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SIRD

Acidification and the Potential Dissolution of CaCO_3 in the Sediments of the South China and Sulu Seas

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INTRODUCTION

Against the backdrop of global climate change and its far-reaching impact on ocean biology, major ecological shifts in the taxonomic composition and physiology of the oceans have been at the center of a flurry of research. Of particular interest have been changes in carbonate chemistry. Among many studies in this regard, that of Sarmiento and Wofsy (1999) is noteworthy for its view that the concentration of carbonate ions should decrease by 30 percent and the pH by more than 0.2 in the mixed layer of the oceans by the middle of this century.

While empirical studies on land plants have consistently shown responses of 20–40 percent higher growth under doubled CO_2 conditions, the effects of elevated CO_2 conditions on increasing growth, known as the CO_2 fertilization effect, have yet to be substantiated in the case of oceans (Schimel et al. 1996). Thus, given the importance of the issue, the IGBP/IHDP/WCRP/DIVERSITAS Global Carbon Project (GCP 2003) still seeks answers as to how marine biota respond to changes in dissolved inorganic carbon (DIC) and pH in the oceans.

It could very well be that diatom growth is limited by the supply of CO_2 (Riebesell 2004), but an increased concentration of CO_2 in the ocean's surface layer is not considered a major contributor to any increase in the gross or net rate of primary productivity. As is well known, however, marine biota plays a crucial role in maintaining the steady-state level of atmospheric CO_2 . About three-quarters of the vertical gradient of DIC are generated by the "biological pump", the process by which CO_2 fixed in photosynthesis is transferred to the

interior of the oceans. This results in temporary or permanent sequestration, or storage, of carbon. The common intuition is that in the open oceans, it is not an abundance of carbon that limits or controls the functioning of the biological pump, but rather the availability of nutrients, light or even phytoplankton population control via grazing (e.g. Stowe 1979).

The view has often been expressed that higher pCO_2 is directly responsible for the ocean surface perhaps becoming under-saturated with respect to CaCO_3 , which could have serious biological consequences. Feely and Chen (1982) are credited with being the first to find concrete evidence that excess CO_2 causes the calcite and aragonite saturation horizons to shoal. This is because increased concentrations of DIC decreases carbonate concentrations, leading to a decreased saturation state. This is in spite of the fact that global warming slightly raises seawater temperature and that this increases the degree of CaCO_3 saturation. Any change in the carbonate/bicarbonate ratio is also indicative of a change in pH.

Though the dissolution of calcareous shells and skeletons may very well be biologically mediated (Milliman et al. 1999), it is still an abiological process mainly affected by the CaCO_3 saturation state of seawater (Feely et al. 2004). The abiological process is controlled by the thermodynamics of the carbonate system in seawater and is easy to model. The results of our attempt to predict the distribution of anthropogenic CO_2 as well as the decreases in pH and in the degrees of saturation of calcite and aragonite in the South China Sea (SCS) and the Sulu Sea (SS) are presented below.

TEMPORAL VARIATIONS IN pH AND CaCO_3 SATURATION STATES

A typical 1997 NDIC (NDIC = $\text{DIC} \times 35/\text{salinity}$, where DIC is the dissolved inorganic carbon) profile for the northern SCS is plotted in Figure 6.6.1a. The values increase from about 1970 mmol kg^{-1} near surface to 2220 mmol kg^{-1} at 450 m. The estimated pre-industrial (i.e., around 1850 AD) profile is plotted after being adjusted for anthropogenic CO_2 input. Also plotted is the projected NDIC profile in light of the fact it is anticipated that pCO_2 will have doubled in the atmosphere by around 2050 AD. For obvious reasons, the largest differences occur near the surface, which when compared with recent values, is about 50 mmol kg^{-1} lower in 1850 AD and a marked 60 mmol kg^{-1} higher in 2050 AD. Such differences dwindle substantially below 450 m. The maximum variation in NDIC with the doubling of CO_2 is only on the order of 6 percent.

A typical 1997 pH profile for the northern SCS is given in Figure 6.6.1b. The pH decreases from about 8.24 near surface to about 7.78 at 450 m. The estimated

pre-industrial (higher pH) and 2050 AD (lower pH) profiles are also plotted. With a doubling of $p\text{CO}_2$, the maximum decrease in pH is on the order of 0.18 pH units, which represents a small change, indeed, especially when compared to the wide oceanic ranges of pH—between 7.5 and 8.3. Nevertheless, even such a small change in pH is expected to have some biological effects (Feely et al. 2004).

Figure 6.6.2 gives the typical profiles for the degrees of saturation of calcite (W_c) and aragonite (W_a), respectively, in 1850, 1997 and 2050 AD. The 1997 recent surface waters in the SCS, like in most other places, are super-saturated with calcite and aragonite, and they are still super-saturated at 450 m. Even with a doubling of $p\text{CO}_2$, the waters remain super-saturated. The results shown in Figure 6.6.2a give a clear indication that the waters on the continental shelf (< 200 m deep) will remain super-saturated with calcite for several centuries to come. Recent studies, nonetheless, reveal that the degree of saturation has a profound impact on the calcification rates of both the planktonic and benthic species (e.g. Feely et al. 2004).

As shown in Figure 6.6.2b, waters below about 450 m, by contrast, may become under-saturated with respect to aragonite around 2050 AD. By that time, benthic organisms with aragonite shells or skeletons may have already started to be severely affected. The aragonite deposits on the continental slope may have also begun to dissolve, thus neutralizing excess CO_2 .

**Figure 6.6.1 Vertical profiles of seawater in the SCS showing typical pre-industrial (~1850), recent (1997) and projected (~2050):
a) NDIC and b) pH (taken from Chen et al. 2006b)**

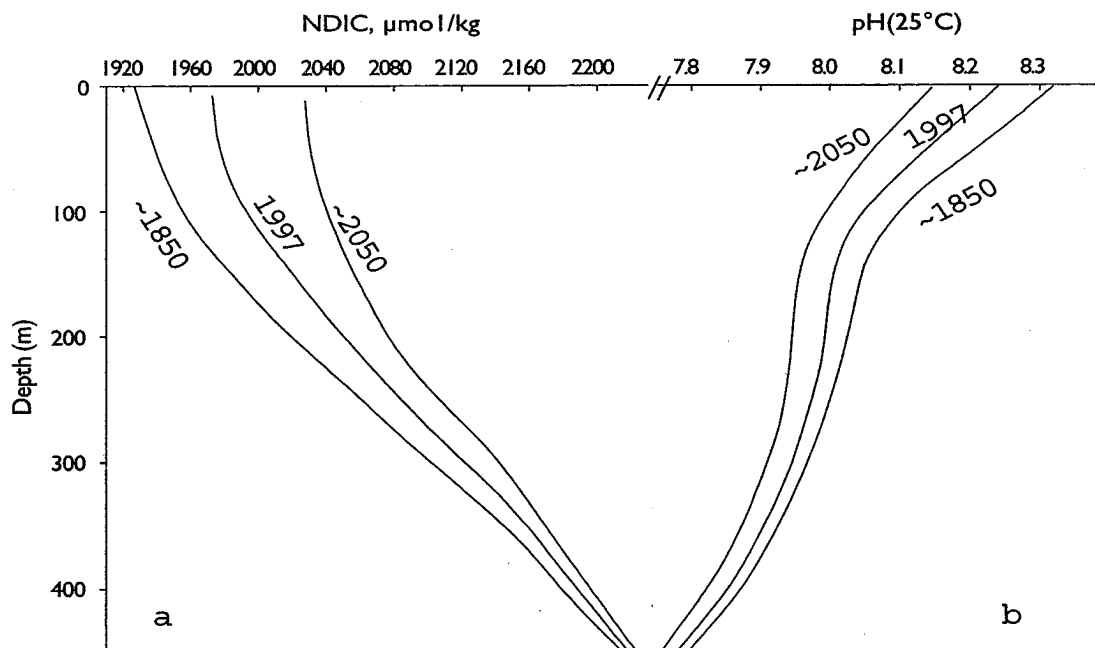
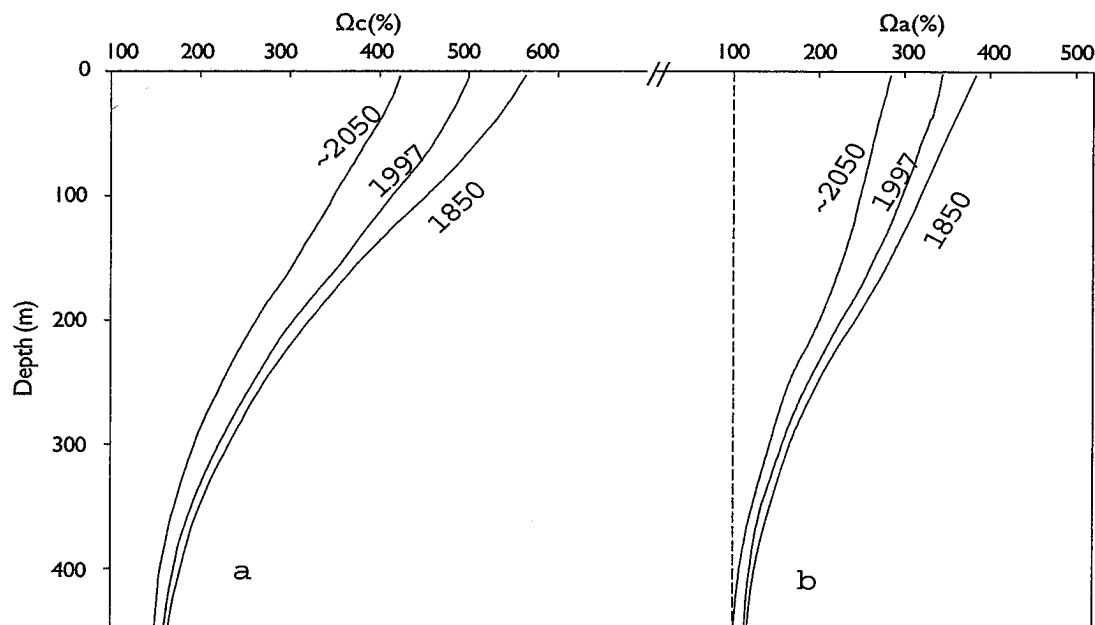


Figure 6.6.2 Vertical profiles of seawater in the SCS showing typical pre-industrial (~1850), recent (1997) and projected (~2050): a) Ω_c and b) Ω_a (taken from Chen et al. 2006b).



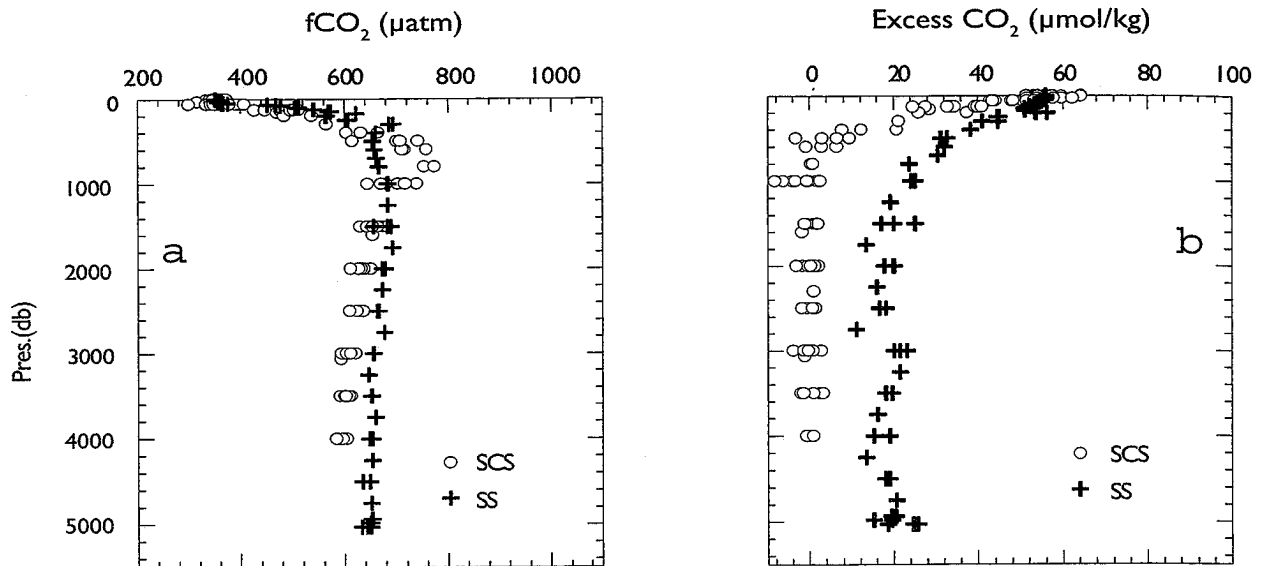
EXCESS CO_2

The fugacity of CO_2 ($f \text{CO}_2$) of surface waters is close to saturation in the SCS and the SS. With depth, the values increase because of decomposition of organic matter (Figure 6.6.3a). The excess CO_2 has penetrated to 1000 m in the SCS (Figure 6.6.3b). On the other hand, in recent times in the SS, the excess anthropogenic CO_2 has penetrated the entire water column (Figure 6.6.3b) because when water at 420 m, which had originated in the SCS, filled the SS basin, it was already laden with excess CO_2 . The total inventory of excess CO_2 in the SS amounted to only 0.28 Gt C. Although this is not large, the SS had an overwhelmingly larger than average excess CO_2 sink per unit area of 800 g C m^{-2} ; contrast this with 229 g C m^{-2} for the SCS and 330 g C m^{-2} for the world's oceans (Chen 2001; Chen et al. 2004; Chou et al. 2005).

POTENTIAL DISSOLUTION OF CaCO_3

Relative to those of the SCS, the bottom sediments of the SS are reportedly rich in CaCO_3 (e.g. Huang et al. 1999 and Zhang et al. 2003), whereas compared to the West Philippine Sea (WPS), the SS is more CaCO_3 -rich (Chen et al. 2006a). The situation may soon change in the SS and SCS, however, on account of the

Figure 6.6.3 Vertical profiles of: a) $f\text{CO}_2$ and b) excess CO_2 in the SCS and SS (taken from Chen et al. 2006a).



impact of the excess CO_2 as the uptake of fossil fuel CO_2 lowers $[\text{CO}_3^{2-}]$, which consequently lowers W . An analysis of a global carbon dataset suggests a significant upward migration (40–200 m) of the aragonite saturation horizon in the world's oceans during the industrial era (Feely et al. 2002; Sabine et al. 2002; Chung et al. 2003) primarily because of the uptake of fossil fuel CO_2 . This upward migration of the aragonite saturation horizon may have caused aragonite particles, which had fallen from the surface, to dissolve at shallower depths than in the preindustrial era, thus influencing the supply of CaCO_3 to the sediments.

Indeed, the aragonite did not become under-saturated in the SS until below 1400 m, compared to 600 m in the SCS. The calcite did not become under-saturated until below 3,800 m in the SS, compared to 2500 m in the SCS. Important here, because of the deep penetration of the excess CO_2 in the SS, in recent times, the saturation horizon has already been lifted up 500 m for both aragonite and calcite, which is considerably more than generally found in global oceans. As a rule, alkalinity increases rapidly, even above the saturation horizons in both seas. In situ dissolution in the water column (Milliman et al. 1999), shelf-generated alkalinity from the large shelves (Chen 2002), coupled with the effect of intensive vertical mixing, may have contributed to such an increase.

CONCLUSIONS

The global nature of greenhouse warming and the acidification of the oceans means that such calcareous organisms as pteropods, forams and corals are likely to suffer (Langdon and Atkinson 2005), but there has been a dearth of related research in Southeast Asia. Evidence from existing oceanic carbonate data demonstrate that DIC in the SCS and SS has increased, while pH has decreased. Thus, as the saturation horizons for aragonite and calcite have been rising, the bottom calcareous sediments may have already started to dissolve in some areas.

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