

# Formation and preservation of calcium carbonate on the deep North Pacific Ocean floor driven by illite weathering

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## 1. Biogenic and abiogenic carbonate minerals presence in the Mariana Trench

In the modern ocean, authigenic calcium carbonate ( $\text{CaCO}_3$ ) formation is thought to occur only in continental margins with anoxic, organic-rich sediments and at depth in the sediment where alkalinity is enhanced by diagenetic reactions, particularly the reduction of sulfate or ferric iron and methane oxidation. In the oxic and suboxic zone of the sediment deposit, the formation of authigenic carbonate is commonly assumed to be inhibited as aerobic respiration of sedimentary organic matter releases  $\text{CO}_2$  and the re-oxidation of reduced compounds (such as  $\text{Fe(II)}$  and  $\text{H}_2\text{S}$ ) releases protons into ambient porewaters, thereby lowering the saturation degree of carbonate phases below 1 (that is the saturation state). However, our new observations during several recent expeditions to the Mariana Trench revealed the ubiquitous occurrence of  $\text{CaCO}_3$  minerals on the deep ocean floor. From scanning electron microscopy (SEM) images of the white mineral crusts collected at the trench, we identified a large number of intact frustules of coccolithopores and foraminifera, and microfossils of extinct star-shaped *Discoaster* with calcareous exoskeletons (Figure 1). SEM images also show extensive authigenic  $\text{CaCO}_3$  precipitation with varying size and morphology.

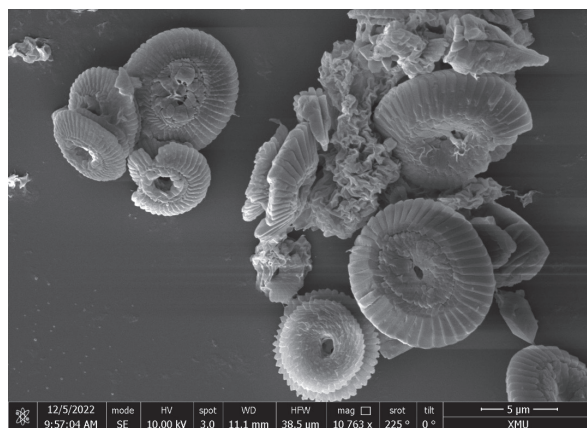


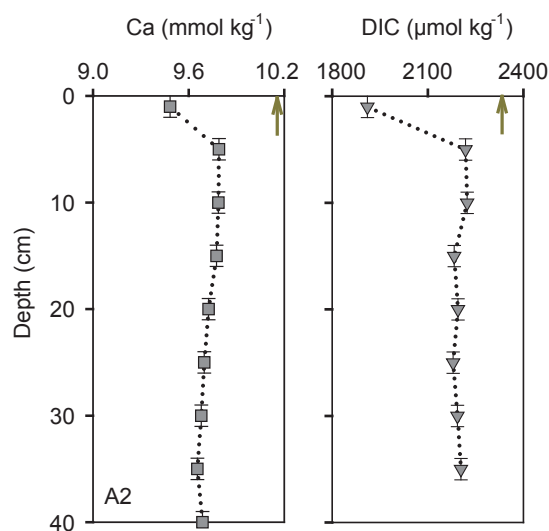
Fig. 1. SEM image of white mineral crust in the surface sediment collected from the Mariana Trench. The image exhibits abundant  $\text{CaCO}_3$ -bearing frustules of coccolithopores.

Many grains are up to ten micrometers in size or larger, and some rice-like grains are in the order of several hundred nanometers. As can be seen from the morphology, the crystals have the foliated structure characteristic of calcite. Energy-dispersive system analyses illustrate that the atomic composition of these aggregates (18.6% Ca, 19.4% C, and 60.3% O) is similar to that of pure calcite crystals ( $\text{Ca}:\text{C}:\text{O} = 1:1:3$ ). Solid phase analyses reveal a low but significant level of  $\text{CaCO}_3$  (~0.8 wt%). These observations provide compelling evidence that in contrary to our expectation,  $\text{CaCO}_3$  frustules are well preserved and authigenic  $\text{CaCO}_3$  is likely to form on the ocean floor below the calcite compensation depth.

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## 2. Porewater evidence on authigenic carbonate formation

We determined relevant porewater constituents and sediment composition from a total of seven sites located around the Mariana Trench. Strikingly, all porewater profiles manifest a marked depletion of  $\text{Ca}^{2+}$  and most of them also show a concomitant depletion of dissolved inorganic carbon (DIC) (Figure 2). The porewater concentration of  $\text{Ca}^{2+}$  ranges from 9.29 to 10.11  $\text{mmol Ca kg}^{-1}$  in the upper 50 cm of sediment, which on average is  $\sim 0.35$   $\text{mmol Ca kg}^{-1}$  lower than the rather constant seawater concentration of  $\sim 10.16$   $\text{mmol Ca kg}^{-1}$ . Measured porewater DIC concentrations are in the typical range of 2100 to 2300  $\mu\text{mol kg}^{-1}$ . The lowest concentrations frequently decline to  $< 2000$   $\mu\text{mol kg}^{-1}$  and generally occur at the topmost 1 cm of sediment, indicating the most vigorous DIC removal there. In contrast, the bottom water concentration is nearly constant at about 2325  $\mu\text{mol kg}^{-1}$ . Therefore, we attribute the mechanism responsible for the concomitant



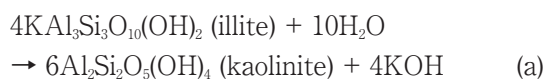
**Fig. 2.** Porewater concentration profiles of calcium (A) and dissolved inorganic carbon (B) in the Mariana Trench. The dark yellow arrows beneath y-axes denote bottom water concentration of the respective constituent.

removal of porewater  $\text{Ca}^{2+}$  and DIC to the formation of authigenic  $\text{CaCO}_3$  in the sediment.

We also conducted glass electrode measurements of pH in selected aqueous samples. Our results show a pH value of 7.72 in the overlying seawater and a 0.3-unit higher pH in porewater (7.99 – 8.09). Calculations using a porewater pH of about 8.04 (that is 7.74 in bottom water plus 0.3) and the range of measured porewater DIC indicate nearly saturated condition with respect to mineral calcite in the sediment.

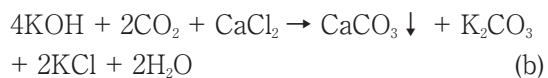
## 3. Illite weathering to kaolinite as the proton sink driving authigenic $\text{CaCO}_3$ formation

The substantial pH rise in porewater indicates that protons are being consumed. We suggest chemical weathering of aluminosilicate minerals as the dominant mechanism because this diagenetic pathway generates  $\text{OH}^-$  ions (or consumes protons) and releases dissolved cations. In the North Pacific near-surface sediment, the porewater concentration of  $\text{K}^+$  falls in the typical range of 11 to 12  $\text{mmol kg}^{-1}$ , drastically higher than the bottom water value of  $\sim 10.11$   $\text{mmol kg}^{-1}$ . In marine sediments, the principal type of potassium-bearing aluminosilicate minerals is illite (chemical formula:  $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ ). Illite is known as a secondary mineral formed during the weathering of orthoclase feldspar (K-feldspar) and can further be converted to kaolinite (chemical formula:  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), which is the stable weathering product of feldspars. This reaction is generally referred to as hydrolysis:

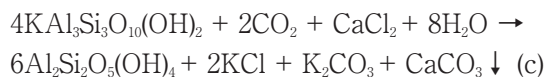


We suggest that the  $\text{OH}^-$  ions generated in this

step react with dissolved  $\text{CO}_2$  and  $\text{Ca}^{2+}$  in porewater to form authigenic calcite:



Combining Reaction (a) and (b) gives



Our porewater measurements reveal a strong correlation between  $\text{Ca}^{2+}$  consumption and  $\text{K}^+$  production. The relationship of the two major cations shows that the porewater concentration of  $\text{Ca}^{2+}$  declines with the rise in  $\text{K}^+$ , and the stoichiometry ratio of  $\text{Ca}^{2+}$  and  $\text{K}^+$  changes (-1:4.1) is very close to the value (-1:4) predicted by Reaction (c). The prevalence of Reaction (c) indicates that the formation of authigenic  $\text{CaCO}_3$  must be attributed to the limited supply of  $\text{CO}_2$ , which in turn is a result of the slow sedimentation rate and low sediment TOC content characteristic of the deep ocean floor. We note that the delicate balance between the supply of  $\text{CO}_2$  by aerobic respiration and the production of  $\text{OH}^-$  ions by illite weathering is an important premise. Otherwise, the excess  $\text{CO}_2$  would dissolve the  $\text{CaCO}_3$  precipitates that have already formed. Then the porewater content of  $\text{Ca}^{2+}$  would not decrease with the increase in  $\text{K}^+$ .

#### 4. $^{226}\text{Ra}/^{230}\text{Th}$ disequilibrium approach to estimate solute transport fluxes

To assess the geochemical significance of authigenic  $\text{CaCO}_3$  formation in slow sedimentation environments on seawater ionic mass balances, we have developed a novel technology, the naturally occurring  $^{226}\text{Ra}/^{230}\text{Th}$  isotope pair in the uranium decay chain, to estimate transport fluxes of dissolved

constituents from (or into) the sediment deposit. The flux of  $\text{K}^+$  out of the sediment deposit fluctuates between 58 and 520  $\text{mmol m}^{-2} \text{yr}^{-1}$  and averages 250  $\text{mmol m}^{-2} \text{yr}^{-1}$ . The average flux of  $\text{Ca}^{2+}$  into the sediment deposit is about 60  $\text{mmol m}^{-2} \text{yr}^{-1}$ , which is about a factor of four lower than that of  $\text{K}^+$  and is consistent with the stoichiometric prediction from Reaction (c). This  $\text{Ca}^{2+}$  flux also means a concomitant carbon removal flux of 60  $\text{mmol m}^{-2} \text{yr}^{-1}$ , which is close to the global average continental weathering rate (98  $\text{mmol C m}^{-2} \text{yr}^{-1}$ ). On the other hand, the average flux of DIC into the sediment is estimated to be 15  $\text{mmol m}^{-2} \text{yr}^{-1}$ , which constitutes only a quarter of the total carbon removal for the formation of authigenic  $\text{CaCO}_3$ . The remaining three quarters of the carbon, or an equivalent rate of 45  $\text{mmol C m}^{-2} \text{yr}^{-1}$ , must come from aerobic respiration of sedimentary organic matter. If we use the Redfield ratio of 106:138 for C and  $\text{O}_2$  changes during aerobic respiration, the oxygen consumption rate estimated from the difference between  $\text{Ca}^{2+}$  flux and DIC flux would fall in a range of 3 to 127  $\text{mmol O}_2 \text{m}^{-2} \text{yr}^{-1}$ . This aerobic respiration rate is consistent with previous benthic chamber measurements that gave a typical range of 20 to 140  $\text{mmol O}_2 \text{m}^{-2} \text{yr}^{-1}$  for organic carbon oxidation rate in this oceanic realm. Notably, the outward flux of silicic acid is ~10 times lower than that of  $\text{K}^+$ . This result is consistent with the prediction from Reaction (c) that no silicic acid is generated during the weathering of illite.

#### 5. Implications for global stable isotope value and ocean $\text{CaCO}_3$ balance

Our work indicates that the formation of  $\text{CaCO}_3$  on the deep ocean floor has important implications for the global Ca and C budget. If

the average uptake flux of  $60 \text{ mmol Ca}^{2+} \text{ m}^{-2} \text{ yr}^{-1}$  is representative for the ocean floor below the compensation depth (total area:  $\sim 1.1 \times 10^8 \text{ km}^2$ ), a simple linear extrapolation reveals that the total production rate of authigenic  $\text{CaCO}_3$  amounts to  $\sim 6.6 \times 10^{12} \text{ mol yr}^{-1}$  or  $\text{Tmol yr}^{-1}$ . This sink is half the annual riverine  $\text{Ca}^{2+}$  supply, and accounts for  $\sim 20\%$  of the annual riverine  $\text{HCO}_3^-$  supply to the ocean. Thus, it appears nearly twice as much calcium is removed from the modern ocean by carbonate burial ( $\sim 38 \text{ Tmol yr}^{-1}$ ) as is estimated to be supplied by rivers and basalt weathering in the Mid-ocean ridges ( $\sim 21 \text{ Tmol yr}^{-1}$ ). In this respect, our study reinforces that the modern ocean may not be in steady state. We must emphasize that authigenic  $\text{CaCO}_3$  formation is also likely to occur on the seafloor above the compensation depth. As long as the premise that the production rate of  $\text{CO}_2$  from aerobic respiration of sedimentary organic matter is slower than the supply rate of  $\text{OH}^-$  ions from the weathering of illite is satisfied, authigenic  $\text{CaCO}_3$  formation can proceed. Thus, this may be a common scenario for most of the global ocean basin floor where sediments are characterized with low TOC content and high abundance of illite. In this regard, our estimate should be treated as a lower limit for the total production rate of authigenic  $\text{CaCO}_3$  in the global ocean. As such, we conclude that the formation of authigenic  $\text{CaCO}_3$  driven by the illite weathering to kaolinite represents an important but previously unrecognized geochemical pathway for calcium and carbon removal in the modern ocean.

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