (Key et al., 2004, 2010; Velo et al., 2009; Suzuki et al., 2013). We have combined and gridded these data products using methods detailed in Supplement document SA. We use our gridded data set in our calculations to limit sampling biases and to enable us to make volume-weighted mean property estimates.

Dickson (1981) defines total alkalinity as the concentration excess “of proton acceptors formed from weak acids (pK ≤ 4.5) relative to proton donors (weak bases with pK > 4.5)” at a reference temperature, pressure, and ionic strength. \( A_T \) can be thought of as a measure of how well-buffered seawater is against changes in pH. This operational definition gives \( A_T \) (expressed in mol kg\(^{-1}\)) several properties that make it an especially useful carbonate system parameter for examining carbonate cycling:

1. It mixes conservatively
2. … and is therefore diluted and concentrated linearly by evaporation and precipitation.
3. It responds in predictable ways to calcium carbonate cycling
4. … as well as organic matter formation and remineralization.
5. It is not changed by air–sea exchange of heat or carbon dioxide.
6. It is, however, affected by anaerobic redox reactions (Chen, 2002).

We are primarily interested in calcium carbonate cycling, item 3 in our list. In Sect. 2 of this paper we therefore define a tracer we call Alk\(^*\) that removes the majority of the influences of organic matter cycling (item 4), freshwater cycling (item 2), and non-sedimentary anaerobic redox reactions (item 6) while still mixing conservatively, remaining insensitive to gas exchange, and responding to calcium carbonate cycling. In Sect. 3 we discuss processes that govern the Alk\(^*\) distribution globally, by ocean basin, and regionally. In Sect. 4 we define a metric to quantify the influence of various processes on the marine calcite saturation state. We use this metric with our gridded data set and Alk\(^*\) to determine the relative importance of the various controls on calcite saturation state in the ocean and at the ocean surface. We summarize our findings in Sect. 5.

### 2 The Alk\(^*\) tracer

In defining Alk\(^*\), we take advantage of the potential alkalinity (Brewer et al., 1975) concept to remove the majority of the influence of organic matter cycling and denitrification, and use a specific salinity normalization scheme (Robbins, 2001) to remove the influence of freshwater cycling. We detail the Alk\(^*\) definition and the reasoning behind it in this section.

The influence of organic matter cycling on \( A_T \) is due primarily to the biologically driven marine nitrogen cycle. Nitrate uptake for anaerobic denitrification and the production of amino acids occurs in a \( \sim 1 : 1 \) mole ratio with the release of molecules that increase \( A_T \) (Chen, 2002). Similarly, nitrate from fixation of nitrogen gas and remineralization of amino nitrogen is released in a \( 1 : 1 \) mole ratio with acids that titrate away \( A_T \) (Wolf-Gladrow et al., 2007). This observation led Brewer et al. (1975) to propose the idea of “potential alkalinity” as the sum of \( A_T \) and nitrate, with the aim of creating a tracer that responds to the cycling of calcium carbonates without changing in response to organic matter cycling. Feely et al. (2002) since used a variant that relies on the empirical relationship between dissolved calcium concentrations, \( A_T \), and nitrate determined by Kanamori and Ikegami (1982). This variant has the advantage of implicitly accounting for the \( A_T \) changes created by the exchange of numerous other components of marine organic matter besides nitrate (e.g., sulfate and phosphate). We thus use the ratio found by Kanamori and Ikegami (1982) to define potential alkalinity (\( A_P \)).

\[
A_P = A_T + 1.26 \times [\text{NO}_3^-] \tag{1}
\]

While the empirical Kanamori and Ikegami (1982) ratio of 1.26 may be specific to the elemental ratios of the North Pacific, Wolf-Gladrow et al. (2007) provide a theoretical derivation from Redfield ratios and obtain a similar value of 1.36.

The sensitivity of the \( A_T \) distribution to freshwater cycling is due primarily to the dilution or concentration of the large background \( A_T \) fraction that does not participate in carbonate cycling on timescales of ocean mixing. This background fraction behaves conservatively, so we call it conservative potential alkalinity (\( A_P^c \)) and estimate it directly from salinity as

\[
A_P^c \equiv \frac{S A_P}{S} \tag{2}
\]

Here, terms with a bar are reference values chosen as the mean value for those properties in the top 20 m of the ocean. We obtain a volume-weighted surface \( A_P \) (2305 µmol kg\(^{-1}\)) to \( \bar{S} \) (34.71) ratio of 66.40 µmol kg\(^{-1}\) from our gridded data set. The mean surface values are chosen in an effort to best capture the impact of freshwater cycling where precipitation and evaporation occur.

Robbins (2001) showed that subtracting an estimate of the conservative portion of a tracer, such as \( A_P^c \), produces a salinity-normalized composite tracer that mixes conservatively. This scheme also retains the \( 2 : 1 \) change of \( A_T \) to dissolved inorganic carbon (\( C_T \)) with carbonate cycling. We follow this approach in our definition of Alk\(^*\). In Supplement document SB we estimate this approach removes 97.5 % of the influence of freshwater cycling on potential alkalinity and reduces the influence of freshwater cycling on Alk\(^*\) to less than 1 % of the Alk\(^*\) variability. In Supplement document SC we demonstrate that Alk\(^*\) mixes conservatively, and
we briefly contrast Alk\(^*\) to traditionally normalized potential alkalinity which does not mix conservatively (Jiang et al., 2014).

In total, we define Alk\(^*\) as the deviation of potential alkalinity from \(A^*_\text{T}\):

\[
\text{Alk}^* = A_p - A^*_\text{P} = A_p - \frac{A_p}{S} \equiv A_p - 66.4 \times S.
\]

where Alk\(^*\) has the same units as \(A_T\) (\(\mu mol \text{ kg}^{-1}\)). The Alk\(^*\) distribution is attributable primarily to carbonate cycling plus the small (in most places) residual variation due to freshwater cycling that is not removed by subtracting \(A^*_\text{T}\). However, hydrothermal vent fluid and non-denitrification anaerobic redox chemistry may substantively affect alkalinity distributions in certain marine environments, and Alk\(^*\) distributions could not be attributed purely to internal and external calcium carbonate cycling in these locations.

Mean global surface Alk\(^*\) is 0 by definition, and thus Alk\(^*\) can have negative as well as positive values. For reference, more than 95% of our gridded Alk\(^*\) data set falls between \(-35\) and \(220 \mu mol \text{ kg}^{-1}\). Comparing gridded Alk\(^*\) to Alk\(^\text{est}\) from measurements suggests a standard disagreement of order 10 \(\mu mol \text{ kg}^{-1}\). We adopt this number as an estimate of standard gridded Alk\(^*\) error despite noting there are reasons to suspect that this value could be either an underestimate (correlated errors) or an overestimate (we are directly comparing instantaneous point measurements to estimates for annual averages for a grid cell).

3 Alk\(^*\) distributions

We consider Alk\(^*\) distributions globally, by ocean basin, and regionally in the context of sources and sinks of the tracer both globally and regionally. We pay special attention to riverine Alk\(^*\) because it is easily identified where it accumulates near river mouths.

3.1 Global distribution of Alk\(^*\)

Figure 1 maps surface Alk\(^*\) (top 50 m) at the measurement stations. We provide this figure to show where we have viable Alk\(^*\) estimates and to demonstrate that our gridded data product adequately captures the measured Alk\(^*\) distribution. Figure 2 maps gridded global surface \(A_T\), salinity, Alk\(^*\), and phosphate distributions and masks the regions that are lacking data in Fig. 1.

The similarity of the \(A_T\) (Fig. 2a) and salinity (Fig. 2b) distributions demonstrates the strong influence of freshwater cycling on the surface marine \(A_T\) distribution (see also Millero et al., 1998; Jiang et al., 2014). The dissimilarity between Alk\(^*\) (Fig. 2c) and salinity (Fig. 2b) suggests Alk\(^*\) removes the majority of this influence. The phosphate (Fig. 2d) and
mean gridded Alk* for each basin (in writing). We attribute the decrease in Alk* as salinity increases – especially visible in the low-salinity bins in the Arctic Ocean (Fig. 5d) – to mixing between high-Alk*, low-salinity river water and low-Alk*, high-salinity open-ocean water. Net precipitation in the tropics and net evaporation in the subtropics widens the histograms across a range of salinities and alkalinites without affecting Alk* in Fig. 5a, b, and c. The Alk* elevation associated with upwelled water is most visible in Fig. 5e where Upper Circumpolar Deep Water upwelling near the Polar Front results in high-frequency (i.e., warm colored) histogram bins at high-Alk*. Similarly, the high-frequency Alk* bins in Fig. 5b with salinity between 32.5 and 33.5 are from the North Pacific Subpolar Gyre, and are due to upwelled old, high-Alk* water (cf. the Si* tracer in Sarmiento et al., 2004). River water contributions can be most easily seen in a scattering of low-frequency (cool colored), high-Alk* as well as low-salinity bins in the Arctic Ocean.

The surface Southern Ocean has the highest Alk* followed by the Arctic and the Pacific. The Indian and Atlantic have similar and low mean Alk*. The high mean Southern Ocean Alk* is due to upwelling. The high mean Arctic surface Alk* is due to riverine input. The Atlantic and the Arctic together receive ~65% of all river water (Dai and Trenberth, 2002). We construct a budget for terrestrial A_T sources to the various surface ocean basins using the following assumptions:

1. the A_T of 25 large rivers are as given by Cai et al. (2008);
2. the volume discharge rates of 200 large rivers are as given by Dai and Trenberth (2002);
3. groundwater and runoff enter each ocean in the same proportion as river water from these 200 rivers;

3.2 Alk* by ocean basin

In Fig. 5 we provide 2-D color histograms of discrete surface Alk* and salinity measurements for the five major ocean basins. Figure 5 also indicates a single volume-weighted
Figure 4. Zonal mean gridded phosphate (in µmol kg\(^{-1}\)) in the (a) Atlantic, (b) Pacific, (c) Indian, and (d) the Arctic oceans plotted against latitude and depth.

4. the \(A_T\) of all water types that we do not know from assumption 1 is the 1100 µmol kg\(^{-1}\) global mean value estimated by Cai et al. (2008);

5. 40\(^\circ\)N is the boundary between the Atlantic and the Arctic, and 40\(^\circ\)S is the boundary between the Southern and the Atlantic oceans (based upon the region of elevated surface phosphate in Fig. 2d).

Our detailed budget is provided as Supplement file SD. We estimate 40% of continentally derived \(A_T\) enters the Atlantic, 20% enters the Arctic, and 40% enters all remaining ocean basins. These ocean areas represent 17, 5, and 78% of the total surface ocean area in our gridded data set, respectively, so the Arctic receives approximately twice as much riverine \(A_T\) per unit area as the Atlantic, and 8 times the rest of the world ocean. The Atlantic has the lowest open-ocean surface Alk\(^*\) value and low basin mean surface Alk\(^*\) despite the large riverine sources. The large riverine \(A_T\) input must therefore be more than balanced by strong net calcium carbonate formation. The Indian Ocean has comparably low mean surface Alk\(^*\) to the Atlantic, but a smaller riverine source. Mean Alk\(^*\) is higher in the Pacific than the Atlantic and Indian, even when neglecting the region north of 40\(^\circ\)N as we do for the Atlantic (Alk\(^*\) = \(-16.5\) µmol kg\(^{-1}\) when omitted vs. \(-22.9\) µmol kg\(^{-1}\) for the Atlantic and \(-22.2\) µmol kg\(^{-1}\) for the Indian). The difference between the

Figure 5. 2-D histograms indicating the log (base 10) of the number of measurements that fall within bins of Alk\(^*\) vs. salinity with color. Data are limited to the top 50 m of the (a) Atlantic, (b) Pacific, (c) Indian, (d) Arctic, and (e) Southern oceans. Where basins connect, the boundary between the Atlantic and the Arctic oceans is 40\(^\circ\)N, between the Atlantic and the Indian it is 20\(^\circ\)E, between the Indian and the Pacific it is 131\(^\circ\)E, between the Pacific and the Atlantic it is 70\(^\circ\)W, and between the Southern Ocean and the other oceans it is 40\(^\circ\)S.
basins and deeper waters or smaller Pacific basin mean net calcium carbonate formation.

3.3 Riverine Alk* regionally

For river water with negligible salinity, Alk* equals the potential alkalinity. This averages around 1100 µmol kg$^{-1}$ globally (Cai et al., 2008) but is greater than 3000 µmol kg$^{-1}$ for some rivers (Beldowski et al., 2010). Evidence suggests that riverine $A_T$ is increasing due to human activities (Kaushal et al., 2013).

The most visible riverine Alk* signals are in the Arctic due to the large riverine runoff into this comparatively small basin and the confinement of this low-density riverine water to the surface (Jones et al., 2008; Yamamoto-Kawai et al., 2009; Azetsu-Scott et al., 2010). Figure 3d shows the high Arctic Alk* plume is confined to the top ~200 m. Figure 1 shows that these high Alk* values extend along the coast of Greenland and through the Labrador Sea. Alk* decreases with increasing salinity in this region (Fig. 5d) due to mixing between the fresh high-Alk* surface Arctic waters and the salty, lower-Alk* waters of the surface Atlantic. Gascard et al. (2004a, b) suggest that waters along the coast of Norway are part of the Norwegian Coastal Current and originate in the Baltic and North seas where there are also strong riverine inputs (Thomas et al., 2005).

Elevated Alk* can also be seen in the Bay of Bengal, with surface values ~100 µmol kg$^{-1}$ higher than those in the central Indian Ocean. This bay has two high-$A_T$ rivers that join and flow into it, the Brahmaputra ($A_T = 1114$ µmol kg$^{-1}$) and the Ganges ($A_T = 1966$ µmol kg$^{-1}$) (Cai et al., 2008). Figure 6b provides an Alk* depth section for this region. The riverine Alk* plume can be clearly seen in the top 50 m. No similar increase is seen in the Arabian Sea (Fig. 6a), where the Indus River (1681 µmol kg$^{-1}$) discharges only ~1/10th of the combined volume of the Brahmaputra and the Ganges.

The Amazon River is the largest single riverine marine $A_T$ source. This river has low $A_T$ (369 µmol kg$^{-1}$; Cai et al., 2008) but has the largest water discharge volume of any river, exceeding the second largest – the Congo – by a factor of ~5 (Dai and Trenberth, 2002). Consequently, the Amazon discharges approximately 50% more $A_T$ per year than the river with the second-largest $A_T$ discharge, the Changjiang (Cai et al., 2008). The Amazon’s influence can be seen as a region of abnormally low salinity and $A_T$ in Fig. 2a and b. Despite the high discharge volume, the influence is only barely visible as a region of elevated Alk* in Fig. 2c due to the comparatively low Amazon Alk*. However, the influence of the Amazon on Alk* can be seen in the seasonal Alk* cycle in the Amazon plume. Figure 7 provides a map of Alk* for this region scaled to show the influence of this low-Alk* river in the Northern Hemisphere (a) winter and (b) summer months. The higher Alk* found for summer months is consistent with Amazon discharge and $A_T$ seasonality (Cooley et al., 2007) and the radium-isotope-based finding of Moore et al. (1986) that Amazon River outflow comprises 20–34% of surface water in this region in July compared to only 5–9% in December.

3.4 Regional abiotic carbonate cycling

The Red Sea portion of Fig. 6a is strongly depleted in Alk* and contains the lowest single Alk* measurement in our data set, −247 µmol kg$^{-1}$. The GEOSCECS expedition Red Sea alkalinity measurements (Craig and Turekian, 1980) predate alkalinity reference materials (Dickson et al., 2007) but are supported by more recent measurements (Silverman et al., 2007). Like Jiang et al. (2014), we attribute low Red Sea Alk* to exceptionally active calcium carbonate formation. Brewer and Dyrrsen (1985) provide seawater chemistry measurements from the neighboring Persian Gulf that suggest
strong calcium carbonate formation results in low Alk\(^*\) there as well (\(< -240 \mu mol\, kg^{-1}\) along the Trucial Coast).

The Red Sea is one of the only regions where \(\Omega_C\) is sufficiently high for abiotic carbonate precipitation to significantly contribute to overall carbonate precipitation (Milliman et al., 1969; Silverman et al., 2007). Notably, saturation state remains high at depth in the Red Sea (see Sect. 4.2). In this region, biogenic aragonitic corals and pteropod shells are progressively dissolved with depth in sediments, and pores left behind are filled in with high-magnesium calcite cement (Geivritz and Friedman, 1966; Almogi-Labin et al., 1986). We hypothesize biogenic carbonates are dissolved by CO\(_2\) from sedimentary organic matter remineralization, as occurs elsewhere (e.g., Hales and Emerson, 1997; Hales, 2003; Boudreau, 2013), and that high deep Red Sea \(\Omega_C\) leads to abiotic re-calcification in sediment pores. Morse et al. (2006) find that synthetic high-magnesium calcite – unlike biogenic high-magnesium calcite – is less soluble than aragonite, so this substitution is favored thermodynamically if the abiotic mineral forms similarly to the synthetic mineral.

Calcium carbonate has recently been found as metastable ikaite (a hydrated mineral with the formula CaCO\(_3\) • 6H\(_2\)O) in natural sea ice (Dieckmann et al., 2008). Ikaite cycling provides a competing explanation for the high Arctic surface Alk\(^*\) values if high-A\(_T\), low-salinity, ikaite-rich ice melt becomes separated from low-A\(_T\), high-salinity rejected brines. However, riverine A\(_T\) inputs better explain the magnitude of the feature: the \(< 5\) mg ikaite L\(^{-1}\) sea ice that Dieckmann et al. (2008) found in the Antarctic could only enrich A\(_T\) of the surface 100 m by \(< 1\) \(\mu\)mol kg\(^{-1}\) for each meter of ice melted, and Arctic surface 100 m Alk\(^*\) is elevated by 59 \(\mu\)mol kg\(^{-1}\) relative to the deeper Arctic in our gridded data set. By contrast, Jones et al. (2008) estimate a \(< 5\%\) average riverine end-member contribution to the shallowest 100 m of this region, which accounts for \(< 55\) \(\mu\)mol kg\(^{-1}\) Alk\(^*\) enrichment. Also, surface Alk\(^*\) in the Southern Ocean – which has sea ice but lacks major rivers – is not similarly elevated relative to surface phosphate (Fig. 2) or deep Alk\(^*\) (Fig. 3).

## 4 Controls on the calcite saturation state

The Alk\(^*\) tracer provides an opportunity to estimate the impact of carbonate cycling on \(\Omega_C\). In addition to (1) carbonate cycling, \(\Delta\Omega_C\) is affected by (2) organic matter cycling, (3) freshwater cycling, (4) pressure changes on seawater, (5) heating and cooling, and (6) A\(_T\) changes from nitrogen fixation and denitrification. For each of these six processes, we estimate the standard deviation of the net influence of the process globally by considering the standard deviation of a "reference" tracer \(R_i\) for the process, \("\sigma_{R_i}\"\), where \(R_i\) is Alk\(^*\) for CaCO\(_3\) cycling, phosphate for organic matter cycling, salinity for freshwater cycling, pressure for pressure changes, temperature for heating and cooling, and N\(^*\) (Gruber and Sarmiento, 1997) for nitrogen fixation and denitrification. We use the standard deviation of the reference tracer as a measure of the oceanic range of the net influence of the corresponding process. We measure the impact of this range on \(\Omega_C\) using a metric \(M_i\), which we define as

\[
M_i = \sigma_{R_i} \left| S_{R_i} \right|, \tag{6}
\]

where \(S_{R_i}\) is the \(\Omega_C\) sensitivity to a unit process change in \(R_i\), which we estimate in Appendix A. We are interested in the relative importance \(I_i\) of our six processes, so we also calculate the percentage that each metric value estimate contributes to the sum of all six metric value estimates:

\[
I_i = 100\% \times \frac{M_i}{\sum_{i=1}^{6} M_i}. \tag{7}
\]

We derive and estimate our metric and its uncertainty in Appendix A. We carry out our analysis for the full water column assuming it to be isolated from the atmosphere (Sect. 4.1), and also for just the top 50 m of the water column assuming it to be well-equilibrated with the atmosphere (Sect. 4.2). Finally, we consider how equilibration with an atmosphere with a changing pCO\(_2\) alters surface \(\Omega_C\).

### 4.1 Process importance in atmospherically isolated mean seawater from all ocean depths

Our metric \(M_i\) is an estimate of the standard deviation of the global distribution of \(\Delta\Omega_C\) resulting from the \(i\)th process. Our relative process importance metric \(I_i\) is an estimate of the percentage of overall variability of the \(\Omega_C\) distribution that can be attributed to that process. We provide \(M\) and \(I\) values for mean seawater from the full water column alongside the \(R_i\), \(S_{R_i}\), and \(\sigma_{R_i}\) values used to estimate them in Table 1. These calculations assume that the seawater is isolated from the atmosphere.

Relative process importance estimates \(I\) indicate organic matter cycling (48 %) is the dominant process controlling \(\Omega_C\) for mean seawater. Changing pressure (28 %) is the second-most-important process, followed by calcium carbonate cycling (17 %), temperature changes (4 %), nitrogen fixation and denitrification (12.1 %), and freshwater cycling (7.8 %).

### 4.2 Process importance in well-equilibrated surface seawater

In Table 2 we provide \(M_i\) values for well-equilibrated seawater in the top 50 m of the ocean alongside the \(R_i\), \(S_{R_i}\), and \(\sigma_{R_i}\) used to estimate them. These surface seawater \(M_i\) values are calculated assuming the water remains equilibrated with an atmosphere with 400 \(\mu\)atm pCO\(_2\). We test the validity of this assumption by also estimating \(M\) for the observed global pCO\(_2\) variability in the Takahashi et al. (2009) global data product. This test reveals transient air–sea disequilibrium are indeed important for surface ocean \(\Omega_C\), but only as a
Table 1. Metric estimates $M_i$, relative process importance percentages $I_i$, calcite saturation sensitivities $S_{R_i}$ to unit changes in the $R_i$ reference properties, and reference property standard deviations $\sigma_{R_i}$ for the $i = 6$ processes in atmospherically isolated mean seawater from all ocean depths. We provide details on how these terms are estimated and $M_i$ and $I_i$ uncertainties are obtained.

<table>
<thead>
<tr>
<th>Process</th>
<th>$i$</th>
<th>$R_i$</th>
<th>$S_{R_i}$</th>
<th>$\sigma_{R_i}$</th>
<th>$M_i$</th>
<th>$I_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonate cycling</td>
<td>1</td>
<td>Alk$^a$</td>
<td>0.0043</td>
<td>53.5 µmol kg$^{-1}$</td>
<td>0.23</td>
<td>17%</td>
</tr>
<tr>
<td>Org. matter cycling</td>
<td>2</td>
<td>Phosphate</td>
<td>−0.0069</td>
<td>0.60 µmol kg$^{-1}$</td>
<td>0.66</td>
<td>48%</td>
</tr>
<tr>
<td>Freshwater cycling</td>
<td>3</td>
<td>Salinity</td>
<td>0.032</td>
<td>0.27</td>
<td>0.011</td>
<td>0.78%</td>
</tr>
<tr>
<td>Sinking/shoaling</td>
<td>4</td>
<td>Pressure</td>
<td>−0.00028</td>
<td>1411 db</td>
<td>0.4</td>
<td>28%</td>
</tr>
<tr>
<td>Warming/cooling</td>
<td>5</td>
<td>Temp.</td>
<td>0.014</td>
<td>4.20 °C</td>
<td>0.06</td>
<td>4%</td>
</tr>
<tr>
<td>Denit./nit. fix.</td>
<td>6</td>
<td>$N^*$</td>
<td>−0.010</td>
<td>1.6 µmol kg$^{-1}$</td>
<td>0.017</td>
<td>1.2%</td>
</tr>
</tbody>
</table>

*standard deviation of the Takahashi et al. (2009) revised global monthly $p$CO$_2$ climatology. $b$ the $M$ value for disequilibria is only calculated to test our assumption of surface seawater air–sea equilibration and is omitted from calculations of $I_i$ for comparison with Table 1.

Table 2. Metric estimates $M_i$, relative process importance percentages $I_i$, calcite saturation sensitivities $S_{R_i}$ to unit changes in the $R_i$ reference properties, and reference property standard deviations $\sigma_{R_i}$ for the $i = 6$ processes in well-equilibrated surface seawater. We provide details on how these terms are estimated and $M_i$ and $I_i$ uncertainties are obtained.

<table>
<thead>
<tr>
<th>Process</th>
<th>$i$</th>
<th>$R_i$</th>
<th>$S_{R_i}$</th>
<th>$\sigma_{R_i}$</th>
<th>$M_i$</th>
<th>$I_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonate cycling</td>
<td>1</td>
<td>Alk$^a$</td>
<td>0.0034</td>
<td>36.9 µmol kg$^{-1}$</td>
<td>0.13</td>
<td>7.8%</td>
</tr>
<tr>
<td>Org. matter cycling</td>
<td>2</td>
<td>Phosphate</td>
<td>−0.0045</td>
<td>0.51 µmol kg$^{-1}$</td>
<td>0.037</td>
<td>2.3%</td>
</tr>
<tr>
<td>Freshwater cycling</td>
<td>3</td>
<td>Salinity</td>
<td>0.20</td>
<td>0.86</td>
<td>0.22</td>
<td>13.2%</td>
</tr>
<tr>
<td>Sinking/shoaling</td>
<td>4</td>
<td>Pressure</td>
<td>−0.00083</td>
<td>15 db</td>
<td>0.011</td>
<td>0.70%</td>
</tr>
<tr>
<td>Warming/cooling</td>
<td>5</td>
<td>Temp.</td>
<td>0.14</td>
<td>8.8 °C</td>
<td>1.2</td>
<td>76%</td>
</tr>
<tr>
<td>Denit./nit. fix.</td>
<td>6</td>
<td>$N^*$</td>
<td>−0.0043</td>
<td>1.5 µmol kg$^{-1}$</td>
<td>0.006</td>
<td>0.40%</td>
</tr>
<tr>
<td>$p$CO$_2$ disequilibria $b$</td>
<td>7</td>
<td>$p$CO$_2$</td>
<td>−0.0086</td>
<td>27 µatm$^b$</td>
<td>0.23</td>
<td></td>
</tr>
</tbody>
</table>

The large increase in $C_T$ lead to surface $\Omega_C$ exceeding 6 despite extremely low Alk$^a$ ($< −200$ µmol kg$^{-1}$). The deep Red Sea is also unusual for having deep water that was warm when it last left contact with the atmosphere (the Red Sea is $> 20$ °C at $> 1000$ m depth). This provides high initial deep $\Omega_C$ that – combined with decreased influence of pressure changes at higher temperatures – keeps deep Red Sea $\Omega_C > 3$. Similarly, the lowest surface $\Omega_C$ values are in the Arctic where there are low temperatures, low salinity, and high Alk$^a$ values from riverine inputs. The importance of warming and cooling is also suggested by the correlation between $\Omega_C$ and the surface temperature ($R^2 = 0.96$). These properties are plotted in Fig. 8.
Figure 8. Gridded global (a) calcite saturation state $\Omega_C$ and (b) temperature at the surface (10 m depth surface) of our gridded CARINA, PACIFICA, and GLODAP bottle data products. Areas with exceptionally poor coverage in the data used to produce the gridded product are blacked out.

5 Conclusions

Alk* isolates the portion of the $A_T$ signal that varies in response to calcium carbonate cycling and exchanges with terrestrial and sedimentary environments from the portion that varies in response to freshwater and organic matter cycling. The salinity normalization we use has the advantage over previous salinity normalizations that it allows our tracer to mix linearly and to change in a 2:1 ratio with $C_T$ in response to carbonate cycling. We highlight the following insights from Alk*:

1. **Alk* distribution**: the Alk* distribution clearly shows the influence of biological cycling, including such features as the very low Alk* in the Red Sea due to the high calcium carbonate precipitation there. We also find evidence of strong riverine $A_T$ sources in the Bay of Bengal and in the Arctic. We show river inputs likely dominate over the small influences of ikaite cycling on the Arctic alkalinity distribution.

2. **Influence of calcium carbonate cycling on marine calcite saturation state**: Alk* allows us to quantify the net influence of calcium carbonate cycling on marine $\Omega_C$. For well-equilibrated surface waters, carbonate cycling is less influential for $\Omega_C$ than gas exchange driven by warming and cooling and freshwater cycling. At depth, the carbonate cycling signal is smaller than the signal from organic matter cycling and from pressure changes. Temperature is the dominant control on $\Omega_C$ of surface waters in equilibrium with the atmosphere. This accounts for the low calcite saturation states in the cold surface of the Arctic and Southern oceans despite high regional Alk*, and high $\Omega_C$ in the warm subtropics despite low regional Alk*.

We intend to use Alk* for two future projects. First, Alk* is superior to $A_T$ for monitoring and modeling changes in marine chemistry resulting from changes in carbonate cycling with ocean acidification. $A_T$ varies substantially in response to freshwater cycling, so Alk* trends may be able to be detected sooner and more confidently attributed to changes in calcium carbonate cycling than trends in $A_T$ (Ilyina et al., 2009). Secondly, we will estimate global steady-state Alk* distributions using Alk* sources and sinks from varied biogeochemical ocean circulation models alongside independent water mixing and transport estimates (e.g., Khatiwala et al., 2005; Khatiwala, 2007). We will interpret findings in the context of two hypotheses proposed to explain evidence for calcium carbonate dissolution above the aragonite saturation horizon: (1) that organic matter remineralization creates undersaturated microenvironments that promote carbonate dissolution in portions of the water column which are chemically supersaturated in bulk, and (2) that high-magnesium calcite and other impure minerals allow chemical dissolution above the saturation horizon.
Appendix A: Definition of the process importance metric $M$

In simplest terms, our metric is the product of the $\Omega_C$ sensitivity to a process and the variability of the net influence of the process globally. The difficulty in this calculation lies in quantifying the “net influence of a process.” We first show how we change coordinates so we can use reference tracers as a proxy measurement for these net influences.

Our metric for $\Omega_C$ variability resulting from the $i$th process is expressed as $M_i$:

$$M_i = \sigma_{R_i} \left| \frac{\partial \Omega_C}{\partial R_i} \right|,$$

(A1)

where $R_i$ is an abstract variable representing the net process influence (that we will later factor out), and $\frac{\partial \Omega_C}{\partial R_i}$ is the $\Omega_C$ sensitivity to the process. We expand $\frac{\partial \Omega_C}{\partial R_i}$ using the chain rule to include a term for $\Omega_C$ sensitivity to changes in the reference tracer $R_i$ (see Sect. 4) and a term $\frac{\partial R_i}{\partial P_i}$ representing changes in $R_i$, resulting from the $i$th process:

$$\frac{\partial \Omega_C}{\partial P_i} = \frac{\partial \Omega_C}{\partial R_i} \frac{\partial R_i}{\partial P_i}. \quad \text{(A2)}$$

In practice, we calculate $\Omega_C$ as a function of $j = 7$ properties: (1) pressure, (2) temperature, (3) salinity, (4) phosphate, (5) silicate, (6) $C_T$, and (7) $pCO_2$ for mean seawater and $pCO_2$ for surface seawater, so we use the chain rule again to expand the $\frac{\partial \Omega_C}{\partial R_i}$ terms as follows:

$$\frac{\partial \Omega_C}{\partial R_i} = \sum_{j=1}^{7} \frac{\partial \Omega_C}{\partial X_{j,i}} \frac{\partial X_{j,i}}{\partial R_i}. \quad \text{(A3)}$$

Here, the $\frac{\partial X_{j,i}}{\partial R_i}$ are assumed terms (assumptions detailed shortly) that relate the effect of the $i$th process on the $j$th property to the effect of the process on $R_i$, and the $\frac{\partial \Omega_C}{\partial X_{j,i}}$ terms reflect $\Omega_C$ sensitivity to changes in the $j$th properties used to calculate it.

We make assumptions regarding the $\frac{\partial X_{j,i}}{\partial R_i}$ terms: we relate changes in temperature from sinking or shoaling to changes in pressure using the potential temperature ($\theta$) routines of Fofonoff and Millard (1983); we assume freshwater cycling linearly concentrates $A_T$, $C_T$, phosphate, and silicate by the same ratio that it changes salinity; we relate $C_T$, phosphate, and $A_T$ changes from organic matter formation to changes in phosphate using the remineralization ratios found by Anderson and Sarmiento (1994) and the empirical relationship of Kanamori and Ikegami (1982); we also use Kanamori and Ikegami’s (1982) constant to relate changes in $A_T$ from nitrogen fixation and denitrification to changes in $N^+$ from these processes; and we assume that an increase in $A_T$ from calcium carbonate dissolution equals the $Alk^*$ increase, and that the corresponding increase in $C_T$ equals half of this $Alk^*$ increase. We neglect any changes in $C_T$ from denitrification and nitrogen fixation because these changes are better thought of as organic matter cycling occurring alongside nitrogen cycling.

We estimate $\frac{\partial \Omega_C}{\partial R_i}$ property sensitivity terms as the differences between $\Omega_C$ calculated before and after augmenting $j$th property by one unit. $\Omega_C$ is calculated with the MATLAB CO2SYS routines written by van Heuven et al. (2009) using the carbonate system equilibrium constants of Mehrbach et al. (1973), as refit by Dickson and Millero (1987). Seawater $pCO_2$ is used in place of $C_T$ for the surface seawater calculations (when $j = 7$) to calculate the change in $\Omega_C$ that remains after the surface seawater is allowed to equilibrate with the atmosphere.

We assume that the distributions of our $R_i$ reference properties are linearly related to the $P_i$ net activities of their associated processes. This assumption implies

$$\sigma_{R_i} = \sigma_{R_i} \left| \frac{\partial P_i}{\partial R_i} \right|. \quad \text{(A4)}$$

We can then substitute Eq. (A3) into Eq. (A2), and substitute this combined equation for $\frac{\partial \Omega_C}{\partial R_i}$ and Eq. (A4) into Eq. (A1).

We then cancel the $\frac{\partial P_i}{\partial P_i}$ and $\frac{\partial R_i}{\partial R_i}$ terms to obtain

$$M_i = \sigma_{R_i} \left| \sum_{j=1}^{7} \frac{\partial \Omega_C}{\partial X_{j,i}} \frac{\partial X_{j,i}}{\partial R_i} \right|. \quad \text{(A5)}$$

We then define $\Omega_C$ sensitivity $S_{R_i}$ as

$$S_{R_i} = \left| \sum_{j=1}^{7} \frac{\partial \Omega_C}{\partial X_{j,i}} \frac{\partial X_{j,i}}{\partial R_i} \right|. \quad \text{(A6)}$$

where $S_{R_i}$ is the $\Omega_C$ sensitivity to a change in the $i$th process scaled to a unit change in the reference variable for that process. We can then substitute Eq. (A6) into Eq. (A5) to obtain Eq. (6). We use Eq. (A6) to define $S_{R_i}$ and Eq. (6) to calculate $M$. We provide the values we use to estimate $S_{R_i}$ for atmospherically isolated seawater from all depths in Table A1 and for well-equilibrated surface seawater in Table A3. We perform a sample $I$ and $M$ calculation in Supplement document SE.

We use a Monte Carlo analysis to estimate variability and uncertainty in our metric $M$ and our percent relative process importance $I$ calculations. We calculate the standard deviations, $\sigma_M$ and $\sigma_I$, of pools of 1000 $M$ and $I$ estimates calculated after adjusting the seawater properties $X_j$ with a normally distributed perturbation with a standard deviation equal to the property standard deviation from the gridded data set. We find $\frac{\sigma_M}{M}$ is typically much smaller than $\frac{\sigma_I}{I}$. This is because $\Omega_C$ sensitivity is typically proportional to the $\Omega_C$ itself, so individual Monte Carlo $M$ estimates vary with the initial $\Omega_C$ and one another. Our $\sigma_M$ estimates are therefore better thought of as measures of the ranges of sensitivities found in the modern ocean, while $\sigma_I$ represent variability in the relative importance of processes. We provide $\sigma_M$ and $\sigma_I$ for atmospherically isolated seawater globally in Table A2, and for well-equilibrated surface seawater in Table A4.
Table A1. $\frac{\partial C}{\partial X_j}$ (bold text) and $\frac{\partial X_{j,i}}{\partial R_i}$ (italic text) terms used in Eq. (A5) for atmospherically isolated mean seawater from all ocean depths. These terms are specific to the $j = 7$ (columns) properties we use to calculate $\Omega_C$ and $i = 6$ (rows) processes we consider. Units for $\frac{\partial C}{\partial X_j}$ are the inverse of the listed $X_j$ units. Units for $\frac{\partial X_{j,i}}{\partial R_i}$ are the $X_j$ units divided by the $R_i$ units given in Table 1.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Pressure</th>
<th>Temp</th>
<th>Salinity</th>
<th>Phos.</th>
<th>Silicate</th>
<th>$A_T$</th>
<th>$C_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Units</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$j$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean seawater values</td>
<td>2235</td>
<td>3.7</td>
<td>34.71</td>
<td>2.15</td>
<td>49.0</td>
<td>2362</td>
<td>2254</td>
</tr>
<tr>
<td>$\frac{\partial C}{\partial X_j}$</td>
<td>$-0.00028$</td>
<td>$0.014$</td>
<td>$-0.011$</td>
<td>$-0.0085$</td>
<td>$-0.00012$</td>
<td>$0.0082$</td>
<td>$-0.0079$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process</th>
<th>$i$</th>
<th>$\frac{\partial X_{1,i}}{\partial R_1}$</th>
<th>$\frac{\partial X_{2,i}}{\partial R_2}$</th>
<th>$\frac{\partial X_{3,i}}{\partial R_3}$</th>
<th>$\frac{\partial X_{4,i}}{\partial R_4}$</th>
<th>$\frac{\partial X_{5,i}}{\partial R_5}$</th>
<th>$\frac{\partial X_{6,i}}{\partial R_6}$</th>
<th>$\frac{\partial X_{7,i}}{\partial R_7}$</th>
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</thead>
<tbody>
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<td>Carbonate cycling</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Org. matter cycling</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Freshwater cycling</td>
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<td>-</td>
<td>-</td>
<td>1</td>
<td>0.062</td>
<td>1.4</td>
<td>68</td>
<td>65</td>
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<tr>
<td>Sinking/shoaling</td>
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<td>1</td>
<td>0.00010</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Warming/cooling</td>
<td>5</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Denit./nit. fix.</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$-1.26$</td>
</tr>
</tbody>
</table>

Table A2. Monte Carlo-derived estimates for $M_i$ variability ($\sigma_{M_i}$) and $I_i$ variability ($\sigma_{I_i}$) for atmospherically isolated mean seawater from all ocean depths.

<table>
<thead>
<tr>
<th>Process</th>
<th>$i$</th>
<th>$\sigma_{M_i}$</th>
<th>$\sigma_{I_i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonate cycling</td>
<td>1</td>
<td>0.09</td>
<td>1 %</td>
</tr>
<tr>
<td>Org. matter cycling</td>
<td>2</td>
<td>0.2</td>
<td>3 %</td>
</tr>
<tr>
<td>Freshwater cycling</td>
<td>3</td>
<td>0.006</td>
<td>0.08 %</td>
</tr>
<tr>
<td>Sinking/shoaling</td>
<td>4</td>
<td>0.2</td>
<td>5 %</td>
</tr>
<tr>
<td>Warming/cooling</td>
<td>5</td>
<td>0.02</td>
<td>2 %</td>
</tr>
<tr>
<td>Denit./nit. fix.</td>
<td>6</td>
<td>0.006</td>
<td>0.1 %</td>
</tr>
</tbody>
</table>

Table A3. $\frac{\partial C}{\partial X_j}$ (bold text) and $\frac{\partial X_{j,i}}{\partial R_i}$ (italic text) terms used in Eq. (A5) for well-equilibrated surface seawater. These terms are specific to the $j = 7$ (columns) properties we use to calculate $\Omega_C$ and $i = 6$ (rows) processes we consider. Units for $\frac{\partial C}{\partial X_j}$ are the inverse of the listed $X_j$ units. Units for $\frac{\partial X_{j,i}}{\partial R_i}$ are the $X_j$ units divided by the $R_i$ units given in Table 2.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Pressure</th>
<th>Temp</th>
<th>Salinity</th>
<th>Phos.</th>
<th>Silicate</th>
<th>$A_T$</th>
<th>$pCO_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Units</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$j$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean seawater values</td>
<td>25</td>
<td>18.3</td>
<td>34.82</td>
<td>0.51</td>
<td>2.5</td>
<td>2305</td>
<td>350</td>
</tr>
<tr>
<td>$\frac{\partial C}{\partial X_j}$</td>
<td>$-0.00084$</td>
<td>$0.14$</td>
<td>$-0.022$</td>
<td>$-0.0038$</td>
<td>$-0.00013$</td>
<td>$0.0034$</td>
<td>$-0.0086$</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Process</th>
<th>$i$</th>
<th>$\frac{\partial X_{1,i}}{\partial R_1}$</th>
<th>$\frac{\partial X_{2,i}}{\partial R_2}$</th>
<th>$\frac{\partial X_{3,i}}{\partial R_3}$</th>
<th>$\frac{\partial X_{4,i}}{\partial R_4}$</th>
<th>$\frac{\partial X_{5,i}}{\partial R_5}$</th>
<th>$\frac{\partial X_{6,i}}{\partial R_6}$</th>
<th>$\frac{\partial X_{7,i}}{\partial R_7}$</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Org. matter cycling</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Freshwater cycling</td>
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<td>-</td>
<td>-</td>
<td>1</td>
<td>0.015</td>
<td>0.072</td>
<td>65.9</td>
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</tr>
<tr>
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<td>1</td>
<td>$0.00010$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Warming/cooling</td>
<td>5</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Denit./nit. fix.</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$-1.26$</td>
</tr>
</tbody>
</table>
Table A4. Monte Carlo-derived estimates for $M_i$ variability ($\sigma_{M_i}$) and $I_i$ variability ($\sigma_{I_i}$) for well-equilibrated surface seawater.

<table>
<thead>
<tr>
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<th>$\sigma_{M_i}$</th>
<th>$\sigma_{I_i}$</th>
</tr>
</thead>
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<td>0.8%</td>
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<tr>
<td>Org. matter cycling</td>
<td>2</td>
<td>0.01</td>
<td>0.2%</td>
</tr>
<tr>
<td>Freshwater cycling</td>
<td>3</td>
<td>0.04</td>
<td>0.5%</td>
</tr>
<tr>
<td>Sinking/shoaling</td>
<td>4</td>
<td>0.001</td>
<td>0.03%</td>
</tr>
<tr>
<td>Warming/cooling</td>
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<td>1%</td>
</tr>
<tr>
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<td>0.002</td>
<td>0.04%</td>
</tr>
<tr>
<td>$p\text{CO}_2$ disequilibria</td>
<td>a</td>
<td>0.05</td>
<td>a</td>
</tr>
</tbody>
</table>

$a$ disequilibria are included only as a test of our assumption of surface seawater air–sea equilibration, so these $M_i$ values are omitted from calculations of $I_i$. 
The Supplement related to this article is available online at doi:10.5194/bg-11-7349-2014-supplement.

Acknowledgements. We thank Eun Young Kwon for contributions to early versions of this research. We also thank the numerous scientists and crew that contributed to the data sets used in this study. R. Key was supported by CICS grant NA08OAR432052. We also thank Judith Hauck and three anonymous reviewers for their helpful and constructive reviews.

Edited by: J.-P. Gattuso

References


