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Faculty of Earth Science and Engineering

Institute of Mineralogy and Geology

Mikoviny Samuel Doctoral School of Earth Sciences

Head of the Doctoral School: Dr. Péter Szűcs, professor

"GEOLOGICAL AND GENETIC MODEL OF METAL-ORGANIC COMPOUNDS FORMATION IN LATE PALAEOZOIC ORGANIC-RICH SEDIMENTS, USING EXAMPLES FROM HUNGARY AND KAZAKHSTAN"

THESES OF PhD DISSERTATION

By

MEDET JUNUSSOV

Scientific supervisors:

Prof. Dr. Ferenc Mádai, & Dr. Hámorné Vidó Mária habil

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Introduction

This dissertation investigated the organic matter (OM) and its genetic roles with metal ores, mainly gold. In this study, I choose two mineral deposits of csulphidearbonaceous-terrigenous formation occurred in the Late Paleozoic, enriched in OM and gold content. The two locations were selected in the W-Mecsek of SW-Hungary and the Bakyrchik open-pit mine of NE-Kazakhstan.

The deposits are hosted by rocks of distinct sedimentary environments and were formed by a hydrothermal-magmatic system. In the W-Mecsek hydrothermal temperature ranges up to 200°C (Barabás & Konrád 2000; Barabás 2013), accompanied by epigenetic uranium ore mineralisation in the Late Permian (P_3) alluvial sandstone where the gold and another gold-containing sulphide minerals are associated to the terrestrial organic matter. The Middle-Upper Carboniferous (C_{2-3}) Bakyrchik gold deposit formed at higher temperatures between 200°C and 340°C in the shear zone of the orogenic belt and accumulated in organic matter rich seriticized sandstone. In both deposits, the OM rich sedimentary sequences formed in a reducing, freshwater environment.

The gold mineralisation in the organic-rich sedimentary sequences of the two deposits relates to tectonic-magmatic events of the Carboniferous Variscan orogenic gold cycling between 350 Ma to 300 Ma (Parnel 2019). Early Carboniferous (C_1) Mórágy granitic complex occurred from 340 Ma to 354 Ma in the W-Mecsek (Klötzli et al. 2004; Lelkes-Felvári and Frank 2006). The Bakyrchik deposit can be associated with the

formation of the Late Carboniferous-Early Permian (C_3-P_1) stages gold-bearing Kunush granitic complex intrusions (Rafaylovich 2009).

This study aims to help identify the source and the form of the metal ores in the deposits and find the relationship between metals and the OM in ore mineralisation zones. Investigations have been carried out on the selected samples' geological and geochemical characteristics for both deposits. Especially the ore mineralisation, mainly the appearance and phase of gold in organic-rich sediments and sulphur minerals were studied. Hence, the source of gold and the role of OM in the mobilisation and precipitation of gold were the major objectives of this study.

Sample and methods

The study of the Western Mecsek deposit was carried out on eight drill core samples (from 34 m to 907 m at Kővágótöttös Sandstone Formation) of the borehole WHE-2, located in 15 km West direction to Pécs city, from the mining area of the closed uranium mine. The study of the Bakyrchik deposit selected nine rock samples from the organic-rich sedimentary bedrocks located near the shear zone in the open pit. The samples of both deposits are organic-rich sedimentary rocks with ore minerals inclusions. The study of organic matter in the ore mineralisation of the deposits was carried out by micro-analytical and experimental investigations in two separations for ore minerals and organic materials. The ore minerals have been analysed by ore microscopy and electron microscopy for textural characteristics; XRPD and WDXRF for mineralogical and chemical composition; ICP-OES and LA ICP-MS for gold content. Organic petrography and electron microscopy have been used to characterize the organic matter for textural features and structural characters; FTIR and Raman analysis for organic elemental content and structural components; and Soxhlet apparatus and proximate analysis for extraction components and physical features. The experiment has chosen a sequential extraction method for releasing gold from organic fractions and evaluating the value of gold content.

Results

The analytical and experimental results show that the organic matter of Western Mecsek is bituminous material, composed of primary vitrinite and solid bitumen accompanying very tiny graphite inclusions. Total organic carbon is less than 1.1 wt% and high sulphur content up to 6 wt%, with the vitrinite reflectance 2.25 %. While the organic

matter of Bakyrchik is bituminous material, veined pyrobitumen and angular-shaped vitrinite particles. Total organic carbon varies from 0.3 to 0.5 wt%, and the reflectance ranges from 3.7 to 3.9 % and sulphur content from 0.8 to 1.27 wt%. Both deposits have extremely low extractable bitumen yield. The sequentially extracted gold content from the organic matter of Western Mecsek reaches an average of 0.82 ppm gold. In comparison, the organic matter of Bakyrchik reaches an average of up to 0.80 ppm gold accompanied by an average of 0.96 ppm Ag, 10.3 ppb Pt and 13 ppb Pd (Junussov et al. 2018c; Junussov, 2020a, b). LA ICP-MS confirmed the results of sequential extraction, regarding the gold content in organic materials.

The LA-ICP-MS analyses on the grains of OM in samples of W-Mecsek, measured mainly on physically destructed vitrinite particles in hydrothermal precipitation zones, show the presence of Au and Ag, ranging from 1.19 ppm to 5.06 ppm Au; and 1 ppm to 90 ppm Ag. The value of Au enriches with increasing the values of radioactive elements (the highest values of 61 ppm U and 9 ppm Th) and arsenic content (the highest value of 2558 ppm). The thirty-three signals for gold content in the sample WH2-065, with the highest values from 5.05 ppm to below the detection limit, while the remaining samples have low signals.

The experimental and analytical results on samples of Bakyrchik show that the gold content increases several times in arsenopyrite (6 times more) and pyrobitumen (3 times more) to pyrite in nine samples from three groups, regarding the first group to the zone rich in the carbonaceous matter (pre-ore mineralisation), the second group to the arsenic sulphide ore zone (the main ore mineralisation), and the third group in the antimony sulphide ore zone (near-surface post-ore mineralisation) (Junussov, 2018a c,d; Junussov et al. 2018 a,b). Three samples show that the arsenopyrite mineral is more enriched in gold, especially from the second group of three samples in the arsenic sulphide ore zone, corresponding to the main ore mineralisation (Junussov et al., 2021). Solid bitumen comprises gold from three groups of samples, mainly from samples of the second group in the arsenic sulphide ore zone. The lowest content of gold is observed in pyrite of three groups gold of pyrite includes mostly in the second group of the arsenic sulphide ore samples.

Discussion

The results from W-Mecsek and Bakyrchik may discuss that the precursor of liquid bitumen in the hydrothermal ore fluid mobilises gold as metal-organic compounds and, as

a part of the organic fraction of gold, undergoes thermal decomposition, releasing dissolved gold and the rest of the preserved organic fraction that occurs gold. When thermally unstable organic matter releases, gold is chemically bound in the structures of arsenic-rich sulphide minerals forming invisible gold (Junussov et al., 2021). The remaining gold in organic functional groups forms gold-containing solid pyrobitumen as metal-organic compounds.

The source of the OM associated with gold mineralisation in both deposits is likely related to the results of the global tectonic Varsican orogenic gold formation within organic-rich sedimentary basins in Central Europe (W-Mecsek) and Central Asia (Kazakhstan).

OM is closely associated with ore mineralisation in both deposits of W-Mecsek and Bakyrchik. In a supergene environment of W-Mecsek and the hypogene environment of Bakyrchik, the OM's complexing, adsorption, and uptake of gold might be important processes that control the enrichment of the gold in the host rocks during sedimentation and diagenesis. Also, humic acids may be important transport agents in supergene/hypogene gold ore mineralisation. OM is unlikely have played an important role in gold transportation in hydrothermal processes. However, organic acids produced by thermal maturation and decomposition of OM and colloidal, or molecular dissolution of hydrocarbon in fluid, might be significant for gold leaching and migration. The high-grade thermal maturation of OM (temperature ranges up to 144^{o}C in W-Mecsek, and 276^{o}C in Bakyrchik, regarding the Raman results) in the ore-containing rocks of both deposits results from hot fluids migration. Finely disseminated vitrinite, secondary macerals and graphite particles associated with gold enrichment confirm that gold in OM occurs due to hydrothermal processes in detrital sedimentary rocks at both locations. While the samples of Bakyrchik have plenty of hydrothermal quartz, closely associated with veins and veinlets of solid bitumen enriched in the gold show that gold occurred as hydrothermal gold mineralisation. The precipitation of gold during the light hydrocarbons release in the metagenesis may have contributed to the thermal reduction of sulphate and thus the pyritisation and gold precipitation.

Conclusion

In my dissertation, I reported about forms and types of OM in both deposits and evaluated their role in ore formations. According to the research data of two ore deposits,

my co-authors and I proposed the primary genetic roles of OMs in gold mineralisation for both sites with the following observational pieces of evidence:

(1) The OM is terrigenous high plant origin at both locations, shows the carboxylic acid organic structure and sulphur-rich aromatic hydrocarbon composition;

(2) The hypo-autochthonous dispersed OM dominantly occurs as vitrinite at both locations, and in a smaller quantity, liptinite and inertinite occur in the Mecsek samples. At both sites, secondary macerals of homogeneous cement of pyrobitumen and brownish, non-fluorescing solid bitumen precipitated in the fractures and fine veins of the host rock;

(3) Occurrence and local enrichments of gold in the OM were confirmed by sequential extraction method with ICP-OES and also by LA ICP-MS. Au in the OM is enriched in reducing zones in solid bitumen types and arsenian pyrite;

(4) Hydrocarbon fluid migration processes in the W-Mecsek played an important role in sulphide and gold transportation because both in the physically destructed vitrinite and secondary macerals of solid bitumen and pyrobitumen of the studied sites, gold was detectable in the OM. This study analytically confirms the occurrence and enrichment of gold in the pyrobitumen heteroaromatic fraction in the form of a metal-organic complex, which is entrapped in the micrometre size or smaller diameter veinlets and voids of the host rock pores;

(5) The thermally stable organic fraction of solid bitumen like asphaltenes preserved a part of the gold. In contrast, the thermally unstable compounds of the organic fraction may liberate some gold during cracking in the metagenesis. With the release of thermally unstable, light-molecule weighted migration products during the thermally driven decomposition and cracking of carboxyl and carbonyl group containing compounds, the gold could be enriched in sulphide minerals with the recrystallisation of pyrite cement and euhedral crystals where gold enrichment is also confirmed. LA-ICP-MS showed that the cement pyrite is enriched in silver in the presence of sulfosalts in its porous centre, which shows that in case the precipitating fluid became depleted in gold, silver was replaced within the sulphide mineral;

(6) In the case of W-Mecsek, the dissolved uranium was transported as a metal-organic complex during hydrothermal processes and at some places precipitated as needle-like uranium oxide in dolomite veins and at the same time formed dispersed subhedral uranium phosphate minerals in the clay matrix. The metal-organic-complex migration is confirmed by reflected light observation where the vicinity of the bitumen veins and

vitrinite particles show medium greenish fluorescence of the mineral matrix at UV excitation;

(7) In the case of Bakyrchik, the reductive OM agent liberated gold above 270°C during the arsenic sulphide ore formation into ore minerals with an arsenic lattice structure in the fracture zone;

(8) Gold is preserved as a lattice gold or structurally bonded metal in the aromatic hydrocarbon fractions of the OM and arsenian pyrite of the deposits of W-Mecsek and Bakyrchik.

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