The Granitoid Series and Related Mineralization in the Earth History

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Granitoids distributed in the Inner Zone of SW Japan were identified to have the accessory components of magnetite and ilmenite to the north, but only small amounts of ilmenite toward the south in 1971, then named later as "magnetite-series and ilmenite-series" granitoids. Associated ore deposits also show characteristic minerals. Native sulfur was mined nearly all from the Quaternary magnetite-series volcanic belts. Native Au-Ag (typically argentite AgS) deposits occur in Neogene to Quaternary magnetite-series terranes. Cu (typically chalcopyrite CuFeS<sub>2</sub>) -Pb (galena PbS) -Zn (sphalerite, ZnS) and Mo (molybdenite, MoS<sub>2</sub>), occur also as sulfides in vein and skarn types of the late Cretaceous to Neogene magnetite-series igneous terranes. On the other hand, the ilmenite-series ores are characterized by none sulfide mineral commodities, such as cassiterite (SnO<sub>2</sub>) and wolframite ((Fe,Mn)WO<sub>4</sub>) and scheelite (CaWO<sub>4</sub>). Therefore, distribution of sulfur in the magmatic stage is the key to the metallogeny of the two series.

Oxidation status of the earth surface has been changed in the earth history. The oldest foliated granitoids in the Greenland showed low  $Fe_2O_3/FeO$  ratios equivalent to the ilmenite series. In the Berberton region of South Africa, the Archean TTG suites appear to belong also to the ilmenite series, but pink granites younger than 3.0 Ga were found to be the first magnetite series. In the western Australia, aeromagnetic map shows the Archean Pilbara craton of the ilmenite-series granitoids, but Proterozoic Yilgarn craton is composed dominantly of the magnetite-series. Au-mineralized sheared zones are hosted in the green stones, with the Au-mineralizing systems: a broadly uniform, low to moderate salinity, mixed aqueous-carbonic fluid capable of carrying Au, but limited capacity to transport base metals. The oldest Sn deposits are known to occur together with biotite and aplitic granites of 1.8 - 1.6 Ga (Rb-Sr), within the Bushvelt ultramafic to mafic body. These granitic magmas were found partial melting products of the middle crust by heat brought-up by the Bushvelt ultramafic magmas. The oldest Li-mica pegmatite-bearing dikes (age: 2.5 Ga) have been mined in the western Australia.

Keywords: Granitoid series, Sulfide mineralization, Oxide mineralization

Granite-series and the origin of granitic magma

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The distribution of magnetite- and ilmenite-series granites (granite-series) shows zonal arrangement in a regional scale, and the ratios of two series granites systematically varied by their age. The facts indicate that the genesis of granite-series is not attributed to local phenomena but is closely related to the origin of granitic magma. The compilation of previous studies on granites in Japan Arc shows that granite activities are positively correlated with the convergence-rate of oceanic plates at the time, and the maximum activity occurred during 95-85 Ma, which comprises mostly ilmenite-series granites. The ratios of ilmenite- and magnetite-series rapidly rose at ca. 110 Ma, and dropped at ca. 70 Ma. The initial Sr isotope ratios (SrI) of ilmenite-series granites systematically rose in Cretaceous, whereas those of magnetite-series were fairly stable regardless of their ages. The similar variations can be found in the initial Nd isotope ratios (NdI). The facts above suggest that the assimilation-rate of sedimentary rocks into granitic magma systematically rose in Cretaceous, and dropped at 70 Ma. The phenomena are hardly explained by lower crustal melting by the ridge-subduction or the assimilation of wall rocks during emplacement of granitic magma.

In the Sr-O isotope diagram, the plots of most granites except for part of high-Sr granites are consistent with the curves of source contamination (convex downward). The SrI-NdI diagram also indicates that most granites were formed by the assimilation-fractional crystallization processes between strongly depleted materials (= mantle materials) and sedimentary rocks. To explain the data consistently, the geological setting of which mantle materials react with sedimentary rocks during magma generation is necessary. The sedimentary rocks should be common and homogeneous materials, and should be drawn into magma source regions. The materials met the above conditions are subducted sediments. Therefore, it can be deduced that the granite-series in Japan Arc depends mainly upon the reaction-rate between primitive magma and subducted sediments. Furthermore, it is also inferable that the main source materials of granitic magma in Japan Arc are not lower crustal materials but subducted sediments reacted with mantle materials. Reference: Takagi, T (2004) Am. Jour. Sci., 304, 169-202.

Keywords: granite, Japan Arc, subduction zone

Hydrothermal alteration, mineralogical description and ore-forming conditions of the Utanobori gold deposit in northern Hokkaido, Japan

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The Utanobori gold deposit is a low-sulfidation type epithermal gold deposit located in northern Hokkaido, Japan. In this study, we investigated geological features of gold-mineralized quartz-adularia veins and hydrothermally altered host rocks from viewpoints of mineral association and paragenetic sequences, bulk chemical compositions, mineral chemical compositions and physicochemical conditions in order to reveal characteristics of gold mineralization and ore-forming environment.

The study area and its surroundings are composed of slate of the Cretaceous to Paleogene Hidaka Supergroup, the Miocene Esashi Formation, the Kemomanai Lava, the Kinkomanai Lava, the Pliocene Penke Formation and the Quaternary terrace and alluvial deposits (Osanai et al., 1963). The gold-mineralized quartz veins are hosted in silicified conglomerate, sandstone, mudstone and tuff of the Esashi Formation. Previous studies based on K-Ar dating reported an ore-forming age of 12.1± 0.6 Ma on adularia from the Utanobori deposits, and a same formation-age of 12.1±0.6 Ma on a bulk dacite from the Kinkomanai Lava (Ministry of International Trade and Industry (MITI), 1997). The Esashi Formation, host rocks of mineralization in the Utanobori deposit, shows hydrothermal alteration with zoning distribution such as 1) quartz + K-feldspar ±chlorite-smectite mixed layer, 2) quartz + K-feldspar + illite ±smectite, 3) quartz + kaolinite ±illite ±smectite, and 4) quartz + plagioclase + chlorite-smectite mixed layer ±calcite, in order from the silicified zone to the periphery zone.

A representative high Au-Ag grades quartz-adularia vein shows three mineralization stages of Stages I, II and III with subdivided twelve sub-stages. Among them, the Stages I and II are the main gold mineralization stages. The veins are composed of gangue minerals of quartz and adularia and ore-minerals of electrum, naumannite, chlorargyrite and Fe-Sb-oxide or hydroxide. Quartz shows fine-grained equigranular, mosaic, microcrystalline, colloform and comb textures. Electrum shows average Au/(Au+Ag) compositions of 52.5, 65.7 and 55.5 atomic % in the Stage I-b, Stage I-d and Stage II-a, respectively. XRF spot analysis along the mineralization sequences revealed that 1) the amount of adularia gradually decreases from the Stages I to III, 2) the gold deposition is not directly associated with adularia, and 3) the highest concentrations of Au, Ag, Se and Sb were observed in a sulfide band of the Stage I-d. On the basis of the fluid inclusions microthermometry data by MITI (1997), frequent ranges of homogenization temperatures are 260-270°C and 220-230°C in the Stages I and III, respectively. Fugacity of selenium based on the electrum tarnish method was estimated to be  $\log fSe_2 = -14.2$  to -12.8 and -13.1 to -11.6 atom for the Stages I-b and I-d, respectively.

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Keywords: The Utanobori deposit, Epithermal gold mineralization, Hydrothermal alteration

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Geochemical mapping using surface water and stream sediments of the mineralized Lom Basin, East Cameroon.

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The Lom Basin is heavily mineralized especially in gold owing to its regional geological setting. Consequently, most research in this region have reported either the rock type, age, and the formation history or the reconnaissance gold investigations. However, the geochemical database of the area is scanty and no regional geochemical mapping has been performed. Although this area has a long artisanal mining history and is a major target for industrialized mining, pollution studies have received limited attention. The present study seeks to i) conduct a systematic stream water and bottom sediment sampling in the area based on the International Geological Correlation Programme (IGCP, 1995) recommendations; ii) determine trace element levels in the sediments and natural water systems and iii) develop geochemical/risk maps of the study area. We target to sample 50 surface water and sediments of streams and major rivers draining the catchment. The geochemical background shall be determined by analysing surface water samples for cations by AAS and anions by Ion Chromatography (IC); and sediments for trace metals using ICP-MS. It is expected that the geochemical baselines and toxic levels of both sampling media shall be established for the construction of a geochemical/risk map of the area. This is important in environmental monitoring. Preliminary results shall be presented in this talk.

Keywords: Geochemical mapping, Surface water, Stream sediments, Lom Basin, East Cameroon

Geochemical Study on Redox Conditions of REE Zone in Nickel Laterie Deposit, South Dinagat Island, Philippines

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Recently, the demand of REE is increasing but its production of REE is limited to a few countries. Therefore it is important to look for alternative sources of REE production. It is economically effective to produce REE as by-product of other resource deposits. Nickel laterite deposits, which account for over 60% of global nickel supply, are being investigated as a possible REE resource because weathering of nickel laterite produces significant concentration of REE, especially Sc. One of the factors that control the geochemical behavior of REE during weathering process is soil pH and redox condition. The objectives of this study are to describe the geochemical characteristics of REE during the formation of nickel laterite in South Dinagat Island and to propose a practical and convenient on-site geochemical tool for REE exploration in nickel laterite deposits. The harzburgite is considered to be the bedrock in this area, and thin section observation revealed that it mainly consists of olivine, orthopyroxene, lizardite, saponite and garnierite. In this study, laterite samples are classified as limonite (Fe0>60%), earthy saprolite (30%<Fe0<60%) and rocky saprolite (Fe0<30%).

The XRF and ICP-MS analysis revealed that there is no apparent correlation between nickel, which is main product of nickel laterite deposits, and scandium, which is investigated as by-product. Nickel is concentrated in the fractures of lower limonite and saprolite as secondary formed hydrous Mg silicate. On the other hand, Sc exhibits correlation with immobile elements such as Fe and Al resulting in Sc concentration in the shallower zone. Weathering caused the Sc concentration to increase about 5.6 times, up to 75ppm, in the shallower zone compared with Sc content in bedrock because mobile elements percolate downward during weathering. Y and the lanthanides, except for Ce, showed different behavior from Sc. Y and Ln are concentrated in the negative Ce anomaly zone in the chondrite-normalized REE pattern. In oxidizing conditions, soluble  $Ce^{3+}$  is oxidized to  $Ce^{4+}$ , which easily precipitates as very insoluble CeO<sub>2</sub>. However, the other REE is drained from the shallower zone and percolates downward. Consequently, positive Ce anomaly is observed in the shallower zone and negative Ce anomaly is observed in the deeper zone. Y and Ln are concentrated to increase up to 57ppm in negative Ce anomaly zone. Combined above geochemical data with on-site soil pH and Eh analyses, there is possibility to practically extract REE concentration zone. SREE (Sc, Y and Ln) is concentrated to increase about 3.2 times up to 126ppm in the horizon where pH values shows less than 7.0 compared with compared with  $\Sigma REE$  content in the horizon where pH values shows more than 7.0. Furthermore limonite and earthy saprolite, where Sc is concentrated, show pH values less than 6.5 and reveal Eh values more than 550mV.

Fractionation between LREE and HREE in granitic rocks in southern Myanmar: Implications for HREE-rich granite

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As crustal abundances of heavy rare earth elements (HREE) except yttrium (Y) are generally smaller than those of light rare earth elements (LREE), HREE are more expensive than LREE in the market. At the present day, minable HREE-rich deposits are confined almost exclusively to ion-adsorption type deposits (e.g., Longnan in China), underlain by highly-differentiated (> 74 -75 % SiO<sub>2</sub>) calcalkaline granites which are enriched in HREE and depleted in LREE. In this study, we collected granitic rocks of 67 -76 % SiO<sub>2</sub> in southern Myanmar to discuss characteristics of HREE-rich granites based on whole-rock geochemistry and the occurrence of REE-bearing minerals. 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. Fractionation of REE-bearing minerals by magmatic differentiation has an important role for the formation of HREE-rich granite rather than the degree of partial melting. In our study, Late Cretaceous to Eocene granitic rocks in southern Myanmar were analyzed and geochemical results indicated that differentiated granites over the approximate boundary of 74 % SiO, tend to be enriched in HREE. This boundary is more distinctly decided by the occurrence of REE-bearing than by the whole-rock chemical composition. Granitic rocks less than 74 % SiO<sub>2</sub> contain either or both of titanite and allanite, whereas granites over 74 % SiO, rarely contain these minerals. In this study, results of the EPMA analysis indicated that some titanite crystals are rich in HREE. Because titanite is the dominant HREE-bearing mineral as much as zircon in granites, undersaturation of titanite may lead to HREE-rich melt eventually. In the strongly-differentiated granites over 74 % SiO<sub>2</sub>, titanite was rarely found and a variety of HREE-bearing minerals such as synchysite-(Y) were observed.

This study result suggests that the HREE-rich granites, as represented by parent rocks underlying ion-adsorption type deposits, were potentially formed by magmatic differentiation under the condition of titanite-undersaturation. Whole-rock chemical compositions of granitic rocks and the occurrence of specific REE-bearing minerals may be indicative of exploration for HREE deposits.

Keywords: HREE, LREE, Granite, Titanite, Allanite, Deposit

Heavy rare earth potential of apatite resources

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Phosphorous is one of the three major nutrients (N, K, P) required by plants and 80-90% of the phosphate mined in the world is used to produce chemical fertilizers. Securing stable supply of phosphate fertilizers is essential to a sustainable food production considering a continuing rapid growth of world population (Van Kauwenbergh et al., 2013). The world resources of phosphate rocks are more than 300 billion tons (U.S. Geological Survey, 2015). "Phosphate rock" is the term generally used in industry to describe mineral assemblages with a high concentration of phosphate minerals, commonly francolite  $(Ca_5(PO_4, CO_3)_3(OH, F, Cl))$  - apatite  $(Ca_5(PO_4)_3(OH, F, Cl))$  series. There are two main types of phosphate deposits: sedimentary and igneous. The former deposits sometimes are called phosphorite and contain varieties of francolite  $(CO_2-rich fluorapatite)$ , the latter mainly consist of fluorapatite (F-rich apatite) (Ihlen et al. 2014). Apatites contain a variety of REEs in concentrations from several thousands of ppm to several wt.%.

Aparites contain a variety of REES in concentrations from several thousands of ppm to several wt.%. They are generally enriched in LREEs (e.g., Roeder et al., 1987), however, some apatites are rich in HREEs: apatites in sedimentary phosphate rocks (Emsbo et al. 2015) and deep sea mud (e.g., Kon et al. 2014), and igneous phosphate rocks (e.g., Hoshino et al., 2015). In addition, both Th and U contents in apatite are very low in contrast to common REE minerals such as monazite and xenotime, and this may be a big advantage over the other types of REE deposits (e.g., alkaline REE deposits). In view of the future of HREE supply (considering both feasibility and sustainability), one of the most promising sources of HREEs is apatite ores that are mined for fertilizer production, because apatite ores are sufficient in reserves and contain enough amounts of the whole REEs that can cover the world demand.

Keywords: apatite, HREE resources

The Origin of the Nangarhar Talc Deposits in the Spin-Ghar Block, Afghanistan

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Talc deposits in the E-W trending Spin-ghar block, southeastern part of Afghanistan, were formed in Paleoproterozoic carbonate rocks. There are two types of talc mineralization in the study area, one in the western part (Dar, Kherwas and Janinaw deposits) and other in the eastern part (Mamond Dara deposits) of the block, hosted by magnesite and dolomite marbles, respectively. The objective of this study is to describe the talc mineralization on the basis of field observations, microscopic observation, XRD, XRF, ICP-MS and SEM-EDS analyses.

In the western part of the block, talc is parallel to sub parallel to magnesite rock and cross cut by intrusive igneous rocks of diabase. Metamorphic rocks of quartz chlorite schist are parallel to sub parallel to talc ore body and magnesite. Massive layers of tremolite about one meter thick were observed at Kherwas. Intrusive rocks have not been identified and a thin layer of talcose quartz has been marked within talc veins at Janinaw. A thick layer of talc contains needle like macroscopic tremolite crystals in the matrix of talc at Janinaw. In the Mamond Dara area at the most eastern part of the block, parallel alternating layers of talc and dolomite marbles occur with quartz chlorite schist mostly altered to chlorite. Massive gneiss occurs at the contact of these talc, dolomite marbles and quartz chlorite schist. Mineral assemblages in the western part are (a) talc + tremolite + calcite, and (b) talc ±cordierite, while those in the eastern deposits are (c) talc + dolomite + calcite  $\pm$ quartz  $\pm$ apatite and (d) talc + dolomite + calcite. Talc was formed by alteration of tremolite and magnesite in Dar and Kherwas deposits, while in Janinaw and Mamond Dara, talc was formed by alteration of dolomite and tremolite and by alteration of dolomite, respectively. Total REE contents of talc bodies, magnesite and dolomite marbles range from 0.9, 5.3 and 13.0 ppm, respectively. The SiO<sub>2</sub> contents of carbonates and talc bodies range from 1.6 to 33.3 wt% and from 52.9 to 65.1wt %, respectively, while MgO contents of carbonate and talc bodies range from18.4 to 48.1 wt% and from 29.4 to 34.0 wt%, respectively. The CaO contents in talc bodies and magnesite are less than 1 wt%, while those of dolomite marbles ranges from 18.0 to 26.0 wt%. The concentration of Al, Ta, Hf, Zr, Th and REE in talc ore and carbonates rocks is very low and inconsistent with a felsic igneous rock protolith, whereas the low concentrations of Cr, Ni, and Co are inconsistent with a mafic igneous protolith. On the basis of this low concentration of trace elements and REE, the Mg-rich carbonate rock is likely the protoliths of talc ore. Magnesium has been derived from pre-existing Mg-rich carbonate host rocks, i.e., magnesite and dolomite marbles.

Keywords: Nangarhar, Spin-Ghar, Talc, Magnesite, Tremolite, Dolomite marble

Evolution of the hydrothermal fluid at the Takatori deposit, Japan - Replacement texture at the rim of wolframite

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The Takatori deposit is a vein type tungsten deposit in Japan. The tungsten-bearing mineral is wolframite ((Fe, Mn)WO<sub>4</sub>), which has a complete solid solution of iron and manganese. Although previous papers pointed out that the replacement texture at the rim of wolframite was formed by a later fluid, the nature of the later fluid was not clear. The purpose of this study is to reveal the characteristics of the later hydrothermal fluid at the Takatori deposit. Samples were obtained from the No.7 vein at -4 Level (60m above sea level) and -7 Level (30m below sea level). They are called the middle and lower samples, respectively in this study. SEM-EDS mapping images of the rim of wolframites showed replace textures. Since the replacement texture can be distinguished by the Mn/Fe ratio in wolframites, the Mn/Fe ratio was measured by EPMA. In the middle samples, the ratio in the center of wolframites was between 40 and 50 mole%, but the ratio increased up to 70 mole% at the rim of some crystals with pyrite. These replacement textures were assumed to form by replacement of iron in the wolframite formation. The later fluid that came into the hydrothermal system after the wolframite formation. The later fluid flowed around wolframite crystals and made replacement texture in the middle samples.

In the lower samples, SEM-EDS mapping images and the change of Mn/Fe ratio showed oscillatory and complicated textures with pyrite and other sulfide minerals. These are also recognized as replacement textures that were formed by the later fluid since the trend of the change of Mn/Fe ratio is the same as that in the middle samples. The textures were formed by the later fluid which flowed thought cracks in wolframite.

Based on the relationship between pH and oxygen fugacity in phase diagrams, the temperature of the later fluid that made replacement textures was lower than that of the fluid, which had precipitated wolframites. The replacement of iron with manganese was occurred because ferberite ( $FeWO_4$ ) was unstable and hubnerite ( $MnWO_4$ ) with pyrite was stable.

Keywords: Takatori deposit, wolframite, replacement texture, hydrothermal deposit

Fluid inclusion study of core samples collected from the Iheya North Knoll in the Okinawa Trough

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From July 9 to 26 in 2014, the dive expedition (Exp. 907, CK14-04) was performed at the Iheya North Knoll in the middle Okinawa Trough to confirm hydrothermal seafloor mineralization. The core samples used in this study were obtained from Hole C9015B and C9016B of the research target area. Microscopic observation and fluid inclusion microthermometry were mainly focused to reveal the ore formation condition. The objective of this study is to clarify geochemical characteristics and the point of similarity between Kuroko deposits and seafloor hydrothermal deposits. The characteristics of the ores collected from Iheya North Knoll are as follows: C9015B samples are pyrite rich but chalcopyrite is minor, therefore, the characteristic of sulfide assemblage is not similar to yellow ore of Kuroko deposits. C9016B samples are divided into two groups. a) At the upper portion, from 29.6 to 32.7 mbsf, only framboidal pyrite could be observed. b) At the lower portion, from 38.1 to 42.1, pyrite is minor, while galena and sphalerite is abundant like Kuroko of Kuroko deposits.

Homogenization temperatures of fluid inclusions in quartz of C9015B range from 266.7 to 338.4°C and the salinity ranges from 0.00 to 6.30 wt. % NaCl eq. Homogenization temperatures of fluid inclusions in anhydrite of C9016B range 271.1 to 348.5°C and the salinity range from 3.2 to 6.1 wt. % NaCl eq. Both the data of fluid inclusion microthermometry of C9015B and C9016B samples are well plotted on the boiling curve of seawater. The fact that low salinity fluid can be observed may support the occurrence of boiling during the formation of the ore in Iheya North Knoll, Okinawa Trough.