低温蛇紋岩化作用から学ぶ地球工学 Earth Engineering Technology Learnt from Low Temperature Serpentinization

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For our sustainable development, engineering technology in 21st century should be in safety, low-cost and environmentally friendly for human living together with the Earth. In such technology, not rare earth and platinum group elements but rather ubiquitous elements such as Si, Al, Mg, Fe should be used. Natural process is a physical, chemical and biological process existing in nature without the intent of human beings. Therefore, products and technology learnt from natural processes are available with low-cost and safety. In the natural processes, of course, ubiquitous elements play a key and major role. Not only civil and geological engineers but also engineering chemists and biologists are interested in natural processes for sustainable engineering technology. Especially, chemical processes at extremely alkaline environments have been attracted their attention for sustainable management of waste disposal used huge amount of concrete, recycling of alkaline materials such as cement, slag and fly ash, and so on. However, an understanding of the processes at such a hyperalkaline condition is not enough for safety assessment of the waste disposals and the recycling. In addition to this, many engineering chemists and biologists are also interested in the hyperalkaline processes for safety CO₂ geological storage, application of Fisher-Tropsch type reaction to natural system, and so on. Therefore, there are many contents to make lessons and be learnt from natural processes at hyperalkaline conditions. Fortunately, we can have the lessons at some ophiolites where occur low temperature present-day serpentinization. Serpentinization has unambiguously been recognized as important geophysical and geochemical processes in mantle wedge and oceanic lithosphere. Serpentinized peridotite generally forms at reaction temperatures of 100-500°C as indicated by chemical, mineralogical and isotopic data. On the other hand, temperatures of present-day serpentinization observed at ophiolites and Lost City vents are considerably lower (40-75°C). This is in strong contrast to other known serpentinization systems. Thus, the temperature variability expressed by vent fluids from ultramafic-hosted hydrothermal systems on or slightly removed from mid-ocean ridge, is not altogether surprising. The low temperature hydrothermal field is characterized by a combination of extreme conditions never before seen in the marine environment. These conditions include venting of hyperalkaline and metal-poor hydrothermal fluids with high concentrations of dissolved H₂, CH₄. Huge amount of CO₂ gas is fixed into carbonate minerals observed in chimneys at the hyperalkaline vents and fissure filling of ultramafic rocks at the ophiolites. In this context, the previous studies on low temperature present-day serpentinization will be reviewed from the engineering points of view (hazardous anion migration, CO₂ geological storage, hydrogen and methane generation, abiogenic hydrocarbon production) in this presentation with introduction of our studies (lessons) at Oman ophiolite.

キーワード:蛇紋岩化、水素、メタン、二酸化炭素貯留、高アルカリ Keywords: Serpentinization, Hydrogen, Methane, Carbon dioxide storage, Hyperalkaline

Carbonate hosted talc deposits in Nangarhar Province, Afghanistan

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Talc deposits in the E-W trending Spin-ghar fault block, southeastern part of Afghanistan, are hosted by Paleoproterozoic carbonate rocks. There are two types of talc mineralization in the study area, one is hosted by magnesite and the other by dolomite marbles. The objective of this study is to describe the talc mineralization on the basis of field observation, microscopic observation, XRD, XRF, ICP-MS and EPMA analyses.

In the study area, talc ore bodies are parallel to sub parallel to magnesite rocks and dolomite marble. The ore bodies are cross cut by intrusive rocks of diabase. Schistosity/foliation of quartz chlorite schist and quartz mica schist are parallel to sub parallel to talc ore bodies. Massive layers of tremolite were observed with most of the talc veins. Thin layers of talcose quartz have been marked within talc veins at places. Quartz veins follow the schistosity/foliation of gneiss all over the study area and cross cut by intrusive rocks at places. Mineral assemblages in the study area are (a) talc + tremolite + calcite, (b) talc \pm cordierite, (c) talc + dolomite + calcite \pm quartz \pm apatite, (d) talc + dolomite + calcite and (e) dolomite + tremolite + calcite. Talc was formed by alteration of tremolite and magnesite in most of the studied areas, while in some deposits talc was formed by alteration of dolomite. Total REE contents of talc bodies, magnesite and dolomite marbles are 0.9, 5.3 and 13.0 ppm, respectively. The SiO₂ contents of carbonates and talc bodies range from 1.6 to 33.3 wt% and from 52.9 to 65.1 wt %, respectively, while MgO contents of carbonate and talc bodies range from 18.4 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 that of dolomite marbles ranges from 18.0 to 26.0 wt%. EPMA analysis of carbonates shows that dolomite and magnesite compositions are close to the ideal composition with Fe ranges from 0.04 to 0.17 wt % and 0.18 to 0.39 wt % respectively, while Mn ranges from 0 to 0.07 wt % and 0 to 0.04 wt % respectively.

The concentrations of Al, Ta, Hf, Zr, Th and total REE in talc ores and carbonates rocks are 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 rock protolith. Therefore, the Mg-rich carbonate rock was likely the protoliths of talc ores. Magnesium has been derived from pre-existing Mg-rich carbonate host rocks, i.e., magnesite and dolomite marbles.

Keywords: Afghanistan, Spin Ghar, Talc, Dolomite, Magnesite, Tremolite

Pb isotope ratios of the Nansatsu gold deposits, Kagoshima, Japan: Implication for gold mineralization

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Elucidating the origin of metals constituting the deposits can provide a crucial key constraint in exploration for new mineral deposits. It is previously considered that the epithermal deposits, one of the most important types of gold deposits, are formed by ore-forming fluids originated from magmatic water discharged from hydrous magmas and/or meteoric water evolved by circulation and reaction within the shallow crust. The fluids extract metals from magmas and/or host rocks and then move to the shallower part of the crust, resulting in deposition of valuable metals due to reduction of pressure and temperature [1]. The previous mineralization model has been proposed on the basis of isotopic study of relatively light elements (e.g., H and O) in the ore-forming fluids. However, recent isotopic studies on heavy metals (e.g., Pb, Sr and Nd) suggest the involvement of another important component, i.e., slab-derived fluid, to the formation of epithermal ore deposits [2].

To detect the source of metals contributing to the formation of epithermal gold deposits, Pb isotopes can provide direct and useful information. Our previous study of the Pb isotopic compositions of sulfide ores from the Akeshi gold deposit (one of the Nansatsu-type gold deposits) demonstrated that the ore samples show three different trends in ²⁰⁶Pb/²⁰⁴Pb-²⁰⁷Pb/²⁰⁴Pb-²⁰⁸Pb/²⁰⁴Pb isotopic compositional space [3]. Two of these trends were interpreted as influences of the bed rock and the slab-derived fluid from the Philippine sea plate. The results suggest that both the bed rock and the slab-derived fluid could have contributed to mineralization of the Akeshi gold deposit. The third trend, however, could not be explained by any geochemical end-member near the deposit.

In the present study, to cover a spatial variation in geochemical signatures, we newly analyzed the samples including bed rocks, host rocks, and sulfide ores from the Kasuga and Iwato gold deposits both in Kagoshima prefecture, which are also among the typical Nansatsu-type gold deposits. We will show the new analytical results, and discuss the origin of the Nansatsu-type gold deposits more comprehensively.

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キーワード:南薩型金鉱床、スラブ起源流体、鉛同位体比、鉱化流体、浅熱水性鉱床

Keywords: Nansatsu-type gold deposits, slab-derived fluid, Pb isotopic ratio, ore-forming fluid, epithermal deposits

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Relationship between high-grade gold mineralization and fluid pressure in the Yamada sub-deposit, Hishikari Epithermal Gold Deposit, Japan

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The Hishikari deposit is a world-class low sulfidation epithermal deposit hosting the most productive gold mine in Japanese mining history. It is composed of the Honko, Sanjin and Yamada sub-deposits. Mixed Bingham distributions have been fitted to the orientation of the ore veins for the clustering of Yamada sub-deposit in order to unravel the paleostress conditions. Furthermore, the relationship between fluid pressure and high-grade gold mineralization has been investigated. Two paleostress states A (of strike-slip faulting regime) and B (intermediate between reverse-faulting and strike-slip faulting regime) were identified. The subsequent analysis of high-grade ore bands (gold grade>100 g/t) shows that although most of Yamada veins were formed by ore fluids with low driving pressures, the high grade veins among them were formed by those with higher driving pressures. If the principal stress magnitudes are assumed to be constant over the sub-deposit, provided that the data were collected at the same elevation, the result also means that high-grade gold mineralization in the Yamada sub-deposit is related to higher fluid pressures. This is further supported by the fact that the high-grade ore bands deposition is controlled by the stress state A which is more likely to be associated with the main hydrothermal activity (thus higher fluid pressure).

Keywords: mixed Bingham distribution, Hishikari, Yamada, orientation , driving pressure, fluid pressure

Subsurface Lithologic and Alteration Mapping and Modelling of the Kay Tanda Epithermal Gold Deposit, Lobo, Batangas, Philippines

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The Kay Tanda epithermal gold deposit is located at the southern flank of Mt. Lobo in the Batangas mineral district, Philippines. It contains approximately 4.9 M metric tonnes of indicated and measured resources at 1.09 g/t Au and 2.15 g/t Ag at 0.5 g/t Au cut-off grade. Situated outside established and well-studied gold districts in the Philippines, its deposit characteristics are among the least studied in the country. This study aims to generate a three-dimensional lithologic and alteration model of the deposit using the data gathered from geologic logging and detailed petrographic and X-ray diffraction analyses.

The deposit is mainly hosted in the Middle Miocene Looc Volcanic Complex (locally named as Talahib Andesite) which is composed of andesitic to dacitic volcaniclastic sequences. Based on the regional mapping conducted by the Bureau of Mines and Geosciences (BMG) in 1980, andesitic sequences dominate the upper sequences of the formation while the lower sequences are dominantly dacitic in composition. Geologic logging showed intertonguing and alternating sequences of the dacitic and andesitic sequences in the deposit. The dacitic sequences are mainly composed of dacitic lapilli tuff. They are composed of strongly hydrothermally altered dacitic fragments with quartz phenocrysts exhibiting embayed to resorbed textures. The andesitic sequences are composed of andesite lava flows. They are hydrothermally altered and exhibit characteristic trachytic and porphyritic textures. The plagioclase phenocrysts are completely altered to clay but their euhedral lath-like habit is still preserved. The Looc Volcanic Complex is intruded by a local multi-facies intrusion called the Balibago Intrusive Complex. It is composed of diorite, quartz diorite and andesite porphyry. The diorite and quartz diorite are phaneroporphyritic while the andesite porphyry exhibits aphanoporphyritic textures. Overlying the Looc Volcanic Complex is the Late Miocene to Early Pliocene Calatagan Formation, a complex sedimentary sequence of sandstones, siltstones, shales, conglomerates, and limestone lenses with minor andesitic tuffs. Weak mineralization was found in some sandstones and limestones of the Calatagan Formation. Overlying the deposit is a post-mineralization Balibago Andesite. It is composed of a slightly to moderately weathered andesitic lapilli tuff.

X-ray diffraction was used to determine the specific alteration mineral assemblages of the samples. The Looc Volcanic Complex is affected by advanced argillic and argillic alteration. The advanced argillic alteration zone is composed of pyrophyllite and kaolinite with minor illite. Argillic alteration zone is composed of illite and smectite with minor amounts of kaolinite. The mineralized portions of the Calatagan Formation are also argillic altered. The intrusive rocks of the Balibago Intrusive Complex are mainly affected by propylitic alteration which is composed of chlorite and illite.

A three-dimensional lithologic and alteration model was generated using the Leapfrog Geo Software. Also, assay values for gold, silver, lead, zinc and copper were inserted in the model to determine the location of the high grade zones of the deposit. The model shows that the gold and silver mineralization are mainly hosted in the dacitic volcaniclastic sequences of the Looc Volcanic Complex which are strongly affected by advanced argillic alteration. Base-metal mineralization is mostly found at the deeper levels of the deposit.

Keywords: Kay Tanda deposit, epithermal, Lobo, Batangas, Philippines, hydrothermal alteration, geologic modelling

Mineralogical and oxygen isotope studies of skarn type tungsten deposit at the Date-Nagai, NE Japan

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The Date-Nagai skarn type tungsten deposit locates at the Abukuma Mountain. The lidateyama body, an ilmenite series granodiorite (102-106 Ma), distributes widely in the area and lenticular hornfelses are accompanied as roof pendant. Small limestone layer is included in hornfels. Skarn develops between hornfels and limestone as a thin layer. Three types of skarn, garnet-vesuvianite skarn, green skarn and fine-grained skarn are distinguished from their appearance and mineral assemblage. Scheelite is accompanied in all these skarns. Paragenetic study suggests that mineral assemblage in skarn differed between early and late stages. Early stage garnet is optically isotropic, whereas that of later stage shows anisotropy. Sheelite precipitated in relatively later stage of mineralization.

Chemical compositions of skarn minerals were examined by EPMA. Garnet of early stage has compositions near grossular, whereas those of later stage contain pylarspite moles up to ~70 %. Andoradite mole in both garnets is very low (<8.0 mole %), which suggests reduced environments since Fe³⁺ in skarn-forming solution was very low. Chemical composition of clinopyroxene is approximately middle between diopside and hedenbergite. Powellite mole in scheelite is very low (<1.4 mole %).

Oxygen isotope compositions of minerals were analyzed by means of CO_2 -laser ablated BrF_5 technique. Garnet and scheelite have variable delta¹⁸O, 4.6-8.2 ‰ and 0.8-2.9 ‰, respectively. Temperature of skarn formation was calculated using oxygen isotope fractionation factor between quartz and scheelite, and T= 283°C was obtained. Using this temperature, delta¹⁸O of skarn-forming solution was calculated. Early stage solution had delta¹⁸O values of 6-8 ‰ and most garnet precipitated from this solution. While later stage solution had lighter delta¹⁸O values 1-5 ‰, and this solution was responsible for precipitation of scheelite and quartz. Origin of skarn-forming solution of early stage was mostly magmatic water, while contribution of meteoric water increased in later stages.

キーワード:スカルン型タングステン鉱床、酸素同位体、ザクロ石 Keywords: tungsten skarn, oxygen isotope, garnet

Characteristics and Ore Genesis of the Clifton Porphyry Copper-gold Prospect, Northern Luzon, Philippines

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The Clifton prospect is one of the priority prospects identified by the renewed exploration campaign of Philex Mining Corporation (PMC), the mining company that has been operating the Sto. Tomas II orebody, an auriferous porphyry copper deposit located in the southern tip of the Baguio District since 1957. Mineralization in Clifton is porphyry copper type associated with a quartz diorite complex emplaced along a ENE-WSW structure. In this study, we investigated the intrusive rocks from the viewpoints of cross-cut relations, alteration and associated vein types, mineral paragenetic sequence, fluid inclusions and sulfur isotopes to reveal the condition of mineralization.

Corelogging and petrographic analyses recognized at least intrusive rocks intruding through the basement consisting of volcanic rocks of the Pugo Formation (PMV): (1) the Early Andesite Porphyry (EAP), (2) the Intra-mineral Diorite Porphyry (IMD), and (3) the Late Andesite Porphyry (LAP). The intrusive rocks have similar mineralogical compositions, and are distinguished via texture of the groundmass, degree of alteration and density of veinlets. The emplacement of the multiple intrusive rocks introduced several alteration types: (1) K-silicate alteration is well-developed in the EAP and its contacts with the PMV. It is characterized by pervasive hydrothermal biotitization, and is accompanied by abundant chalcopyrite, bornite and magnetite with ilmenite-hematite and sphene as disseminated grains. Associated wavy quartz veinlets cross-cut the host rocks. (2) Quartz-dominated K-silicate alteration, occurring within the

"Stockwork Zone" ("SQZ"), introduced addition of silica accompanied by chalcopyrite-pyrite-magnetite-hematite with rare gold. It is accompanied by sheeted quartz, quartz-magnetite, and chalcopyrite-rich quartz veinlets. (3) Chlorite-sericite overprint accompanied by chalcopyrite-pyrite affects the bottom portion of the "SQZ", and cross-cuts the earlier quartz veinlets. Chalcopyrite grains appear to be rimmed by an unidentified silver-bearing mineral. Lastly, (4) propylitic alteration, characterized by chlorite-actinolite, in the IMD and LAP.

A direct correlation of copper and gold concentration is evident in the early stage biotite-dominated K-silicate alteration. Higher concentrations of copper in the quartz-dominated K-silicate alteration are associated with the later chalcopyrite-rich mineralization. Higher silver contents correspond to the higher silver content of the electrum, Ag/(Au+Ag) = c.a. 46.7 atomic% was measured in a minute gold globule found in the later chalcopyrite-rich mineralization.

Abundance ratios of vapor-rich fluid inclusions to polyphase hypersaline fluid inclusions vary from 18% to 47% and from 95% to 287%, for the veins related to the "SQZ" and the later quartz veins at the shallower parts, respectively. The significant increase in the vapor to brine ratio at the shallower depth compared to the deeper portions indicates the transport of vapor in the shallower part.

Formation depth of Clifton is shallow, estimated to be 2.2 km, 58MPa at 650°C, 58 MPa during the earliest stage, and uplifted to 1.5 km, 38.5MPa at 525°C, during the chalcopyrite-rich stage, based on fluid inclusion microthermometry.

Sulfur isotope analyses measured +1.0 to +6.0 $\delta^{34}S_{CDT}$ (‰) indicating that the source of sulfur is enriched in ³⁴S similar to the other hydrothermal ore deposits in the western Luzon arc.

Keywords: Clifton prospect, Baguio District, porphyry copper-gold mineralization

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伊豆小笠原弧ベヨネース海丘におけるチムニー鉱石中の銀に富む硫化鉱物 の鉱化作用

Mineralization of Ag-rich Sulfide Minerals in Chimney Samples at Bayonnaise Knoll, Izu-bonin Arc.

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我が国周辺海域に賦存が知られている海底熱水鉱床は他国の資源政策に影響しない資源であり、開発が可能 になれば需要の大半を海外に依存している金属鉱物資源の新たな供給源として期待される。伊豆-小笠原弧に 属するベヨネース海丘は島弧・海底火山である。陸上の黒鉱鉱床の鉱石平均値、同海丘に隣接する明神礁カル デラ鉱石の平均値と比較すると前者の平均値よりも金と銀の品位が高く、また後者の平均値とは概ね同等の品 位を示すことが知られており、主要元素の品位は金 (4.635 ppm),銀 (354 ppm),銅 (0.406 wt%),鉛 (0.252 wt%), 亜鉛 (11.841 wt%)である。本研究では同海丘から採取された熱水噴気孔から噴出する熱水によって形成 されたチムニー鉱石と、それが物理的要因によって崩壊して形成したとされるマウンド鉱石の関係及び、チム ニー鉱石中の銀に富む硫化鉱物の鉱化作用を議論することを目的とした。

肉眼観察、顕微鏡観察、電子マイクロアナライザー(EPMA)の順に巨視的から微視的に分析を行った。黒鉱鉱 床の鉱石中にも確認される分類であるが、筒状かつ成長軸は外側から内側に延びていると考えられる形状で外 側から順に表面に付着するマンガン酸化物、重晶石を多く含む白色部分(G1)、閃亜鉛鉱・方鉛鉱を主とする硫 化物を多く含む灰色部分(G2)、G2と同じ硫化鉱物を主とするが黒色多孔質で重晶石の大きな結晶が確認される 部分(G3)に大別できることが確認された。また、先行研究の流体包有物の均質化温度より重晶石(G1)の形成温 度が150-215℃、閃亜鉛鉱(G2-G3)の形成温度が205-225℃であることが知られている。加えてEPMAの特性 X線像よりBaはG1とG2に広く分布するが、G3では晶洞内のみ重晶石の分布が確認された。またG1-G2には黒 鉱鉱床の黒鉱にあたる閃亜鉛鉱・方鉛鉱・黄銅鉱が多く観察されたことより、黒鉱鉱床の鉱石と現在海底面に 存在するチムニー鉱石とマウンド鉱石の成長過程・鉱物組み合わせが類似していることが明らかとなった。特 に銀に富む硫化鉱物は、EPMAの定量分析により重晶石と閃亜鉛鉱と共生して銀・銅・鉛を含む硫化鉱物とし て確認された。加えて、銀はG2内のG1-G2の境界に分布することと、チムニー鉱石の形成温度は成長軸に 沿って上昇することから、銀・銅・鉛を含む硫化鉱物は200℃付近で形成されたと推測される。よって以上の 点より、黒鉱鉱床の鉱石に対してベヨネース海丘のチムニー鉱石とマウンド鉱石は主要元素 (銅, 鉛, 亜鉛)の濃 集は陸上の黒鉱鉱床の鉱石と類似しているが、黒鉱鉱床の鉱石よりも品位の高い金・銀が見られた。特に金に 比べ、銀の品位が高いチムニー鉱石中に確認される銀を含む硫化鉱物の分布から200℃付近の熱水から沈殿し たと見られる。その濃集場所は主に重晶石からなる硫酸塩と主に黒鉱(閃亜鉛鉱・方鉛鉱・黄銅鉱)からなる硫 化物の境界付近に位置し、重晶石と閃亜鉛鉱と共生していることが明らかとなった。

キーワード : ベヨネース海丘、チムニー、銀の硫化鉱物 Keywords: Beyonnaise Knoll, Chimney, Ag-sulfide Minerals

Resistivity Structure around Off-Okinawa Hydrothermal Area Using Two-Dimensional Inversion of Marine DC Resistivity Survey

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Global demands for metal resources have increased interest to development of deep-ocean hydrothermal ore deposit called as SMS (Seafloor Massive Sulfide). SMS deposits, including rare and precious metals, have been often found out around hydrothermal active areas; for example in the Okinawa and Izu-Bonin areas, located in the Japanese Exclusive Economic Zone, and in the mid-Atlantic ridge. Geophysical explorations with electromagnetic (EM) methods are recently carried out around the SMS deposits because the SMS deposits are known as low resistivity material and the resistivity distribution below the seafloor can be a good indicator for the buried SMS deposits. However, the resistivity structure below hydrothermal active areas has not been clearly investigated. In this study, I developed a two-dimensional inversion of a marine deep-towed DC resistivity survey as an effective tool to exploration of SMS deposits. Marine deep-towed DC resistivity survey system was originally developed as a sensitive tool to gas hydrate, but the numerical simulations how the survey is sensitive to the SMS deposits have never been conducted. The inversion developed in this study is based on the model space Occam' s inversion method and the finite-difference method is applied in the forward modeling calculation to solve potential difference between electrodes at the electric-current injection to the seawater. We tested the system using the synthetic data and found that the inversion can estimate the buried SMS deposits effectively. The first test is based on newly-developed inversion with smoothness constraint, frequently used to solve ill-posed inverse problems. Although the ordinary constraint assuming a smooth model can detect the low resistivity anomalies, the real distributions of SMS deposits are concentrated at narrow (thin) zones, and cannot be treated as the smooth model. In order to obtain sharp-change of resistivity matching the petrophysical information, I add a guided Fuzzy C-Means (FCM) clustering constraint into the objective function in the inversion procedure. Two balance parameters in this objective function should be controlled in the inversion, but the optimal ways to adjust these parameters have not been proposed. Therefore, I propose an algorithm to choose these parameters properly. The new algorithm is based on the two stages; the first stage with the ordinary Occam scheme, then the second stage with the FCM constraint where the inverted model and parameter in the first stage are the initial model and the fixed parameter. The other parameters are decided with the scaling scheme. The refined inversion results show that the inversion with the FCM constraint can produce sharp boundaries in resistivity structure, which can handle with the realistic petrophysical information. Finally, I applied the inversion code to the field data obtained at the Okinawa Trough; the inverted resistivity anomalies are consistent with the known geological investigations of hydrothermal fluid flows and the observed distributions of seafloor venting sites.

キーワード:電気探査、海底熱水鉱床、逆解析 Keywords: Direct Current resistivity survey, Seafloor massive sulfide deposits, Inversion SRD39-09

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熱水鉱床開発における重金属汚染と表層光合成生態系に対する影響評価 ーちきゅうCK16-05航海で採取したコアを用いた環境影響評価 Evaluation of metal dissolution from fresh hydrothermal core samples collected at Izena Hole during CK16-05 and rapid detection of their toxicity on marine phytoplankton community

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Environmental impact assessment is essential to reduce loads of seafloor metal-mining operations to marine environments. Accidental leakage of crushed hydrothermal ores from mining vessel is one of the possible concerns. Metals and metalloids could be released from mineral particulates and damage marine phytoplankton communities, the primary producers at the base of the marine food chain. Our previous study found that high amounts of metals can be released from fine particulates of oxidized hydrothermal ores into seawater, and they inhibit the growth of a marine phytoplankton species. In this study, metal leaching potential of deoxidized (fresh) ores was evaluated using whole round core (WRC) samples collected from Izena Hole, Okinawa Trough, by D/V Chikyu (CK16-05). Also, the toxicity of the leachates on marine phytoplankton was estimated onboard using delayed fluorescence (DF) -based bioassay method which is a useful tool to estimate rapidly and easily toxic metals (Yamagishi et al., 2016). Four whole round core samples (C9025A 6H-2, C9026A 7X-CC, C9027B 1X-CC, and C9028A 7S-CC) were taken from sulfide mineral rich sections and powdered manually with agate mortars. Approximately 3 g of each powdered sample was mixed with 30 mL of artificial seawater, and then the mixture was shaken at room temperature for 6 h. After shaking, the solid phase was separated by centrifugation and filtered. Dissolved metals and metalloids in the liquid phase is quantified using an inductively coupled plasma-mass spectrometry.

A newly developed bioassay technique was applied to evaluate the toxicity of the core-leachates onboard. A test organism for the bioassay was a marine Cyanophyceae of *Cyanobium sp.* (NIES-981), which had been cryopreserved and was resuscitated onboard just before the bioassay test. The inhibition effect of the leachates on the algal photosynthetic activity or growth was quantitatively determined by a custom made ultra-weak luminescence detector system (Type 7600, Hamamatsu Photonics) at 15 min, 1, 3, 6, 9, 12 and 24 h after the exposure to those leachates.

Zn (4–15 ppm), Pb (2–16 ppm), Cd (20–130 ppb), and Mn (130–160 ppb) were detected from the leachates of samples C9025A 6H-2, C9027B 1X-CC, and C9028A 7S-CC. These metal contents in the leachate from the core samples were 2–3 order of magnitude lower than in the leachates from the oxidized ore samples. On the other hand, the contents of these elements in the leachate from sample C9026A 7X-CC was significantly low.

On the bioassay experiment for the leachates from C9025A 6H-2, C9027B 1X-CC, and C9028A 7S-CC, the DF-intensities of *Cyanobium sp.* greatly decreased at 24 h comparing to the control, i.e., without the

leachate. On the other hand, the leachate from C9026A 7X-CC which contained low amounts of metals did not cause the significant inhibition effect on *Cyanobium sp.*

Our results clearly show that non-oxidized fresh hydrothermal ores can release various toxic metals into seawater as same as the oxidized hydrothermal ores (e.g., weathered chimney ores), and such contaminated seawater leachates could inhibit the growth activity of natural marine phytoplankton. Therefore, appropriate management systems for controlling the leakage and disposal of mining ores and wastes to the marine surface area should be devised to preserve the natural marine ecosystem.

キーワード:熱水鉱石、金属汚染、海産植物プランクトン

Keywords: hydrothermal ore, metal contamination, marine phytoplankton

火山性塊状硫化物鉱床における鉄同位体分別と鉱床形成プロセス Fe isotope fractionations relating to the ore formation processes in volcanogenic massive sulfide deposits

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The Hokuroku district in Northeast Japan hosts many large volcanogenic massive sulfide (VMS) deposits called Kuroko deposits, which were formed around 15 Ma by ancient submarine hydrothermal activity. Because they are composed of sulfide minerals that are stable in a reducing environment, redox environment on the seafloor during the formation of Kuroko deposit may play an important role in the preservation of the sulfide ores. Furthermore, factors controlling the size and grade for VMS deposits have not been well understood. Previous studies have shown that Fe isotope ratios as well as Rare Earth Element (REE) patterns of ferruginous cherts that associated with Kuroko deposits may reflect the depositional environments. However, sulfides containing in the sedimentary rocks may affect the bulk Fe isotope ratio. Therefore, the objective of this study is to understand formation processes of a large and high-grade VMS deposit based on Fe isotope variations in the sulfide ores and ferruginous cherts with considering the effect of Fe mineralogy to the bulk Fe isotope ratios.

Studies samples were obtained from several VMS deposits from the Hokuroku district as well as Palmer deposit in Alaska, USA. Microscopic observations of the polished sections and the major element contents obtained by X-ray Florescence (XRF) analysis demonstrated that the samples are typical black ores, containing sphalerite and galena, yellow ores, containing chalcopyrite and pyrite, and ferruginous cherts, containing quartz and minute grains of hematite. Some ferruginous cherts also contains iron sulfide (e.g., pyrite, pyrrhotite) as it was concerned. Most ferruginous chert samples also show a distinct positive Eu anomaly in their REE patterns, suggesting that they are affected by high temperature hydrothermal fluids. Fe isotope ratios of sulfide minerals physically separated from ferruginous chert samples were not significantly different from those of the bulk samples, indicating that the presence of iron sulfides in the ferruginous cherts does not affect the bulk Fe isotope ratio. The bulk Fe isotope analysis of ferruginous chert samples from all the studied deposits using multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) shows large variations in the δ^{56} Fe values (-1.55–+2.04‰). The variations in Fe isotope ratios suggest that partial oxidation of dissolved ferrous iron occurred by mixing ferrous iron-bearing anoxic water with oxygen-bearing seawater, and therefore that the sea-floor of the Hokuroku basin was likely anoxic during the formation of Kuroko deposits. Furthermore, while samples from some deposits (e.g., Matsumine, Kosaka) tend to show more negative δ^{56} Fe values, those from other deposits (e.g., Fukazawa, Palmer) tends to show more positive δ^{56} Fe values. The difference may be stemmed from their formation processes. Near equilibrium conditions between hydrothermal fluids and sulfides in the ore bodies by a long-term circulation may have lead to a steady δ^{56} Fe value (e.g., -0.5%) of dissolved iron in the hydrothermal fluids and negative values of ferruginous chert by a Raleigh-type fractionation. On the other hand, rapid precipitation of sulfides ore body under dynamic conditions may have caused a kinetic isotope fractionation, leading to shift δ ⁵⁶Fe value of both hydrothermal fluids and ferruginous cherts to

more positive values.

キーワード:鉄同位体、火山性塊状硫化物鉱床、化学堆積岩、海底熱水活動 Keywords: Fe isotope, VMS deposit, Chemical Sedimentary rock, Seafloor hydrothermal activity インドネシア、パプア州、グラスベルグ鉱山、DMLZ鉱床における、銅-金鉱化作用に伴われる鉱物組み合わせに関する先行研究 Initial study on the mineral assemblages associated with Cu-Au mineralization,DMLZ deposit, Grasberg mine, Papua, Indonesia

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グラスベルグ鉱山は世界でも最大規模の銅-金鉱山の一つとして知られている(Cu: 341,099t, Au: 35t, 2015)。鉱山の歴史は1936年にオランダの地質学者により発見されたことに始まり、1972年からのPT Freeport Indonesiaによる大規模採掘へとつながった。現在操業中の鉱床は全部で3つあり、グラスベルグ露天 掘り鉱床、Deep Ore Zone (DOZ)坑内掘り鉱床、そしてDeep Mill Level Zone(DMLZ)坑内掘り鉱床である。鉱床のタイプとして、グラスベルグ露天掘り鉱床は斑岩銅鉱床、残り二つの坑内掘り鉱床はスカルン鉱床 となっている。グラスベルグ露天掘り鉱床は、現在のグラスベルグ鉱山全体の生産量の70%を占める鉱床であるが、高品位の坑内掘り鉱床を開発するという計画に沿って、1990年から始まった操業を2017年末期に終了し、グラスベルグ鉱山内すべての鉱床が坑内掘り鉱床へとなる予定である。一方、DMLZ鉱床は2015年に操業を開始した最も新しい鉱床であり、かつ2021年までに鉱石生産量を8万t/日を見込まれている鉱床であるが、DMLZ鉱床は操業を開始して間もないため学術的調査もあまり進んでいない。そこで、本研究ではDMLZ鉱床におけるスカルン鉱物組み合わせと鉱石鉱物の分布について理解し、金属鉱化作用とスカルン作用の関連について明らかとすることを目的とした。

DMLZ鉱床での金属の鉱化作用は、白亜紀から第三紀のKembelangan GroupやNew Guinea Limestone Groupの石灰岩や砂岩に、鮮新世に貫入した貫入岩である閃緑岩が、密接に関連している。貫入岩の閃緑岩か ら離れるにつれて、岩相がホルンフェルス帯、スカルン帯、そして結晶質石灰岩へと変わり、それらすべての 岩相を貫くコア試料(TE-17-09)を中心に、鉱物組み合わせの分布を明らかにするために均一間隔でサンプルを 採取した。なお、本研究では、特にエクソスカルン変質地帯(コア試料の坑口から約320m⁻⁴⁸⁰m地点)に着 目し実験を行った。研究手法としては現地調査による肉眼観察に加え、研磨片・薄片の作製、SEM-EDXによる 鉱物同定、XRFによる化学分析を行った。

スカルン鉱床には高温の前行過程と低温の後退過程という二つの異なる変質の過程が存在しており、前行過 程においてザクロ石などの無水鉱物が形成され、後退過程において緑簾石などの含水鉱物や硫化鉱物が形成さ れることが分かっている。顕微鏡観察より、前行過程における主な鉱物としてザクロ石、後退過程における主 な鉱物として緑簾石、黄銅鉱、黄鉄鉱が確認された。また、主な鉱石鉱物は黄銅鉱と黄鉄鉱、脈石鉱物は緑簾 石であったことから、DMLZ鉱床のエクソスカルン変質地帯では後退過程において形成された鉱物が卓越して いると言える。顕微鏡観察により観察された自然金はすべて黄銅鉱に付随していたことから、DMLZ鉱床にお ける金の鉱化作用も後退過程において起こっていると考えられる。また、高温の前行過程に形成される主な鉱 物であるザクロ石がコア試料の坑口から約360m地点の試料を境に観察できなくなったことと、母岩中の方解 石が対照的にその地点付近より遠い地点において卓越してきたことから、貫入岩からもたらされた熱水はその 地点までに前行過程の鉱物ができない温度にまで冷却されたと考えられる。

結論として、前行過程に形成されるザクロ石は貫入岩近傍(コア試料の坑口から約360m地点まで)の試料 でのみ観察された一方で、後退過程に形成される緑簾石や、黄銅鉱と黄鉄鉱が広範囲にわたり発達していたこ とから、DMLZ鉱床のエクソスカルン変質地帯における主なスカルン鉱物と鉱石鉱物は後退過程において形成 されており、自然金もすべて黄銅鉱に付随していたことから、金の鉱化作用も同様に、後退過程に発達してい ることが解明された。 キーワード:スカルン、鉱物組み合わせの分布、銅-金鉱化作用 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 $_2$ O inclusions and minor H₂O vapor inclusions. Laser Raman detected CO₂ and N₂ 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 CO₂ rich mineralizing fluid as it was confirmed by the presence of CO₂ 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 \pm Cu \pm Pb \pm 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 (\pm 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 \pm chalcopyrite), and some with xenoliths of porphyritic andesites. Plagioclase crystals exhibit alteration to clay minerals (chlorite, interstratified illite-montmorillonite \pm kaolinite). Veins/veinlets cutting across these units are generally quartz \pm 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 \pm kaolinite).

Petrographic study of the veins in Co-O is partly used for fluid inclusion microthermometry. The quartz \pm 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

鹿児島湾若尊海底熱水系における輝安鉱の沈澱条件 Precipitation condition of stibnite at Wakamiko submarine Hydrothermal system in Kagoshima Bay, Japan

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鹿児島湾湾奥部の水深約 200m の海底に若尊熱水系と呼ばれる活発な熱水噴出活動が確認されている。過去 の潜航調査から少なくとも3か所でチムニーを伴う熱水噴出活動が見つかっており、これらのチムニーは主に 輝安鉱の塊状硫化物から成るマウンドの上に形成されている。先行研究より、この硫化物マウンドはかつて海 底下で形成され、その後小規模な水蒸気爆発のような噴火活動が起こり、海底面上に噴出した可能性が示され ており、海底下において鉱床規模での硫化物沈殿が生じていることが期待されている。

本研究では、若尊海底下において輝安鉱沈殿適した条件が存在するのかを明らかにすることを目的とし、鉱物の共生関係、EPMA分析による元素分析、硫黄同位体比測定を行い、その結果と先行研究で明らかとされている熱水の化学的、物理的条件に基づいて熱力学計算を行った結果を合わせて輝安鉱沈殿条件について検討した。

検鏡およびEPMA分析を行った結果、微量ではあるが黄鉄鉱、閃亜鉛鉱、黄銅鉱、方鉛鉱の存在が認められ た。硫黄同位体比測定の結果、輝安鉱の硫黄同位体比は試料ごとにあまり差が無いのに対し、黄鉄鉱の硫黄同 位体比には比較的大きな差が認められた。産状と合わせて考えると、これらの硫化物が輝安鉱と共生関係にあ るとは見なせないと結論づけた。閃亜鉛鉱中のFeS含有量についてEPMA分析を行った結

果、0.5~41.0mol%とおおきなばらつきを示し、このことから閃亜鉛鉱は様々な酸化還元条件で沈殿している と考えられた。よって、熱水の酸化還元条件は一様ではなく、輝安鉱も様々な酸化還元条件で沈殿していると 考えられる。輝安鉱の硫黄同位体比と、本海域の噴気ガスや熱水試料から得られた硫化水素の同位体比を用い て硫黄同位体地化学温度計を用いて形成温度を見積もったところ110~220℃と算出された。

アンチモンに関する熱力学データから、アンチモンは $H_2Sb_2S_4$, $HSb_2S_4^{-7}$, $Sb_2S_4^{2-7}$, $Sb(OH)_3$ の錯体で熱水 中に溶存していると推定された。酸化還元条件はアンチモンの溶解度と関係がなく、さらに硫化水素濃度の変 化による溶解度への影響もほとんどないと考えられた。また、pH条件について、若尊では熱水中に火山ガス由 来もしくは堆積有機物分解起源のCO₂が多量に溶解していることによりpH=6でほとんど一定であるた

め、pH変化に伴う溶解度の変化は無視できる。このような条件下において熱水が200℃以上になると1ppm以 上のアンチモンが熱水中に溶け込み、鉱液として有効な熱水になると考えられた。その一方で、温度が170℃ より低温になると溶解度は劇的に低下し、それに従って輝安鉱の沈殿も生じると推測された。この温度条件は 硫黄同位体比から推測された輝安鉱の沈殿温度と矛盾しない。熱水の温度低下は、上昇に伴う伝導的なもの と、海水との混合によるものが考えられる。いずれの場合も、輝安鉱の沈澱に影響しないが、本海域からはマ グネシウムを含む熱水性粘土鉱物が報告されており、その形成温度が約130℃とされていることから、海水の 混合が温度低下の主因だと考えられる。なお、本海域の硫化物には最大500ppmほどの金の濃縮が認められる が、金の濃縮は、酸化的な海水の混合に起因すると考えられる。

以上より、若尊熱水系における輝安鉱の沈殿は温度によるコントロールが主体であり、輝安鉱の沈殿には高 温の熱水が噴出するチムニーよりも海底下におけるおだやかな温度低下が生じている環境のほうが適している と考えられる。

キーワード:輝安鉱、海底熱水系、鹿児島湾

Keywords: stibnite, submarine hydrothermal system, Kagoshima Bay

秋田県北鹿地域におけるR2流紋岩の地質学的研究:黒鉱鉱床分布との関係

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

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1500万年間に形成された黒鉱鉱床は、熱水変質を被った火成岩などの上盤岩石に覆われ保存されてきてい る。上盤岩石の熱水変質分布と黒鉱鉱床の空間分布に関する研究は皆無である。上盤岩石の変質と黒鉱の分布 が明らかになれば、現在の海底下に埋没した黒鉱鉱床の探査指針を与えるものとなり重要である。そこで本研 究では秋田県北鹿地域の黒鉱鉱床上盤のR2流紋岩を対象とし、火山岩層序とそれらが被った熱水変質の産状を 明らかにすること、後黒鉱期の海底火山活動と熱水活動域の分布、黒鉱鉱床との空間的関係に関して地質学 的・岩石学的研究を行うことを目的とする。

深沢鉱山および餌釣鉱山近傍地域の野外調査を行った結果、この地域に分布するR2流紋岩岩体の内部構造が 明らかになった。岩体内部には成層した3種の岩石が見出された。最下層岩石は、数十cm大の礫〜細礫からな り、珪長質溶岩ドームの自破砕した外殻部と解釈した。細礫内部には石英や同一方向に伸びる不定形〜レンズ 形岩片を伴う流離構造が認められたが、全体的に粘土化が著しい。特に礫間の基質には約500 μm幅の石英脈 が発達しており、自形黄鉄鉱が点在し、熱水変質が著しいゾーンと考えられる。この上位には、火山礫凝灰岩 が存在した。緑色粘土化変質を受けた基質に材木状軽石礫や流紋岩質溶岩礫、玄武岩質溶岩礫を含む。材木状 軽石は最大数cmの亜角礫であるが、一方で流紋岩質および玄武岩質溶岩礫は数十cm大の巨礫から細礫の亜角 礫として存在していた。水中火砕流起源、あるいは再堆積性の火山砕屑岩であると考えられ、堆積後、熱水変 質を被ったと考えられる。この火山砕屑岩は、角礫岩により貫かれていた。調査地域最上位層として変質の度 合いの低い流紋岩質溶岩流が見出された。

一方、大茂内沢地域では、R2流紋岩岩体は複数のflow unitで構成され、少なくとも厚さ100m分の厚さに達 する。個々のflow unitは塊状相とその上部に発達する板状節理からなる。flow unit内部は数cm幅のシリカ脈を 伴うことが多いが、著しく変質した板状節理部にはセレドナイトなどの緑色鉱物が卓越する。以上の結果によ り、黒鉱鉱床近傍上盤では、硫化鉱物(黄鉄鉱)をともなう熱水変質を確認できた。これは、鉱床形成後の継 続的な海底熱水活動の痕跡である可能性がある。その一方で黒鉱鉱床から離れた地域では、熱水変質は認めら れるが、溶岩噴出・流動時の海水との反応によるものであると考えられる。

キーワード:北鹿地域、黒鉱層準上盤、後黒鉱期活動、珪長質火山岩類、熱水変質

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

レーザーアブレーションICP-MSを用いたラテライト質ニッケル鉱石中の スカンジウムの定量分析

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

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スカンジウムは広義の希土類元素に含まれるが、マグマの分化や岩石の風化の過程での地球化学的挙動は イットリウムやランタノイドとは異なる。そのため、スカンジウムは希土類鉱床に限らず、様々な鉱床の副産 物として生産されてきたが、主要なスカンジウム含有鉱物が何であるかは明らかになっていない。本研究で は、ラテライト型ニッケル鉱床のスカンジウム含有鉱物を特定するため、インドネシアのSoroako鉱床の ニッケル鉱石についてLA-ICP-MSを用いて局所元素分析を行った。LA-ICP-MSによる分析径はおよそ10 μm程 度であるため、ミクロン-サブミクロンオーダーの微細な鉱物単体の元素分析は困難である。そのため、鉱物単 相に加えて複数の鉱物粒からなる部分の測定を行い、各元素組成の分布から各端成分の元素組成を推定した。

その結果、Soroako鉱床においては、針鉄鉱中のスカンジウム濃度が80-300 ppm程度であることが分かった。また、シリカやスピネル中のスカンジウム濃度は10 ppm以下であった。一方、針鉄鉱中のニッケル 濃度は低いため、全岩元素組成において、スカンジウム濃度とニッケル濃度に負の相関が見られることと調和 的である。本研究結果から、Soroako鉱床では針鉄鉱が主要なスカンジウム含有鉱物であることが分かった。

キーワード:スカンジウム、ニッケル、ラテライト、リモナイト鉱、鉱床、針鉄鉱 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 bastnä site-(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.