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Role of sulfur isotopes to classify geochemically Pb-Zn mineralisation

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The first attempt to classify geochemically Pb-Zn deposits was made by Schroll et al. (1994). Amongst other geochemical parameters, sulfur isotopes in sulfide and sulfate minerals play an essential role. Sulfur originates: i) from the hydrothermal source produced .by magmatic processes or by fluid-rock reaction or by organic matter; ii) from the reduction of sulfate, originating from coeval seawater or evaporites in the geochemical environment of metal precipitation. Sulfate is not stabile under high temperature condition,. and is reduced by Fe (II), C and organic matter. Sulfate reducing bacteria are responsible for H_2S production, if porosity, moisture and nutrients within the temperature limit (~ < 100°C) are available.

In the high temperature range (~>370°C) H_2S and SO_2 are the mayor components of magmatic gases. The isotope composition is commonly around $\delta^{34}S$ 0‰. Isotopic equilibrium dominates within sulfide minerals ($\delta^{34}S$ FeS_2>ZnS>PbS, Ohmoto & Rye 1974). In hydrothermal deposits <370°C) isotopic equilibrium between sulfide and sulfate is observed > 300°C. Isotopic equilibrium between the sulfide phases $\delta^{34}S$ FeS_2>ZnS>PbS is reported > 150°C (Ohmoto & Rye 1974). Organic matter produces H_2S by decomposition of organic sulfur-compounds or thermochemical reduction of sulfate (TSR). The sulfide sulfur isotopes are heavy ($\delta^{34}S > 0$‰), and the $\delta^{34}S$ difference between sulfide and sulfate is <20 ‰. Bacteriogenic sulphate reduction (BSR) reveals the largest isotope fractionation, i.e. $\delta^{34}S$ values around -100 to +100‰. Bacteriogenic activity is indicated by wide spread of isotope data due to environmental influences and mixing of heavy sulfur from hydrothermal sources. Indications of BSR are macro-, micro- and nano-textures of the ores, oxisulfides, valency states of sulfur, organic compounds etc (Kucha et al 2001). Newly, fossil bacterial bodies were indicated in zinc-ores of Bleiberg (Kucha et al. 2004). However, light sulfur may originate also from the metal-bearing hydrothermal fluids by leaching of sedimentary iron sulfides in the depth or in the environment of the deposit (Ohmoto and Goldhaber 1997). At temperature of > 200°C, isotopically light sulfide sulfur may produced by sulfate reduction in isotopic equilibrium under special conditions.

Sulfur isotopes are useful to characterize low temperature carbonate-hosted Pb-Zn deposits (Schroll and Rantitsch 2003). The precipitation temperatures are commonly lower than 150°C. The temperature range of the oil window (~ 110°C °C) is important for the transition from bacteriogenic sulfate reduction (BSR) to thermochemical reduction (TSR) in deep horizons (Machel 2001). The sulfur isotope characteristics in the three main types, i.e. MVT (Mississippi type), IRT (Irish type) and ATP (Alpine type), is shown in Table 1. MVT-deposits are formed by burial processes, IRT- and APT deposits by pre-burial events. Late mineralisation stages may be influenced by the thermical history.

Multiple sulfur isotopic analysis using a new ion microprobe multicollector technique promises to be an additional mean to identify biological and abiological sulfur fractionation.

Table 1: Sulfur isotope characteristics of MVT -, IRT - and ATP - Pb-Zn deposits.
An attempt considering natural diversity.

	MVT	IRT	APT
Community	Disequilibrium of $\delta^{34}S$ in FeS_2<(PbS, ZnS) and in $\Delta\,\delta^{34}S_{\text{sulfate-sulfide}}$		
$\Delta\,\delta^{34}S_{\text{sulfide to sulfate}}$ (Mostly coeval seawater)	Low (<20‰)	~ 40‰	up to ~ 40‰
Sulfate reduction	TSR	BSR	BSR
Hydrothermal sulfur (Second sulfide sulfur source)	Not present	around 0‰ $\delta^{34}S$	around 0‰ $\delta^{34}S$

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