

Rb-Sr dating of sphalerites from Pomorzany, Upper Silesia (Poland)

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The world-class, carbonate-hosted Zn-Pb deposits in Upper Silesia (Poland) represent one of the largest productive base metal sulfide ore districts in Europe. Proven original reserves are in excess of 500 Mt of crude ore, with a grade of 4-6% combined Zn and Pb (Leach et al., 1996). Ores occur in Devonian to Jurassic rocks but most sulfides (95 %) are confined to epigenetic dolosparites of the Middle Triassic Muschelkalk sequence (Sass-Gustkiewicz et al., 1982). Despite numerous studies, the age and genesis of the Zn-Pb deposits has been the subject of much debate in the past. Models of gravity-driven fluid flow induced by uplift of the Carpathian orogenic belt (Leach et al., 1996), apparently supported by a mid-Tertiary paleomagnetic age, are competing with those proposing upward migration of mineralizing basement brines within an extensional setting (Mucchez et al., 2000).

In order to shed light on this controversy, we have applied the Rb-Sr method to distinct sulfides (sphalerite, marcasite) related to the main, economic mineralization stage. Samples were taken from the Pomorzany mine near Olkúsz. Aliquots of sphalerite samples were subjected to a crush-leach procedure using a BC mortar (e.g. Christensen et al., 1995) and separate Rb-Sr analyses were carried out on bulk samples (U), crushed sphalerite residues (R) and corresponding fluid leachates (L).

Well-correlated mixing lines for these U-R-L triplets in a ⁸⁷Sr/⁸⁶Sr vs. ⁸⁷Rb/⁸⁶Sr diagram testify to a good control on the crush-leach experiments. Five sphalerite residues and a marcasite display a straight line corresponding to an isochron model age of 135 ± 2 Ma ($Sr_i = 0.70881 \pm 11$, MSWD = 2.1), which we interpret as the age of main-stage Zn-Pb mineralization in Upper Silesia. This age appears to be in accordance with available field evidence and clearly refutes the model of gravity-driven fluid flow during the Cenozoic in favour of a scenario in which the ores formed in response to Late Jurassic/Early Cretaceous extension.

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Looking for equilibrium: the determination of an equilibrium constant to describe the formation of hydroxyaluminosilicates (HAS)

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Silicon and aluminium are respectively the second and third most abundant elements in the lithosphere. The predominant form of dissolved Si, i.e. the monomeric silicic acid Si(OH)₄, has been proposed as a geochemical control of the biological availability of aluminium [1]. Silicic acid reacts with aluminium to form hydroxyaluminosilicates (HAS) [2], [3], thereby ameliorating the toxic effects of aluminium [4], [5], [6]. Over the past few years, many studies have been carried out in order to elucidate the mechanism of formation of HAS, culminating in an important breakthrough in the structural characterisation of HAS [7]. However, no equilibrium constant has been available to complete the description of the reaction occurring between Si(OH)₄ and Al. In order to clarify this point, we used the fluorescent reagent morin to measure Al by fluorimetry in the presence or not of Si(OH)₄. The competitive reaction of HAS formation was then observed as the effect of Si(OH)₄ on the formation of Al-morin complex. Using experimentally obtained fluorimetric data and calculations based on the different equilibria involved in systems containing (i) Al, (ii) Al and morin or (iii) Al, morin and Si(OH)₄, we have determined a constant which will describe the formation of HAS. The presented results are believed to be an important advance in understanding the role of HAS in controlling the biological availability of Al in our environment.

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