Identification of factors affecting partitioning of rare arth elements between calcite and seawater

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[Introduction]

Concentrations of 14 rare earth elements (REEs) in carbonates are considered to reflect that of seawater via partitioning coefficients, which may be controlled by chemical conditions of seawater. Therefore, partitioning coefficients could be used as a proxy of either REE composition of seawater or chemical conditions. However, the reported partitioning coefficients of rare earth elements are inconsistent, and it has not been certain whether it could be applied to an actual seawater column. In the ocean, carbonate particles are supplied at the surface layer and absorb dissolved elements during settling through a column. In this study, we devised an experimental system mimicking a natural seawater column, where carbonate particles were introduced to carry out partitioning. We have identified several factors that affect the partitioning.

[Method]

Calcite particles of various sizes were added to seawater in a reaction vessel, and were left to partition REEs for a certain period under slightly saturated conditions with respect to calcite by modulating carbon dioxide partial pressure in bubbling air. The calcite particles in half of the seawater were size-separated by elutriation and analyzed for REEs and Ca using ICP-MS and ICP-OES (Stage 1). The calcite particles in another half the seawater were further subjected to the partitioning under an unsaturated condition with respect to calcite by increasing the carbon dioxide partial pressure in bubbling air (Stage 2). They were treated in the same manner as in Stage 1. The partitioning coefficient under each condition was determined by analyzing the relationship between particle size and Ln/Ca.

[Results]

Thermodynamic analysis of the system using pH and calcium concentration data revealed that the presence of REEs significantly inhibits the dissolution of calcium carbonate. REEs have been reported to inhibit calcium carbonate growth, but inhibition of dissolution has not been reported. The partitioning pattern was significantly affected by the addition of iron, but it was found that Mn in seawater had little effect. Also, iron appeared to form an independent hydroxide phase. In addition, it was found that the overall pattern sensitively changes depending on pH of seawater. We also conducted experiments with a fairly small amount of REEs added. Partitioning values higher than most of the reported values were obtaine.

Keywords: Rare earth elements, Calcite, seawater, partitioning experiments