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Hydrothermal evolution recorded by trace-element composition in sulphides and bismuth sulphosalts from the Karkonosze Granite, Szklarska Poręba (SW Poland)

KAROLINA MIL[1], BOZENA GOLEBIOWSKA[1], DIMITRINA DIMITROVA[2], TOMÁŠ MIKUŠ[3] AND ADAM PIECZKA[1]

[1]AGH University of Krakow
[2]Geological Institute, Bulgarian Academy of Sciences
[3]Earth Science Institute, Slovak Academy of Sciences

Within the Variscan Karkonosze pluton (NE Bohemian Massif), the Szklarska Poręba–Huta quarry hosts a multistage post-magmatic mineralisation disseminated in aplogranites, small pegmatites, and quartz veins. It includes W–Sn–Mo–Bi assemblages accompanied by various sulphides, sulphosalts, and Th–Nb–(REE+Sc) minerals, all derived from (pneumo-)hydrothermal solutions [1]. To reconstruct the hydrothermal evolution, trace-element analyses (LA-ICP-MS) of base-metal sulphides were integrated with chemical (EPMA) and textural characteristics of bismuth mineralisation.

The strongest geochemical contrasts occur between sulphides from aplogranite and quartz veins. Pyrite is the most trace-element-enriched, with maximum concentrations [ppm] of: As – 4117, Mo – 3259, Co – 1201, Ni – 146. It shows a wide Co/Ni range, indicating highly variable physicochemical conditions [2]. Aplogranite-hosted pyrite has higher total Co and Ni and Co/Ni <10, consistent with higher-temperature crystallisation. Vein-hosted pyrite shows lower Co and Ni, with stronger nickel decrease, resulting in Co/Ni ratios up to 91.6. In pyrrhotite from aplogranite Mo, W, and As are nearly absent and Co/Ni <22. Quartz-vein pyrrhotite is Co- and Ni-free and Se-enriched (~22 ppm), reflecting progressive fluid fractionation during cooling.

Silver shows strong affinity for chalcopyrite in quartz veins with lower-temperature assemblages, reaching concentrations <480 ppm. Chalcopyrite in aplogranite or veins with W–Sn–Mo mineralisation contains <45 ppm Ag, indicating higher-temperature crystallisation.

Sphalerite from both aplogranite and quartz veins shows high Fe (<9.7 wt%), In (<627 ppm), and Ag (<329 ppm). Later-stage sphalerite coexisting with Bi-sulphosalts contains lower Fe (<2.54 wt%), In (<146 ppm), and almost no Ag, indicating crystallisation after chalcopyrite when Ag was removed from the system.

Early Pb–Bi(Sb)–Ag(Cu)–S sulphosalts (galenobismutite, lillianite–gustavite) formed at ~390–350 °C, followed by cannizzarite and cosalite. As temperatures dropped to ~320–270 °C, fluids became progressively enriched in Bi and Cu, forming emplectite, cuprobismutite homologues, padéraite, and bismuthinite derivatives. Bismuth chalcogenides (<250 °C) and matildite (<230 °C) represent the final stage. Selenium occurs in minor amounts, mainly controlled by ΣSe/S ratios, whereas tellurium was mobilised only during the latest stage.

These results provide insights into metal partitioning within a post-magmatic system.

[1] Mikulski, S.Z. 2007, Granitoids in Poland, AM Monograph (1), 123-145.

[2] Keith, M., et al. 2022, GCA, 329, 185-205.