

## Chapter 1

### **Extreme Acidification of the Ocean during the Paleocene-Eocene Thermal Maximum**

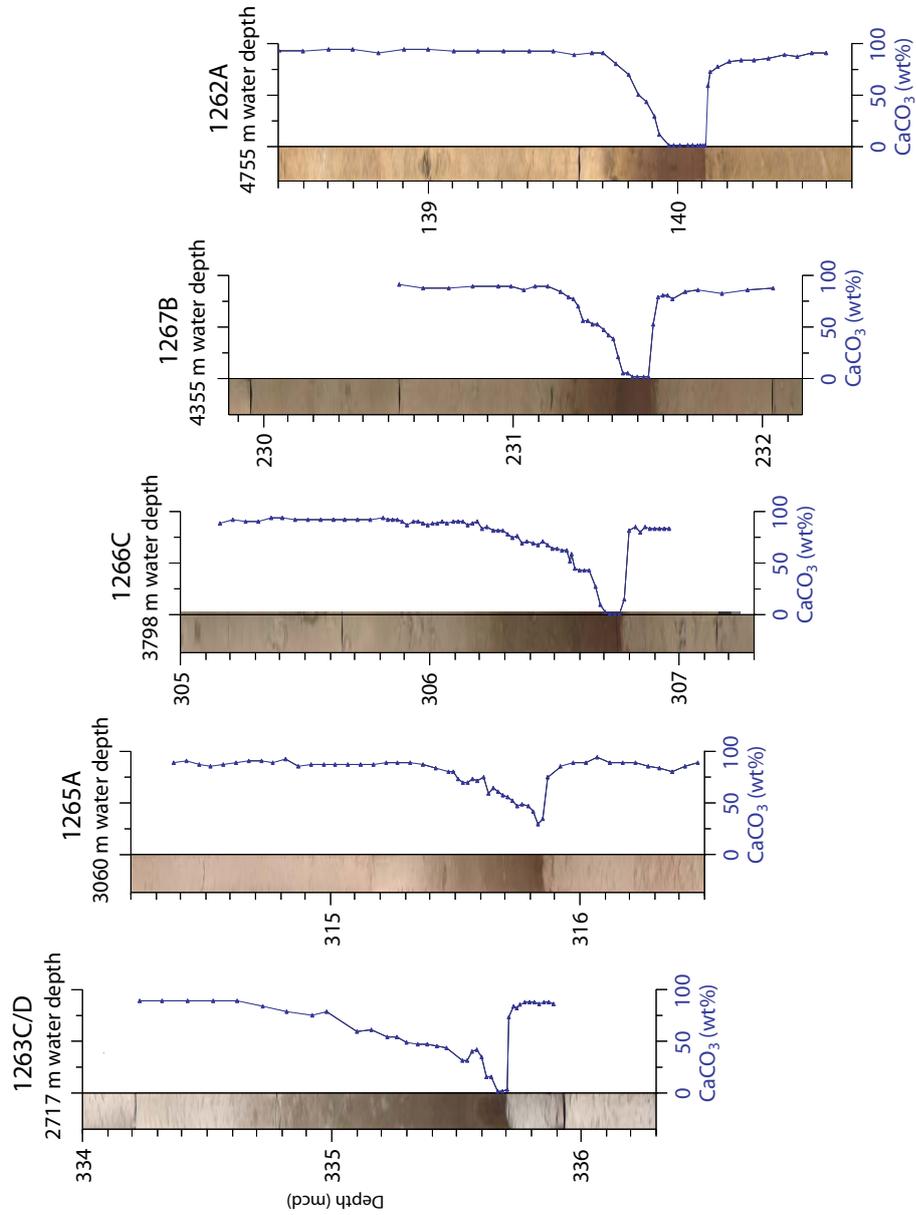
The Paleocene–Eocene Thermal Maximum (PETM) has been attributed to the rapid release of  $\sim 2000 \times 10^9$  metric tons of carbon in the form of methane. In theory, oxidation and uptake of this carbon by the ocean should have lowered deep-sea pH, thereby triggering a rapid ( $<10,000$ -year) shoaling of the calcite compensation depth (CCD) followed by gradual recovery. Here, we present geochemical data from 5 South Atlantic deep-sea sections that constrain the timing and extent of massive seafloor carbonate dissolution at the P-E boundary. The sections, from between 2.7 and 4.8 km water depth, are each marked by a prominent clay-layer, the character of which indicates that the CCD shoaled rapidly ( $<10,000$ -years) by more than 2 km, and recovered gradually ( $>100,000$  years). These findings suggest that an anomalously large mass of carbon ( $>>2000 \times 10^9$  metric tons of carbon) dissolved in the ocean at the Paleocene-Eocene boundary and that permanent sequestration of this carbon occurred via the silicate weathering feedback.

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During the PETM sea surface temperature (SST) rose by 5°C in the tropics and as much as 9°C in the high latitudes (Kennett and Stott, 1991; Zachos et al., 2003; Tripathi and Elderfield, 2004) whereas bottom-water temperatures rose by 4-5°C (Thomas and Shackleton, 1996). The initial SST rise was rapid, on the order of  $\sim 10^3$  yr, although the full extent of warming was not reached until some  $\sim 30,000$  years (30 kyr) later (Thomas et al., 2002). The most compelling evidence for greenhouse forcing is coeval global carbon isotope excursion (CIE) of roughly  $-3.0$  per mil (‰) in deep sea cores (Thomas and Shackleton, 1996). The pattern of the CIE – an initial rapid decrease ( $\sim 20$  kyr) followed by a more gradual recovery (130-190 kyr) (Kennett and Stott, 1991; Kelly et al., 1996; Röhl et al., 2000) – indicates the input of a large mass of  $^{13}\text{C}$ -depleted carbon into the ocean and atmosphere. Quantitatively, methane hydrates, with a mean  $\delta^{13}\text{C}$  of  $< -60$ ‰, appear to be the most plausible source of this carbon (Dickens et al., 1995). For example, only  $\sim 1200 \times 10^9$  metric tons of carbon (GtC) of biogenic methane would be required to produce a CIE of 2.5‰ (Dickens et al., 1997; Dickens, 2000). Thermogenic methane has been implicated as well (Svensen et al., 2004), although the mass required to produce the P-E CIE would be roughly double that of biogenic methane.

Regardless of source, the released methane was rapidly oxidized to  $\text{CO}_2$ . Subsequent oceanic dissolution of this  $\text{CO}_2$  would alter ocean carbon chemistry, principally by lowering the pH and carbonate ion content [ $\text{CO}_3^{2-}$ ] of seawater. These changes would be partially neutralized by a transient rise in the level of the lysocline and calcite compensation depth (CCD), resulting in widespread dissolution of sea-floor carbonate. Eventually,  $\text{CO}_2$  would be sequestered and ocean carbonate chemistry would be restored, primarily through chemical weathering of silicate rocks (Dickens et al., 1997). The extent and duration of lysocline/CCD shoaling and subsequent recovery would depend largely on the source, mass and rate of carbon input. For example, modeling of a 1200-GtC input over 10 kyr produces a lysocline shoaling of 300 m (less in the Pacific), with a recovery of  $\sim 40$  ky (Dickens et al., 1997). Such changes in [ $\text{CO}_3^{2-}$ ] should produce distinct patterns in pelagic carbonate sedimentation and lithology, characterized by an abrupt transition from carbonate-rich sediment to clay, followed by a gradual recovery to carbonate. Moreover, the clay layer should increase in thickness with increasing water depth.

Clay or low-carbonate layers coincident with the PETM were previously identified in several deep-sea cores and land-based marine sections (Bralower et al., 1997; Thomas, 1998; Thomas et al., 1999). However, these sections, which are either geographically isolated or not completely recovered, or both, are inadequate for constraining CCD variations and for testing the methane hypothesis. Ocean Drilling Program Leg 208 was designed to recover an array of pelagic cores spanning the Paleocene-Eocene (P-E) boundary over a broad depth range. The primary drilling target was the Walvis Ridge, southeastern Atlantic (Appendix



**Figure 1:** Digital core photos and weight percent CaCO<sub>3</sub> plotted versus composite depth (MCD) across the P-E boundary interval at ODP Sites 1262 (Hole A), 1263 (Hole C/D), 1265 (Hole A), 1266 (Hole C), and 1267 (Hole B) on the Walvis Ridge (Appendix Fig. 2.1). Records are plotted from left to right in order of increasing water depth. The core photos for each site represent composites of the following sections; 1262A-13H-5 & 6; 1263C-14H-1 & 2; 1263D-4H-1 & 2; 1265 A - 2 9 H - 6 & 7; 1266C-17H-2, 3 & 4; 1267B-23H-1,2 & 3.

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Fig. 2.1) where DSDP Leg 74 rotary cored portions of the P-E boundary sequence near the base and summit of the ridge (Sites 527 & 525) (Moore et al., 1984). By using advanced piston coring in multiple offset holes at five sites (1262, 1263, 1265, 1266, & 1267), Leg 208 successfully recovered stratigraphically complete and undisturbed upper Paleocene-to-lower Eocene successions at four of five sites between 2.7 and 4.8 km water depth (Zachos et al., 2004). At each site, the P-E boundary sequence is characterized by an abrupt transition from carbonate-rich ooze to a dark red “clay layer”, which then graded back into ooze (Fig. 1). Carbonate content is <1 weight percent (wt%) in the clay layers, and >80 and 90 wt% in the under- and overlying oozes, respectively; the only exception is Site 1265, where the basal portion of the clay layer was not recovered. The thickness of the clay layers increases with depth, from 5 cm at the shallowest site (1263 at 2717 m; paleodepth ~1500 m; Zachos et al., 2004) to 35 cm in the deepest site (1262 at 4755 m; paleodepth ~3600 m) (Fig. 1). The benthic foraminiferal extinction horizon, which is characterized by the disappearance of long-lived Paleocene species and a rapid drop in diversity, occurs at the base of the clay layer in each site (Moore et al., 1984).

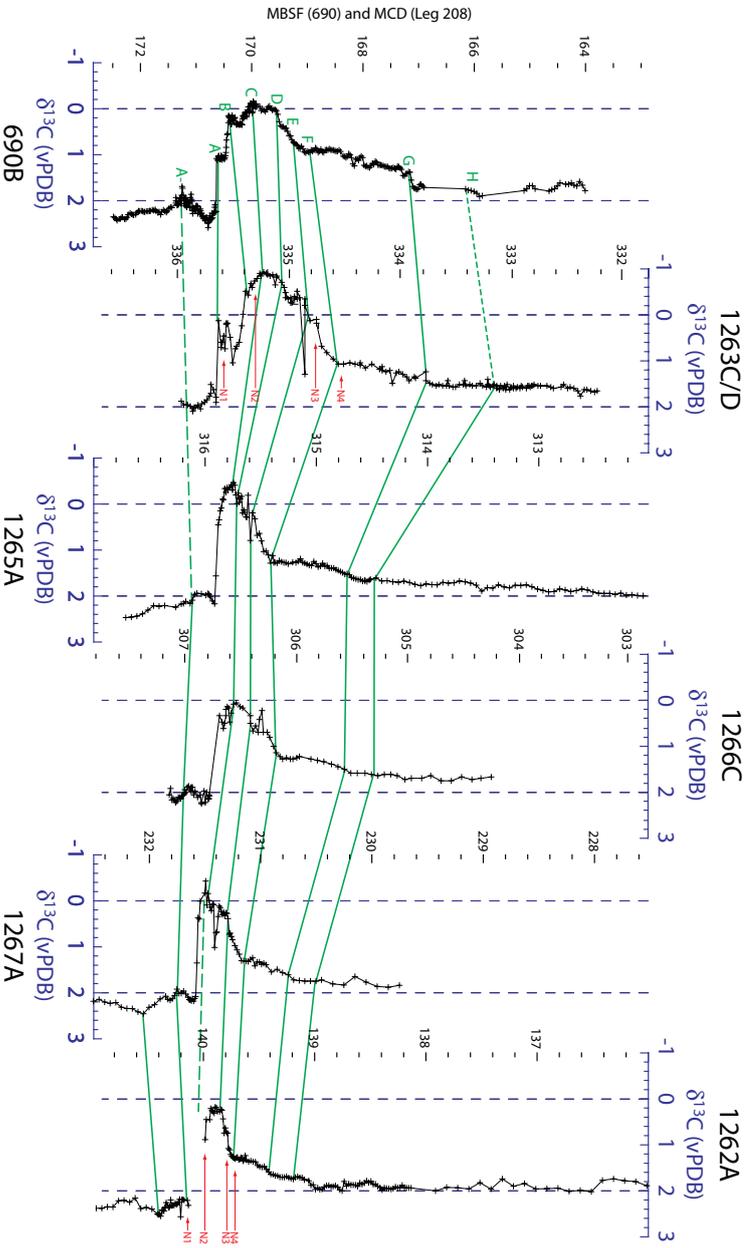
Bulk sediment carbon isotope records ( $\delta^{13}\text{C}$ ) were constructed at 1-5 cm resolution for each P-E boundary interval. Each record is marked by a decrease in  $\delta^{13}\text{C}$  at the base of the clay layer, followed by gradual recovery. Minimum carbon isotope values within the clay layer are not uniform, but increase from the shallowest to deepest site (minimums of  $-0.9\text{‰}$  and  $0.0\text{‰}$  at Sites 1263 and 1262, respectively), a feature we attribute to truncation by dissolution and the presence of residual pre-excursion calcite (Bains et al., 1999). Also, the base of the CIE also differs across sites, occurring in two steps at Site 1263 and in a single step in the deeper sites. As a result, the excursion layer from the onset of the CIE to the point of full recovery (i.e., stability) decreases in thickness from 2.1 m at Site 1263 to 1.0 m at 1262.

In this spatially tight array of sites, the production and export of carbonate and the accumulation of clay should be similar at any given time, leaving dissolution as the major process affecting differences in carbonate accumulation between sites. We can therefore infer from the wt% carbonate and carbon isotope data that rapid shoaling of the lysocline/CCD followed first by a more gradual descent or recovery of the CCD and then by the recovery of the lysocline. The duration of the lysocline/CCD to descend from the shallowest to deepest sites was estimated by first correlating several key inflection points in the carbon isotope records of the 208 sites (Figure 2, tie points A to G), as well as in the Fe concentration and the bulk magnetic susceptibility (MS) records (Appendix Fig. 2.2). The tie points, particularly E and F, were then verified with biostratigraphic data (Appendix Table 2.2). We then correlated the Site 1263 carbon isotope record to that of south Atlantic ODP Site 690 (Bains et al., 1999), which has an orbitally-based age-model (Röhl et al., 2000), and ordinated the weight %

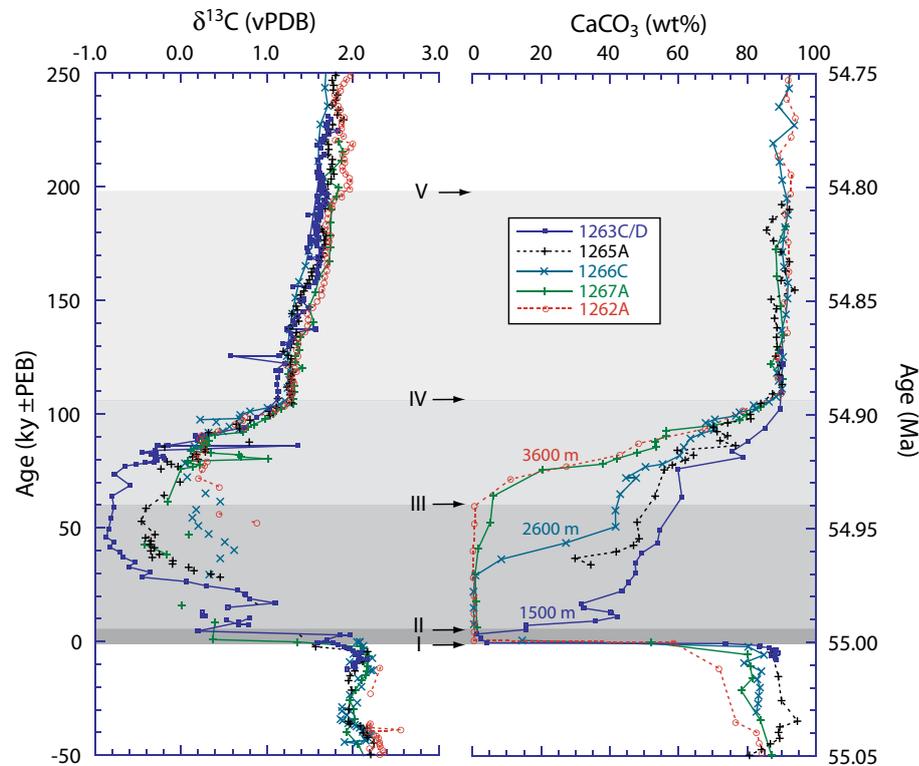
carbonate and isotope data for each site within that age model (Figure 3; Appendix Table 2.2). An alternate age model based on  $^3\text{He}$  exists for Site 690 (Farley and Eltgroth, 2003). But the models are roughly similar for the first 100 kyr of the PETM; thus choice of model makes little difference in our interpretation of events up to that point. The greatest uncertainty in the site-to-site correlations and the age estimates is in the basal portion of the clay layer, where the carbon isotope and other records are compromised by dissolution. The correlations (Fig. 1, tie points D to G) are most reliable in the recovery interval where the weight % carbonate is higher and the ocean  $\delta^{13}\text{C}$  is rapidly shifting.

Given these age constraints, the CCD is inferred to have shoaled more than two kilometers within a few thousand years (Fig. 3). Recovery was gradual with the CCD descending to the shallowest site (1263) within ~10 to 15 kyr of the CIE onset and to the deepest site (1262) within ~60 kyr. At 110 kyr, carbonate content had fully recovered. This pattern of change, particularly the recovery, has important implications. According to theory, initial uptake of  $\text{CO}_2$  and buffering should occur mainly via deep-sea calcite dissolution, but eventually, chemical weathering of silicate rocks takes over accelerating the flux of dissolved ions (including  $\text{HCO}_3^-$ ) to the ocean, thereby increasing  $[\text{CO}_3^{2-}]$  and the rate of calcite accumulation. The weathering of silicates on land is generally represented by the following equation:  $\text{CaSiO}_3 + 2\text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + \text{Ca}^{2+} + \text{SiO}_2$ . Ensuing precipitation of calcite from the bicarbonate (and carbonate) ions supplied by the above reaction is represented by this equation:  $\text{HCO}_3^- + \text{Ca}^{2+} \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ , so that there is a net uptake of one unit of  $\text{CO}_2$  for each unit of silicate weathered. The distribution of carbonate between +60 and +100 kyr indicates that the CCD had descended, but the lysocline was still shallow and the deep sea was largely undersaturated. The percentage of  $\text{CaCO}_3$  continued to increase, and by +110 kyr, it had reached 90% over the entire transect, a state that implies that the lysocline descended below the deepest site (>3.6 km) as well as its pre-excursion level. This phenomenon consistent with theory (Dickens et al., 1997) and likely represents a transitional period during which the excess ions supplied to the ocean by weathering of silicate rocks greatly increased deep-sea  $\text{CO}_3^{2-}$  concentration and thus carbonate accumulation. The Site 690 records is marked by a similar pronounced interval of high carbonate content (Farley and Eltgroth, 2003; Kelly et al., 2005) demonstrating that  $\text{CO}_3^{2-}$  oversaturation was not a local phenomenon.

This scenario for acidification of the deep sea initial subsequent neutralization by carbonate dissolution is not unlike that simulated by models in response to anthropogenic rise in anthropogenic  $\text{CO}_2$  (Caldeira and Wickett, 2003; Feely et al., 2004; Archer, in press). Because dissolution layers are also present in P-E sections in the Pacific and Tethys Oceans and at depths <1 km (Coccioni et al., 1994; Ortiz, 1995; Speijer et al., 1996; Schmitz et al., 2001; Bralower, 2002), it appears that for a brief period of time, much of the ocean beneath the mixed



**Figure 2:** Bulk sediment carbon isotope records for Holes 1262A, 1263C/D, 1265A, 1266C, and 1267A plotted versus MCD. Also plotted are the nanofossil horizons (N1 to N4, arrows in red) for Holes 1262B and 1263C/D (Appendix 2). Data for ODP Site 690 (Bains et al., 1999) are plotted to the far left versus meters below the seafloor (MBSF). Lines of correlation are based on inflections in the carbon isotope (A to G above the P-E boundary, A- below), Fe/Ca, and magnetic susceptibility (MS) records vPDB, Vienna Peedee Belemnite.



**Figure 3: A)** Bulk sediment  $\delta^{13}\text{C}$  and **B)** weight percent carbonate content plotted versus age for ODP Sites 1262, 1263, 1265, 1266, and 1267. Age (kyr) relative to the P-E boundary is plotted on the left axis and absolute age (Ma) along the right. Age models (Appendix Table 2.2) are based on correlation to Site 690 (Röhl et al., 2000) using the carbon isotope stratigraphy as verified with the nannofossil events in Figure 2 and with the Fe and MS cycles in Appendix Fig. 2.2. Transferring the 1263 age model to deeper sites with carbon isotopes could only be achieved where sufficient carbonate was present. Ages within the clay layers for Sites 1266, 1267, and 1262 were derived through linear interpolation from tie points E and A. Paleodepths ( $\sim 55$  Ma) are provided for Sites 1263 (1500 m), 1266 (2600m), and 1262 (3600 m). Key events in the evolution of south Atlantic carbonate chemistry: I rapid drop in content to  $<1\%$  for all sites with the exception of Site 1265 where the lowermost Eocene is absent; II return of the CCD to Site 1263 roughly 5 kyr after the excursion; III the return of the CCD to Site 1262 at 60 kyr; IV the lysocline descending to a point below the deepest site at 110 kyr after the excursion. PEB, Paleocene-Eocene boundary.

layer was highly undersaturated with respect to calcite. The mass of  $\text{CO}_2$  required to shoal the CCD to  $<1$  km water depth in the modern ocean would be substantial. In a series of simulations with an ocean/sediment carbon-cycle model designed to evaluate the ocean-buffering capacity in response to a range of anthropogenic  $\text{CO}_2$  fluxes, 4500 GtC was required to terminate carbonate

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accumulation over the entire ocean (Archer, in press). For the PETM, the release of >4500 GtC would be more consistent with the large magnitude of global temperature rise (Dickens et al., 1995; Zachos et al., 2003; Tripathi and Elderfield, 2004). Such a large mass carbon, however, would require a reevaluation of the source of the carbon and its isotopic composition. With bacterially produced methane at  $-60\text{‰}$ , the total input from hydrates is limited by the  $\delta^{13}\text{C}$  to <2000 Gt (Dickens et al., 1997). To increase the mass of carbon added while adhering to the isotope constraints requires input of isotopically heavier carbon such as thermogenic  $\text{CH}_4/\text{CO}_2$  ( $\sim -30$  to  $-20\text{‰}$ ) or oxidation of organic carbon (standing or stored,  $-20\text{‰}$ ) (Kurtz et al., 2003). In this regard, recent documentation of an unusual concentration of upper Paleocene fluid/gas seep conduits associated with volcanic intrusions in the North Atlantic (Svensen et al., 2004) merits additional attention. An alternative explanation, that the magnitude of the marine CIE has been significantly underestimated because of dissolution or damping by pH effects, seems unlikely given constraints provided by continental isotope records (Bowen et al., 2004). Finally, proximity to where carbon ( $\text{CO}_2$  or  $\text{CH}_4$ ) enters the deep sea via circulation will dictate where neutralization by carbonate dissolution is most intense (Dickens, 2001b). For example, severe dissolution in the Atlantic may indicate direct input of methane into bottom waters entering this basin.

Excessive carbonate undersaturation of the deep ocean would likely impede calcification by marine organisms and thus, represents a potential contributing factor to the mass extinction of benthic foraminifera at the P-E boundary. Although most plankton species survived, carbonate ion changes in the surface ocean might have contributed to the brief appearance of weakly calcified planktonic foraminifera (Kelly et al., 1996) and the dominance of heavily calcified forms of calcareous algae (Bralower, 2002). What, if any, implications might this have for the future? If combustion of the entire fossil fuel reservoir ( $\sim 4500$  GtC) is assumed, the impacts on deep-sea pH and biota will likely be similar to those in the PETM. However, because anthropogenic carbon input will occur within just 300 years, which is less than the mixing time of the ocean, the impacts on surface ocean pH and biota will probably be more severe.