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Iodargyrite from Zalas (Cracow area, Poland) as an indicator of Oligocene–Miocene aridity in Central Europe

Bożena Gołębiowska *, Adam Pieczka, Grzegorz Rzepa, Jacek Matyszkiewicz, Marcin Krajewski

AGH-UST University of Science and Technology, Faculty of Geology, Geophysics and Environment Protection, al. Mickiewicza 30, 30-059 Kraków, Poland

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ABSTRACT

Iodargyrite, the hexagonal silver iodide, was found in the Permian rhyodacite quarry at Zalas (near Cracow, Southern Poland) in a fault zone cutting Middle Jurassic sandy limestone. It occurs within a tectonic breccia encrusted by chalcopyrite, pyrite, Ag-containing chalcocite, covellite, galena, native bismuth, malachite, cuprite, Fe- and Mn-dominant oxides, Cu sulfates and barite. The hydrothermal encrustacion is most likely connected with rejuvenation of Old–Paleozoic faults in the Sava phase of the Alpine orogeny on the Oligocene–Miocene boundary. The periods of aridity when iodargyrite precipitated, determined by evaporation of salt lakes or the inland Miocene sea that delivered halide ions to the groundwater oxidation system, or leaching of weathered Ag-containing mineralization by saline, I^--rich deep formation waters derived from Paleogene sediments during folding and formation of the Carpathians nappe structure, are connected rather with the Low to Middle Miocene period. At this time, steppe areas with a dry climate existed on the north foreland of the Carpathians in southern Poland as a result of a displacement to the north of a dry subtropical zone because of uplift of the Carpathians and regression of the inland Miocene sea.

1. Introduction

The group of Ag halide minerals includes chlorargyrite, AgCl, bromargyrite, AgBr, and miersite, (Ag,Cu)I, all crystallizing in the cubic system. Iodargyrite, AgI, however crystallizes in the hexagonal system. Tocornalite, (Ag,Hg)I, is a questionable, probably hexagonal species. Of the silver iodide minerals known in nature, miersite occurs occasionally — it has been found so far only in the Broken Hill deposit, Australia (Millsteed, 1998), Municipalidad de Moctezuma, Mexico (Braith et al., 2001), the Bisbee deposit, the Mildren Mine and the Steppe Mine in Arizona, USA (Williams, 1963; Graeme, 1993). Bloch and Moller and Barclay and Jones (see Millsteed, 1998) proved that an excess of Ag promotes the crystallization of AgI as the cubic miersite, whereas an excess of iodine favours the formation of hexagonal iodargyrite. An admixture of CuI in AgI, more than 1 mol%, stabilizes the regular miersite. The solubilities of silver halides (1.9×10^{-3} g/L AgCl, 1.4×10^{-4} g/L AgBr and 2.2×10^{-6} g/L AgI) clearly show that in the case of simultaneous presence of Cl^-, Br^- and I^- in groundwater, iodargyrite precipitates at the smallest distance from the parental ores. Therefore, iodargyrite is concentrated in the deeper oxide and underlying supergene sulfide zones, whereas bromargyrite and, particularly, chlorargyrite, precipitate as expected near the Earth's surface. However, as Cl^- is a much more common component of groundwater than Br^- and, in particular, I^-, chlorargyrite precipitates more quickly than bromargyrite or iodargyrite, and is found more often. Boyle (1997) indicated three main features resulting in the tendency of Ag halide precipitation in reverse to their solubilities (AgCl>AgBr>AgI): i) higher concentration of Cl^- than Br^- and I^- in groundwaters; combined with rapid increase of AgCl solubility relative to AgBr and AgI with increasing temperature in near-surface waters, groundwater saturation in AgCl and precipitation of AgCl in downwelling fluids as temperature decreases, ii) higher solubilities of AgI and AgBr than AgCl in alkali chloride solutions (Emmons, 1917), and iii) a much stronger oxidizing effect of ferric ion on Br^- and I^- than on Cl^- , lowering the concentrations of bromide and iodide ions (Knopf, 1918).

All the Ag halides are rare and sometimes are found in weathering zones around silver ores. It has been known for a long time that minerals of the group, particularly bromargyrite and iodargyrite, are restricted to extremely semi-arid and arid environments, in contrast to chlorargyrite, which is a good indicator of a slightly moister climate (Boyle, 1997). In temperate and humid climates, the oxidized zones of polymetallic sulfide deposits containing Ag are devoid of silver halides. Currently, the climate favouring the formation of silver halides predominates among others in Chile (the Atacama Desert), Mexico, the SW part of USA (Arizona, Colorado, Nevada and New Mexico), Australia, Central Asia, and Namibia. Numerous examples, and extensive discussion on Ag halide minerals as climatic indicators were presented by Boyle (1997).

At the village of Zalas, in the southern part of the Cracow–Silesia Monocline (Cracow Upland, S Poland; Fig. 1), only iodargyrite has been found. Zalas is known, first of all, for an abundant assemblage of Middle and Upper Jurassic fossils, occurring within the cover of a Permian rhyodacite laccolith, 281(4) million years old (Nawrocki et al., 2005),

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* Corresponding author. AGH-UST University of Science and Technology, Department of Mineralogy, Petrography and Geochemistry, al. Mickiewicza 30, 30-059 Kraków, Poland. Fax: +48 126334330.
E-mail address: goleb@agh.edu.pl (B. Gołębiowska).

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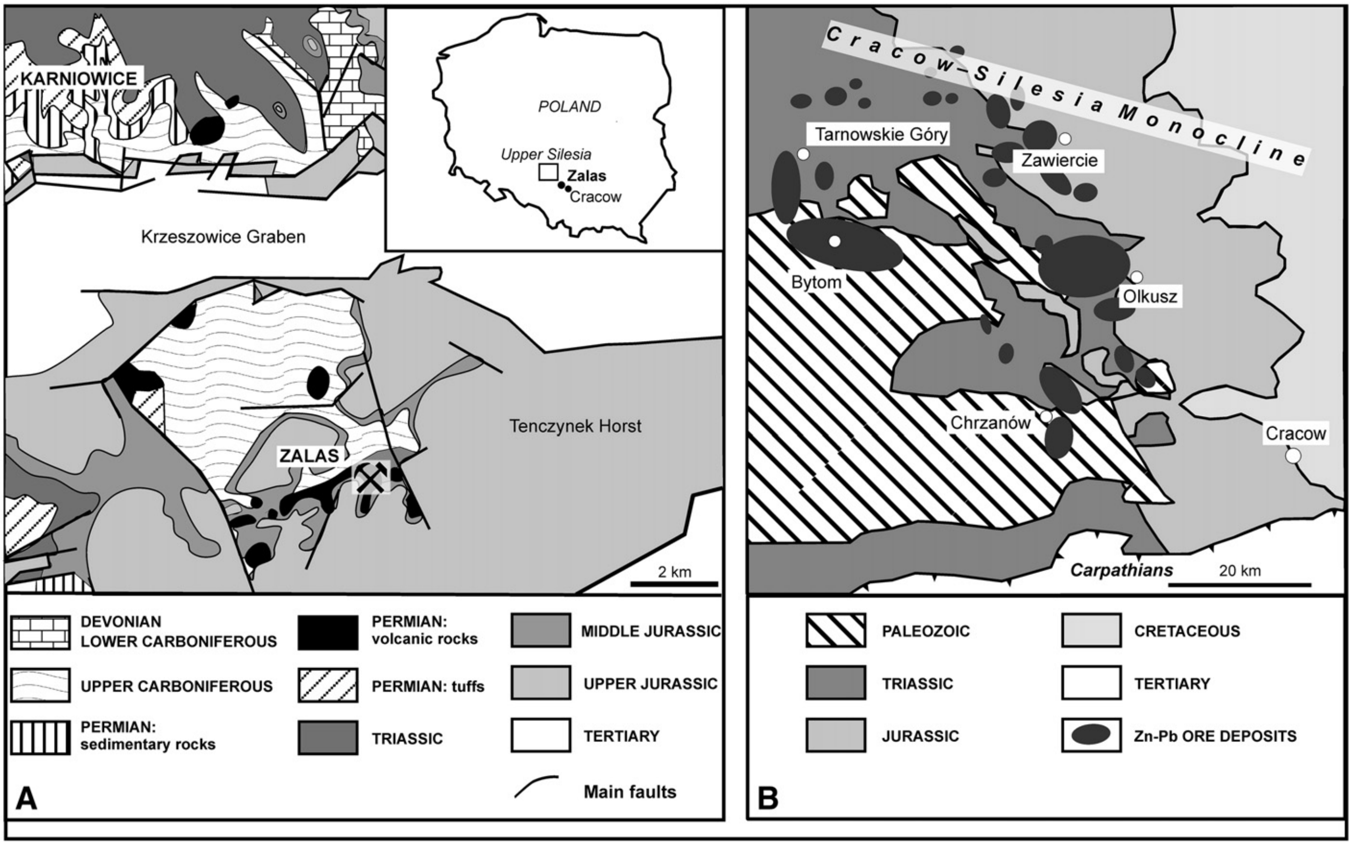

Fig. 1. A — geological map of the Cracow area, without Quaternary (after Gradziński et al., 1994, simplified), and B — distribution of Upper Silesian Zn–Pb strata-bound ores (after Sass-Gustkiewicz and Dżułyński, 1998, simplified).

exploited in a large local quarry. The surprising composition of the supergene assemblage, containing AgI, is a basis for an evaluation of the paleoclimate in the southern part of the Cracow–Silesia Monocline (CSM) and its correlation with similar indications from other localities, suggesting that a subtropical climate with periodic aridity existed locally over central Europe during the late Oligocene–Middle Miocene period.

2. Geological setting and materials

Zalas is located about 5 km south of Krzeszowice (about 20 km west of Cracow), in the southern margin of the CSM, which was formed during the Laramide orogeny from Triassic, Jurassic and Cretaceous deposits (Fig. 1). The southern part of the monocline is arranged in a system of horsts and grabens, resulting from the northward overthrusting of Carpathian flysch nappes in Paleogene during the Alpine orogeny. The basement of the monocline embraces strata from Precambrian (Wend) to Carboniferous sediments with numerous sequences of Upper Carboniferous and Permian volcanic rocks occasionally exposed at the surface (Buła, 2002).

The rhyodacite laccolith at Zalas has been exploited for a few decades (Dżułyński, 1955; Harańczyk, 1989). The intrusion was formed about 260–280 Ma during the Early Permian transtensional, sinistral tectonic regime predominating in central Europe at that time (Nawrocki et al., 2005). In the CSM, the transtension propagated along the broad Cracow–Lubliniec deep-fracture zone, which separates the Małopolska and the Upper Silesian Blocks. The zone originated in the Early Paleozoic and was active until the Cenozoic (Żaba, 1999; Buła, 2002; Matyszkiewicz et al., 2006). The Zalas area is located in the Upper Silesian Block, close to the Krzeszowice–Charsznica Fault, a branch of the Cracow–Lubliniec Fault (Żaba, 1999; Buła, 2002).

The succession exposed in the Zalas quarry includes Permian and Middle to Upper Jurassic deposits. Permian volcanic rocks are overlain by a Middle–Upper Jurassic sedimentary sequence with a total thickness of about 18 m, of which Middle Jurassic deposits (Lower and Upper Callovian) constitute about 8 m. The Lower Callovian consists of cross-bedded sands grading into sandy crinoid limestones, capped by the so-called nodular layer followed by a hardground. Upper Callovian sediments, at most about 1 m thick, overlay these rocks. The Upper Callovian succession starts with a brownish, reddish or black stromatolite, about 40 cm thick. At the top and base, and within the stromatolite layer, Matyszkiewicz (1997) noted several-centimetres-thick intercalations of pink limestones with clasts of Callovian sandy limestones, covered by Fe- and Mn-dominant oxide crusts. The Callovian–Oxfordian boundary occurs within a lens of yellowish-green limestones with oncoliths (e.g. Giżejewska and Wieczorek, 1977).

The Lower Oxfordian includes pink, yellow, brownish and greenish, layered marly limestones and marls at the base with a total thickness ≤4 m. Above there occur Middle Oxfordian gray thin-bedded limestones with sponges. The Middle Oxfordian strata called the Jasna Góra Beds (Trammer, 1989) contain small carbonate buildups formed by siliceous sponges and, subordinately, by microbial structures (Matyszkiewicz, 1997; Krajewski and Matyszkiewicz, 2004).

In 2005, quarrying operations exposed a fault zone cutting the Middle Jurassic sandy limestones, with a breccia locally encrusted by a subordinate hydrothermal mineralization filling fissures and small caverns, as well as forming thick veinlets cutting the limestone, or surrounding the breccia clasts. In hand specimen, the mineralization is composed mainly of aggregates of Fe- and Mn-dominant oxides and malachite. Relics of sulfide mineralization occur only in the malachite-oxide aggregates and are represented by chalcopyrite (up to 0.5 mm), covellite, Ag-enriched chalcocite (up to 1.0 wt.% Ag), pyrite, traces of