

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 nontronite, 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 nontronite was likely formed by weathering. Furthermore, the K enrichment in nontronite agrees with downward diffusional K flux from seawater to the basaltic basement through overlying sediments, which supports the inference that subseafloor 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