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学位論文題目（英文）	Evolution of the Gold and Base Metal Mineralization of the Kay Tanda Epithermal Gold Deposit, Lobo, Batangas, Philippines: Insights from Fluid Inclusion Studies, Ore Mineral Chemistry and Stable Isotope Systematics (フィリピン, バタンガス州ロボ, カイタンダ浅熱水金鉱床の金およびベースメタル鉱化作用の進化: 流体包有物, 鉱石鉱物の化学組成および安定同位体比)
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論文内容の要旨

The Kay Tanda epithermal Au deposit in Lobo, Batangas is one of a few known Au deposits in the Batangas Mineral District in southern Luzon, Philippines. It was formed at the southern flank of an inactive volcano located at the southern tip of the Western Luzon Arc, and is less than a kilometer from the coastline of southern Batangas. The geology of Kay Tanda is composed of: (1) the Talahib Volcanic Sequence, a Middle Miocene dacitic to andesitic volcanoclastic sequence which hosts the majority of the epithermal mineralization, (2) the Balibago Diorite Complex, an intrusive complex cogenetic to the Talahib Volcanic Sequence, (3) the Calatagan Formation, a Late Miocene to Early Pliocene volcano-sedimentary sequence overlying the Talahib Volcanic Sequence and hosts minor mineralization, (4) the Dacite Porphyry Intrusives which intruded the older lithologic units, and (5) the Balibago Andesite, a Pliocene post-mineralization volcanoclastic unit.

The mineralization at Kay Tanda evolved from an early-stage extensive epithermal mineralization characterized by Au-Ag-bearing quartz stockworks hosted in the shallower levels of the Talahib Volcanic Sequence, to a late-stage epithermal base metal

(Zn, Pb, and Cu) mineralization with local bonanza-grade Au mineralization hosted in veins and hydrothermal breccias at deeper levels. Paragenetic studies defined six mineralization stages. Stage 1 is characterized by the formation of localized quartz \pm pyrophyllite \pm dickite/kaolinite \pm diaspore alteration which was later cut by Au-bearing quartz veins. This was formed due to the intrusion of the Balibago Diorite Complex into the volcanoclastic host rocks. Magmatic volatiles were released from the intrusions and then condensed into the groundwater which generated strongly acidic solutions. Fluid inclusion studies on Stage 1 quartz veins indicate that mixing with meteoric water is the main ore-forming process. With the intrusion of the Dacite Porphyry Intrusives, the hydrothermal system developed over a wider area which formed the pervasive illite \pm quartz \pm smectite \pm kaolinite alteration and the Stage 2 Au-Ag-bearing quartz stockworks. K-Ar dating on two Stage 2 illite samples collected from alteration halos surrounding mineralized Stage 2 quartz veins revealed a mineralization age of 5.9 ± 0.2 to 5.5 ± 0.2 Ma (Late Miocene). Also, a boiling condition under hydrostatic pressure was estimated around 500 m below the paleowater table. The late base metal mineralization commenced with the deposition of Stage 3 carbonate veins with minor base metal sulfides. Stage 4 is composed of quartz \pm adularia \pm calcite veins and hydrothermal breccias which host the main base metal and bonanza-grade Au mineralization and is associated to chlorite-illite-quartz alteration. Native gold is the dominant Au-bearing mineral which contains 81.2 to 94.2 atomic% Au. Silver is mainly hosted in native gold (up to 18.8 atomic% Ag), electrum (up to 21.6 atomic% Ag), galena (up to 0.58 atomic% Ag), and Bi-Pb-Cu-Ag minerals (up to 7.5 atomic% Ag) which occur typically as chalcopyrite inclusions. Boiling is the main mechanism of ore deposition in Stage 4 based on the occurrence of rhombic adularia, the heterogeneous trapping of fluid inclusions of variable liquid-vapor ratios, the distribution of homogenization temperatures of measured fluid inclusions, and the ratio of fluid inclusion gas compositions (CO_2/N_2 vs total non-aqueous gas content). Stage 5 is composed of epidote-carbonate veins associated to epidote-calcite-chlorite alteration. Towards the end of the mineralization, the Stage 6 anhydrite/gypsum-base metal veins which contain sub-economic amounts of Au and Ag were formed. Fluid inclusion microthermometry indicates that the temperature of the system increased from the Stage 1 (220-280°C) to Stage 2 (260-310°C), remained at high temperatures towards the Stage 4 (270-310°C) which were attributed to the continuous intrusion of the Dacite Porphyry Intrusives at depth, and then gradually decreased at the Stage 6 (240-290°C). The salinity slightly decreased from 5.8 wt% NaCl equivalent in the Stages 1, 2 and 4 to 4.6 wt% NaCl equivalent in the Stage 6.

Based on the CO_2/CH_4 vs N_2/Ar diagram, Ar/He vs N_2/Ar diagram and $\text{N}_2/100\text{-}10\text{He-Ar}$ ternary diagram derived from the fluid inclusion gas data, meteoric water is an important component of the hydrothermal system. A small amount of arc-type derived magmatic fluid is also suggested from the $\text{N}_2/100\text{-}10\text{He-}2\text{Ar}$ ternary diagram. The possibility of

incorporation of seawater into the hydrothermal system of Kay Tanda was suggested by the moderate salinity of measured fluid inclusions and the results of oxygen and hydrogen isotope analyses of the two Stage 2 illite samples that were used from K-Ar dating. The calculated $\delta^{18}\text{O}_{\text{water}}$ and $\delta\text{D}_{\text{water}}$ values of the two Stage 2 illite samples approach the $\delta^{18}\text{O}$ and δD value of SMOW. This suggests the incorporation of seawater into the hydrothermal system since the formation of the early mineralization stages. Sulfur isotope analysis on the Stage 2 and Stage 4 sulfides and the Stage 6 sulfide-sulfate pairs also shed light to the evolution of the hydrothermal system. Sulfur isotope analysis was conducted on Stage 2 sulfides (-5.8‰ to +2.8‰), Stage 4 sulfides (-2.1‰ to +3.3‰) and Stage 6 sulfides (+0.1‰ to +2.3‰) and sulfates (+21.6‰ to +22.9‰). Although the sulfur isotopic compositions of the sulfides point to magmatic sulfur as the principal sulfur source, the sulfur isotopic compositions of the Stage 6 sulfates approach that of Late Miocene seawater suggesting incorporation of seawater into the hydrothermal system.

The deposit was formed due to the complex interaction of the volcanoclastic host rocks, the two intrusive rock units at depth, and the circulating hydrothermal fluids with components of magmatic, meteoric and seawater origin. During the early mineralization stages, as the seawater enter the deposit, seawater-derived sulfate minerals precipitate at the recharge zone where the seawater-derived fluids encounter increasing temperatures. The resulting fluids became seawater sulfate-depleted which later circulated in the system. This is consistent with absence of sulfates in the early mineralization stages. However, at the last mineralization stage where the temperature of the system decreased and the meteoric water circulated into the deeper levels, the seawater-derived sulfate minerals started to dissolve which introduced seawater-derived sulfate into the hydrothermal fluids. The mixing of these fluids is an effective mechanism for the co-precipitation of the Stage 6 sulfates and sulfides.

Thermodynamic calculations of physicochemical conditions (pH, $\log f\text{S}_2$, $\log f\text{O}_2$) during the Stage 4 bonanza grade Au mineralization were also conducted. Ore mineral assemblage and sulfur fugacity determined from the FeS content of sphalerite at temperatures estimated by fluid inclusion microthermometry indicate that the base metal mineralization evolved from a high sulfidation to an intermediate sulfidation condition. Assuming that the system is in equilibrium, the $\log f\text{O}_2$ varies from -32.2 to -37.5 atm from $T = 300$ to 250°C at $\text{pH} = 5.11$ and $\Sigma\text{S} = 10^{-2}$ mol/kg. Gold was mainly transported as $\text{Au}(\text{HS})_2^-$ complex. In Kay Tanda, evidence of fluid boiling were observed. Boiling might have caused the removal of H_2S from the hydrothermal fluid, which triggered the decomposition of $\text{Au}(\text{HS})_2^-$ complex leading to the precipitation of gold.

論文審査結果の要旨

提出された博士論文、博士論文要旨及び論文目録について、所属する資源学専攻の教員および外部審査委員により構成される審査委員会において審査し、不備がないことを確認した。記載内容は適正であり、また、査読のある学術誌に投稿された論文が受理されていることを確認し、書類審査は合格とした。申請者は、フィリピン、ルソン島南部バタンガス州ロボ地域の、Kay Tanda 鉍脈鉍床について、流体包有物、鉍石鉍物の化学組成および安定同位体比の詳細な検討に基づいて、鉍化作用と鉍化流体の変化を明らかにした。

まず著者は、Kay Tanda 鉍床周辺の地質について概説した後、鉍化作用は大きく2つのステージに分けられることを明らかにした。早期鉍化作用は、Talahib 火山岩類の浅部に胚胎される金銀を含む網状石英脈、後期鉍化作用は深部の鉍脈および熱水角礫中のベースメタル（亜鉛、鉛、銅）鉍化作用で局所的に高品位の金鉍化作用を伴っている。

次に著者は、鉍物の共生関係に基づいて鉍化ステージが6つに細分されることを示した。ステージ1は、石英±葉ろう石±ディッカイト/カオリナイト±ダイアスポアの熱水変質作用を金を伴う石英脈が切っており、石英脈の流体包有物は、熱水と天水の混合を示唆する。引き続きステージ2では、広範囲にわたってイライト±石英±スメクタイト±カオリナイト変質が生じ金銀を伴う網状石英脈が形成した。古地下水面下 500m の深度で静水圧下での沸騰が推定された。後期の鉍化作用は、少量のベースメタルの硫化物を伴う炭酸塩脈で始まった。ステージ4の石英±氷長石±方解石脈と熱水角礫がベースメタルと局所的に高品位の金鉍化作用を胚胎しており、緑泥石+イライト+石英からなる変質作用を伴っている。沸騰が鉍石の主たる沈殿メカニズムであった。ステージ5は緑簾石-炭酸塩鉍物脈で、緑簾石+方解石+緑泥石からなる変質作用を伴っている。ステージ6が最末期の鉍化作用であり、硬石膏/石膏脈にベースメタルと低品位の金銀鉍化作用が伴われている。流体包有物マイクロサーモメトリより、ステージ1 (220-270°C) からステージ2 (260-310°C) は温度が上昇し、その後ステージ4 (270-310°C) まで高温状態が継続した後、ステージ6 (240-290°C) へ徐々に温度が低下した。流体包有物の塩濃度（ステージ1, 2および4は 5.8wt%NaCl 相当、ステージ6は 4.6wt%NaCl 相当）、ステージ2の石英脈を伴う変質帯のイライトの水素および酸素同位体比は海水起源と天水起源の熱水の混合を示唆する。また、イライトの K-Ar 年代は、 $5.9 \pm 0.2\text{Ma}$ および $5.5 \pm 0.2\text{Ma}$ である。

続いて著者は、ステージ2 ($\delta^{34}\text{S}$ 値 $-5.8\text{‰} \sim +2.8\text{‰}$) および4 ($-2.1\text{‰} \sim +3.3\text{‰}$) の硫化物と、ステージ6の硫化物 ($+0.1\text{‰} \sim +2.3\text{‰}$) - 硫酸塩 ($+21.6\text{‰} \sim +22.9\text{‰}$) の硫黄同位体比を詳細に検討し、熱水系の進化を論じた。初期には、海水起源の熱水から流入帯において海水起源の硫酸根が沈殿して除去されたが、温度が低下した後期には深部を循環した天水によって硫酸塩鉍物が溶解したことにより硫酸根が熱水に溶存した。

さらに著者は、ステージ4の高品位金鉍化作用の熱水について熱力学的に物理化学条件を考察した。鉍石鉍物組み合わせ、閃亜鉛鉍の FeS 含有量および流体包有物から推定された温度において高硫化状態から中間硫化状態の環境であったことが示された。また沸騰が金の沈

殿のメカニズムであったことを示した。

本学位論文は、これまで研究例がなく鉱床の詳細についてほとんど知られていなかったロボ地域における鉱化作用について、鉱化作用の特徴、熱水の化学的特徴と起源、鉱石の沈殿メカニズムを明らかにした。博士の学位に値する業績であると認め、本審査は合格と判定した。