Exploring the hydrogen isotopic composition of deep-sea corals

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Despite the widespread use of hydrogen isotopic analyses in environmental investigations, no previously-published work has attempted to measure or utilize the hydrogen isotopic composition (δ D) of deep-sea corals. Geographically widespread, forming annual growth rings, and having lifespans on the scale of hundreds of years, δ D measurements of deep-sea coral skeletons have the potential to elucidate oceanographic parameters at well-resolved spatial and temporal resolutions.

We present a method for the determination of annually-resolved δ D in gorgonin, a complex proteinaceous material making up the horny skeletal component of gorgonian corals. We address the issue of exchangeable hydrogen in gorgonin by controlling the isotopic composition of the exchangeable fraction of the total hydrogen pool using a heated batch equilibration technique. Coupled with seawater δ D profiles, the δ D of particulate organic matter (POM) filtered from seawater, and the δ D of plankton trawl samples, we attempt to identify the relationships between trophic exchange, physical oceanographic parameters, and the δ D of gorgonin from 3 species of live-collected coral.

Results include a 43-year record from a Primnoa pacifica colony collected from the Gulf of Alaska, three 10-year records from Primnoa resedaeformis colonies collected from the Labrador Sea, and a 40-year record from a Keratoisis grayii colony collected from southern Baffin Bay. Preliminary data show an unprecedented range of δ D values in all three species, ranging from -40‰ to -110‰. Final results will determine the suitability of gorgonin δ D as a potential marine environmental proxy by testing the reproducibility of δ D values between adjacent colonies.

Keywords: Deep-sea, Coral, Hydrogen, Isotopes, Experimental, Geochemistry

Evaluation of heterogeneity of reaction-transport phenomenon in rock by sequential pore water extraction

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Heterogeneity of dissolution/precipitation and solute transport in rock pores has been drawing attention in recent years. This phenomenon has been often studied using numerical calculation, but direct analysis of pore water is important to know what is actually occurring in pores. However, most previous studies have analysed the composition of bulk pore solution and it is difficult to discuss the detail of reactive-transport behaviour in pores using the bulk composition. In the present study, an experimental technique to sequentially extract pore water by applying various gas pressures to wet sample was used. With this technique, pore water can be extracted for each pore radius, which provides information on the heterogeneity of reaction and transport in pores. In the experiment, pure water was first passed through a sandstone core to induce dissolution in pores (flow-through reaction), then pore water was extracted for each pore size and solute concentrations were measured. The result of the experiment showed that the concentrations of Na, Ca, Mg, and Si increased with decreasing pore radius and that the concentration increases of Ca, Mg, and Na were greater than that of Si. Qualitatively, this result can be explained by a numerical model of the advection and dissolution in a single tube for different pore radii. However, the observed concentration increases were significantly greater than the model calculation, and it seems possible to evaluate the extent of the mixing of solutions in narrow pore and large pore by comparing the model calculation and experimental result.

Keywords: pore water, dissolution, advection

Subseafloor weathering of cretaceous basaltic basement revealed by nanomineralogical and conventional clay characterizations

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Areal coverage of basaltic ocean crust overlain by oxygenated sediments reaches up to 25% on Earth. During 10 million years after formation, porous basaltic lava erupted at mid-ocean ridges generally become impermeable due to infilling of secondary minerals formed by hydrothermal alteration. Although chemical reactions between basalt and seawater might continue to influence the elemental distribution between ocean and crust around the globe, it remains unknown whether or not porous fractions filled with secondary minerals are susceptible of low-temperature rock water interactions collectively referred to as weathering. By integrated ocean drilling program (IODP), 84-120-Ma basaltic basement covered by 70-m-thick oxygenated sediment was drilled down to 121 meters below seafloor, and nanomineralogical and conventional clay characterizations were conducted for three basaltic core samples with different fracture-filling secondary minerals (Ca carbonate in U1365E7R-2, celadonite in U1365E8R-4, Fe oxyhydroxides in U1365E12R-2). X-ray diffraction (XRD) pattern analysis of clay fractions collected from powdered core samples after particle dispersion in water revealed that the presence of clay minerals with basal spacings (d_{001}) of 1.5 nm after air dry and d_{001} of 1.7 nm after glycolation in all samples. As (060) reflections of the clay minerals are characteristics of trioctahedral smectite in U1365E7R-2, Fe-rich dioctahedral smectite in U1365E12R-2, and both the smectite clays in U1365E8R-4. Scanning electron microscopic (SEM) observations with energy dispersive X-ray spectroscopic (EDS) analysis clarified that chemical compositions of the trioctahedral and dioctahedral smectite clays are identical to those of saponite and notronite, respectively. SEM-EDS analysis of thin sections across the basalt-fracture transect revealed the infilling of Ca carbonate-bearing fractures with saponite in U1365E7R-2, whereas nontronite, which was located at the rim of celadonite in U1365E8R-4 and randomly in the partially filled fracture in U1365E12R-2, was highly enriched with Fe. By focused ion beam (FIB) milling coupled to high- resolution transmission electron microscopy (HR-TEM), it was revealed that the excess Fe is resulted from the co-occurrence of goethite nanoparticles. As the occurrence of nontronite is clearly correlated with textural features that indicate the high porosity and permeability around grain boundaries, it is suggested that notronite was likely formed by weathering. Furthermore, the K enrichment in notronite agrees with downward diffusional K flux from seawater to the basaltic basement through overlying sediments, which supports the inference that subsefloor weathering is ongoing and associated with microbial colonization. From this study, it is concluded that the upper oceanic crust might be globally reactive to control the chemical composition of seawater.

Keywords: nontronite, oceanic crust, weathering, FIB-TEM

Microstructure and geochemistry of organic matters associated with iron minerals in 3.2 Ga banded iron formations, Moodies Group, Barberton Green stone Belt, South Africa

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The iron oxidation process in Banded iron formations (BIFs) is still controversial especially before the Great Oxidation Event. Previous studies suggest that microbial activity, either free oxygen produced by cyanobacteria or anoxygenic iron-oxidizing bacteria was involved in the formation of BIFs. Therefore, geochemical characteristics and occurrence of organic matters relating to the iron mineralogy may give an insight to the oxidation process. Here, we performed geological, petrological, and geochemical investigations on ~3.2Ga BIFs deposited in a shallow ocean, where high microbial productivity were expected, in the Sheba gold mine, Moodies Group, Barberton Green stone Belt, South Africa. Rock samples were classified into the MT type (magnetite-rich sandstone, 13-50 wt% Fe_2O_3) and SD type (magnetite-poor silty clastics, 10-30 wt% Fe_2O_3) based on the dominant iron mineral. MT type consists of alternating magnetite-rich layers and silicate-rich layers, containing euhedral magnetite, carbonates, quartz, biotite and chlorite. SD type is subdivided into SD-1, which consists of alternating carbonates (siderite, ankerite and dolomite)-quartz-rich layers and biotite-chlorite-rich layer, and SD-2, which contains the smaller grains of quartz, chlorite and biotite.

These samples contain 0.03-0.29 wt% of carbonaceous matters, which are observed as aggregates of 20 μm round or oval flakes in diameter. Wrinkles and folding structure are often observed on the surface of the flake structures. Carbon stable isotope ratio of the carbonaceous matters shows -26~-27‰, suggesting that it is likely to be derived from organisms. Microfossil-like strucstures in Moodies shales observed by Javaux et al., (2010) have the similar characteristics to this study, though they shows the wider range in the size distribution (31-298 μm in diameter). Organic matters extracted by acid dissolution has ~0.002 of N/C ratio, which is consistent with that of kerogen in Archean rocks that were subjected to a similar metamorphic grade. Raman microspectroscopy of the extracted organic matters indicates that they have experienced ~500 °C metamorphic temperature, which is slightly higher than the regional metamorphism in Moodies group. This may be due to an influence by the later hydrothermal fluids involving gold mineralization.

In both sample types, the iron content show a negative correlation with the organic carbon content, but a positive correlation with the carbonate carbon content. Most SD-1 samples show higher carbonate carbon to iron ratios than that of siderite. The carbon stable isotope ratios of carbonates in MT and SD-1 samples were ~-4‰. These results suggest that most carbonates in SD-1 and MT samples were ankerite and/or dolomite derived from mineralizing fluids. Previous studies indicate that organic matters in BIFs can be consumed as CO_2 or converted to siderite by a reaction with primary iron oxides during diagenetic and metamorphic process (Perry et al., 1973, Kohler et al., 2013). However, SD-2 samples showing high organic carbon contents are poor in carbonates and iron. Moreover, considering carbonate carbon stable isotope ratio in MT and SD-1 type samples and relatively high organic carbon contents in MT type samples (0.03-0.26 wt%), we suggest that the negative correlation between the organic carbon and iron contents is a primary signature during the deposition of BIFs. Assuming that a model proposed by Kohler et al. (2013) can be applied to this study, SD-2 samples, which are organic carbon-rich and iron-poor, and MT samples, which are carbon-poor and iron-rich, may reflect the activities of cyanobacteria and iron-oxidizing bacteria, respectively, in different depositional settings. Then, our results imply that cyanobacteria would flourish nearby coast, whereas iron-oxidizing bacteria would be active relatively far from the coast, or below the cyanobacteria in 3.2Ga shallow ocean.

Keywords: Banded Iron Formations, Barberton Green stone Belt, organic matters

Depositional environment of graphite-bearing metasedimentary rocks and banded iron formations in >3.7 Ga Isua Supracrustal Belt, West Greenland

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Biogenic graphite in > 3.7 Ga metasedimenrary rocks, Isua Supracrustal Belt (ISB), West Greenland, has been reported as the oldest remnants of life (Rosing, 1999; Ohtomo et al., 2014). However, ecosystem spreaded in the >3.7Ga ocean is still poorly understood. Depositional environments of metasedimentary rocks containing biogenic graphite and surrounding banded iron formations (BIFs) could give an insight into microbial activities in the >3.7Ga ocean. Graphite-rich schist reported by Ohtomo et al. (2014) contains rare earth element (REE) minerals such as monazite, zircon and xenotime. These REE minerals could have been deriven by one or some of the following processes: detrital transport, precipitation from a seafloor hydrothermal fluid, generation during diagenesis and precipitation from a metamorphic fluid. Occurrence, geochemical composition and chronological information of the REE minerals might constrain their origin and provide information of depositional and/or alteration process of the graphite-rich schist. Here, we performed a geological survey in the west side of the ISB and investigated the petrographic and geochemical characteristics of sedimentary rocks to reconstract the depositional environment. Chemical Th-U-total Pb Isochron Method (CHIME) was conducted on monazite to determine the age.

Samples collected in the whole west side of the ISB consist of alternate layers of magnetite-amphibote-chlorite-rich and quartz-rich layers. The samples were roughly divided into magnetite-rich type, which distributed at northeast to south, and silicate-rich type, mostly distributed at northwest, based on the dominant minerals. Bulk chemical compositions of the examined samples showed that magnetite-rich type are abundant in Fe, whereas silicate-type are rich in Mg. Magnetite-rich type primarly composed of Fe-rich amphibole, grunerite, whereas silicate-rich type contains more Mg or Ca-rich amphibole. Similarly, chemical compositions of chlorite in magnetite-rich type are Fe-rich, whereas that of silicate-rich type are Mg-rich. Amphibole and chlorite compositions in graphite-rich metasedimentary rocks are Mg-rich, which is similar to silicate-type BIF samples. The results suggest that Mg-rich characteristics of BIFs and graphite-rich metasedimentary rocks at north west, and Fe-rich characteristics of BIFs at north east to south are a primary signature. Ti and Al concentrations in BIFs and graphite-rich sedimentary rocks showed a positive correlation, indicating contribution of detrital components to them. Graphite-rich schist sample consisted of graphite-chlorite- and quartz-cummingtonite-dominated microlayers, containing high amounts of REE compared to samples showing low graphite content. The graphite-rich sample contained euhedral monazite, zircon and minor xenotime 2-10 μm in diameter, which were accumulated in graphite-chlorite microlayers and concordant with orientation of lamination, whereas most of the monazite in samples showing low graphite content were anhedral. CHIME age of the monazite in graphite-rich schist samples indicated 3630±91Ma, which ranges in the ages of prograde metamorphism and detrital zircon in previous report (Nutman et al., 2009). Considering monazite occurrence concordant with lamination of the graphite-rich schist, it is most likely that monazite was syngenetic with host rocks, probably derived from detritus and the age was modified during metamorphism, or crystalized during diagenesis to early metamorphism. Our results suggest that BIFs and graphite-rich schist at north west of west side of the ISB deposited where clastic components such as Mg, Al, Ti and REE were supplemented at a relatively high rate, evoking that photosynthetic

microorganisms might have been flourished in >3.7Ga shallow ocean.

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Keywords: Isua Supracrustal Belt, rare earth element, monazite, graphite

Abiotic Nitrogen Fixation and Organic Synthesis by Photochemistry on Early Mars

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Detailed studies of Mars in recent years have provided many progress on understanding the possible view of environment on early Mars. With the fact that liquid water was present on early Mars, and the discovery of organic molecules as well as nitrogen-bearing compounds on Mars, there is possibility that life could have emerged on early Mars. Thus, it is important to understand the abiotic organic synthesis and nitrogen fixation process to evaluate the possible origin of life on Mars or other terrestrial planet. Previous studies suggested that organic matters can be produced by photochemistry. Total pressure of Martian atmosphere is lower than Earth. Thus, UV may penetrated down to the surface and can directly photolyze liquid water. This suggests that UV-induced photochemistry may have been more important. However, little is known about abiotic nitrogen fixation by UV light. This experimental study examines the nitrogen photochemistry at the surface of water. In the experiment, initial gas contains N_2O or N_2 with or without CO under the presence of liquid water. The starting condition may have existed on early Mars. The results showed that NH_3, methylamine, glycine and other amino acids was produced from $N_2O + CO + H_2O$, whereas only trace amount of NH_3 was formed from $N_2 + CO + H_2O$. When gas phase do not contain CO, nitrate and nitrite were produced instead of NH_3. A numerical model including 296 photochemical reactions was constructed, and can qualitatively explain the formation of NH_3 from N_2O. However, the concentration of NH_3 in the model is order of magnitude lower than the observed amount in the experiment, suggesting that current photochemical model still lack some possible reactions to generate NH_3. The results provide important insights on chemical evolution theory that lead to the origin of life and the atmospheric evolution on Mars when the reaction pathway of NH_3 starting from N_2O and N_2 by UV light is confirmed.

Keywords: Mars, Nitrogen fixation, amino acid synthesis, UV