

Geochemical behavior mechanism of base metal and rare earth elements in water-rock interaction

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Water-rock interaction is divided into high temperature type and low temperature type. Hydrothermal alteration and formation of hydrothermal ore deposits occur in high temperature, while weathering and diagenesis in low temperature. Large number of studies on high temperature water-rock interaction and interpretation of mass transfer mechanism associated with the water-rock interaction have been carried out from experimental and computer simulation works.

For instance, chemical compositions of geothermal water in reservoir in geothermal system were successfully interpreted in terms of chemical equilibrium model (Shikazono, 1978). However, chemical equilibrium model cannot be applied to chemical composition of hydrothermal solution and precipitating minerals at discharge zone of hydrothermal system and fluid flow - precipitation kinetics coupling model and other complicated models have been used to interpret the characteristics of discharge zone (e.g. Shikazono et al., 2012).

On the other hand, interpretation of mass transfer mechanism in low temperature water-rock interaction process is generally difficult because many factors (dissolution, precipitation, adsorption, desorption, ion exchange, advection, diffusion) affect the process, although some efforts to elucidate the chemical weathering process of granitic rocks and secondary mineral distribution around ore deposits.

In previous works the geochemical behaviors of major elements (e.g. alkali, alkali earth, Si) associated with water-rock interaction process have been studied, while a few studies on minor elements (base metals, rare earth elements) are available. Therefore, here, the studies on these elements are focused on, and are compared with major elements.

As examples of these studies, the analytical results and interpretations on distribution of base metals and rare earth elements in volcanic soil (andosol, loam) with depth (Kanagawa Pref.), enrichment of rare earth elements in chemical weathering of Japanese and Chinese granitic rocks, base metals, rare earth elements, Cs and Sr behavior in high alkaline ground water-bentonite interaction (Mangatarem, Phillipine), formation process of high alkaline groundwater (Mangatarem, Phillipine) are presented and interpreted based on chemical analytical, experimental (dissolution experiments, step wise extraction experiments) and computer simulations (dissolution kinetics model) results.

Geochemical behaviors of base metals and rare earth elements in these processes are discussed in relation to ionic radii, surface complexes and elemental mobilities controlled by these parameters.

Keywords: base metal elements, rare earth elements, water-rock interaction, geochemical behavior mechanism, formation of water quality mechanism, weathering

Depositional Environments of Hydrogenetic Ferromanganese Crusts in the NW Pacific Oceans

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We report the preliminary results of the two cruises of ROV (HyperDolphin 3K, operated by JAMSTEC) mapping of sea floor occurrence and in-situ sampling of hydrogenetic ferromanganese deposits. This is the first systematic joint scientific research on the crusts over the deep-sea floors, which unveiled the ubiquitous distribution of the crusts covering the rock substrates. The results of physical measurements of morphology and thickness of the crusts, geochemical characterization of very surface portions of intact samples, distribution patterns of occurrences and thickness. The successful operation and ongoing shorebased geochemical and geological analyses proved that the ROV is one of the best methods in careful mapping, sampling and in-situ observation of sea bottom.

Keywords: ferromanganese crust, manganese nodule, ferromanganese nodule, cobalt-rich, seamount, minor elements

Estimation of lithium origin in salt lakes at Nevada by using lithium isotope ratio

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Lithium is a useful element for industrially purposes. Lithium has unique characteristics such as lowest Oxidation-reduction potential and the third-lightest element among all elements. These properties are valuable for lithium-ion secondary battery that is high-power, lightweight and the highest energy density among batteries in practical use.

Salt lakes are the most major lithium resources on earth. Highly concentrated lithium resources have been formed in salt lakes by repetition of water evaporation and inspissation with an arid climate. As a result of rising consumption of lithium carbonate, lithium-rich brine in salt lakes have been developed all over the world. Therefore, it is essential for understanding the origin of highly concentrated lithium in salt lakes for future exploration.

Lithium has two stable isotopes and its ratio is known for newly useful tool understanding water-rock interaction. Amount of lithium leached from rock to fluid at high temperature, and once leached lithium is kept in fluid while decreasing temperature, because lithium is a fluid-mobile element. Therefore, lithium isotope ratio of samples collected from salt lakes has a potential for tracing lithium origin in salt lakes.

In this study, we report lithium isotope ratio, as well as major and trace element compositions and strontium isotope ratio, of samples collected from some salt lakes at Nevada, USA. These lithium isotopic values of samples have a large variation among each sample, however all the values are much lower than the values of river water reported previously, and are close to values of upper continental crusts. These results suggest that highly concentrated lithium in these salt lakes were not formed during surface weathering processes, but were supplied by the result of water-rock interaction below the surface of the earth at high temperature. In the future, further detailed studies must be required such as the initial values of host rocks.

Keywords: Lithium isotope ratio, Salt lakes, Lithium resources, Water-rock interaction, Nevada

The fractionation mechanism between indium and arsenic originated from the acidic thermal water during river transport

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The Kusatsu and Tamagawa hot springs contain toxic elements such as arsenic and lead as well as rare metals such as indium and rare earth elements. Because of the strong acidity and large discharge, both thermal waters are neutralized by lime input and construction of dams.

The neutralization of the Kusatsu thermal waters was rapidly completed, when the lime suspension was dropped. After the rapid neutralization, most of dissolved As and In is removed by suspended hydrous ferric oxide (HFO). Consequently, As and In are transported as sorbate onto the suspended HFO to the bed sediments of man-made lake without the significant fractionation. On the contrary, the Obuki thermal water is neutralized by not only lime addition but also the mixing with tributary. Consequently, the pH values gradually increased toward the downstream. Arsenic tends to be sorbed by HFO from the upstream region, leading to wide distribution in the entire watershed. Indium is transported until the lake inlet as stable chloride- and/or sulfate-complexes without significant removal, and then, is mostly precipitated in the man-made lake. As a result, In is effectively accumulated in the downstream lakebed compared to As.

The apparent difference in geochemical mobility of these elements in the Kusatsu and Tamagawa fields indicates that we could purposely control elemental mobility in the natural river system. For example, we could preferentially concentrate the useful metals in the lakebed sediments by the toxic metal exclusion. If possible, we could obtain the rare metal resource from the man-made mineral deposits.

Keywords: indium, arsenic, Tamagawa hot spring, Kusatsu hot spring

Factors controlling dissolution rate of basalt for underground sequestration of carbon dioxide

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1. Introduction

Underground sequestration of CO₂ attracts attention these days as a measure which can expect an instantaneous effect on reducing anthropogenic CO₂ emission.

After injecting CO₂ into underground, CO₂ will react with rock and water, and will be finally fixed as carbonate (solubility trapping and mineral trapping). However, behavior of its chemical reaction is not revealed. When considering the above mentioned chemical reactions, dissolution rate of rock reacting with water is important as fundamental data, however dissolution rate of basalt changes greatly with different samples and/or experimental conditions. As factors controlling dissolution rate of basalt, Si:O ratio, crystal:glass ratio, structure of glass, experimental system (open system or closed system) and condition of agitation may be important.

Thus, we studied the influences of crystal:glass ratio and structure of glass on the dissolution rate of basalt (experiment 1). Moreover, we also studied the influence of experimental system (open system or closed system) and agitating on dissolution rate of basalt (experiment 2).

2. Sample preparation and experimental methods

In experiment 1, the basalt used was basaltic lava of younger stage Mt. Fuji and basaltic glass melted from its basalt lava and gradually cooled or rapidly cooled. This sample was put in a pressure tight vessel with solution, and CO₂ was injected into its vessel, and left in closed system. After reacted, the solid phase and liquid phase were separated. For the solid phase, before and after the reaction, analyzing the compositions of mineral and main element with XRD and XRF, and observing surface with SEM. The liquid phase was analyzed for cations(Ca²⁺ etc) and Si by ICP-MS.

In experiment 2, the basalt used was basalt lava. By changing the conditions of experimental system (open system or closed system) and agitation, the solution and solid phase were analyzed by the method same to experiment 1.

3. Results and discussion

In experiment 1, although the dissolution rate was about 1~2 times high and the increase order of dissolution rate was lava < gradually cooled < rapidly cooled, indicating much difference was not found. When it assumes injecting CO₂ in aquifer below 1000m depth, actual condition is in close to closed system. Therefore, under conditions of underground sequestration of CO₂, this result indicates that the difference in cooling rate from magma, the crystallinity do not affect dissolution rate significantly.

In experiment 2, the dissolution rate became higher for open system than closed system. Moreover, observing sample surface after the react with SEM, the surface did not change in open system, while the surface changed for closed system. This observation implies that in closed system, Si, Al, etc. precipitated when concentration of solution became high and covered the sample surface, forming alteration layer, and preventing dissolution. Assuming CO₂ is stored in aquifer below 1000m depth, the actual condition is in close to closed system. Until now, simulation assuming that dissolution rate of basalt is surface reaction controlled had been performed in Japan. But the simulation taking into account diffusion through alteration layer should be consideration.

Keywords: CCS, geochemical trapping, dissolution rate