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Geochemical and mineralogical characteristics of ion-adsorption type REE mineralization: A case of Phuket, Thailand

Kenzo Sanematsu¹, Yoshiaki Kon¹, Akira Imai^{2*}, koichiro watanabe³, Yasushi Watanabe¹

¹Geological Survey of Japan, AIST, ²Faculty of Engin & Resource, Akita Univ, ³Faculty of Engin., Kyushu University

Ion-adsorption type rare earths (REE) deposits are composed of weathered granite formed in warm and moist climate, providing both light REE (LREE) and heavy REE (HREE) resources. As REE are chemically adsorbed onto weathering products such as clays, they can be extracted by ion exchange reaction with electrolyte solutions. The REE deposits have been mined only in southern China and similar mineralization is locally identified outside China. In order to elucidate the genesis of ion-adsorption type deposits, particularly the transportation and adsorption of REE in the process of weathering, we studied geochemical behavior of REE and occurrences of REE-bearing minerals in weathered crust on the Kata Beach Granite in Phuket Island, Thailand.

The Kata Beach Granite is ilmenite-series biotite granite with transitional characteristics from I-type to S-type (ASI = 1.01), and is abundant in REE (595 ppm). REE are contained in fluorocarbonate and subordinate allanite and titanite with lesser amounts of apatite and zircon. Chondrite-normalized REE pattern of the parent granite indicates the enrichment of LREE relative to HREE and without Ce anomaly. The upper part of the weathering profile from the surface to 4.5 m deep are mostly characterized by positive Ce anomaly, showing lower REE contents ranging from 174 to 548 ppm and lower percentages of adsorbed REE (adsorbed REE / whole-rock REE x 100) from 34 to 68 %. In contrast, the lower part of the profile from 4.5 to 12 m deep are characterized by negative Ce anomaly, showing higher REE contents ranging from 578 to 1084 ppm and higher percentages from 53 to 85 %. These REE contents, percentages of adsorbed REE and thickness of weathered crust are comparable to those of ion-adsorption type REE deposits in China. The upper part of the weathering profile is a leached zone in which Ce^{4+} is immobilized as CeO_2 in an oxidizing condition and REE with the depletion of Ce are dissolved in acidic soil water. The lower part of the profile is an accumulation zone in which REE with the depletion of Ce transported from the upper part of the profile are adsorbed onto weathering products or are distributed into the structure of secondary minerals such as rhabdophane. The immobilization of REE results from the increase of pH due to the contact with higher-pH groundwater. In ion-adsorption type ores (weathered granite with >50 % adsorbed REE) the majority of REE is present in the ion-adsorption phase with negative Ce anomaly, not in mineral structures, leading to the negative Ce anomaly of whole-rock geochemical data. Thus, the percentages of adsorbed REE are positively correlated with whole-rock negative Ce anomaly. Fractionation between LREE and HREE is not simply explained because it is controlled by occurrences of REE-bearing minerals and adsorption affinity. However, La/Yb ratios indicate that LREE tend to be more adsorbed onto weathering products than HREE.

The result of this study suggests that the occurrence of easily-soluble REE fluorocarbonate is important for formation of ion-adsorption type REE deposits. Whole-rock negative Ce anomaly of weathered granite suggests the ion-adsorption type mineralization and is a useful geochemical indicator for exploration of the deposits. As LREE tend to be more adsorbed than HREE in the process of weathering, identification of HREE-rich parent rocks is required to explore HREE-rich ion-adsorption type deposits.

Keywords: REE, granite, weathering, adsorption, mineralization, Phuket

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Origin of lithium in Uyuni salt flat, Bolivia: constraints from Li isotope ratio

Yoshiro Nishio^{1*}, Wataru Tanikawa¹

¹Kochi Institute, JAMSTEC

Lithium (Li) is one of important natural resources. The South American salt lakes contain abundant Li. The Li enrichments of the South American salt lakes are attributed to the effective drying of the influent Li-enriched river water (Rettig et al., 1980; Aloso and Risacher, 1996). The Li contents in the Grande river that flows into the Uyuni salt flat range from 3.1 to 26ppmLi (Rettig et al., 1980). Because the average Li content in river water is 1.5 ppb (Huh et al., 1998), the high Li content in the Grande river cannot be explained as the simple rock-fluid interaction at low temperature. Accordingly, the high Li content in the Grande river should due to the Li-enriched volcanic fluid and/or Arima-type deep fluid. To constraint on the origin of Li in the Uyuni salt flat, the author analyzed Li isotopic compositions of salt and brine from the Uyuni salt flat. The author will discuss the origin of Li in the Uyuni salt flat based on the Li isotopic data on Uyuni salt flat, volcanic fluid, non-volcanic Arima-type deep fluid.

Reference: Rettig et al., 1980, Chem. Geol. 30, 57-79. Alonso and Risacher, 1996, Revista Geol. Chile 23, 113-122. Huh et al., 1998, GCA 62, 2039-2051.

Keywords: lithium isotope, geofluid, Uyuni salt flat, volcanic fluid, Arima-type deep fluid, mud volcano



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Relationship between granitic magmatism and formation of hydrothermal ore deposits: An example from Naegi granitic body

Yuta Yoshie^{1*}, Kenichi Hoshino²

¹Fac. Sci., Hiroshima Univ., ²Grad. Sch. Sci., Hiroshima Univ.

Late Cretaceous to Paleogene granitoids located in the Inner zone of Southwest Japan are classified into three belts: the Sanin-Shirakawa belt, the Sanyo-Naegi belt and the Ryoke belt (Ishihara, 1971). W-Sn-Cu mineralizations are characteristically associated with the granitoids of the Sanyo-Naegi belt. Although numerous geochemical studies have been made for the hydrothermal ore deposits accompanied with these granitoids, the entire process from the granitic magma crystallization to the formation of hydrothermal ore deposits is still in debates.

The Naegi granitic body in the eastern part of the Sanyo-Naegi belt and related ore mineralizations have been investigated in this study to clarify detailed chemical characteristics of ore forming fluids for a future discussion of the process.

The Naegi granite intrudes into the felsic ignimbrites called the Nohi rhyorite. A high Rb/Sr ratio and an REE pattern with a distinct negative Eu anomaly were reported from the granite (Ishihara et al., 2001), implying its origin as a highly fractionated magma. The granitic body is associated with numerous hydrothermal ore deposits, from center of the body to the surroundings: (1) U-Th-REE-bearing pegmatites, (2) W-Sn-Bi-Be deposits, (3) W-As-Bi deposits, and (4) Cu-Pb-Zn-As deposits. Compositions and the physicochemical conditions of ore fluids have been estimated from detailed petrographic studies, EPMA analyses of minerals and LA-ICP-MS microanalyses of fluid inclusions for 14 elements (Na, K, Mn, Fe, Cu, Zn, Rb, Mo, Sn, Sb, Cs, W, Pb and Bi). Temporal relations of fluid inclusions trapped in quartz and topaz crystals were investigated by microscopic observations. Characteristics of the deposits are as follows:

(1) U-Th-REE-bearing granitic pegmatites are consisted of quartz, feldspar, biotite, muscovite and trace amounts of REE minerals. Fluid inclusions show homogenization temperatures of 200-470C with salinities ranging 1-7wt%. Base metal (Cu, Pb, Zn) concentrations in fluid inclusions are 2-3 times higher than those of W, Sn and Bi concentration, while Sb concentrations are relatively stable.

(2) W-Sn-Bi-Be deposits are of wolframite-cassiterite-native bismuth-topaz-beryl-quartz veins in the granite and the ignimbrites. Fluid inclusions show homogenization temperatures of 250-430C with salinities ranging 1-33wt%. Base metal concentrations are higher than those of W, Sn and Bi.

(3)W-As-Bi deposits are of wolframite-loellingite-arsenopyrite-native bismuth-quartz veins in the ignimbrites with silicification. Fluid inclusions show homogenization temperatures of 185-360C with salinities ranging 1-7wt%. Base metal concentrations are higher than those of W, Sn and Bi.

(4)Cu-Pb-Zn-As deposits are of sulfide (Cu-Fe-As-Zn-S) -chlorite-quartz veins in the ignimbrites. Fluid inclusions show homogenization temperatures of 150-360C with salinities ranging 1-6wt%. Almost all the metal concentrations, especially Cu, Pb, Zn, Fe, W and Mo, of fluid inclusions in (4) are 2-3 times higher than those of the other deposits.

Although the above physicochemical characteristics of the ore forming fluids have been clarified in the present study, much detailed examinations are required to investigate the entire process of ore formations and geneses and evolutions of the fluids.

Keywords: LA-ICP-MS, fluid inclusion, Naegi Granite, rare metal, base metal, hydrothermal ore deposit



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Precipitation condition of antimony-rich and gold bearing hydrothermal minerals associated with shallow-water hydrotherm

Ryota Komiyama², Toshiro Yamanaka^{1*}, Kotaro Maeto¹, Hiroyasu Murakami³, Jun-ichiro Ishibashi⁴, Kazuhiko Shimada⁴, Takashi Nakatani⁵, Hitoshi Chiba¹

¹Okayama University, ²Okayama University, ³AIST, ⁴Kyushu University, ⁵University of Tokyo

The eastern part of the innermost part of Kagoshima Bay contains a small, crater-like depression called Wakamiko Crater, where maximum water depth is approximately 202 m. Active fumaroles have been reported in this area (Kagoshima Prefectural Government, 1978; Oki and Hayasaka, 1978), resulting in its designation as an active volcano named Wakamiko. In addition, occurrences of hydrothermal petroleum and mineralization related to hydrothermal fluid-sediment interaction have also been reported within the crater (Yamanaka et al., 1999, 2000; Ishibashi et al., 2008; Nakaseama et al., 2008), strongly suggesting occurrence of hydrothermal activity at the crater floor. In 2007 during the dive study of ROV/HyperDolphin belonging to Japan Agency for Marine-Earth Science and Technology (JAMSTEC) we found vigorous hydrothermal venting at the northwest area in the crater at depth 200 m, measured temperature of the venting fluid was reached up to 192?C. We found three vents, and the venting fluid were emitting from the top and foot of the chimney like cone-shaped mineral precipitations (about 2 m in height and 3⁴ m in diameter at the foot), respectively. The chimneys are composed mainly talc and carbonate with minor amount of anhydrite and stibnite. It is very rare that shallow water hydrothermal venting involve forming chimney like mineral precipitation. On the other hand, those talc-rich chimneys were formed on the mounds, which deposit of blackish boulder size (up to 50 cm in diameter) lump of sulfide minerals. The lump was aggregate of almost stibnite with minor amount of talc and pyrite. The stibnite aggregate was composed ~1 mm length needle-sharp stibnite. Although any characteristic inner structure was not observed to the aggregate, pumice-like vague vestiges replaced by talc was rarely found in the aggregate. From the bulk analysis Au was detected in the those precipitations, bulk concentration of Au in the stibnite aggregate was reached 19 ppm. Therefore, we considered the precipitation condition of the stibnite aggregate using REE pattern.

Significant contents of REEs were detected in barite minerals occurred in the stibnite aggregate. The condrite-normalized REE patterns of the aggregate shows a pronounced positive Eu anomaly that is probably inherited from the hydrothermal fluid, suggesting insignificant contribution of seawater during precipitation. Total REE contents of the aggregate were higher than those of the chimney precipitations, it may reflect low growth rate of precipitation minerals in the aggregate.

Au and Ag were concentrated significantly on stibnite relative to talc and barite, and their contents in the aggregate and chimney precipitation formed inner part of the chimneys were one order of magnitude higher than those of the chimney precipitations formed outer part of the chimney. The precipitation temperature of the chimneys between the inner and outer parts were expected different based on the oxygen isotope geothermometer using talc, the estimated precipitation temperatures were 195 deg-C for the inner part and 174 deg-C for outer part. Although the oxygen isotope data of the aggregate was not measured, the high Au and Ag concentrations in the aggregate suggests that the precipitation temperature of the aggregate is close to the inner part of the chimney precipitations.

From those results the stibnite aggregate is expected to form beneath seafloor and erupted on the seafloor. It suggests that such antimony-rich precipitation is expected to distribute extensively beneath the seafloor, and the estimated amount of the precipitins is not negligible compared to the case of aggregate depositing as hydrothermal mineral mound as a result of collapse of chimney precipitations.

Keywords: shallow-water hydrothermal activity, hydrothermal precipitation, Antimony, gold, REE



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Bazman epithermal gold-silver mineralization, Sistan and Baluchestan province, Iran

Mohammad Boomeri^{1*}, Kazuo Nakashima², M. J. Gholami³

¹Univ. of Sistan and Baluchestan, ²Yamagata Univ., ³Univ. of Sistan and Baluchestan

The study area is located 160 km northwest of Iranshar in Sistan and Baluchestan province, southeast of Iran. The area is geologically located in the SE-trending part of the Central Iran magmatic arc zone known as Sahand-Bazman magmatic zone. This zone extends to Turkey to the northwest and to Pakistan to the southeast. The Arabian Plate was subducted and collided beneath Eurasian plate to form a few arc-trench systems in Turkey, Iran and west of Pakistan from Cretaceous to recent days. Among them is the active Makran subduction zone formed by the convergence of the Arabian plate and Lut block in Iran and Helmand block in Afghanistan. The Neogene volcanoes of Bazman, Taftan in Iran and Sultan in Pakistan have spatial link with this subduction zone. Epithermal mineralization occurs in Sahand?Bazman magmatic zone of Iran as a result of the Neogene volcanism and related processes. The study area is located in the northeastern slopes of Quaternary Mount Bazman. Geology of the mineralized area consists of andesite, andesitic basalt, basalt, olivine basalt, and pyroclastic rocks that had all been erupted from the Mount Bazman. Preliminary studies revealed considerable potential of gold and silver mineralization in the area. Mineralization occurs in a vast area and ore grade is high (up to 16 ppm Au and 120 ppm Ag). The mineralization mainly occurs in and around a few veins. The mineralized veins strike N 25 to 35 E and vary from 50 cm to 2 m in width and from 500 m to over 1000 m in strike length. The veins are generally crustiform banded to brecciated with colloform to cockade banding. Pure white and milky quartz and chalcedony occur in central part of the veins (along axial line of the veins). The volcanic rocks close to the milky pure quartz and chalcedony veins (seems as halo) are brecciated and strongly silicified and contains abundant pyrite. Phyllic, argillic and propylitic alteration occur peripheral to the veins. Mineralization is associated with the pyrite-rich brecciated parts around the axial line of the veins. Other sulfides are chalcopyrite, covellite, silver-rich covellite, galena, sphalerite, tetrahedrite and an unknown Ag-rich phase. Quartz is main gangue mineral and occurs as large euhedral to microcrystalline grains. Chalcedony occurs with quartz periodically in crustiform banded veins. Other gangue minerals are adularia, calcite and phyllosilicates. The brecciation is first stage followed by silica precipitates as cockade structure. Finally crustiform quartz and chalcedony were formed along central part of the veins. Pyrite is the most common sulfide. It occurs in every rock samples. Chalcopyrite and Ag-minerals occur as late veinlets. Gold (less than 1 micron up to 2-3 microns) occurs in the hydrothermal breccias of final phase. This paper will discuss many data that obtained by polarization microscope, XRD, XRF and EPMA.

Keywords: Bazman deposit, epithermal gold-silver mineralization, Neogene volcanism, hydrothermal breccias, XRD, XRF and EPMA



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Hydrothermal alteration and minerlization in Abdar Caldera, Kerman province, Iran

Mohammad Boomeri^{1*}, Kazuo Nakashima², Gh. Abasszadeh³

¹Univ. of Sistan and Baluchestan, ²Yamagata University, ³Univ. of Sistan and Baluchestan

The Abdar Caldera is located in 35 km northeast of Shaher-e-Babak, southeast of Iran. This area is geologically a part of northwest of the Dehaj-Sardueih Belt (a part of Uromieh-Dokhtar magmatic arc) that consists of a thick sequence of Eocene volcanic, pyroclastic and volcanoclastic rocks and Oligo-Miocene intrusions. Post-collisional processes also produced adakitic and alkaline rocks in this zone during the Plio-Pleistocene and Plio-Quaternary. Local geology consists of Eocene fine-grained tuffs, andesitic tuff, andesite, andesitic basalt, trachyandesite and basalt, and Oligo-Miocene, diorite and granodiorite. The above rocks are mainly porphyry in texture and contain plagioclase, K-feldspar, quartz, biotite and hornblende and minor titanite, magnetite, apatite and zircon. The volcanic and pyroclastic rocks were cut by numerous quartz veins in the area. Every vein surrounded by an intense alteration halo. The quartz veins show banding and comb structures in their central part where contains large (up to 3 cm) pyramidal quartz. The quartz crystals decrease in size outward. Phyllic and propylitic alterations occur at the periphery of the veins. Although hydrothermal alterations occur around the veins in a vast area but the veins are weakly mineralized. Most of the assemblages and fluid inclusions can be assigned to epithermal alteration and mineralization. Mineralization occurs as sulfides and oxides. The sulfides are pyrite, galena, sphalerite, chalcopyrite, stibnite, tetrahedrite, tennantite, arsenopyrite and covellite. The oxides are hematite, magnetite, pyrolusite and iron hydroxides. The gangue minerals are mainly quartz, barite, calcite and phyllosillicates. In this paper we document and interpret petrography and geochemistry of volcanic rocks using microscopic and XRF data. Alteration mineralogy checked by XRD. Sulfide and oxide minerals were analyzed by EPMA and the mineral chemistry will be discussed in this paper.

Keywords: Abdar Caldera, Oligo-Miocene intrusions, porphyry copper, hydrothermal alteration, Iran