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, deasorption, 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 sorbates 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 CO\textsubscript{2} attracts attention these days as a measure which can expect an instantaneous effect on reducing anthropogenic CO\textsubscript{2} emission.

After injecting CO\textsubscript{2} into underground, CO\textsubscript{2} 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 CO\textsubscript{2} 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(Ca\textsuperscript{2+} 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 CO\textsubscript{2} in aquifer below 1000m depth, actual condition is in close to closed system. Therefore, under conditions of underground sequestration of CO\textsubscript{2}, 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 CO\textsubscript{2} 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
Boron and lithium concentrations of vent fluids from submarine hydrothermal systems

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Boron and lithium concentrations were determined for vent fluids from arc-backarc hydrothermal systems in West Pacific. The hydrothermal vent fluids were collected from the Suiyo Seamount in the Izu-Bonin arc, the Mariana Trough (Alice Springs and Forecast vent sites), the Manus Basin (Vienna Woods and PACMANUS sites), the North Fiji Basin (White Lady, Kaiyo, and LHOS sites), and the Okinawa Trough (JADE, CLAM, and South Ensei sites) twenty years ago. The boron and lithium concentration of vent fluids basically showed negative correlation with the magnesium concentration for each hydrothermal system, which indicates mixing of hydrothermal end member and ambient seawater. In hydrothermal fluids, Li concentrations are always higher than those in seawater (0.026 mmol/kg), while B concentrations are various compared with the seawater value (0.41 mmol/kg). Especially, at the sediment-hosted hydrothermal systems in the Okinawa Trough, the Li and B concentrations are significantly higher than those in seawater. The hydrothermal end members of Li and B concentrations in the Okinawa Trough are 4-6 mmol/kg and 4-5 mmol/kg, respectively. This suggests that large amounts of B and Li are derived from sediment during reaction between sediment and fluid. In sediment-starved hydrothermal systems, the vent fluids from the Suiyo Seamount and PACMANUS site in the Manus Basin were more enriched in B (1.6-1.8 mmol/kg) relative to other sites (0.4-0.8 mmol/kg). This difference is probably resulted from type of rock which fluid reacts with. It is suggested that dacitic rocks in the Suiyo Seamount and PACMANUS site provided more boron than basaltic rocks in other sites. On the other hand, the Li concentrations of the hydrothermal end members in sediment-starved sites ranged from 0.4 to 1.2 mmol/kg with no relationship with rock type. Further isotopic study on the vent fluids will help to reveal the behaviors of boron and lithium in submarine hydrothermal systems.

Keywords: Hydrothermal system, Boron, Lithium
Natural radionuclides included in the deposits and water of Oga-Yumoto hot springs, Oga Peninsula

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Large scale travertine mounds which accumulated from approximately 30,000 to 5,000 years BP are exposed in the Oga-Yumoto hot springs in the north coast of the Oga Peninsula. They are expected as a recorder of hot spring activity during late Quaternary. Radiation was found in the hot spring water and present calcareous deposit (Takashima, et al., 2008). However it has not been conducted quantitative analysis of concentration of radionuclides included in the water and deposits in Oga-Yumoto hot springs, and therefore not been identified their origin. In this study, in order to determine radionuclides and their concentrations, both ICP-MS analysis and gamma-ray measurement with Ge detector were performed on the hot spring water, present and past deposits in Oga-Yumoto hot springs. Radioactivity concentrations of U-series nuclides range from 243.6 to 1083.7 Bq/kg in the deposits and 12.3 Bq/kg in the hot spring water. In the past deposit, radiation is only detected samples younger than several thousand years. On the other hand, Th-series nuclides were not detected in the past deposits. However the concentrations of Th series nuclides in the present samples are relatively high ranging from 304.1 to 4594.0 Bq/kg. The values of both radioactivity concentration tend to change depending on mineral species and distance from spring well. Deposits rich in iron oxide-hydroxide show obviously higher radioactivity concentration than those rich in the carbonate. The concentration of Th and U in the deposits are very low, almost hundreds and tens ppt order, respectively. Therefore it can be said that parent nuclides included in the Oga-Yumoto hot springs are Ra-226 in U-series and Ra-228 in Th-series. The fact the presence of Ra-228, a relatively short-lived nuclide suggests prompt upwelling of hot spring water without holding after reaction with the source rocks.

Keywords: natural radionuclide, Oga-Yumoto hot springs, travertine
Is dawsonite, NaAl(CO3)(OH)2, a mineralogical trump to fix CO2 underground? - its changing roles in GCS

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An option storing CO2 in a saline aquifer is recently considered to be vital for successful deployment of CO2 sequestration in many countries including Japan. The injected CO2 is expected to be, in a long period, fixed into newly formed carbonates through a variety of geochemical processes operative in the underground CO2 reservoir initially filled with saline groundwater. Dawsonite, NaAl(CO3)(OH)2, which is a carbonate composed only of elements concentrated in the upper crust, is one of the promising candidates of CO2-trapping minerals in the early phase of the geochemical study on geological CO2 storage (GCS). Through the accumulation of studies, however, the possible role of dawsonite is gradually changing although it is still a geochemically important carbonate in GCS. In my presentation, the possible roles of dawsonite will be summarized and introduced: one of them is a carrier of Al released from aluminosilicates, and the other is a self-sealing mineral filling fractures formed by the invasion of CO2-rich fluid.

Keywords: geological CO2 storage, dawsonite, water-rock interaction, saline aquifer, mineral trapping
Variation of the seawater Sr isotope on a geological time scale: implications for solid earth and environmental change.

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In order to reveal the petrogenesis of ore deposits, it is necessary to elucidate origin and age of oceanic crust forming the deposits and the earth environment at that period. In this respect, the seawater strontium isotope ratio (87Sr/86Sr) recorded in marine sediments is regulated by a balance between weathered materials originated from continents and mantle-derived materials by hydrothermal reaction, which could be a useful proxy for the ancient crustal production and environmental change. We point out the reasons for the variation of seawater 87Sr/86Sr and its related problems based on the recent geochemical knowledge.

With regard to continental weathering, young volcanic rock is important. It would contribute to the variation of the seawater 87Sr/86Sr because the strontium isotopic value of this type of rocks is low and they have high reactivity. Moreover, metamorphosed carbonate in the orogenic zone is significant. It has higher 87Sr/86Sr than marine carbonate since the metamorphosed carbonate is formed by reactions with surrounding silicate minerals. Concerning the hydrothermal reaction, recent studies indicate that the hydrothermal reactions take place at ridge flank and that the off-axis hydrothermal reaction as well as the ridge axial reaction on high temperature should be taken into account as a controlling factor on the seawater 87Sr/86Sr value.

On a geological time scale, temporal change of continental area and sealevel is often discussed which alter the seawater 87Sr/86Sr variation. In Achaean, a sudden increase of the seawater 87Sr/86Sr due to the formation of the juvenile continents is pointed out. Also, the correspondence to Wilson cycle and sealevel fluctuation from Paleozoic to Cretaceous in Mesozoic area is known. However, in Cenozoic, the seawater 87Sr/86Sr variation is not consistent with the sealevel change. Instead, the elevation and denudation in the Himalaya and Tibet, weathering of Columbia flood basalt, specific weathering accompanied with glaciations, and link to the atmospheric CO2 variation are discussed.

Among these geochemical factors, seafloor spreading in the early Cenozoic is possibly a part of the factors controlling the seawater 87Sr/86Sr at that period. In respect of the uplift of Himalayan and Tibetan region, in general terms, there are two kinds of the explanations about the cause of the seawater 87Sr/86Sr in the late Cenozoic, that is, increase in the weathering amount, and/or the high 87Sr/86Sr value of weathered materials of those regions, although some numerical studies oppose the former case. In terms of the atmospheric CO2 variation, its concentration in the late Cenozoic is roughly same as that at present and it does not match the trend of variation of the seawater 87Sr/86Sr. Thus, the seawater 87Sr/86Sr could not be used as a proxy for the atmospheric CO2 level during this period.

Finally, the seawater 87Sr/86Sr variation on a geological time scale cannot be explained by a simple factor, but combination of them. Accordingly, for example, it is useful to elucidate the reasons for the seawater 87Sr/86Sr variation by using the numerical models which parameterize the possible controlling factors on the seawater 87Sr/86Sr variation. Especially, because the relationship between the variation of the seawater 87Sr/86Sr and the change of atmospheric CO2 and development of glaciation would indicate a close link between behavior of a specific element and environmental change, it should be further discussed in the future.

Keywords: strontium isotope, weathering, hydrothermal reaction, Cenozoic, Himalaya, glaciation
Application of a New Relationship between Effective Porosity and Specific Capacity on a Hypothetical Aquifer System

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Previous researches lead to the establishment of a relationship between effective porosity and specific capacity. This paper shows how this relationship can simplify the volumetric evaluation of a hypothetical aquifer system based solely on specific capacity data. Preliminary results of this type of application showed excellent results and that it can be used with confidence on aquifer systems without regard to well construction or the lithology of the aquifer. This relationship is useful for distributing effective porosity within 2 or 3 dimensional groundwater and particle tracking models on a cell-by-cell basis. More importantly, this relationship can be used for parameter estimation to determine effective porosity for contaminant transport models. The importance of this breakthrough is that can it be used based only on specific capacity data and can be used with different units of measure. This is important for the widespread application of this relationship among the international scientific community. In this presentation the solutions for the relationship in other measurement systems will be revealed to enable the widespread application of this new relationship in all conditions.

Keywords: effective porosity, specific capacity, groundwater, parameter estimation, hydraulic properties, modeling
Quantitative analysis on hydrothermal alteration on fault rocks in the borehole core penetrating the MTL

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We will more precisely reconstruct the history of the condition of deformation and alteration in the hangingwall by especially advancing quantitative analysis on alteration mineral by principle component analysis (PCA). We studied hydrothermal alteration along the Median Tectonic Line (MTL) which has a long history of displacement and the fault rocks deformed under variable conditions.

AIST drilled a borehole penetrating the MTL for predicting Tonaikai-Nankai Earthquake at Itaka, Matsusaka, Mie prefecture. The drilling length is 600m. It crosses MTL at the depth of 473.9m. Hangingwall of the MTL consists of Ryoke-derived tonalitic mylonite and footwall of the MTL consists of fractured rocks derived from Sanbagawa metamorphic rocks.

The rocks in the hangingwall experienced the four kinds of stress pattern after the mylonitization. These are stresses which caused normal faultings (vertical compressive stress and North-South tensional stress, order of the two is unknown), North-South compressive stress and East-West compressive stress (present stress pattern) in turn with time (Shigematsu et al., oral presentation in the 117th Annual Meeting of the Geological Society of Japan, 2010).

In addition, based on the analysis of deformation structure and alteration minerals, prehnite generated before the stresses which caused normal faultings, laumontite had produced since the stresses which caused normal faultings until the present stress pattern and then has decomposed later on in the hangingwall (Fujimoto et al., oral presentation in the 117th Annual Meeting of the Geological Society of Japan, 2010).

We sampled the 124 bulk samples and fault material on the 129 slip surfaces of the small brittle faults in the borehole core the depth from 138m to 473.9m, analyzed mineral composition of those samples by X-ray diffraction and the bulk and the fault material mineral composition data sets are analyzed by PCA respectively. We obtained these principle components (PC).

1) First principle component of the bulk samples: explained variance is 0.536.
   It explains how much degree the wall rock is altered.
2) Second principle component of the bulk samples: explained variance is 0.203.
   It explains which hydrothermal alteration mineral is mainly distributed, carbonate or chlorite.
3) Third principle component of the bulk sample: explained variance is 0.127.
   It reflects the alteration zones (K-feldspar zone, chlorite zone and laumontite zone).
4) First principle component of the fault materials: explained variance is 0.798.
   It explains carbonate filling fractures.
5) First principle component of the fault materials: explained variance is 0.101.
   It explains chlorite and laumontite replacing rock-forming minerals.

We inferred these points from the five PCs.
1) The alteration of the bulk samples is more variable than the fault materials.
2) Laumontite and carbonate occur together in the bulk samples, but not together in the fault materials resulting from different mode of occurrences.
3) Quartz is similar to carbonate in the second PC of the two.

Keywords: Median Tectonic Line, Fault, Borehole core, Hydrothermal alteration, Mineral composition, Principle component analysis
Determination of critical point of H\textsubscript{2}O-CO\textsubscript{2}-X systems by spectrum measurement

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Physicochemical state of H\textsubscript{2}O are divided into three phases, solid, liquid and vapor. Especially, the vapor-liquid phase boundary is called the saturated steam pressure curve. The highest point of this curve is called the critical point. Liquid density becomes equal to gas density at that point. The fluid of that state is called supercritical fluid (water). Supercritical fluids exist near the deep-sea hydrothermal vent or in the Earth’s crust.

Supercritical fluid has a characteristic property that chemical reactivity, solubility and/or ion product. It is very important for the understandings of crustal rocks and fluid interaction. Therefore, decision of state and supercritical point of crustal fluid is very important.

The fluid near a critical point has intense density fluctuation, so, it is considered that the optical transmissivity is very low.

The purpose of this study is to observe the state of the optical property of the fluid near the critical point, in order to develop a method for the critical point determination of multicomponent fluid by the spectral measurement of the transmitted light through the fluid.

Keywords: critical point, supercritical fluid, spectrum measurement