Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

SRD41-01 Room:106 Time:May 25 09:00-09:25

# Chemical analysis of individual fluid inclusion by SXRF: application to hydrothermal ore deposits

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Information on chemical composition of ore-forming fluid is significant when discuss the origin and evolution of ore-forming fluid, dissolution and transportation mechanisms of heavy metals and precipitation mechanisms of ore minerals. Salinity of fluid inclusion has been extensively reported, however data of heavy metals is scarce. Chemical compositions of individual fluid inclusion are measured recently with a development of micro-analytical techniques. Examples of SXRF analysis of individual fluid inclusion are described.

Chemical compositions of ore-forming fluid responsible for vein-type W deposit at the Takatori mine was measured. Four mineralization stages are distinguished at the deposit, such as early wolframite-fluorite-topaz-muscovite-lepidolite, middle sulfide-fluorite, late carbonate-cassiterite and final carbonate-clay mineral stages. Quartz is accompanied in all these stages. Pseudosecondary fluid inclusions hosted in quartz are selected for chemical analyses. Temporal relation of these inclusions is determined from cross-cut nature of trails that accompany fluid inclusions. SXRF analyses suggest compositions of ore-forming fluid as follows. Metal concentrations in early stage fluid are very high as 1400-3700 ppm W, 4100-6200 ppm Fe, 1000-1800 ppm Mn, 1500-3000 ppm Cu and 1800-2900 ppm Zn. Middle to late stage fluids contains 300-600 ppm Fe, 100-300 ppm Mn, 50-100 ppm Cu and 50-100 ppm Zn with less than detection limit of W. Concentrations of ore-forming metals in fluid decreased remarkably with mineralization.

Vapor-liquid partitioning coefficients for Cu and Zn in aqueous fluid were determined under boiling conditions at 500-650 ℃ and 35-100 MPa in sulfur-bearing and sulfur-free systems. A synthetic fluid inclusion technique was used to sample the experimental system coexisting vapor-rich and liquid-rich fluid inclusions, with the Cu and Zn concentrations in individual fluid inclusions then analyzed by SXRF. The vapor-liquid distribution constant of Cu ($K_D = m_{Cu(vapor)}/m_{Cu(liquid)}$) is found to be strongly dependent on the sulfur content in the experimental solutions. In sulfur-bearing systems, Cu preferentially partitions into the vapor phase, whereas Zn preferentially fractionates into the hypersaline liquid. The $K_D$ values for Cu and Zn obtained in this study correspond well with those obtained from natural fluid inclusions in hydrothermal ore deposits. The results suggest that differential volatility of metals is an important factor affecting the enrichment of certain metals in different hydrothermal ore deposits.

Keywords: fluid inclusion, SXRF, chemical analysis, ore-forming fluid

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# Characteristics of Magmatic Hydrothermal System at Southeastern Martabe High Sulfidation Epithermal Deposit, Indonesia

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The Martabe Au-Ag deposit, North Sumatra Province, Indonesia is a high sulfidation epithermal deposit, which is hosted by Neogene sandstone, siltstone, volcanic breccia, and andesite to basaltic andesite of Angkola Formation. The deposit has six ore bodies that occur as silicified massive ore (enargite-luzonite-pyrite-tetrahedrite), quartz veins (tetrahedrite-galena-sphalerite-chalcopyrite), banded sulfide veins (pyrite-tetrahedrite-sphalerite-galena) and cavity filling. All ore bodies were controlled by N-S and NW-SE trending structures. The Barani and Horas ore bodies are located in the southeast of the Purnama ore body. Fluid inclusion microthermometry and alunite-pyrite pairs sulfur isotopic geothermometry show slightly different forming temperature among the ore bodies. Formation temperature of the Purnama ore body ranges from 215 to $260^{o}$C and salinity from 5 to 8 wt% NaCl equivalent. Formation temperature of the Barani ore body ranges from 200 to $240^{o}$C and salinity from 0 to 2.5 wt% NaCl equivalent and those of the Horas ore body ranges from 240 to $260^{o}$C and from 2 to 3 wt% NaCl equivalent, respectively. The general sequences of mineralization at Martabe are divided into the early stage as main high sulfidation mineralization stage and the late stage of oxidation and brecciation, which were followed by weathering. Sulfides (enargite-luzonite-pyrite-tetrahedrite) that were associated to gold and silver are abundant at the Purnama ore body. The Barani and Horas ore bodies are less silicified and sulfide abundance is less than the Purnama ore body. The salinity and sulfur isotopic values indicate a mixing trend among different fluids. Salinity of fluid inclusion decrease from higher salinity (› 5 wt% NaCl equivalent) in the Purnama ore body to lower salinity (‹ 3 wt% NaCl equivalent) in the Barani ore body which is directly located in southeast of the Purnama ore body. The sulfur isotope ratio values of sulfide and sulfate in Purnama range from -4.2 to +5.5 ‰ and from +1.2 to +26.7 ‰ , and those in the Barani range from -4.3 to +26.4 ‰ and from +3.9 to +18.5 ‰, respectively. The Horas ore body shows low salinity but higher formation temperature compared to Barani which possibly indicate different mixing condition unrelated with Purnama and Barani ore bodies. The sulfur isotope ratio values of sulfide and sulfate in the Horas ore body range from -11.8 to +3.5 ‰ and from +1.37 to +25.7 ‰. At the Purnama and Barani ore bodies, alteration assemblages consist of quartz-kaolinite-dickite - alunite - illite - pyrophillite and ore mineral assemblages are mostly composed of enargite-luzonite-pyrite-tetrahedrite. In contrast, mineralization style at the Horas ore body including the alteration assemblages (quartz - alunite - illite - dickite - muscovite) and ore forming temperature is different from the Purnama and Barani ore bodies.

Keywords: epithermal high sulfidation, sulfur isotope, fluid inclusion microthermometry

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# Lithium isotope index as powerful research tool for earth resource

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Lithium (Li) is one of important natural resources, because Li is used for secondary battery of electric and/or hybrid vehicles. The lightest alkali element, Li, is one of fluid-mobile elements. The leaching of Li from sediments into fluids is dramatically elevated together with increasing temperature, and the fact that subsequent re-uptake of the leached Li from the fluid by sediments (which occurs as the fluid cools) takes a considerable time. Li is relatively unaffected by surface water contamination because the Li contents of deep-rooted fluid samples are much greater than the surface water content. The two stable isotopes of Li are $^{6}$Li and $^{7}$Li, and their relative abundances are about 7.5% and 92.5%, respectively. Furthermore, the difference in the $^{7}$Li/$^{6}$Li ratio between fluid and solid phases varies with the reaction temperature. As a result, the Li isotope ratio is a potentially useful geothermometer because the Li cation is monovalent and hence not redox sensitive, and it is not a nutrient, so it does not participate in biologically mediated reactions.

In this presentation, I'll talk about fundamental feature of Li isotope tool at first, and after then I show the potential of Li isotope tool for earth resource science.

Keywords: lithium isotope, deep crustal fluid, geochemical thermometer, fluid inclusion

SRD41-04 Room:106 Time:May 25 10:00-10:15

# Li isotopic composition of submarine vent fluids from arc and back-arc hydrothermal systems in the western Pacific

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Submarine hydrothermal systems significant contribute to heat and elemental fluxes to the ocean. Vent fluid geochemistry in mid-ocean-ridge (MOR) hydrothermal systems were well-studied, while studies on vent fluid geochemistry in arc and back-arc systems with various geological characteristics were insufficient, especially in terms of lithium. To reveal control factors on lithium in arc and back-arc hydrothermal systems and lithium isotopic behavior in water-rock interaction at high temperature, we determined Li contents and its isotopic compositions of 11 vent fluids collected from 5 submarine arc/back-arc hydrothermal systems in the western Pacific.

Based on mass balance calculation, Li in vent fluids are dominated by seawater-rock (seawater-sediment) interaction in sediment-starved (sediment-hosted) hydrothermal systems in arc and back-arc basins at equilibrium. Li contents in vent fluids is also influenced by phase-separated processes, by temperature-related portioning of rock Li into fluid phase, and by host rocks and sediments. In contrast, Li isotopic composition in vent fluids is affected by host rocks and sediments, but not by phase-separated processes. These results demonstrate that lithium is a useful tracer for investigating geological processes occurred underground such as a phase separation process and water-rock/water-sediment interaction at high temperature.

Keywords: submarine hydrothermal system, lithium isotope ratio, vent fluid, arc, back-arc basin

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# Salinity of pore waters in sedimentary basins under geothermal gradients

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The pore waters in sedimentary basins are crucial in the control of diagenesis, sediment-hosted ore formation, and generation and transport of hydrocarbons. The chemical and hydrological properties of the pore waters are therefore of importance in the understanding of these geological phenomena. An increasing number of studies reported that the pore waters often have higher salinity than seawater, and the salinity generally increases with the increase of the depth (e.g., Kharaka and Hanor, 2003). Such salinity distribution has been often attributed to infiltration of brines from underlying halite beds. However, the downward salinity increase is observed also in basins that are lacking halite beds (e.g., Xie et al., 2003). Therefore, more general mechanisms may exist for the formation of the salinity distribution.

In this study, I demonstrate on the basis of thermodynamics that the chemical equilibrium of the saline water in a sediment column under gravity and the pressure and geothermal gradients results in the downward salinity increase. The chemical potential of solute is the function of pressure, temperature, concentration, and gravity potential. The pressure term increases with increasing the depth, whereas the temperature term and the gravity potential decrease. The sum of these terms generally decreases with the increase of the depth. In the final equilibrium state, the chemical potential should be constant along the column. Therefore, we consider that the concentration term increases to keep the chemical potential constant, leading to the downward salinity increase. Assuming that the pore water is the NaCl-H2O mixture, I calculated the concentration of NaCl in the solution using the model of Pitzer et al. (1984) and Rogers and Pitzer (1982). The calculations showed that the salinity increased from 32 to 208 g/L in the 2000 m-thick sediment column under the geothermal gradient of 0.05 K/m. Such a salinity increase is in the same order to those observed in many sedimentary basins. In an isothermal case, the salinity increased only weakly, and it reached 36 g/L. This result is consistent with the conclusion of Mangelsdorf et al. (1970) that gravity alone does not explain the observed enrichment of salinity. If we set the salinity at the top of the column at 1 g/L, it increased to 24 g/L under the identical condition. Therefore, the high-salinity waters are generated in fresh to brackish environments.

This study showed that the simple chemical equilibrium along the sediment column resulted in the downward salinity increase. The method proposed here may be applicable to studies of fluids in other geological systems, such as in mantle, crustal rocks, hydrothermal environments, and magmatic systems.

Keywords: pore waters, salinity, sedimentary basins

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# Distribution of rare earth elements between deep granitic groundwater and fracture filling carbonate

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The chemical properties of rare earth elements (REEs) and yttrium (YREE) have been widely studied as geochemical tracer in aqueous environments. The YREE abundances in groundwater are mainly regulated by mineral-water interaction. The YREE variability in natural groundwater system is very complex and dependent upon geologies, water flow-path, mixing and chemical condition of groundwater. We investigated distribution of rare earth elements (YREE) between deep granitic groundwater with diverse geochemical character and fracture filling calcite in order to understand YREE behavior in natural groundwater systems.

In Tono area, central Japan, the chemical types of groundwater varied with depth; Na-$HCO_3$ type of groundwater in sedimentary rock, Na-Cl type in upper part of base rock granite and Ca-Cl type in deeper granite. The Na-Cl type groundwater was collected using boreholes from 200, 300 and 400 m, the Ca-Cl type from 650 and 1150 m below ground surface. The concentrations of YREE were measured by ICP-MS. The fracture filling calcite was obtained from drill core of boreholes similar to the groundwater sampling. The collected samples were dissolved into 1M $NH_4$-acetate buffer solution (pH = 4.8) and the concentrations of YREE in the leached solutions were measured by ICP-MS. Furthermore, in order to assess the precipitation condition, we measured isotopic composition of O and C for calcite.

Chondrite-normalized YREE patterns of Na-Cl type groundwater exhibited enrichment in heavy REEs relative to light REE, which was well explained by the predominance of YREE carbonate aqueous complex in the groundwater. On the other hand, YREE patterns of Ca-Cl type groundwater were enriched in middle REEs (MREEs). In addition, Y/Ho of the Ca-Cl type groundwater was significantly lower than that of chondrite. MREE-enrichment in natural water occurs from dissolution of MREE-enriched Fe-oxyhydroxide [1], and lower Y/Ho than chondrite is common in distribution patterns of Fe-oxyhydroxide [2]. The concentration of Fe in the groundwater increased with depth and the Eh measurement of the groundwater showed strongly reducing condition. Consequently, YREE in the Ca-Cl type groundwater can be explained by dissolution of MREE-rich Fe-oxyhydroxide with sub-chondritic Y/Ho.

Oxygen isotopic composition of fracture filling calcite varied regardless of depth. The correlation between precipitation temperature and depth was not observed. On the other hand, carbon isotopic composition became heavier with depth. This result indicates the fracture filling calcite precipitated from mixture of seawater and freshwater. For YREE patterns of fracture filling calcite collected from 200˜400 m depth exhibited negative Eu anomaly, while the samples from 670˜1294 m along borehole showed positive Eu anomaly when the YREE contents were normalized by granite. For the fracture filling calcite from 200˜400 m depth were precipitated from groundwater with YREE eluted from granite, because the negative Eu anomaly has been observed in mother rock granite [3]. Therefore, the positive Eu anomaly in calcite indicates that the groundwater precipitated calcite was enriched in Eu.

[1] Johannesson and Zhou, 1999, Geochim. Cosmochim. Acta 63, 153-165.
[2] Bau, 1999, Geochim. Cosmochim. Acta 63, 67-77.
[3] Takahashi et al., 2002, Chem. Geol. 184, 311-335.

Keywords: rare earth elements, granite, groundwater

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# Fractionation between LREE and HREE in hydrothermal fluids associated with felsic magmatism

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As crustal abundances of heavy rare earth elements (HREE) are generally smaller than those of light rare earth elements (LREE), HREE are more expensive than LREE in the market. HREE-rich deposits (e.g., Longnan in China, Nechalacho in Canada) are associated with hydrothermally-altered felsic igneous rocks such as granite and syenite. This study aims to discuss what caused the fractionation between LREE and HREE in such igneous rocks.

Alkaline rocks, formed by magma with a low degree of partial melting, are significantly enriched in LREE and are weakly enriched in HREE because LREE are more incompatible than HREE in magma because of their larger ionic radii. Igneous rocks, which can be HREE-rich deposits, are probably formed by either process of alkaline magmatism enriched in certain elements and fractional crystallization. The former is represented by intercontinental alkaline rocks such as the Nechalacho deposit and is rich in REE, HFSE (high field strength elements), fluorine and carbonate. Previous experimental studies found that solubility of zircon is high when magma is rich in alkali elements and/or fluorine and this causes the residual melt to contain more HREE and Zr. On the other hand, calc-alkaline granite can be a source rock of HREE-rich deposits, as represented by the Longnan deposit. The intensive magmatic differentiation and fractionation of LREE-bearing minerals may cause the residual melt to be enriched in HREE relative to LREE. For REE ore formation, however, such deposits require further processes including the deuteric alteration, dissolution of REE-bearing minerals and adsorption of REE during weathering.

Fractionation between LREE and HREE by complexing with various ligands is likely to occur in hydrothermal fluids produced from felsic igneous rocks. Different previous works have suggested that $REE^{3+}$ ions are complexed with carbonate, bicarbonate, fluorine, chlorine and sulfate ions. A recent study indicates that REE-fluoride complexes do not have a significant role in transportation or fractionation of REE because of their lower stability than REE-chloride and sulfate complexes above 150 ℃ (Migdisov et al., 2009). However, it appears that footprint of saline fluids or sulfate minerals are not very common compared to abundant carbonatite and fluorite in REE deposits.

The HREE-rich igneous rocks are commonly accompanied by alkali alteration and fluoritization in many ore deposits and prospects, however alkali igneous rocks containing high alkali or fluorine contents are not necessarily rich in HREE. REE-fluoride complexes are not significant in hydrothermal fluids, however there are insufficient data to determine an importance of chlorine or sulfate ions in complexing with REE. Fractionation between LREE and HREE in REE deposits still remains unclear and further studies are expected to elucidate which is the more significant process for the REE fractionation, magmatism or hydrothermal alteration.

Reference

Migdisov, A.A., Williams-Jones, A.E. and Wagner, T. (2009) Geochimica et Cosmochimica Acta, 73, 7087-7109.

Keywords: HREE, LREE, hydrothermal fluids, fractionation, ore deposits, felsic igneous rocks

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# Petrogenesis of granitoids in northern Palawan (Philippines) and its implications on rare-earth element mineralization

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Global attention brought about by the increasing demand of rare earth elements (REE) has paved the way for various exploration efforts worldwide. Areas with promising REE deposits were revisited. In the Philippines, explorations are now on-going with studies focused on several granitic intrusions. Some of these granitic bodies are distributed in northern Palawan, which is a rifted fragment of the southeastern Eurasian margin during the opening of the South China Sea basin in the Oligocene.

The granitic bodies were investigated for possible concentration of REE during magmatic differentiation. The Kapoas granitoids include granites and granodiorites that are metaluminous, high-K calc-alkaline, and belong to the I-type and ilmenite-series. The granitoids are mostly biotite-rich and contain xenoliths of schists and diorite, quartz xenocrysts, and mafic enclaves. Two separate intrusive bodies are observed: the Mt. Kapoas which is 13.2 Ma in age; and the Bay Peak granite which is dated 14.1 Ma. However, both intrusives have similar geochemical signature, which show LREE enrichment. These granitic rocks were more evolved or highly differentiated I-type, probably generated in the middle to lower continental crust . The REE-bearing minerals are allanite and monazite. The weathered crust also show LREE enrichment. Weathered crust profile shows Ce-anomaly in the B-horizon portion where kaolinite, muscovite and illite act as absorptive materials.

This study also confirmed the presence of the Cretaceous Daroctan granitoids aside from the well-studied Middle Miocene Kapoas granitoids. The Daroctan granitoids include granodiorites and granites which belong to ilmenite-series. The granodiorites contain xenoliths of metasedimentary rocks, quartz xenocrysts and mafic enclaves. It is also sporadically distributed in the northern part of the island but these different intrusive bodies have almost similar ages. The REE-bearing minerals are monazite. Enrichment of LREE in the weathered crust is relatively higher than that of the Kapoas.

Allanite and monazites in the study areas are enriched in Ce, La, Nd, and Sm with associated radioactive element Th. Heavy minerals concentrated in the beach in Erawan and Ombo, which is part of the Kapoas granitoids, contain up to $>$10,000 ppm of La, Ce, and Sm.

Keywords: Palawan Continental Block, Kapoas granitoids, rare earth element mineralization, monazite, allanite