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**Lithogenic,
atmospheric, and
biogenic cycles**

S. V. Smith and
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Linking the lithogenic, atmospheric, and biogenic cycles of silicate, carbonate, and organic carbon in the ocean

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Abstract

Geochemical theory describes long term cycling of atmospheric CO_2 between the atmosphere and rocks at the Earth surface in terms of rock weathering and precipitation of sedimentary minerals. Chemical weathering of silicate rocks takes up atmospheric CO_2, releases cations and HCO_3^- to water, and precipitates SiO_2, while $CaCO_3$ precipitation consumes Ca^{2+} and HCO_3^- and releases one mole of CO_2 to the atmosphere for each mole of $CaCO_3$ precipitated. At steady state, according to this theory, the CO_2 uptake and release should equal one another. In contradiction to this theory, carbonate precipitation in the present surface ocean releases only about 0.6 mol of CO_2 per mole of carbonate precipitated. This is a result of the buffer effect described by Ψ, the molar ratio of net CO_2 gas evasion to net $CaCO_3$ precipitation from seawater in pCO_2 equilibrium with the atmosphere. This asymmetry in CO_2 flux between weathering and precipitation would quickly exhaust atmospheric CO_2, posing a conundrum in the classical weathering and precipitation cycle.

While often treated as a constant, Ψ actually varies as a function of salinity, pCO_2, and temperature. Introduction of organic C reactions into the weathering–precipitation couplet largely reconciles the relationship. ψ in the North Pacific Ocean central gyre rises from 0.6 to 0.9, as a consequence of organic matter oxidation in the water column. ψ records the combined effect of $CaCO_3$ and organic reactions and storage of dissolved inorganic carbon in the ocean, as well as CO_2 gas exchange between the ocean and atmosphere. Further, in the absence of $CaCO_3$ reactions, Ψ would rise to 1.0. Similarly, increasing atmospheric pCO_2 over time, which leads to ocean acidification, alters the relationship between organic and inorganic C reactions and carbon storage in the ocean. Thus, the carbon reactions and ψ can cause large variations in oceanic carbon storage with little exchange with the atmosphere.

1 Introduction

Weathering and precipitation, among others processes, work in concert and coupled with other cycles to control the composition of the atmosphere and oceans (Arvidson et al. 2006). In particular, weathering and precipitation of silicate and carbonate miner-
5 als have long been recognized as key processes in the long-term global carbon cycle. Equations describing these reactions were apparently first written by Urey (1952), but Berner and Maasch (1996) have traced the concept to the much earlier work of Ebelmen (1845). The following two equations (from Urey, 1952) can be used to represent silicate mineral weathering and carbonate mineral precipitation, respectively:

10
$$CaSiO_3 + 2CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2\downarrow \qquad (1)$$

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3\downarrow + CO_2\uparrow + H_2O \qquad (2)$$
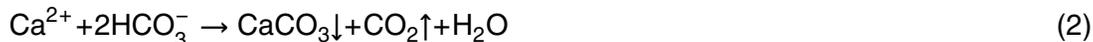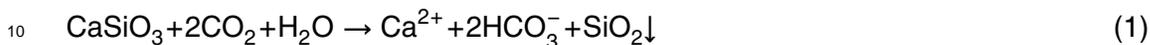
The two equations taken together provide the geochemical explanation for the counterintuitive fact that $CaCO_3$ precipitation releases CO_2 to the atmosphere, rather than taking up atmospheric CO_2 (Gattuso et al., 1999a). Carbon incorporated into $CaCO_3$
15 during precipitation is directly derived from HCO_3^- ions, not from atmospheric CO_2. That HCO_3^- is, in turn, derived from atmospheric CO_2 via the chemical weathering of rocks. These equations can be combined to describe the net reaction of igneous and metamorphic silicate minerals and CO_2 from the Earth interior to form sedimentary carbonate (e.g., $CaCO_3$) and silica (SiO_2) at the Earth surface:

20
$$CaSiO_3 + CO_2 \leftrightarrow CaCO_3\downarrow + SiO_2\downarrow \qquad (3)$$

While both sedimentary $CaCO_3$ and SiO_2 can form by inorganic chemical precipitation, their precipitation in the contemporary ocean is driven overwhelmingly by biotic processes (biomineralization).

At steady state according to Eq. (3), there is no net CO_2 flux between air and water.
25 Deviations from steady state would cause changes in the carbon content of all carbon reservoirs (rocks, water, air, organic matter). Of immediate relevance to this paper, the

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atmosphere (by far, the smallest of these reservoirs) equals about 2% of the mass of inorganic carbon dissolved in water (primarily the ocean; Berner, 1990; Sigman and Boyle, 2000). Therefore the atmosphere is particularly sensitive to deviations from steady state.

5   Herein, we summarize a problem we have recognized from oceanic ecosystems that we have studied; we use data from a well described oceanic site to explore the problem at an ocean-basin scale; and we develop geochemical scenarios in order to explore and resolve the problem.

2   Observations and calculations leading to the "carbonate conundrum"

10 Our field studies and geochemical calculations over some years for two types of calcifying marine ecosystems initially brought our attention to an apparent problem within the Ebelmen-Urey cycle; ongoing consideration of the problem has eventually led us to a plausible resolution. The relevant types of ecosystems we have studied are: (1) coral reefs, which are characterized by very rapid rates of $CaCO_3$ precipitation and
15 organic metabolism; and (2) shallow, confined basins, which typically have low rates of carbonate precipitation and organic metabolism and lack significant terrigenous or marine inputs of materials.

Both types of system receive little other than dissolved inorganic carbon from outside of the systems (much of that via the atmosphere). Both produce organic C more
20 rapidly than $CaCO_3$. Yet both types of ecosystem have residual products (sediments) dominated by $CaCO_3$, indicating that most organic C produced in the systems oxidizes there. Both show clear signals of altered water composition with respect to dissolved inorganic carbon, relative to surrounding water, in response to compositional dominance by net internal reactions. These $CaCO_3$ dominated ecosystems provide insight
25 into aspects of the oceanic CO_2 system, because of their well-defined biogeochemical signals with respect to $CaCO_3$. Lessons learned in these systems also apply to other calcifying ecosystems and communities (e.g., oceanic plankton).

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The Ebelmen-Urey reaction for carbonate precipitation and dissolution (Eq. 2) adequately characterizes these processes in freshwater, but analysis of the aqueous CO_2 system of ecosystems that we have studied led us to recognize a problem with the quantitative application of Eq. (2) in surface seawater. We found that this equation does not represent the quantitative balance between $CaCO_3$ precipitation and CO_2 gas evasion from surface seawater (Smith, 1985; Ware et al., 1991; Frankignoulle et al. 1994).

Total dissolved inorganic carbon ($DIC=[CO_2^*]+[HCO_3^-]+[CO_3^{2-}]$) is the sum of the various species or inorganic carbon, where $CO_2^*=CO_2+H_2CO_3$. The partitioning among these species is controlled by pH (as well as temperature, salinity and hydrostatic pressure). Un-dissociated H_2CO_3 is hydrated CO_2, which is in approximate gas equilibrium with atmospheric CO_2. For water of any given temperature and salinity, any two variables of the carbonate system can be used to partition the carbonate system into its various components (Park, 1969). The choice of variables is often determined by a consideration of easy or accurate measurements. This choice can also be based on scenario testing, which may be viewed as "conceptual experiments" requiring manipulation of specific variables.

Precipitating $CaCO_3$ according to Eq. (2) would remove two moles of HCO_3^- and two equivalents of total alkalinity (TA) from water for each mole of $CaCO_3$ precipitated, where TA is the number of moles of hydrogen ion equivalent to the excess of proton acceptors over proton donors (Dickson, 1981), i.e., $2HCO_3^-$ in Eq. (2). The quantitative problem with the equation may be illustrated by the following simple scenario. We begin with seawater in pCO_2 equilibrium with the atmosphere; the two variables describing the aqueous CO_2 system in this case are TA and pCO_2. Precipitate $CaCO_3$ according to Eq. (2) (removing one mol of HCO_3^- as CO_2 gas for each mol of HCO_3 removed as $CaCO_3$; this removes two equivalents of TA). Finally, calculate the pCO_2 of that water with the prescribed changes in TA and DIC. For seawater, the removal of TA and HCO_3^- as described by Eq. (2) would cause $pCO_{2(water)}$ to drop below $pCO_{2(air)}$.

It is well recognized that the physical force that causes CO_2 gas evasion from water at

pCO$_2$ equilibrium with the atmosphere is the CO$_2$ partial pressure differential between water and air, so the amount of gas flux predicted by Eq. (2) is physically impossible (Smith, 1985). The sequence of events is as follows. CaCO$_3$ precipitation immediately causes the pCO$_2$ of the water to rise. Over time, some amount of CO$_2$ will escape to the atmosphere, and the pCO$_2$ of the water will return towards atmospheric equilibrium. The maximum amount of CO$_2$ that can evade in response to the precipitation is just sufficient to return pCO$_2$ back to equilibrium.

Ware et al. (1991) pointed out that the problem of gas flux against a pressure differential could be readily circumvented by using a coefficient smaller than 1.0 in Eq. (2) for the ratio of CO$_2$ efflux to CaCO$_3$ precipitation. The coefficient they determined (for tropical surface ocean seawater (T=25°C, S=35, pCO$_{2(water)}$=pCO$_{2(air)}$=350 ppmv) was 0.6. Calculations using experimental data available in Wollast et al. (1980) were used to demonstrate that this coefficient is observed in real data. Ware et al. (1991) termed this the "0.6 rule." Frankignoulle et al. (1994) confirmed the calculations of Ware and colleagues; most importantly, they also recognized that this coefficient (which they termed ψ) is not constant, but varies as a function of temperature, salinity and pCO$_2$.

Equation (2) can be re-cast into a general expression that includes ψ:

$$Ca^{2+}+2HCO_3^- \rightarrow CaCO_3\downarrow+\psi(CO_2\uparrow+H_2O)+(1-\psi)(HCO_3^-+H^+) \qquad (4)$$
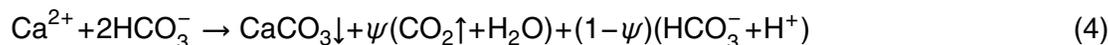
This equation demonstrates that the HCO$_3^-$ that does not escape to the atmosphere as CO$_2$ gas is retained in the water as a result of the buffer capacity of the water. Because freshwater has very low buffer capacity, the CO$_2$ is released rather than retained in the water as HCO$_3^-$ (i.e., ψ=1.0), with a concomitant decrease in pH once the water returns to partial pressure equilibrium. This formulation includes an accounting for the pH change associated with the reaction.

Frankignoulle (1994) presented the buffer factors by which ψ can be calculated directly. The calculations as performed by Ware et al. (1991), before and after precipitation or dissolution of some hypothetical amount of CaCO$_3$, implicitly invoke these buffer factors.

The "0.6 rule," or relationship between $CaCO_3$ precipitation and CO_2 gas evasion, has come to be generally recognized and treated as approximately constant, without apparent recognition that it poses a conundrum with respect to the Ebelmen-Urey cycle. We term this, the "carbonate conundrum." If the equations of that cycle are accepted as a qualitatively correct representation of the long-term carbon cycle of weathering and precipitation of silicate and carbonate minerals, then replacing Eq. (2) with (4) (that is, with $\psi < 1.0$) sets up a large asymmetry between the uptake and release of atmospheric CO_2 (Eq. 1).

If we assume steady state, more CO_2 is apparently removed from the contemporary atmosphere by $CaSiO_3$ weathering than is released by $CaCO_3$ precipitation. The magnitude of this asymmetry is substantial. Application of the "0.6 rule" to estimated present rates of net $CaCO_3$ burial ($\sim 30 \times 10^{12}$ mol yr^{-1}; from Milliman and Droxler, 1996) suggests that the asymmetry would be sufficient to exhaust atmospheric CO_2 ($\sim 60 \times 10^{15}$ mol) in $< 10^4$ years. Clearly atmospheric fluctuations of this magnitude do not occur on this time scale. Oceanic processes must have some internal mechanism to allow for substantial fluctuation of internal DIC with relatively little atmospheric exchange.

Despite this obvious problem, let us tentatively continue to accept that the cycle of rock weathering and mineral precipitation is a reasonable representation of a "slow geochemical cycle" for these materials in the absence of biota. Biota obviously play a major part in the carbon cycle, and Berner (1990) explicitly recognized organic production and respiration as a "rapid cycle" that accompanies the standard Ebelmen-Urey cycle. In fact, Ebelmen and other early researchers discussing the weathering cycle recognized the importance of biota (Berner, 1995; Berner and Maasch, 1996). Representing organic matter as CH_2O, the following reaction describes the synthesis of organic matter from CO_2 and water, and its remineralization by respiration:

$$CO_2 + H_2O = CH_2O\downarrow + O_2\uparrow \tag{5}$$

Smith and Veeh (1989) pointed out that some shallow-water calcifying ecosystems with long water residence time approach CO_2 compensation between CO_2 evasion

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associated with $CaCO_3$ precipitation and CO_2 uptake associated with organic carbon production:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3\downarrow + CH_2O\downarrow + O_2\uparrow \qquad (6)$$

Equations (4) and (7) can be combined in the following manner to include ψ in a reaction that eliminates gas flux:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3\downarrow + \psi(CH_2O\downarrow + O_2\uparrow) + (1-\psi)(HCO_3^- + H^+) \qquad (7)$$
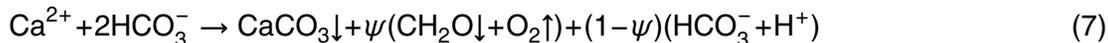
Thus, a combination of $CaCO_3$ precipitation and organic production in surface waters can maintain pCO_2 relatively constant, even though pH and TA are depressed. This provides a mechanism by which oceanic $CaCO_3$ and organic C reactions can cycle carbon internally, with relatively little interaction with the atmosphere.

3 The aqueous CO_2 system in the open ocean

The central oceanic water column may be considered to be an isolated system analogous to the shallow-water isolated ecosystems that led to the above concept, although with an important difference. The production of reactive organic and inorganic and inorganic particles from dissolved materials in the upper ocean and the sinking and subsequent decomposition of these particles back to dissolved materials at depth effectively divide the oceanic system into two geochemically distinctive but strongly interactive sub-systems. The surface ocean production, sinking, and decomposition of particles links the two sub-systems, while together they remain an isolated total system. Little accumulation of either organic or inorganic sediment occurs in the open ocean at depths >4000 m in the North Pacific Gyre, so the only effective exchange of carbon is between the atmosphere and the upper ocean.

Figure 1 presents 20-year average conditions of water composition and ψ for an oceanographic station 100 km north of Oahu, Hawaii (~4700 m water depth). A log scale is used for depth, and raw data (in m) have been bin-averaged into intervals of 0.1

log units in order to highlight both the compositional difference between the upper and lower water column and the composition gradients between the two. For these data, TA and DIC (measured to high precision at the station) were used as the master variables to partition the CO_2 system. Calculations include hydrostatic pressure effects on the CO_2 system. Also included are calculations of ψ and carbonate mineral saturation state ($\Omega = [Ca^{2+}] * [CO_3^{2-}]/K'_{sp}$; where [ ] denotes concentration, and K'_{sp} is the mineral solubility product constant) for the two prominent carbonate minerals precipitated by planktonic organisms, low-Mg calcite and aragonite.

Salinity varies vertically. In order to visualize the non-conservative behavior of DIC and TA relative to salinity, both DIC and TA were normalized to a constant salinity of 35 (represented by DIC* and TA*, respectively). With these normalizations, it is seen that DIC* is constant above ~100 m (the long-term averages of the base of the euphotic zone and the mixed layer depth approximately coincide at this station), then increases between that depth and about 1000 m. It decreases slightly below 1000 m. TA* is constant to a depth of approximately 300 m (well below the mixed layer and euphotic zone), increases to a depth of ~1000 m, and then is constant.

Both net organic carbon production and $CaCO_3$ precipitation obviously occur in the upper water column. Therefore, constant, low values for DIC* and TA* in the euphotic zone relative to the deep ocean represent the combined effects of uptake of both DIC and TA into $CaCO_3$, uptake of DIC into organic matter, release of HCO_3^- from calcification-mediated CO_2 gas evasion, and mixing of this water to constant composition.

The surface water pCO_2 averages about 340 ppmv, about 20 ppmv below atmospheric pCO_2 over the duration of the sampling period. For purposes of this analysis, we may consider this to be in approximate equilibrium with the atmosphere. Net $CaCO_3$ precipitation (represented by constant and low TA* relative to the deep ocean) persists downward to about 300 m, while both respiration and calcification elevate DIC*, pCO_2, and ψ. Rising DIC* and TA* between 300 and 900 m represent the net effect of decomposing organic matter and $CaCO_3$, with no gas exchange with the atmosphere. Organic

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decomposition is complete by ∼1000 m, and there is little further downward change in Ω for either calcite or aragonite. The dramatic $p\text{CO}_2$ decrease below 1000 m, a slight continuing rise in TA, and a slight decrease in ψ represent some continuing CaCO_3 dissolution in the absence of organic oxidation.

5   ψ and Ω are constant in the euphotic zone/mixed layer. ψ rises from 0.6 to 0.9 between 100 and 800 m, in response to both oxidation of organic matter and diminished temperature. Below 1000 m, ψ decreases slightly as $p\text{CO}_2$ is lowered by CaCO_3 dissolution in the absence of additional organic oxidation products.

    CaCO_3 dissolution above the lysocline is contrary to long-held beliefs dating back
10 to the Challenger Expedition. However, the trend we observe and our interpretation of it are consistent with the growing body of recent evidence (e.g., Milliman and Droxler, 1996; Milliman et al., 1999; Feely et al., 2002), that most CaCO_3 dissolution occurs in water shallower than 1000 m. The lysocline marks the depth above which – rather than below which – most dissolution of CaCO_3 occurs. Further, only a small proportion of
15 the water column (∼3% of its volume, 2% of the DIC mass) has ψ constrained by gas exchange between the air and water; about another 15% is a mixing transition zone; the remainder has ψ slightly below 1.0.

4   Scenarios of "no CaCO_3" and "no organic C" reactions in the open ocean

The data shown in Fig. 1 can be used to develop scenarios for the distribution of CO_2-
20 related variables under regimes of no CaCO_3 precipitation and dissolution, and no organic C production and respiration. These scenarios are not intended to be realistic, but rather to explore the geochemical implications of these end member conditions. A scenario in which there are no C reactions is used as a baseline for comparison. For these calculations, observed temperature distribution is used; DIC and TA are again
25 normalized to a salinity of 35. Further, it is assumed that in the absence of CaCO_3 reactions, TA in the oceanic water column would homogenize to the present water column average value of 2420 µeq kg^{-1}. Finally, the calculations use contemporary

mixed layer pCO$_2$ (i.e., 340 ppmv).

Numerical integration of Fig. 2a to the bottom of the sampled profile (4450 m) provides information on the magnitude of the water-column DIC reservoir. Relative reservoir sizes are also scaled to the C-neutral reservoir value of 9500 mol m^{-2} (Table 1).

5 The observed contemporary ocean reservoir is about 13% above C-neutral. This reflects the results of combined contemporary organic and inorganic C particle production in the upper water column, downward transport of those particles, and their total decomposition at depth. In the absence of CaCO$_3$ reactions, the reservoir is about 33% above C-neutral, indicating the strength of the biological C pump. The reservoir without

10 organic C reactions is 3% below C-neutral; that is, CaCO$_3$ reactions are a net source of CO$_2$ release to the atmosphere. The contemporary ocean is only slightly closer to the no-CaCO$_3$ end member than to the no-organic C end member. Thus the CaCO$_3$ dissolution at depth and with higher values for ψ during dissolution than during surface precipitation apparently is an important component of the net oceanic biogeochemical

15 C pump.

Water column pCO$_2$ in deep water in the absence of CaCO$_3$ reactions would be about 8 times the contemporary value (Fig. 2c), while pCO$_2$ in the deep water would actually diminish below surface ocean values in the absence of organic carbon reactions. Note that the pCO$_2$ scale is logarithmic, so that variations for all three conditions

20 can be visualized on a single graph. One oceanic consequence of the no-CaCO$_3$ scenario would be that any region with outcropping deep water (i.e., upwelling zones) would effectively ventilate CO$_2$ to the atmosphere because of the extremely elevated pCO$_2$.

A useful metric for comparison is that the C reservoir size for the contemporary

25 atmospheric column above the Earth surface is about 120 mol m^{-2}. Thus, the oceanic reservoir variations among these various scenarios are all far larger than the magnitude of the atmospheric reservoirs size.

The results for Ω (shown only for calcite, the dominant form of planktonic CaCO$_3$) are also interesting, particularly with respect to the no-CaCO$_3$ scenario. Water below

the mixed layer would be very undersaturated ($\Omega_{calcite} < 0.5$ by 500 m and near 0.1 by 1000 m). This compares with contemporary Ω only slightly below 1.0 even at the base of the sampled water column. The highly corrosive water of the no-$CaCO_3$ scenario would tend dissolve any calcareous sediments in contact with the water, acting as

5   a feedback on the other variables. In the no-organic C scenario, $\Omega_{calcite}$ would remain well above 1.0. In fact, the modeled drop below surface ocean values is, to a great extent, an artifact. The contemporary $CaCO_3$ dissolution above the lysocline is clearly related to biotically mediated dissolution, and this mediation would not occur in the absence of organic C reactions.

10   Finally, note ψ (Fig. 2e). The upper water column value is quite stable, near 0.6 for all scenarios, to a depth of about 200 m. In the absence of organic metabolism, it remains near 0.6 through the lower water column. In the absence of $CaCO_3$ reaction, it rises to 1.0 throughout in the deep water column (where most of the DIC storage occurs). This reflects the importance of organic reactions (specifically, oxidation, without gas

15   evasion) in elevating ψ to unity. Varying ratios of $CaCO_3$:organic C delivery to the deep ocean would both alter ψ and store greater or lesser amounts of DIC in the deep ocean.

5   Implications with respect to ocean acidification

With present concerns about ocean acidification resulting from the oceanic uptake of

20   anthropogenic CO_2, it is appropriate to consider ψ for surface seawater in response to changing atmospheric and upper ocean pCO_2. Brewer and Peltzer (2009) showed that pCO_2 could be expected to reach water column values greater than 3500 ppmv in a station of the eastern tropical Pacific, owing to the diminished buffer capacity of the increasingly acidified water both at the sea surface and with increasing water column

25   oxidation of organic matter. The scenarios presented in Fig. 2 would suggest that ψ should rise and Ω should fall in response to rising atmospheric pCO_2.

There is mounting evidence that acidification is affecting calcification, although it is

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by no means certain that there will be a single general rule to describe this effect. The decline of calcification will have two concomitant and antagonistic impacts on the carbonate chemistry of the surface ocean (Gattuso et al., 1999b). On the one hand, less calcification means less CO_2 released to the water column. On the other hand, the
5   increase in ψ will lead to a greater release of CO_2 per each mole of $CaCO_3$ precipitated (Eq. 4). The reverse of this effect is propagated downward into the water column, as $CaCO_3$ dissolves.

    We make a simple assumption and develop a surface water calcification index (CI) that scales calcification proportional to $\Omega_{calcite}$ (Table 2). We use CI, surface TA* scaled
10 to CI, present deep-water TA*, and a constant water-column average TA* in order to develop profiles for TA*. We assume that release of DIC from OC oxidation does not change from contemporary. With these assumptions, we calculate profiles of DIC* , pCO_2, $\Omega_{calcite}$, and ψ for surface water at pCO_2 values of pre-industrial (~280 ppmv), contemporary (~380), 2, and 3 times contemporary (Fig. 3). In effect, our treatment
15 extends the calculation made by Brewer and Peltzer (2009) in the Eastern Tropical Pacific to include effects of ψ. There is an upward shift of ψ from about 0.57 to 0.77 in the upper ocean over this range of conditions. The combined effect of the two mechanisms described above is towards less CO_2 released (Table 2).

    The Hawaii station is more oligotrophic than the station analyzed by Brewer and
20 Peltzer (2009). Despite the lower amount of organic C produced and consumed at the Hawaii station, maximum water-column pCO_2 values (2300 ppmv, 2×atmospheric CO_2; 3300 ppmv, 3 ×) are very similar to the values reported by those authors. At 2×atmospheric pCO_2, ψ reaches or exceeds 0.95 throughout the water column below 700 m at the Hawaii station.

25   The changing size of the oceanic carbon reservoir with increasing pCO_2 and decreasing upper water column calcification can be seen in Table 1. It is evident that the net sink strength will diminish as atmospheric CO_2 rises and calcification decreases.

    Note that this assessment of sink strength in response to ocean acidification is greatly simplified. In particular, physical considerations, temperature, and more com-

plex relationships between $CaCO_3$ reactions and acidification can be considered (see, for example, Heinze, 2004; Gehlen et al., 2007).

6 Conclusions

The introduction of organic carbon reactions into the weathering-precipitation couplet provides a plausible conceptual reconciliation between the Ebelmen-Urey reactions and the quantitative chemical behavior of $CaCO_3$ reactions in seawater. The heretofore problematic coefficient, ψ, is a sensitive variable related to $CaCO_3$ and organic matter reactions, DIC storage in the ocean, and CO_2 gas exchange between the ocean and atmosphere. Variation in ψ vertically in the water column, with changing atmospheric pCO_2, and in response to changing proportions of $CaCO_3$ and organic C reactions affect air-sea gas exchange and the oceanic carbon storage reservoir. An important aspect of this coefficient is that relatively subtle variations in the characteristics of both $CaCO_3$ and organic C reactions in the oceanic water column, acting in concert with ψ can dramatically alter the magnitude of the oceanic storage of C relative to the much smaller size of the atmospheric C reservoir.

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Lithogenic, atmospheric, and biogenic cycles

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Table 1. Water-column reservoir sizes for contemporary (observed) conditions and the 6 scenarios described in Figs. 2 and 3.

Carbon flux scenarios (340 ppmv)		
Scenario	$mol\,C\,m^{-2}$	% of C-neutral
Observed	10 700	113
no $CaCO_3$	12 600	133
no organic C	9200	97
C-neutral	9500	–
Atmospheric CO_2 Scenarios		
Scenario	$mol\,C\,m^{-2}$	% of observed
pre-industrial (280 ppmv)	10 100	94
2x pre-industrial (560 ppmv)	11 300	105
3x pre-industrial (840 ppmv)	11 500	108

Table 2. Effect of pCO_2 on $\Omega_{calcite}$ and ψ for surface seawater of $T=25\,^{\circ}$C, $S=35$. Surface TA* is calculated to match the diminished CI, based on deviation from water column average TA*. A "calcification index" (CI) for each scenario (X) is scaled relative to contemporary conditions (CI=1.0) and a value of 0 at $\Omega=1.0$. CI=$(\Omega_X-1)/(\Omega_{contemp}-1)$. Relative CO_2 flux from calcification in the upper ocean is calculated as CI*ψ.

pCO_2 (ppmv)	TA*	$\Omega_{calcite}$	CI	ψ	CO_2 flux
280 (pre-industrial)	2272	6.2	1.2	0.57	0.68
340 (contemporary)	2300	5.3	1.0	0.63	0.63
560 (2x pre)	2342	4.2	0.7	0.70	0.49
840 (3x pre)	2370	3.2	0.5	0.77	0.39

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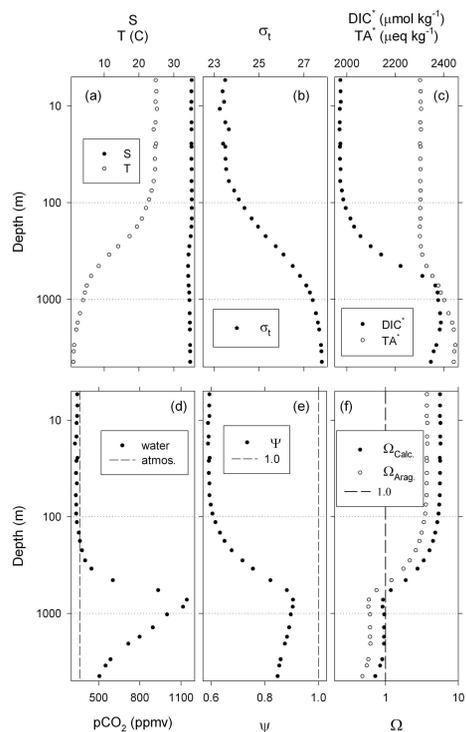
Fig. 1. 1988–2007 average data for temperature, salinity, sigma-t, dissolved inorganic carbon, and TA at Station Aloha (22.75° N, 158.00° W) and pCO_2, from which we calculate ψ and Ω for calcite and aragonite calculated from these data. DIC* and TA* are normalized to S=35, to remove conservative effects. Data online at http://hahana.soest.hawaii.edu/hot/hot-dogs/interface.html.
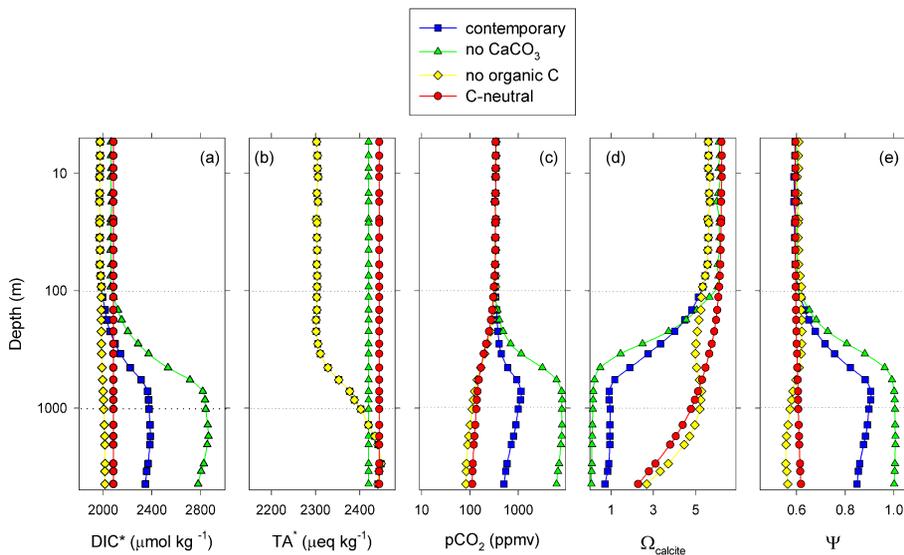
Fig. 2. Water column composition according to the three scenarios of oceanic carbon reactions discussed in the text. These scenarios are derived from the data used in Fig. 1, as discussed in the text. All calculations are based on DIC* and TA* (data normalized to S=35).

Fig. 3. Observed water column composition according to the three scenarios of elevated atmospheric CO_2 discussed in the text. These scenarios are derived from the data used in Fig. 1. All calculations are based on DIC^* and TA^* (data normalized to S=35).

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