Initial study on the mineral assemblages associated with Cu-Au mineralization,DMLZ deposit, Grasberg mine, Papua, Indonesia

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Grasberg mine is one of the biggest Cu-Au mine in the world. The Deep Mill Level Zone (DMLZ), a skarn mineralization, is one of the operating mine in the Grasberg mineral districts. The DMLZ underground deposit started in 2015, and is expected to produce approximately 80,000 t/d in 2021. It is important to conduct scientific research of DMLZ deposit which is the newest and most prospective mining area in the Grasberg mine. Therefore, this study is focused on the DMLZ deposit, and the objective is to understand the zonation of mineral assemblages. Mineralization in this district is associated with Pliocene diorite, emplaced into Cretaceous sandstone and limestone that underlie the Tertitary limestone. The drill hole (TE17-09) which cuts the DMLZ deposit horizontally, is about 630m length and run through from Ertsberg diorite to limestone, and marble. Samples were collected at equal intervals (20m) of core TE17-09. In this study, mineral assemblages in exoskarn (about 320m to 480m part of the drill hole) is focused.
Based on the microscopic observation, garnet is a main mineral of prograde stage, and chalcopyrite, pyrite and epidote are the main minerals of retrograde stage in the exoskarn. In addition, minerals formed in retrograde stage are specially developed. Native gold is associated with chalcopyrite. Gold mineralization in the exoskarn of DMLZ deposit mainly developed in the retrograde stage. Garnet can be observed in samples which are relatively proximal with intrusion. In contrast, calcite in host rock can be observed in samples which are relatively distal with intrusion. The border between garnet and calcite is about 360m part of this drill hole. For these things, it is guessed that hydrothermal fluids were cooled to the temperature in which minerals formed in prograde stage cannot be developed by about 360m part.

Keywords: skarn, zonation of mineral assemblages, Cu-Au mineralization

Characteristics of Gold Mineralization in the Salu Bulo Prospect, South Sulawesi, Indonesia

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The Salu Bulo prospect is one of the gold prospects in Awak Mas project which is located in Luwu District, South Sulawesi Province, Indonesia. The prospect is hosted in meta-sedimentary rocks of pre-Cenozoic Latimojong Formation which consists of dark (graphitic), green (chloritic) and red (hematitic) mudstone, siltstone, sandstone and intercalated meta-volcaniclastic rocks. The mineralized zones are approximately three meters thick and associated with stockwork veins and cataclastic breccias with an orientation sub-parallel and discordant to the foliation of the host rocks. Carbonatization (ankerite ±calcite or dolomite), silicification, albitization and sulfidation (pyrite) are common in addition of minor sericitization.

Pyrite is the most abundant sulfide mineral which is commonly more abundant as disseminated in the altered host rocks than in veins. It shows different morphologies and textures: fine-grained, porous and deformed pyrites. Trace amounts of tennantite-tetrahedrite, chalcopyrite, bornite, galena, hematite and rutile are also present as inclusions in pyrite and rarely as discrete minerals. Covellite and chalcocite occur on the rim of some chalcopyrite, which are possibly of supergene origin. Bulk chemical compositions of strongly altered rocks and ore bodies indicate that Au content is correlated with Ag, Ni, Na_2O and Mo contents and show Au/Ag ratio ranges from 1.5 to 7 (average 4.4). Gold occurs as electrum and native gold as fracture filling and inclusion in pyrite with Au/(Au+Ag) ratio ranging from 66.2 to 78.5 atomic % and from 81.4 to 82.3 atomic %, respectively.

Fluid inclusions in mineralizing veins and matrix of cataclastic breccia are mainly liquid rich vapor-liquid H_2O inclusions and minor H_2O vapor inclusions. Laser Raman detected CO_2 and N_2 gases in these inclusions. Homogenization temperature (Th) of fluid inclusions in mineralizing veins ranges from 132 to 336 ˚C and that in the matrix of cataclastic breccia ranges from 148 to 368 ˚C, which homogenized into the liquid phase. Salinity of fluid ranges from 4.3 to 9.3 wt.% (average 7.4 wt.%) NaCl equivalent in mineralizing veins and from 5 to 9.5 wt.% (average 7.1 wt.%) NaCl equivalent in matrix of cataclastic breccia. Carbonate alteration was probably formed by CO_2 rich mineralizing fluid as it was confirmed by the presence of CO_2 in fluid inclusions, while albite alteration and the occurrence of albite in veins and matrix of cataclastic breccia indicates the presence of sodium-rich mineralizing fluid. Hydrothermal activity accompanied with deformation during formation of cataclastic breccia formed pyrite and gold. In the alteration halo of quartz-carbonate±albite vein and stocwork, gold precipitated as fracture filling and inclusion in pyrite.

Keywords: Meta-sedimentary rocks, pyrite, quartz-carbonate±albite vein, CO2

Fe isotope and trace element variations in Shilu iron deposit, Hainan province, China: an early Neoproterozoic iron formation

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The Shilu Fe ore deposit in Hainan province, China is known as the richest Fe-ore deposit in Asia, with proven ore reserves exceed 460 Mt of Fe-ore at an average grade of 51% FeO. It is dominated by high-grade hematite-type Fe ores, which are hosted in dolomite marble of Shilu Group. The constrained age of the ores is early Neoproterozoic, between ca. 0.8Ga and ca. 1.0Ga. The genesis of the deposit is still under debate due to its complicated geological characteristics. The proposed models include: 1) skarn type deposit; 2) magmatic-volcanic origin (erupted volcano); 3) exhalative sedimentary origin.

Here Fe isotopes and trace elements for iron ores and jasper from the main orebody (Beiyi Orebody) of Shilu deposit were systematically investigated based on carefully petrographic studies. It is observed under the microscope that fine-grained jasper is widely distributed in the Fe ores. The Fe isotopes and PAAS-normalized REE patterns vary regularly for iron ores from different layers. There are three layers of iron ores in Beiyi Orebody. The iron ores from the bottom (lower) layer have highly positive δ^{56}Fe values of ca. 1‰ ~ 1.5‰. Their PAAS-normalized REE patterns show remarkably positive Eu anomalies and negligible Y anomalies, indicating partly sourced from high-temperature hydrothermal fluids. On the other hand, the iron ores from the middle layer have slightly positive δ^{56}Fe values of ca. 0.2‰ ~ 0.4‰, whereas those from the upper layer have δ^{56}Fe values of ca. -0.2‰ ~ 0.2‰. Their PAAS-normalized REE patterns imply a mixed source from seawater and low-temperature fluids, with LREE depleted and HREE enriched, no or negligible Eu positive anomalies, and slightly positive Y anomalies.

The positive and variable Fe isotope compositions, and characters of REE patterns, as well as the fact that jasper is widely distributed in the iron ores, convincingly demonstrate that the Shilu Fe deposit is of chemical-sedimentary origin, or in other word, banded iron formation (BIF).

Shilu iron formation is not the only one of the early Neoproterozoic iron formations. Another one, the Aok iron formation in NW Canada, has also been previously reported. They likely deposited in a same period according to stratigraphic correlation. It seems that the early Neoproterozoic iron formations are not of local occurrence, but may be widely in globe, although their scale is not as large as that of Cryogenian iron formations. The origin and significance of occurrence of the early Neoproteorzoic iron formations are interesting issues worthy of further studies, but obviously they are not related to the “Snowball Earth”.

The Fe isotope and REE variation trend in Shilu iron deposit provide insights into the temporal evolution of iron deposition. The variation of REE patterns among different layers of ore deposit indicates that the degree of mixing of high temperature hydrothermal fluids is not constant during Fe precipitation. The correlation between Fe isotopes and REE patterns indicate that the Fe isotope variation may be affected by changes of physico-chemical conditions (such as pH, Eh and T) during Fe-oxide precipitation.

Keywords: iron deposit, iron isotopes, rare earth element, iron formation, early Neoproterozoic

Petrographic study of geological units and veins of the Co-O epithermal gold deposit, Mindanao, Philippines

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Located in the eastern Mindanao Island, Philippines, the Co-O mine of the Philsaga Mining Corp. (a Philippine subsidiary of the Medusa Mining Ltd. of Australia) hosts two mineralization types, namely: intermediate sulfidation epithermal gold (+ Ag ±Cu ±Pb ±Zn) quartz vein and porphyry copper-gold. Eastern Mindanao belongs to the Pliocene-Quaternary calc-alkaline magmatic zone of the Central Mindanao Volcanic Zone (Mines and Geosciences Bureau, 2004). Stratigraphic units in this region include andesitic and pyroclastic basement rocks of the Eocene Anoling Andesite, intrusive rocks of the Early Oligocene Diwata Diorite, and sedimentary sequences of the Late Oligocene to Early Miocene Bislig Formation. Younger limestone units are the Lower Middle Miocene Rosario Limestone and Pleistocene Hinatuan Limestone. This study is part of a research on the structural geology characterization of this deposit and vicinity. It is a review of the general geology and mineralogical characteristics of the study area through field surveys and petrography of the main geologic units and veins, integrated with XRD analyses of clay minerals.

In the Co-O mine, the main geologic units are Eocene to Oligocene basaltic-andesitic to andesitic volcanic flows and volcaniclastic basement deposits, Oligocene andesitic to dioritic stocks and dikes intruding the volcanic basement rocks, a diatreme-maar complex that cuts and overlies these volcanic and intrusive rocks, and overlying sedimentary sequences (e.g., Sonntag and Hagemann, 2010). The porphyry copper-gold mineralization and overprinting intermediate sulfidation epithermal gold mineralization are mainly hosted in an intrusive stock and surrounding volcanic rocks. The epithermal vein system is characterized by structurally-controlled early stage hydrothermal breccias and main stage epithermal quartz veins.

The volcanic basement rocks generally contain phenocrysts of plagioclase, clinopyroxene, and hornblende crystals set in a microcrystalline matrix. In most samples, sub-angular to sub-rounded plagioclase crystals (~1-5 mm) show alteration to clay minerals. As verified through XRD, the clay minerals are smectite (montmorillonite) and chlorite (± kaolinite). The andesite porphyry and dioritic intrusive rocks mainly contain large crystals (>1 mm) of plagioclase, hornblende, and minor quartz. Andesite porphyries contain plagioclase, clinopyroxene, and opaque minerals (pyrite ±chalcopyrite), and some with xenoliths of porphyritic andesites. Plagioclase crystals exhibit alteration to clay minerals (chlorite, interstratified illite-montmorillonite ±kaolinite). Veins/veinlets cutting across these units are generally quartz ±calcite, with opaque and clay minerals. The diatreme portion of the diatreme-maar complex consists of monomictic to polymictic breccias containing clasts of andesite porphyry to diorite and andesitic volcanics. The clasts are generally lithic fragments and partly detrital crystals set in patches of fine-grained quartzofeldspathic, calcitic and chloritic minerals. Plagioclase crystals appear to be bloated and altered to clay minerals (smectite/montmorillonite, chlorite, interstratified illite-montmorillonite ± kaolinite).

Petrographic study of the veins in Co-O is partly used for fluid inclusion microthermometry. The quartz ± calcite veins are generally white to smoky/gray and exhibit massive, banded, comb/crustiform, and mosaic textures. Initial results indicate a dominance of small inclusions (<2 microns) with only a few measurable inclusions (>5 microns). These inclusions occur within quartz and calcite crystal grains as internal trails and clusters of two-phase inclusions, including dominant liquid-rich vapor-liquid inclusions with rare vapor-rich inclusions. Previous consultancy works (Hagemann and Grignola, 2012; Hagemann and Roudaut, 2014), which investigated similar crystal grains of quartz and calcite veins, interpreted the occurrence of these inclusions as pseudosecondary, from which microthermometric analyses were measured. The occurrence of such assemblages is consistent with fluid boiling during fluid inclusion entrapment and formation of the quartz ±calcite veins (Hagemann and Grignola, 2012).

Keywords: petrography, geology, Philippines, Co-O mine

Precipitation condition of stibnite at Wakamiko submarine Hydrothermal system in Kagoshima Bay, Japan

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Active hydrothermal venting have been occurred on a shallow-seafloor in the most inner part of Kagoshima Bay, Southern Kyushu, Japan. That area is called Wakamiko hydrothermal field and at least three active vents with chimneys are recognized. Those chimneys are standing on sulfide mounds, which almost consist of stibnite. The previous studies suggested that those sulfide deposits possibly ejected from beneath the seafloor where they once formed. Therefore, it is likely that those sulfides may form ore body below seafloor.

In this study, to confirm prevailing favorable condition for stibnite precipitation below the seafloor, mineral paragenesis, elemental analysis using EPMA, and stable isotope analysis were performed together with thermodynamic calculations based on chemical and physical data obtained from previous studies at the area.

From the microscopic and EPMA analysis, pyrite, sphalerite, chalcopyrite, and galena were found as minor components in the sulfide deposits. Sulfur isotope compositions of stibnite were almost uniform among the samples ($\delta^{34}S = +2.3$ to +3.3‰), while those values of co-occurred pyrite were relatively variable (form +1.7 to +7.0‰). It suggests that source of sulfide to form pyrite is variable. Therefore, it was considered that most of them were not paramedic relation with stibnite. The FeS contents of sphalerite measured by EPMA showed significant variations ranging from 0.5 to 41.0 mole percent. It may suggest that sphalerite precipitate at variable redox condition. Sulfur isotope geothermometer (Ohmoto and Goldhaber, 1997) suggests that precipitation temperature of stibnite is ranging from 110 to 220 degree-C.

Thermodynamic calculation with respect to antimony suggested that the element dissolved in the fluid as several complexes, such as $H_2Sb_2S_4$, HSb_2S^-, $Sb_2S_4^{2-}$, and $Sb(OH)_3$. Those solubility is not likely affected by redox condition and sulfide concentration of fluid. Furthermore pH condition of the fluid is expected to be strongly constrained approx. 6 due to high concentration of dissolved CO_2, so the effect of pH to solubility is not considered. Under such condition, at the high temperature (>200 degree-C) sufficient antimony (1ppm) can be dissolved in the fluid, while at the low temperature (<170 degree-C) the solubility is estimated dramatically decrease. This estimation is almost consistent with that of the sulfur isotope geothermometer.

Drop of the fluid temperature is occurred by conductive cooling or mixing with cool seawater. According the calculation, both cooling is effective to stibnite mineralization. Mixing with seawater involve oxidation of the fluid. Some hydrothermal clay minerals contained magnesium have been observed in the core sediment obtained around the vent sites, and the formation temperature was estimated around 130 degree-C. It may suggest that mixing with seawater is a plausible cause of cooling the fluid. Those sulfide deposits contained significant amount of gold (up to 500 ppm), it's mineralization may also occur due to cooling and oxidation of the fluid.

Accordingly, temperature is the main control factor for stibnite precipitation in the Wakamiko system, and it may suggest that slow temperature dropping of fluid temperature in sedimentary layer relative to fluid venting from the chimney is favorable to form massive stibnite deposit below seafloor.

Keywords: stibnite, submarine hydrothermal system, Kagoshima Bay

Geological study on R2 ryolite in the Hokuroku District, Akita: their alteration patterns and relationship to Kuroko ores

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Kuroko ores (15 Ma) in the Hokuroku district are covered by hanging-wall rocks, mostly felsic volcanic rocks (termed as R2 rhyolite). Those felsic volcanic rocks also suffered from submarine hydrothermal alteration. However, relationship between alteration patterns in R2 rhyolite and spatial distribution of Kuroko ores is still unclear. Understanding such relationship has importance to provide an indicator to explore modern volcanogenic massive sulfide ores buried in sub-seafloor. Therefore, geological and petrological studies are performed on R2 rhyolite in Hokuroku district, Akita. Geological survey of R2 rhyolite was conducted in two areas: one is distal zone from Fukuzawa and Ezuri mines (A area), and the other is barren zone along Oshigenai stream (B area).

R2 rhyolite in A area can be divided into three stratigraphic layers. The lowermost layer is composed of volcanic breccia and lapilli with size from dozens to a few centimeters, and interpreted as an autobrecciated outer rim part of a felsic lava dome. The interspace of breccia is hydrothermally altered intensively, although some un-altered parts retain fluidal texture as elongated-unidirectional cluster of quartz inside each lapillus. Quartz veins with disseminated pyrite fills also common in the interspaces. Matrix-supported lapilli tuff (green colored) overlies the above lava dome. This layer contains lapilli-sized woody pumice and lapilli- to block-sized rhyolitic and basaltic lava. This layer represents submarine pyroclastic flow or resedimented one. Hydrothermal breccias intrude into this pyroclastic rock. Rhyolite lavas, which were less altered compared to others, occur as uppermost layer.

On the other hand, R2 rhyolite body in B area consists of several flow units, which pile more than 100 m in thickness. Each flow unit comprises two parts, massive and upper planer joint parts. Silica veins in several centimeters width occur in flow unit, while green-colored minerals such as celadonite are distinguished in the planer joint part. Sulfidic alteration is absent or much less in B area.

From the above results, sulfidic hydrothermal alteration is only limited in the distal zone of Kuroko mines. Therefore, it is concluded that submarine hydrothermal activities continued from Kuroko-forming to post-Kuroko periods in the same region. On the other hand, in the barren zone, the alteration of R2 rhyolite was caused by simultaneous interaction with seawater and hot R2 rhyolite lavas.

Keywords: Hokuroku district, Hanging-wall sequence of Kuroko ores, Post-Kuroko activity, Felsic volcanic rocks, Hydrothermal alteration

Petrochemistry of Plutonic Rocks along Loei Fold Belt, Northeastern Thailand

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Petrography and geochemistry of Permo-Triassic plutonic rocks from different provinces along the Loei Fold Belt, northeastern Thailand were studied. The Loei Fold Belt is an 800-km north-south trending fold belt that hosts an epithermal Au and several skarn Cu-Au deposits. Petrographic analysis of the granodiorites, diorites and granites in the area shows that the rocks consist mainly of quartz, plagioclase, hornblende and biotite. Orthoclase feldspars has been noted from samples in the Loei Province. Accessory minerals such as magnetite and ilmenite were also present. Magnetic susceptibilities of granitoids vary from 0.01 to 11.14×10^{-3} SI in the Loei Province, from 0.07 to 9.9×10^{-3} SI in the Petchabun Province and 0.02 to 2.81×10^{-3} in the Chantaburi Province. Concentrations of major elements suggest that these intermediate to acid igneous rocks have calc-alkaline affinities. Trace element geochemistry upon normalization to chondrite shows moderately elevated LREEs and relatively flat HREEs, with distinct depletion of Eu. Plotting concentrations of Rb versus Y/Nb and Nb/Y in tectonic discrimination diagrams for granitoids show that the rocks formed in volcanic-arc setting. New age data from radiometric K-Ar dating of orthoclase from granodiorite in the provinces of Loei and Nakhon Sawan yielded ages of 171 and 221 Ma, respectively. Age data of hornblende separated from diorite in Lopburi Province yielded ages of 219 Ma. Sulfur isotope data of pyrite separated from limestone and skarn deposit in Wang Saphung, Loei Province, show negative values of $\delta^{34}S$ (CDT) from -9 to +1‰. The sulfur isotope values suggest that the magma had been influenced by light biogenic sulfur from local country rocks.

Keywords: Loei Fold Belt, Geochemistry, Petrology, Calc-alkaline, Thailand

Quantitative analysis of scandium in lateritic nickel ores using LA-ICP-MS

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Scandium (Sc) is included in rare earth elements in the broad sense, its however geochemical behavior during magmatic differentiation and weathering is different from yttrium and lanthanides. Scandium is produced from a variety of deposits as by-product and little attention has been paid to dominant Sc-bearing minerals of each deposit. We present results of microanalysis of nickel ores from the Soroako deposit using LA-ICP-MS in order to identify the most dominant Sc-bearing minerals. Because crater diameter of the LA-ICP-MS is ~10 μm, quantification of fine-grained minerals in the order of micron to submicron were difficult. We performed quantitative analyses of single mineral-grains and also mineral aggregates to determine elemental composition of each end-member.

According to LA-ICP-MS analysis, Sc content of goethite range mainly from 80 ppm to 300 ppm, whereas SiO_2 and spinel are very low in Sc (< 10 ppm). These results are consistent with a negative correlation between whole-rock Sc and Ni contents in the Soroako deposit, because goethite is poor in typical Ni-rich ores (saprolite). This study result indicates that goethite is the most dominant Sc-bearing mineral in Soroako.

Keywords: scandium, nickel, laterite, limonite, ore deposit, goethite

Characteristics and genesis of ion adsorption type REE deposits and related granites in South China

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Rare Earth Elements (REEs) are strategically important in high-technology industrials. Currently, China dominates the global production of REEs while the widespread “ion-adsorption type” deposits in South China are some of the major REE sources especially the more demanding heavy rare earth elements (HREEs). Therefore, it is critical to have an in-depth understanding on the characteristics and genesis of this type of deposit. This review will summarize the geochemical and mineralogical features of these deposits as well as their parent granite, and suggest the factors controlling the formation of these deposits.

Although prospects of ion adsorption type REE deposit have been discovered and explored in Vietnam, Myanmar, Thailand, Brazil, Malawi, and Madagascar recently, the majority of this type of deposit is located in South China, distributing over the Jiangxi, Guangdong, Fujian, Hunan and Yunnan provinces. In general, deposits can be categorized into the HREE-enriched, for example the famous Zudong deposit in southern Jiangxi province and the LREE-enriched type, such as the Heling and Dingnan deposit in southern Jiangxi province. Numerous geochemical analyses have indicated that the maximum REE enrichment, normally two- to three-fold enrichment compared to the parent granite, mostly occurs within the completely weathered zone (B horizon) with less concentration in the semi-weathered zone (C horizon). Accumulation of LREE at comparatively upper part while that for HREE at the lower part is also frequently observed in these deposits. Mostly, the REE pattern of the regolith is similar to the parent rock, except for Ce. Strong positive Ce anomaly is commonly observed in the upper part of the weathering profile while it shifts to a negative one at the lower part. It is likely due to the oxidation of Ce^{3+} to Ce^{4+} and the precipitation of cerite that removes Ce from fluids at shallow level. As for the mineralogy, clay minerals, particularly kaolinite and halloysite, are the key components on which the REEs are adsorbed. Nevertheless, organic substances and Fe-Mn oxyhydroxides likely play an important role. Furthermore, SEM observations show that a variety of secondary REE minerals exist in the regolith. Residual zircon, monazite, and xenotime may also contribute a certain amount of the resources. Traditionally, REEs are thought to be adsorbed onto clay minerals in ionic state, however, recent studies start to reveal that nano-REE particles and colloids are also adsorbed on clay minerals. These deposits are dominantly developed from the weathering of biotite and/ or muscovite-bearing alkali granite from Caledonian to Yanshanian period in the region. The nature of the parent granites is various, including S-type, A-type and highly-fractionated I-type. However, it is common that late stage metasomatism took place transferring part of the REEs into hydrothermal minerals, which are more susceptible to weathering, such as bastnäsite-(Ce), synchysite-(Y), fergusonite, and allanite.

Under a tropical to sub-tropical climate, REEs are released from the parent REE-enriched granites during weathering. Along with infiltration of meteoric water, REEs are leached from broken down of REE-bearing minerals, and transported to the lower part, at where they are adsorbed by clay minerals and precipitate as secondary minerals. After a long period of weathering, REE accumulates at the lower part of the profile to form the deposit. Therefore, climate and duration of weathering, that control the intensity and extent of weathering, are significant to the ore formation. Exhumation is also important in keeping weathering active. Low-lying relief and slow denudation rate in South China help reduce the erosion of the regolith

and preserve of the ore bodies. pH and redox environment of the regolith are other major factors and they control REE adsorption and secondary mineral precipitation in the regolith.