Nucleation pathways and energetic controls during templated nucleation of calcite by MHA and MUA self-assembled monolayers

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Organic templates in living systems are believed to control nucleation rates and crystallographic orientations of nuclei. Self-assembled monolayers (SAMs) have been frequently used as a simple model to reproduce the function of natural templates. In particular, SAMs made of alkanethiol molecules have been demonstrated to effectively induce highly-oriented nucleation of calcium carbonate [1, 2].

Although a mechanistic understanding of templating requires knowledge of the thermodynamic and kinetic barriers, no experimental work has been done to quantify these factors. Moreover, the importance of indirect nucleation pathways via amorphous precursors during templating remains unresolved. The objective of this study is to use measurements of nucleation rates to determine the interfacial energies between template-directed calcite nuclei and 16-mercaptohexadecanoic acid (MHA) and 11-mercaptoundecanoic acid (MUA), and to determine whether nucleation occurs via the amorphous phase. The results reveal that (1) MHA and MUA both significantly reduce the effective surface energy of calcite from about 97 mJ/m2 in solution to about 45.3 and 52.7 mJ/m2 on MHA and MUA respectively, providing a thermodynamic basis for the strong capacity of MHA and MUA to promote calcite nucleation; and (2) at solute activities below the solubility limit of amorphous calcium carbonate, calcite forms directly.

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Late Cenozoic history of deep water circulation in the western North Pacific: Evidence from Nd isotopes of ferromangnese crusts

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Despite the importance of deep ocean circulation in regulating the global climate, its past variations in the western North Pacific are still poorly understood. Nd isotopes of ferromanganese crusts have proven a good proxy for paleoceanic circulation changes. We obtained late Cenozoic Nd isotopic data of two ferromanganese crusts located near Mariana arc but at different water depths (MKD13: 1500m, MDD53: 2700m), and studied their implications for paleocirculation changes in this area. From early to late Miocene, Nd isotopic compositions of MDD53 remained stable. MDD53 was also characterized by the least radiogenic feature (Nd: -4.0 to -5.0) compared with crusts of similar water depths in the Miocene North Pacific. Afterward in the Pliocene Nd value of MDD53 increased sharply. In contrast, Nd isotopes of MKD13 became more and more radiogenic in the Miocene and were almost invariable afterwards. We interpret the continual increase in Nd of the shallower crust MKD13 as reflecting progressive closure of Indonesian Seaway in the Miocene, while the deep western boundary current originated from the Southern Pacific may have dominated Nd isotopes of the deeper crust MDD53 during the same time interval. The lack of Nd isotopic variation of MKD13 in the Pliocene indicates that there were no changes in Nd sources in the shallower water. Therefore the observed large shift to more radiogenic Nd isotopes of MDD53 in the Pliocene should not be caused by change in vertical input from shallower to deeper water. Instead, we suggest that the ventilation of deep southern component current along the studied water depth range (~2700m) may have evidently decreased in the early Pliocene.

This study was funded by the Chinese Association for Research of Oceanic Mineral Resources (DY-115-01-2-2) and the Education Ministry of China.