Behavior of phosphorus during hydrothermal alteration of basalt under CO_2-rich condition

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It is well known that a unique environment is created around seafloor hydrothermal systems by element exchange between circulating seawater and surrounding rocks: enrichment in transition elements and sulfide, emission of quite hot water, and even even electric current flow. In addition, a number of hyperthermophilic microorganisms inhabit around hydrothermal vents. 16S rRNA-based phylogenetic tree suggests that the hyperthermophilic organisms are closest to the earliest lineage; thus the hydrothermal environment is one of the candidates for habitat and evolution of early life.

Phosphorus is one of essential elements for life. In order to maintain an early ecosystem around the hydrothermal vent, phosphorus should have been supplied from the hydrothermal vent through high-temperature water-rock reaction. In the modern basalt-hosted hydrothermal systems, phosphorus is removed due to its adsorption to iron oxide precipitated from hydrothermal fluid and/or formation of metamorphic apatite in the hydrothermally metamorphosed basalt. On the other hand, it is well known that middle Archean basaltic rocks, which constituted upper part of oceanic crust, suffered from severe carbonation during hydrothermal alteration due to quite high atmospheric CO_2 content on the early Earth. Under the CO_2-rich condition, calcium was removed from the seawater/hydrothermal fluid due to extensive carbonate formation. Because the carbonate formation inhibits the formation of apatite, the phosphorus might be released from hydrothermally altered rocks. Actually, the hydrothermally altered basaltic rocks in the Archean are more depleted in phosphorus than hydrothermally altered modern mid-ocean ridge basalt.

In order to quantify phosphorus content of fluid supplied from the basalt-hosted hydrothermal system on the early Earth, we conducted hydrothermal experiments involving hypothetical seawater and basalt under both CO_2-free and CO_2-rich conditions at 200 ˚C, 100 bars. The basalt used in this study was collected from the Indian Ocean Marie Celeste Fracture Zone. The initial solution was prepared by mixture of standard reagents by reference to modern seawater, except for Ca and P. The calcium and phosphorus contents in the solution were regulated to 30 mmol/kg and 0.60 ppm, respectively. The latter is ten times higher than the modern equivalent. For the CO_2-rich experiment, $NaHCO_3$ and HCl were added to the hypothetic seawater to substantialize 400 mmol/kg of ΣCO_2 at the beginning of the experiment.

The CO_2 concentration decreased from 400 mmol/kg to 250 mmol/kg as water-rock reaction advanced, indicating precipitation of carbonate minerals. The SEM-EDS observation demonstrated that the run products contain calcite, dolomite, and magnesite. Phosphorus content of the fluid decreased to *ca.* 0.10 ppm under the CO_2-rich condition and *ca.* 0.04 ppm under the CO_2-free condition, respectively. The pH value of the produced fluid for the CO_2-rich experiment, measured at room temperature, was 6.6, by *ca.* 2 unit higher than that of the CO_2-free experiment. Calcium concentration decreased from 30 mmol/kg to 25 mmol/kg under the CO_2-free condition. On the other hand, calcium concentration of the formed fluid under the CO_2-rich condition decreased to 18 mmol/kg at 96 hours, and then increased to 25 mmol/kg. The formation of high alkaline and Ca-poor fluid under the CO_2-rich condition suggests that the fluid was oversaturated with carbonate, whereas undersaturated with apatite. Because the produced fluid under the CO_2-rich condition contained more phosphorus than the modern seawater, the basalt-hosted hydrothermal system may have served as a source of phosphorus under the CO_2-rich condition, probably on the early earth.

