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# Behavior of phosphate during the submarine hydrothermal alteration of ca. 3.455 Ga Apex Basalt, Australia

**YUYA TSUKAMOTO**[1] AND PROF. TAKESHI KAKEGAWA, PH.D.[2]

[1]Japan Collection of Microorganisms, RIKEN
[2]Graduate School of Science, Tohoku University

A phosphate-poor ocean model is popular for the Archean oceans. On the other hand, recent studies have suggested the possibility of high phosphorus flux from the Archean submarine hydrothermal activity, yielding phosphate-rich oceans. Here, we performed mineralogical and geochemical analyses for the 3.455 Ga Apex Basalt in ABDP#1 core from the Pilbara Craton, Australia, to examine if Archean submarine hydrothermal activity could play the role of a phosphate source to contemporary oceans.

In this study, the 60 m section of Apex Basalt was divided into three zones. Zone A (top 10 m section) is the least altered zone, containing actinolite, epidote, albite, and chlorite with low chemical index of alteration (CIA) values (0.42 to 0.44). Concentrations of $P_2O_5$ in Zone A were 0.10±0.01 wt%. Euhedral apatite crystals were observed in Zone A, interpreted as the remnants of igneous phosphates in Apex Basalt. Zone B (middle 25 m section) was extensively chloritized, with abundant siderite and quartz. Zone C (lower 25 m section) comprised chlorite, sericite, and sulfides. CIA values of both Zones B and C ranged from 0.77 to 0.99, suggesting intensive hydrothermal alteration. Most parts of Zones B and C were depleted in $P_2O_5$ (0.01±0.01 wt%), but minor enrichment of $P_2O_5$ (0.06±0.01 wt%) with secondary apatite, xenotime ($YPO_4$), berlinite ($AlPO_4$), and florencite (Ce, La, Nd)$Al_3(PO_4)_2(OH)_6$) were found. A similar relationship between P depletion and CIA values, and the different occurrences of phosphate mineralogical compositions between Zone A, and Zones B and C indicate that such P depletion was caused by 3.455 Ga submarine hydrothermal activity.

Calculations of apatite solubility suggested that hydrothermal fluids percolating Zone B could contain at least similar level as the modern marine phosphorus concentration (2.3 μM) and could reach up to 2 mM. The estimated phosphate flux from Archean hydrothermal activity could be more than $3.6 \times 10^{12}$ g/yr, which is comparable to the riverine flux, modern primary phosphorus source of the ocean. Its flux could have been significant for the early biosphere, even if the exposed landmasses had been very limited.