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論文内容の要旨

The different styles of mineralization in the Mankayan District that evolved within at least 5 million years include several porphyry Cu-Au deposits, epithermal enargite-Au orebodies, carbonate-base metal-Au-Ag veins and quartz-pyrite-gold (QPG) veins. Among the four types of mineralization styles, the QPG veins has just been recently delineated extensively. This study focuses on the characterization of the QPG veins and determining its temporal and spatial relationship with the adjacent enargite orebodies and porphyry-type mineralization.

The QPG veins are mainly hosted by the Cretaceous to Eocene Lepanto metavolcanics basement rocks. Different sets of QPG veins have been delineated: The Northwest deposit is situated 500 m to the east of the Lepanto Fault, while Carmen and Florence are located further to the south. In general, the paragenesis of the QPG veins include five mineralization stages. The earliest stage, Stage 1, is characterized by sphalerite + chalcopyrite + pyrite ± magnetite veins that cut the host rocks that were altered to chlorite ± illite ± epidote. The Stage 2 is the start of precious metal deposition as electrum, native gold and gold-silver tellurides deposited with pyrite, quartz and carbonate. Deposition of gold and silver tellurides continued during the formation of Stage 3a and Stage 3b veins with pyrite, tennantite-tetrahedrite solid solution

intergrown with chalcopyrite, bornite and minor sphalerite. Gangue minerals deposited during the Stage 3a include abundant muscovite and quartz, while the Stage 3b veins and alteration contain quartz, pyrophyllite, alunite and dickite. Abundant luzonite and enargite were deposited during the Stage 4 as dissemination in silicified host rocks or as inclusions in quartz veins. Stage 5 is characterized by less amount of quartz and abundant pyrite deposition. The paragenetic sequence of the QPG veins shows a change in the sulfidation state of the ore-forming environment from a distal porphyry (stage 1) to an intermediate sulfidation (stages 2 and 3a) and then a high sulfidation (stages 3b to 5) condition. All the five mineralization stages have been documented in the observed drill holes from the Northwest deposit. However, only the QPG and enargite veins associated with quartz + alunite ± pyrophyllite ± kaolinite/dickite alteration zones, which may be equivalent to Northwest stages 3b and 4, have been observed in the available drill holes and underground exposures in Carmen and Florence.

Radiometric $^{40}Ar/^{39}Ar$ dating on alunite separated from the Stage 3b vein from the Northwest deposit yielded an age of 2.2 ± 0.1 Ma, while the alunite from the Carmen deposit yielded an age of 1.62 ± 0.04 Ma. These new age data, in comparison with previously published ages of the adjacent deposits, substantiate the idea that there is more than one intrusive center that caused acid leaching and alteration, which coalesced to form a large, continuous district-wide alteration zone in Mankayan.

The ore-forming fluids of the Northwest, Carmen and Florence QPG and enargite veins were characterized by fluid inclusions microthermometry and bulk gas analysis. Fluid inclusions in quartz of the Northwest QPG stage 1 are mostly bi-phase liquid-rich fluid inclusions that homogenized between 220 °C and 280°C. These bi-phase liquid-rich fluid inclusions co-exist with minute polyphase fluid inclusions that did not homogenize at 450°C. Microthermometric data of bi-phase liquid-rich fluid inclusions in the Northwest QPG stage 2 and stage 3a quartz indicate that precious metals were deposited due to boiling of fluids that occurred from 270°C to 250°C and 250°C to 210°C, respectively. The deposition of alunite, pyrophyllite and quartz during the stage 3b occurred at higher temperatures (250°C to 270°C), indicating hotter pulses of hydrothermal fluids. The deposition of abundant enargite and luzonite during the stage 4 also occurred with fluid boiling at a temperature lower than the earlier stages (220°C). Gas compositions of fluid inclusions in stage 2 quartz from the Northwest deposit have N_2/Ar ratios ranging from 16 to 53, which are lower than that of air (N_2/Ar = 84) or air-saturated water (N_2/Ar = 40 to 50). These low N_2/Ar combined with elevated He content indicate that the stage 2 fluids were derived from basaltic magma. In contrast, the fluid inclusions in quartz of the enargite-bearing stage 4 veins from Northwest and Florence deposits have elevated N_2/Ar indicating contribution of a fluid derived from andesitic magma. The fluid inclusions in quartz of the QPG veins in Carmen have elevated He content and N_2/Ar ratios are between 60 and 106, indicating that the

hydrothermal fluids are deeply-circulated meteoric waters.

The QPG and enargite veins in Carmen and Florence were found to have overprinted earlier porphyry-type quartz veinlet stockwork and veins that host polyphase hypersaline fluid inclusions that homogenized above 500 °C. The mineral chemistry of the high-temperature quartz exhibits distinctly different mineral chemistry compared to the quartz veins related to QPG and enargite mineralization. The Ti content of the porphyry-type quartz is above 100 ppm, while the Ti content in epithermal-type quartz is below detection limit. On the contrary, Fe concentration in epithermal vein quartz reaches above 300 ppm, whereas Fe is nearly undetected in the porphyry-type stockwork veinlet quartz. This shows that several high-sulfidation epithermal gold orebodies in the Mankayan District were formed in an environment that have been already affected by earlier porphyry-type mineralization.

Stable isotopic ratios of the sulfides, sulfates, dickites and quartz were measured to determine the characteristics of the ore-forming fluids. The $\delta^{34}S$ of the sulfides from the Northwest QPG deposit shows a decreasing trend from Stage 1 to Stage 5, which is parallel to the general decrease in temperature measured from fluid inclusions microthermometry. The $\delta^{34}S$ of alunite range from +13 to +24 ‰, suggesting hypogene origin. The bulk $\delta^{34}S$ measured from alunite-pyrite and anhydrite-pyrite pairs from Northwest and Carmen indicate a nearly uniform value of +5 ‰. The narrow range of the $\delta^{34}S$ values of sulfides and the wider range of the $\delta^{34}S$ of associated alunite indicate the predominance of H_2S in hydrothermal fluids.

The calculated $\delta^{18}O$ and δD values of the fluids that formed the stage 4 dickites in the Northwest deposit indicate a significant contribution by magmatic fluids, while the $\delta^{18}O$ and δD values of the fluids that formed the Stage 3b dickites of the Northwest deposit indicate dilution by meteoric water. The calculated $\delta^{18}O$ and δD of the fluids that formed the dickite that occur as an overprint to the porphyry-type stockwork veins are significantly greater than the isotopic ratio of the dickites that occur as veins, indicating possible contribution of heavier isotopes by the earlier alteration.

The available ages, fluid inclusions microthermometry, bulk gas analysis and stable isotopes geochemistry of the different deposits in the Mankayan District suggests multiple hydrothermal events that occur adjacent and overprinting each other. In general, the different episodes of enargite mineralization were formed from fluids whose major components were derived from a magma, whereas the hydrothermal fluids that formed the QPG were largely meteoric in origin. In both type of mineralization, boiling is an important mechanism for deposition.

The effects of the different styles of mineralization and their associated alteration can also be seen in the geochemical signature of the host rocks. N-MORB-normalized multi-element diagrams show that the host rocks preserve the negative anomalies of the high-field strength elements (HFSEs) that are typical of magmas generated in a

suprasubduction zone setting. The non-mineralized diorites and metavolcanics rocks show variable signature of the large ion lithophiles (LILEs), while the altered rock samples show a more consistent signature, indicating that pervasive alteration causes geochemical homogeneity. The host rocks that have been altered by acid-sulfate alteration assemblage show negative Rb anomaly, while those that show a near-neutral alteration assemblage has a positive Rb anomaly. The rare earth elements (REEs) are severely depleted in rocks that underwent acid-sulfate alteration. Mass balance calculations indicate that the host rocks in Mankayan gained significant amounts of Al, Si and S, while Na, Ca, Mg and Fe were considerably leached.

The new findings of this study provide new constraints for understanding the prolific mineralization in the Mankayan District, which was produced by multiple hydrothermal events. This study contributes information for the exploration of overprinted hydrothermal systems that may not show typical alteration patterns but contain economic precious metal deposits.

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，ルゾン島北部マンカヤン地域において，特に最近発見された石英–黄鉄鉱–金（QPG）鉱脈鉱床について，その鉱物学的および地球化学的特徴を明らかにするとともに，近接する斑岩型銅–金鉱床、浅熱水硫砒銅鉱金鉱床との時間的および空間的関係を明らかにした。

まず著者は， Lepanto 断層の東 500m に位置する Northwest 鉱床，さらに南方に位置する Carmen 鉱徴地，Florence 鉱徴地で発見された白亜系～始新統の Lepanto 変火山岩類に主として胚胎する QPG 鉱脈について，鉱物の共生順序が５つのステージに分けられることを明らかにした。それらは早期のものから順に，ステージ１は，緑泥石±イライト±緑簾石の熱水変質作用を受けた母岩を切る閃亜鉛鉱＋黄銅鉱＋黄鉄鉱±磁鉄鉱で特徴付けられる。ステージ２の黄鉄鉱，石英，炭酸塩鉱物に伴われるエレクトラム，自然金および金銀テルル化物の晶出により貴金属鉱化作用が始まった。ステージ３a および 3b の間，黄鉄鉱，砒四面銅鉱–安四面銅鉱固溶体，黄銅鉱，斑銅鉱，閃亜鉛鉱に伴われる金銀テルル化物の晶出が続いたが，ステージ 3a の脈石鉱物は石英–白雲母であるのに対し，ステージ 3b に伴われる変質鉱物は葉ろう石，明礬石，ディッカイトを含む。ステージ４では珪化母岩中の鉱染および石英脈中に多量の硫砒銅鉱およびルゾン銅鉱が生じた。ステージ５では少量の石英と多量の黄鉄鉱

が晶出した。斑岩銅鉱化作用の縁辺部の熱水系（ステージ１）から中間的硫化状態（ステージ２および３a），高硫化浅熱水系（ステージ３b から５）へ変化した。

次に著者は，Northwest 鉱床および Carmen 鉱徴地のステージ３b の鉱脈の明礬石の $^{40}Ar/^{39}Ar$ 年代をそれぞれ 2.2±0.1Ma，1.61±0.04Ma と求め，他の鉱体から報告されている年代値と比較し，マンカヤン地域において複数の熱水活動が時間的，空間的に広く生じたことを示した。

さらに著者は，Northwest 鉱床および Carmen 鉱徴地，Florence 鉱徴地の鉱化流体について，流体包有物のマイクロサーモメトリーとガス分析により詳細に論じた。Northwest 鉱床のステージ１の石英は 220–280℃で均質化する気液二相包有物を含有し，450℃以上の均質化温度をもつ多相包有物を僅かに伴う。ステージ２および３a の QPG 脈の鉱化作用はそれぞれ 270-250℃，250-210℃で沸騰した熱水により生じた。ステージ３b の葉ろう石，明礬石，ディッカイトはより高温（250-270℃）の熱水から晶出したことから，新たなマグマの寄与が考えられる。ステージ４の多量の硫砒銅鉱およびルゾン銅鉱の晶出温度は 220℃で、早期の熱水よりも低温であった。

また著者は，Carmen 鉱徴地および Florence 鉱徴地において QPG 鉱脈が，すでに存在していた斑岩型鉱化作用の石英細脈に重複して生成したことを示した。斑岩型鉱化作用の石英細脈の流体包有物は 500℃以上で均質化する多相包有物を含む。またこの細脈の石英の Ti 含有量は 100ppm 以上であり，浅熱水鉱化作用により生成した石英とは異なる。

本学位論文はマンカヤン地域における鉱化作用の多様性を明らかにし，それぞれの鉱化作用の特徴と熱水の化学的特徴を明らかにしたこと，長期間、複数の活動が重複したことにより世界的にも著名な大規模な鉱床地帯が形成されたことを示した。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。