Behavior of rare earth elements during chemical alteration of deep granitic rocks at Tono, Central Japan

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Behavior of rare earth elements (REEs) in deep subsurface (from 85 to 1010 meter below ground level) during groundwater–granite interaction was investigated using chemical analysis of bulk rock and microscopic observation. It was revealed that REEs provide information on chemical alteration of granite even in the early stage of alteration, when the chemical index of alteration (CIA) using major element composition does not reflect the effect. REE patterns of granite with higher phosphorous concentration show a steeper slope in the lighter REE part relative to patterns of granite with lower phosphorous concentration. The relationship between the relative shape of REE patterns and phosphorous concentration suggests that phosphate minerals play a significant role in the release and incorporation of REEs at depth in granite, as they do in the surface environment. Allanite also plays a role as a REE host phase in granite indicated by the similarities in the relative shape of REE patterns, especially those with steep slopes. The steep slope in REE patterns corresponds to fresh granite, whereas the gentle slope in REE patterns corresponds to relatively altered granite in terms of chemical alteration. Change in the REE host minerals as granite alteration progress has an effect on the relative shape of the REE pattern of granite. Slope of REE pattern of granite can be explained using the patterns of accessory minerals. Presence of the accessory minerals and their alteration were also observed by electron microscopic analysis. Our results demonstrate that, during granite alteration, behavior of REEs in deep subsurface depends on dissolution and precipitation of accessory minerals, similar to the behavior in surface environments. REE pattern of granite is sensitive to the early stage of granite alteration, suggesting that the relative shape of REE pattern can be used as an indicator of the weak water–rock interaction in deep subsurface.

D/H exchange of hydrogen on fatty acids

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Compound-specific stable isotope analysis of biomarkers has been employed in a number of geochemical studies as a powerful tool to track delivery of organic matter and to reconstruct climates and ecosystems in the geological past. Stable hydrogen isotopic composition of lipid molecules such as fatty acids has been employed as an effective tool to understand modern to paleo environments. In this study, to further evaluate the reliability of hydrogen isotope information (δD) of H-C bounds on organic compounds, we examine the isotope exchanges on fatty acids in phospholipid bilayer of pseudo cell membranes that exposed with 0 to 50% of D_2O at room temperature or 85ºC for 12 hours. Exchange of D/H is the maximum when 50% D_2O is used, in which increase of δD values is between 93 and 328‰. These results indicate that hydrogen isotopes are clearly exchanged even hydrogen on C-H bound in fatty acids and that its magnitude may depend on type of fatty acids (chain-length and unsaturation degree) and state of bilayers (gel vs liquid crystal). Based on these results, we roughly estimated that hydrogen isotopic composition should be change by up to a maximum 0.0099‰ when it is expected in water with enrichment in D by 100‰ for 12 hours.

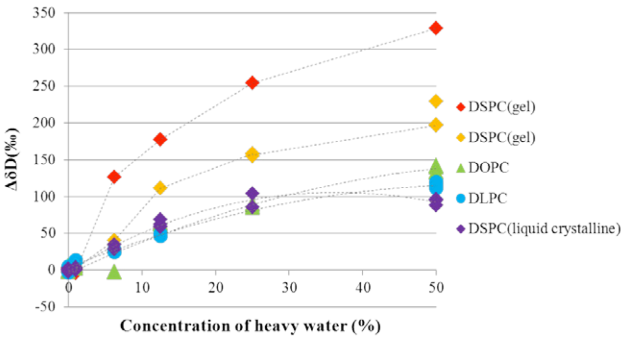

Figure 1: Change in δD value with respect to difference concentration of heavy water.