

Concentration of Elements Related to Redox Evolution in Oceanic Environments

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Chemical sedimentary rocks, which are precipitates from ancient seawater, not only concentrate useful elements (e.g., Fe, Mn, Co, Ni, Rare Earth Elements (REEs)), but may also reflect changes in Earth's surface environments (e.g., pH, redox conditions, surface temperature). The temporal distribution of Banded Iron Formations (BIFs), the main economic Fe source, has been proposed to indicate changes in atmospheric and ocean chemistry in early Earth related to the evolution of the biosphere. However, to acquire a better understanding of the surface environments, BIFs deposited in various sedimentary setting need to be investigated. In this study, geological and geochemical investigations of BIFs that were deposited in a shallow ocean in the Archean Barberton Greenstone Belt, South Africa, show that the Cr/Ti and U/Th ratios are higher in the BIFs compared with the underlying and overlying clastic sedimentary rocks. Oxygen isotope compositions in each chromite grain, a host mineral of Cr, were determined by SIMS. The results show the chromite has lower $\delta^{18}\text{O}$ values compared with igneous and metamorphosed chromites, indicating that they were formed under hydrothermal conditions. The results suggest that dissolved Cr and U species in ocean were coprecipitated with ferric (hydr)oxides during the formation of the BIFs, and that chromite was formed by later hydrothermal alteration. Therefore, the results of the study indicate that enrichments of redox-sensitive elements (e.g., Cr, U) in BIFs have already occurred through chemical processes as early as 3.2 billion years ago due to the oxygenation of a shallow part of the ocean.

Volcanogenic Massive Sulfide (VMS) deposits such as Kuroko deposits in the Hokuroku district, Akita Prefecture were formed by ancient submarine hydrothermal activity, and are also associated with Fe-rich chemical sedimentary rocks. Because VMS deposits are primarily composed of sulfide minerals that are unstable in an oxic environment, such as pyrite and chalcopyrite, an anoxic environment in the Hokuroku basin may play an important role in the preservation of sulfide ores. Therefore, REE patterns and Fe isotope compositions of the Fe-rich chemical sedimentary rocks were investigated since geochemical evidence of such an environment being present in the Hokuroku basin is currently lacking. The results of these analyses show that the $\delta^{56}\text{Fe}$ values of samples occurring directly on and above Kuroko deposits were -1.5 to 0.5 ‰. These values are largely fractionated from the $\delta^{56}\text{Fe}$ value of the standard (i.e., 0 ‰), which is similar to that of igneous rocks. The samples that have a large negative value also bears negative Ce anomaly. These signatures indicate that partial oxidation of dissolved ferrous iron occurred by mixing ferrous iron-bearing anoxic water with oxygen-bearing seawater, and therefore that the seafloor of the Hokuroku Basin was anoxic. On the other hand, $\delta^{56}\text{Fe}$ values of chemical sedimentary rocks formed 2 - 3 Ma after the Kuroko deposits formed ranges from -0.8 to -0.3 ‰. These values are similar to those of dissolved ferrous ion in a modern seafloor hydrothermal fluid. Therefore, the $\delta^{56}\text{Fe}$ values of the samples indicate near complete oxidation of dissolved ferrous iron in an oxic environment. Therefore, these results suggest that the depositional environment in the Hokuroku basin shifted from anoxic to oxic after the formation of Kuroko deposits.

Keywords: Chemical sedimentary rock, Banded Iron Formation, Barberton Greenstone Belt, Chromium, Volcanogenic Massive Sulfide deposit, Iron isotope

Os isotope stratigraphy of a ferromanganese crust: Its principles and applications

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Sedimentation age determination by using an Os isotope stratigraphy is one of the effective dating methods for a ferromanganese crust. This dating method is applicable to the almost whole sedimentation age of a ferromanganese crust from the Late Cretaceous to present. So far, we have applied the Os isotope dating method to various ferromanganese crust samples collected from Northwestern Pacific, South Atlantic Oceans and Philippine Sea. In this presentation, we introduce the principles and applications of the Os isotope dating method, and discuss our recent results especially focusing on the growth hiatus of a ferromanganese crust.

Keywords: ferromanganese crust, Os isotope, geochemistry, growth hiatus, paleoceanography

Occurrence of hydrothermal alteration minerals at the Jade hydrothermal field, in the Izena Hole, mid-Okinawa Trough

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Mineralization at the Jade hydrothermal field, in the Izena Hole, mid-Okinawa Trough, resembles in many aspects the Kuroko type ore mineralization. In the Kuroko type ore deposits, zonal distribution of hydrothermal clay minerals was recognized around the deposit. This study aims to reveal occurrence of hydrothermal clay minerals below the seafloor in the Jade hydrothermal field. We report mineralogy and geochemistry of hydrothermal clay minerals identified in surface sediments in the Jade field and compare with those in the Kuroko type ore deposits.

Surface sediment cores (~30 cmbsf (centimeters below the seafloor)) were collected by an acrylic push corer (MBARI-type corer) attached to remotely operated vehicle (ROV) Hyper-Dolphin. The core sampling was conducted during the NT10-17 cruise of R/V Natsushima (Japan Agency for Marine-Earth Science and Technology (JAMSTEC)) in September 2010. Minerals in the sediment were identified by X-ray diffraction (XRD), at the Department of Earth and Planetary Sciences, Kyushu University. For some sediment samples, clay fractions (<2 μ m) were collected from suspending particles in the distilled water according to the Stokes' law. Clay minerals in the clay fraction samples were identified by the XRD and analyzed chemically using a transmission electron microscope (TEM) equipped with an energy dispersive spectrometer (EDS) in the Research Laboratory for High Voltage Electron Microscopy (HVEM), Kyushu University.

A surface sediment core collected near the sulfide chimney venting high temperature fluid up to 320°C was characterized by occurrence of kaolinite, with sulfide minerals such as sphalerite and galena. The kaolinite would be related to be formed under acidic condition caused by oxidation and dissolution of the sulfide minerals by penetrating seawater. Surface sediment cores collected near clear hydrothermal fluid venting of about 100°C, which is located in 400 m distant from the sulfide chimney, were characterized by assemblage of chlorite and smectite. The chlorite had chemical composition close to Al-rich chlorite (sudoite) which was found around a few Kuroko type ore deposits. In the Kuroko type ore deposits, sudoite was considered to be stable under acidic condition because of the associated clay minerals. This study revealed occurrence of acidic alteration minerals in surface sediment at the Jade hydrothermal field, in the Izena Hole, mid-Okinawa Trough.

Keywords: clay mineral, hydrothermal alteration, Okinawa Trough

Geochemistry of hydrothermal fluids collected from submarine volcanoes in the Izu-Bonin Arc

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The Izu-Bonin Arc is an intraoceanic arc related to subduction of the Pacific Plate beneath the Philippine Sea Plate. At some submarine volcanoes on the volcanic front, active hydrothermal fields have been located. Hydrothermal fluids were collected from two active fields, the Suiyo Seamount and Myojin Knoll, and analyzed. Geochemical characteristics of hydrothermal fluids collected from the Izu-Bonin Arc hydrothermal fields will be presented, comparing with those of Okinawa Trough hydrothermal fields.

Hydrothermal fluid samples were collected from the Suiyo Seamount during the NT07-08 cruise in 2007, and from the Myojin Knoll during the NT12-10 cruise in 2012. Fluid samples were collected with ROCS (Rotary Clean Seawater Sampler) installed on ROV Hyper Dolphin (JAMSTEC). Temperature monitored during the fluid sampling showed up to 296 degC at the Suiyo Seamount, and 235 degC at the Myojin Knoll.

Fluid chemistry was characterized as 1) Depletion in Mg and SO₄, 2) Enrichment in K and Ca compared with seawater; especially Ca enrichment is notable, and 3) Low concentration of organic derived species such as NH₄. The fluid chemistry is explained by high-temperature water-rock interactions. Notable enrichment in Ca would be in accordance with low- and Mid-K series chemical composition of volcanic rocks. Low NH₄ concentration would be related to depletion in organic-rich terrestrial sediment around the volcanoes. Concentration of minor elements including metal elements will be present, to discuss linkage with mineralogy of hydrothermal deposits in these hydrothermal fields.

Keywords: seafloor massive sulfide deposit, Suiyo Seamount, Myojin Knoll, fluid-rock interaction

Relationship between the formation of mercury deposits and the occurrences of organic minerals in subduction zones

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Karpatite and idrialite occur in mercury deposits in the West Coast in the USA. In addition, organic matter was also found in mercury deposit in Hokkaido. Both mercury deposits are epithermal type and formed in subducting zone. The relationship between organic minerals and mercury deposits in subducting zone will be discussed.

Keywords: Mercury deposits, Organic minerals, Subducting zone, Polycyclic aromatic hydrocarbons

A pilot magnetotelluric survey for geothermal exploration in northern Thailand

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One of Thailand's most prominent geothermal field is located in Maechan district, Chiangrai province, along the active Maechan fault which is East-West left-lateral strike-slip fault. Its surface temperature is 99.5 degree Celsius with the flow rate of 3 l/s. Magnetotelluric (MT) survey is proposed to help delineating geothermal fluid and controlling features of the hydrothermal system. In July 2013, 7 magnetotelluric stations were deployed covering the area of Maechan geothermal field. Horizontal magnetic and electric fields (H_x , H_y , E_x and E_y) were collected with the remote reference site located 70 km away in Fang district, Chiangmai province. To obtain 3-D resistivity model, 18 periods of off-diagonal (Z_{xy} and Z_{yx}) elements ranging from 0.003 to 300 second were applied with WSINV3DMT, a 3-D MT inversion widely used among many authors. The obtained resistivity model shows the shallow conductive zones which their locations coincide with the hot springs manifestation. These conductive zone locates from the surface to not more than 500 m and referred as the reservoir of hot geothermal fluid heated by the deeper resistive batholith granite basement. The resistivity contrast in the obtained model up to 2 km northward is corresponding to the lineament of Maechan fault. This also confirms the hypothesis from previous studies that the hot fluid is being stored in fractures of weathered granite which is the damage zone of Maechan fault and reaches the surface where the springs are located through shallow fractures and faults.

Keywords: magnetotellurics, geothermal field, three-dimensional inversion, electrical resistivity, Maechan fault

Development of in-situ Cu isotope ratio measurement by femtosecond-LA-MC-ICP-MS and its applications to ore minerals

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A new method for determining copper isotope compositions of copper-rich minerals (native copper, cuprite, chalcocite, chalcopyrite, cubanite and malachite) using a femtosecond LA-MC-ICP-MS has been developed. The standard-sample-standard bracketing technique was applied to correct the instrumental mass fractionation. Matrix effects found in chalcocite, chalcopyrite, cubanite and malachite can be corrected using the matrix-matched calibration standard. The analytical precision ($<0.14\text{ ‰}$, 2σ) and accuracy were significantly improved compared with those of previous works using a nanosecond-LA-MC-ICP-MS.

The developed LA-MC-ICP-MS method was applied to the measurements of copper isotope ratios of minute copper ore minerals in igneous rocks (e.g., Horoman peridotite complex) and seafloor hydrothermal deposits (modern: Mariana Trough; ancient: Besshi-type and Kuroko-type volcanogenic massive sulfide deposits) in order to investigate variability of copper isotopic compositions in these samples.

The $\delta^{65}\text{Cu}$ (where $\delta^{65}\text{Cu} = [(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}} / (^{65}\text{Cu}/^{63}\text{Cu})_{\text{NIST-SRM976-1}}] \times 1000$) values of copper-rich sulfide minerals of the active seafloor hydrothermal deposits are significantly large ($\delta^{65}\text{Cu} = -0.7$ to 4.0 ‰) compared to those of the ancient submarine hydrothermal deposits ($\delta^{65}\text{Cu} = -0.3$ to 0.4 ‰) and the igneous rocks ($\delta^{65}\text{Cu} = -0.3$ to 0.3 ‰). These large copper isotope variations in the modern active seafloor hydrothermal deposits are most likely explained in terms of a redox-controlled isotope fractionation during hydrothermal reworking or alteration of precipitated copper-rich minerals. These results also suggest that sub-seafloor and metamorphic recrystallization effects probably have reduced the original range of copper isotopes.

Secondary malachite ($\delta^{65}\text{Cu} = 2.6$ to 3.0 ‰) and native copper ($\delta^{65}\text{Cu} = 1.4$ to 1.7 ‰) in the Besshi-type deposit have heavier copper isotope values compared to precursor copper-rich minerals. These variations are mainly due to isotope fractionation during redox reactions (weathering) at low temperatures involving the preferential incorporation of heavy copper isotope in secondary Cu(II) solutions. Therefore, copper isotope geochemistry could be a useful tool for understanding geochemical processes of copper transport and deposition in ore-forming systems.

Keywords: copper isotope ratio, femtosecond-LA-MC-ICP-MS, ore minerals

Origin of Heavy-REE-rich apatite in deep-sea mud from Minami-Torishima area, south-eastern Japan

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We have conducted geochemical and mineralogical investigations of the rare earth and yttrium (REY)-rich mud from Minami-Torishima area in the Pacific in order to clarify the concentration of REY and their host-phase in the mud. X-ray diffraction analysis shows that the mud is mainly composed of phillipsite, fluorapatite, quartz, albite, illite and montmorillonite. Whole-rock CaO, P₂O₅ and total REY contents of the mud are positively correlated. Relative abundance of apatite is also positively correlated to P₂O₅ and total REY contents. These correlations suggest that apatite is the main host of the P₂O₅ and REY in the mud. In order to quantitatively estimate the REY-host phase, we make in-situ compositional analyses of constituent minerals in the REY-mud. The result shows that the apatite is abundant in REY (9300 to 32000 ppm) and characterized by negative Ce-anomaly. In contrast, phillipsite is less abundant in REY (60 to 170 ppm). We conclude that the main REY host phase of the mud is apatite.

Keywords: REE, deep-sea mud, apatite, Minami-Torishima, LA-ICPMS, Nd isotope

Upgradation of silica rich fluvial sands of Bangladesh: Proposals for alternate uses

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Major rivers of Bangladesh are carrying billions of tons of sediments from the Himalayan mountain range from the north, forming bars almost on every river. These bars inundate in floodwater every year, eroding some sediments as well as depositing more. Thus, almost all the rivers are getting filled with the sediment in course of time. The government of Bangladesh has undertaken a mega plan for Capital Dredging, for raising navigability of the main and important rivers across the country. But there is not enough space to keep those dredged materials. Hence, most of the time, the dredged materials are thrown only in the vicinity of dredging area. In course of very short time, those materials eventually return back to river bed with the precipitation and surface runoff. This makes wastage of time and money.

The river sediments are rich in silicate mineral, mainly quartz and feldspar, along with others, like heavy and micaceous minerals. Quartz (SiO_2) is the raw material for glass production. River sands of Bangladesh also contain some heavy minerals like magnetite, ilmenite, rutile, zircon, garnet, leucosene, pyroxene etc., and some Mica group minerals like muscovite, biotite, chlorite etc. Industrial use of these minerals are widely accepted. Upgradation of river silica by some physical separation procedures like density, magnetic and electric separators, and chemical composition revealed from X-ray fluorescence analysis shows that 60-70% silica of river sediment can be easily enriched up to 94%. Very low amount of Fe, Al, Ca, Mg and absence of Cr and Ti indicates the probable use of this upgraded silica as glass producing sand.

For industrial use, advance research is necessary for potential use of such silica for silicon extraction or other silicon products e.g. silicon chip, if the upgradation can be reached more than 99%. The heavy and magnetic minerals associated with silica also can be used economically as by-products of the process. Mining of this sediment from the rivers will increase the navigability of the rivers. As dredging is a must in almost every river of Bangladesh, the mining will work as alternative work of dredging, saving huge amount of money to be spent for dredging. This will also lessen the risk of dangerous flood problem of the country.

Moreover, since fluvial sands has been used as earth filling materials for long time and is suitable in many technical aspects, potentiality of using such sediments for artificial islands can be thought. Japan has been implementing several artificial islands where materials like solid waste, soil from mountains are mostly used as filling materials which are not always environment friendly. Feasibility study for using bulk fluvial sand from Bangladesh as earth filling materials for future artificial islands of Japan can a better alternative. This will decrease the risk of potential environmental hazards that can be created from solid waste or hill-cutting. Use of dredged materials from Bangladesh will help decreasing environmental hazards like floods too. Economical sustainability can be achieved through such reduction of hazard risk.

Keywords: Fluvial Sand, Bangladesh, Silica, Heavy Minerals, Capital Dredging, Artificial Islands

Iron isotopic composition of the Palaeoproterozoic Hotazel Formation in the Kalahari Manganese Field, South Africa

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Kalahari manganese deposit in the Palaeoproterozoic Hotazel Formation of Transvaal Supergroup of South Africa is the world's largest layered manganese deposit. It has alternating layers structure of three manganese rich layers and banded iron formation. This banded iron formation and manganese deposits of Hotazel Formation were formed at approximately the same time as Global Oxidation Event, which was the period of explosive growth of oxygen in Earth's atmosphere. In addition, the relevance of the snowball Earth event of Huronian glaciation has also been suggested from its formation age. Iron isotopes are sensitive indicators of the redox state, and it is suitable for estimating the marine environment when the banded iron formation was formed. Although a prior study on the iron isotope analysis of manganese deposits and banded iron formation of Hotazel Formation has been reported by Tsikos et al. in 2010, it is hard to say enough data is gathered.

In this study, drill core that was collected from the Kalahari manganese deposit in South Africa was subjected to iron isotope analysis with MC-ICP-MS and XRD analysis, and the results were compared with those of Tsikos et al.(2010). In isotopic analysis, $\delta^{56}\text{Fe}$ values of drill core samples for the standard sample IRMM-14 were measured.

From the results, low $\delta^{56}\text{Fe}$ values (not higher than -0.70‰) throughout the all samples were measured. When limited to manganese-rich layers, $\delta^{56}\text{Fe}$ values are between -1.66 and -2.86‰ . Relationship between Fe-Mn ratio and $\delta^{56}\text{Fe}$ value showed that $\delta^{56}\text{Fe}$ value have a tendency to drop to a lower value with the increasing abundance ratio of manganese to iron in a formation. This results are consistent with those of Tsikos et al.(2010). In other words, this results support their theory that banded iron formation has a role as a sink of heavy iron isotopes, and manganese are deposited in an environment that was rich in light iron isotopes.

Reference

Harilaos Tsikos, Alan Matthews, Yigal Erel, John M. Moore, 2010. Iron isotopes constrain biogeochemical redox cycling of iron and manganese in a Palaeoproterozoic stratified basin. *Earth and Planetary Science Letters* 298, 125-134. doi: 10.1016/j.epsl.2010.07.032

Keywords: iron isotope, banded iron formation, Kalahari manganese deposit