

Sulfur isotope systematics of sulfide oxidation intermediates: implications for organic geochemistry

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Bacterial sulfate reduction in natural anoxic aquatic systems produces hydrogen sulfide. Chemical and biological oxidation of sulfide results in formation of sulfate as well as variety of intermediate species, such as polysulfides (S_n^{2-}), elemental sulfur (S_8), thiosulfate ($S_2O_3^{2-}$), sulfite (SO_3^{2-}) and polythionates ($S_nO_6^{2-}$). Many of sulfide oxidation intermediates are highly reactive toward other inorganic and organic species. Such reactions result in formation of secondary products including dimethylpolysulfanes, carbonyl sulfide, and sulfur cross-linked organic macromolecules [1-3]. Sulfurization of organic matter during early diagenesis occurs due to reactions of organic molecules with polysulfides and possibly with other sulfide oxidation intermediates (e.g. thiosulfate, sulfite) [4,5].

Bacterial sulfate reduction and bacterial sulfur disproportionation are known to result in relatively high sulfur isotope fractionation. On the other hand, processes involved in reoxidative part of sulfur cycle produce only small sulfur isotope fractionations. For example, $\delta^{34}S$ values of fractionation between H_2S and HS^- were reported to be up to 2.7‰ [6], between sulfur and hydrogen sulfide (by anaerobic bacterial sulfide oxidation) – 2‰ [7], between HS^- and inorganic polysulfides (S_n^{2-}) – up to 4‰ [8], and between thiosulfate and sulfide during bacterial reduction of thiosulfate – 10‰ [9].

A new powerful tool, simultaneous measurement of abundances of all four stable isotopes of sulfur, was recently applied for studying reoxidative part of biogeochemical sulfur cycle [10-12]. First multiple sulfur isotope fractionation fingerprints look promising for future decoupling of various pathways of sulfide reoxidation in natural aquatic systems.

Future application of multiple sulfur isotope approach to formation of sulfide oxidation intermediates as well as to reactions between sulfide oxidation intermediates and organic molecules have a potential to shed a light on mechanisms of diagenetic sulfurization of organic matter as well as on oil formation scenarios.

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Biominingeralization of Mg-rich calcite by aerobic microorganism enriched from rhodoliths

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Introduction

The formation of carbonate minerals by biological processes may play an important role in carbon and metal geochemistry in natural environments. The objectives of this study were to investigate biominingeralization of the carbonate minerals using microorganisms enriched from rhodoliths and to identify environmental factors that control the formation of calcite by the microorganisms.

Materials and Methods

Carbonate forming microorganisms were enriched from rhodoliths, which were sampled at Seogwang-ri coast in the western part of Wu Island, Jeju-do, Korea. Microorganisms enriched from rhodoliths were aerobically cultured at 25°C in D-1 media containing various concentrations (0, 30, 100 mM) of Ca and Mg-acetate, and the microorganisms were analyzed by 16S rRNA gene DGGE analysis to confirm microbial diversity. Mineralogical characteristics of the rhodoliths and carbonate minerals precipitated by the enriched microorganisms were determined by XRF, XRD, and SEM-EDS analyses.

Results and Conclusion

XRF and XRD analyses showed the rhodoliths mainly consisted of CaO (46%) and MgO (5%) and major mineral is Mg-rich calcite. A 16S rRNA sequence analysis showed the enriched microorganisms contained carbonate forming microorganisms such as *proteus mirabilis* and *marinobacterium coralli* [1, 2]. The enriched microorganisms precipitated carbonate minerals using D-1 media containing Ca and Mg-acetate (30, 100 mM) and mineralogy of the precipitated carbonate mineral was Mg-rich calcite. Whereas, the microorganisms did not form carbonate minerals without Ca and Mg-acetate in D-1 media. SEM-EDS analyses showed that the Mg-rich calcite formed by the microorganisms had a rhombohedron shape and consisted of Ca, Si and Mg with extracellular polymeric substance (EPS). These results indicate that the microorganisms induce precipitation of Mg-rich calcite on the cell walls and EPS via the accumulation of Ca and/or Mg ions on the cells. Therefore, microbial precipitation of carbonate minerals may play one of important roles in metal and carbon biogeochemistry as well as carbon sequestration in natural environments.

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