Trace element geochemistry and isotopic data of sulphides in Alpine-type Pb-Zn deposits in the Eastern and Southern Alps

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More than 500 occurrences of Pb-Zn ores are documented in Mesozoic carbonate sequences of the Eastern and Southern Alps. They are invariably hosted by shallow lagoonal and reef carbonates of Middle and Upper Triassic (Anisian and Carnian) age and are collectively termed "Alpine-type" (APT) deposits. The district has a long mining history starting in Roman times and terminating in the early 1990ies when the last operations closed at Bleiberg (Austria), Cave del Predil/Raibl (Italy), and Mežica/Mies (Slovenia) (Schroll 2008). The Bleiberg deposit was closed in 1993 after more than 700 years of mining. It is regarded as a world-class deposit (Leach et al. 2005) and represents the type locality of APT Pb-Zn deposits. The historical total metal production from APT deposits exceeded 6 x 10^6 tons (Mt) Zn and Pb from a resource exceeding 110 Mt (Cerny 1989; Cerny & Schroll 1995; Leach et al. 2003; Spangenberg & Herlec, 2006). Renewed interest in base metals, and especially in their by-products such as Ge, Ga, In and Cd, has initiated modern exploration activities in some of the mining districts. Germanium and Cd have been recovered from ores in the past; about 200 tons Ge, mostly from Bleiberg and Raibl, were produced from APT deposits.

Although the deposits occur in a wide region, they share common features such as a simple mineralogical composition, complex ore textures, light sulphur isotopic compositions, Late Palaeozoic Pb model ages, and trace element compositions in sphalerite, galena and pyrite. Ore textures are complex and often equivocal. They include rare examples indicating syngenetic to early diagenetic origin, besides abundant epigenetic textures such as crosscutting veins and breccia ores. However, biogenic textures and relict bacteria colonies are present (Kucha et al. 2010). Therefore, some mineralization must have precipitated at shallow level at low temperature.

Sphalerite is low in Fe (commonly 0.01-0.5 %), Mn, Co, Ga and In, but commonly contains elevated Cd, Ge, As, Tl and Pb concentrations. Median concentrations of Ge determined by LA-ICP-MS are 846 ppm in the Fladung deposit, 229 ppm at Bleiberg and 222 sppm at Raibl where the highest contents of As and Tl have been determined. Sphalerite chemistry indicates that temperatures of formation range from 60 to 140 °C. This is lower than suggested by previous fluid inclusion data, but in line with results of thermal modelling. Metamorphosed sphalerite (>450 °C) in the Brenner and Stangalm Mesozoic reveals metal exchange to higher Fe and Mn, and lower Ga, Ge, As and Tl concentrations. Galena is Ag-poor, although Ag concentrations both in sphalerite and galena increase towards the north of the Austroalpine nappe system. Pyrite- and marcasite-rich ores display an As-Tl-(Hg) association, and are low in Co and Ni. Pyrite is stable to higher temperatures, keeping its original low-temperature trace element compositions.

The sulphur isotope composition of sulphides in APT deposits varies over a wide range and is often bimodally distributed, attaining a maximum at highly negative values ($\delta^{34}S \leq$-20 ‰) explained by bacteriogenic sulphate reduction, and a second maximum at $\delta^{34}S$ = -10 to 0 ‰ explained by thermogenic sulphate reduction from a second source (Schroll & Rantitsch 2005). APT ores in general show lead isotopic compositions above the crustal lead growth curves. The variable enrichment in ^{207}Pb and ^{208}Pb originated from an isotopically enriched continental source (Köppel 1997). Local differences in the bedrock geology and/or its variable common Pb composition are responsible for the Pb isotopic variability of the individual APT deposits. A metal source from the Paleozoic basement and Triassic sedimentary rocks is most likely.

Rb-Sr isochrons of sphalerite from the Bleiberg deposit indicate two phases of ore deposition: a first one at about 229 Ma and a second at about 207-201 Ma. Initial $^{87}Sr/^{86}Sr$ of the early (229 Ma) sphalerite agrees with Carnian seawater composition. The Carnian Rb-Sr isochron age corresponds to U-Pb ages of calcite associated to ore minerals of the (Southalpine) Gorno deposit (Giorno et al. 2022). The younger (≈205 Ma) age reflects fluid flow within the carbonate sequence, probably due to fracturing of the platform during initial rifting of the Penninic Ocean. This process is probably related to ongoing tectonic instability following sedimentation of the Upper Hauptdolomit with formation of deep basins, where hydrocarbon source rocks were deposited. In a wider context of central and southern Europe, mineralizing processes during the Mesozoic have been explained as a response to the Pangaea breakup (Burisch et al. 2022). The oldest hydrothermal processes in the circum-Mediterranean are related to the initial rift axes. Mineralization spans a range from 230 to 160 Ma with a maximum at 230-200 Ma.

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