Minor and trace element geochemistry of a branching coral *Acropora sp.* skeleton

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Incorporations of chemical elements and isotopes, into coral skeletons are influenced by ambient water conditions which may provide important information on past climate in the tropics. The geochemistry of *Acropora* is significantly important for the past-temperature reconstruction because *Acropora* is one of the main genera constituting the coral reefs. *Acropora* may also provide unique opportunity to evaluate the effects of physiological processes on the elemental incorporation. Branching coral *Acropora* consists of fast-growing axial corallite and slowly growing radial corallite at the visible scale. On the other hand, at the micro-scale, there are several types of skeletal elements precipitated under different biological mechanisms. However, geochemistry of branching corals has not been well understood. To investigate the mechanisms of elemental incorporation into *Acropora* skeletons, chemical and isotopic compositions in the skeleton were analyzed at various spatial resolutions.

The chemical profiles of both axial and radial corallite along with growth axes were measured by conventional ICP-MS and Stable Isotope Mass Spectrometry. The tip and basal parts of *Acropora* skeletons were also analyzed at micro-scale. The Mg/Ca, Sr/Ca, Ba/Ca, and U/Ca ratios were measured in ~8μm diameter spots by using NanoSIMS, and Mg, Sr, Ca, and S distributions were analyzed by Electron Probe Micro Analyzer (EPMA), with a spatial resolution of ~2μm.

Based on the elemental distribution obtained by EPMA, we found that the *Acropora*'s skeleton is composed of more than three types of the skeletal elements, “Framework”, “Infilling” and “High-Mg Low-S” skeletons. Observation of skeletal structure revealed that the skeletal porosity decreased with distance from the tip, because “Infilling” skeletons possibly filled the space between “Framework” skeletons. Micro-scale elemental analyses (EPMA and NanoSIMS) revealed that “Infilling” skeletons have lower Mg/Ca and higher Sr/Ca and U/Ca than “Framework” skeletons. Since the “Infilling” skeletons were probably formed under the slower calcification rate than “Framework” skeletons, the elemental fractionation pattern between two skeletal elements is consistent with the model of elemental incorporations dependent on calcification rate. The chemical profiles of axial corallite along with the growth were significantly affected by the proportions of “Infilling” skeletons.

Mantle and crustal processes in the Hadean and Archean: Evidence for the onset of subduction at 3.8 Ga

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Considerable geochemical evidence supports initiation of plate tectonics on Earth shortly after the end of the Hadean. The present upper mantle retains old heterogeneities, some of which likely derive from subduction in the early Eoarchean. Nb/Th and Th/U ratios of mafic-ultramafic rocks from the depleted upper mantle begin to change from 7 to 18.2 and 4.7 to 2.9 (respectively) at 3.6 Ga. This signals the appearance of subduction-altered slabs in general mantle circulation from subduction initiated at 3.8 Ga. Juvenile crustal rocks begin to show derivation from progressively depleted mantle with typical igneous ε Nd:ε Hf = 1:2 after 3.6 Ga. Cratons with stable mantle keels that have subduction imprints begin to appear at 3.5 Ga. These changes all suggest that extraction of continental crust by plate tectonic processes was progressively depleting the mantle from 3.6 Ga onwards. Neoarchean subduction appears largely analogous to present subduction except for the production of large cratons with thick mantle keels. The earliest Eoarchean juvenile rocks and Hadean zircons have compositions that reflect the integrated effects of separation of an early enriched reservoir and fractionation of perovskite from the Mars-sized, impact-derived magma ocean, rather than separation of voluminous continental crust or oceanic plate tectonics. Hadean zircons most likely were derived from a continent-absent, initially mafic to ultramafic protocrust that was multiply remelted between 4.4 and 4.0 Ga under wet conditions to produce more evolved (felsic) rocks. If the protocrust was produced by global mantle overturn at ca 4.4 Ga, then the transition to plate tectonics resulted from radioactive decay-driven mantle heating. Otherwise, such protocrust would have been the typical product of mantle convection and the transition to plate tectonics resulted from cooling and stabilization of lithospheric plates.