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### **Sulfur isotope distribution at Bleiberg lead-zinc deposit (Austria) and its genetic implication.**

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Bleiberg (Carinthia, Austria) is the Alpine type deposit (ATP) of the low-temperature carbonate-hosted lead-zinc mineralisations. The ores are hosted by 350m Ladinian to Carnian platform carbonates. Genetically related lead-zinc deposits are found in Mežica (Slovenia) and Raibl (Italy). These deposits are located along the Periadriatic lineament, which separates the Austroalpine from the Southalpine tectonic unit. Mining ceased at the end of the 20<sup>th</sup> century. With a total production of 2.4 Mio t Pb+Zn, the deposit of Bleiberg is the largest deposit of the ATP.

The genesis of this deposit is discussed controversially. A Carnian sedimentary-sydiagenetic origin (Brigo et al. 1977, Schroll 1996) is opposed against a (MVT) model of migrating brines during post-Norian (Jurassic) age (Zeeh et al. 199?, Kuhleemann et al. 2002).

The interpretation of the sulfur isotope distribution in the Alpine ore district is an efficient contribution to evaluate these contrary models.

The Bleiberg deposit is characterized by a complex mineralisation, distributed in six ore horizons. In spite of the uniformity of the ore mineralization, differences in mineralogy, trace element geochemistry of sphalerite, and sulfur isotopes of sulfides are observed in dependence of the stratigraphic position and the structural setting of the mineralisation (Table 1). Geochemical data, e.g. Ga/Ge-ratio of sphalerite, indicate a leaching temperature around 100°C. The burial temperature of Carnian sediments at Bleiberg is estimated with ca. 130°C (Rantitsch 2001).

Ore horizon	Metal Zn+Pb mio t	Zn/Pb	Gangue	Ge (ppm)	$\delta^{34}\text{S}\%$ sulfides	$\delta^{34}\text{S}\%$ barite
3 <sup>rd</sup> Cardita	0.1	6/1	Ba, F		-22.1 to -15.1 (19)	15,3 to 16,3 (2)
2 <sup>nd</sup> Cardita	Subeconomic		Ba, F		-19.3 to -5.0 (5)	12.1 to 14,8 (2)
1 <sup>st</sup> Cardita	0.2	8/1	F	340	-31.9 to -13.7 (44)	
Crest	0.5	6/1	F	160	-31.9 to -10.2 (29)	
Erzkalk	1.5	1/1 to 10/1	Ba, F	180	-27.0 to -3.0 (181)	12.0 to 17,1 (27)
Maxer Baenke	0.1	8/1	F	550	-31.6 to -13.7 (48)	

Table 1: General characteristic (F=fluorite, Ba=barite, n=number of samples) of the Bleiberg ore horizons (Cerny 1989, Schroll 1996).

348 sulfur isotope data from the Bleiberg deposit, obtained during thirty years of exploration, are available for this study. The sulfur isotope distribution of the Bleiberg deposit is shown in Tab. 1 and Fig. 1. The  $\delta^{34}\text{S}$ -values of sulfides (n=303) display a wide variation from -3.0 (ZnS) to -31.6 (PbS). Three populations of  $\delta^{34}\text{S}$ -mean values around  $\delta^{34}\text{S}$  -7, -17 and -25 ‰ are identified. The  $\delta^{34}\text{S}$ -values of barite (n=28) vary between 12.0 and 17.1‰ (mean 14.7‰). An isotopic equilibrium between the mineral phases is not recognisable.

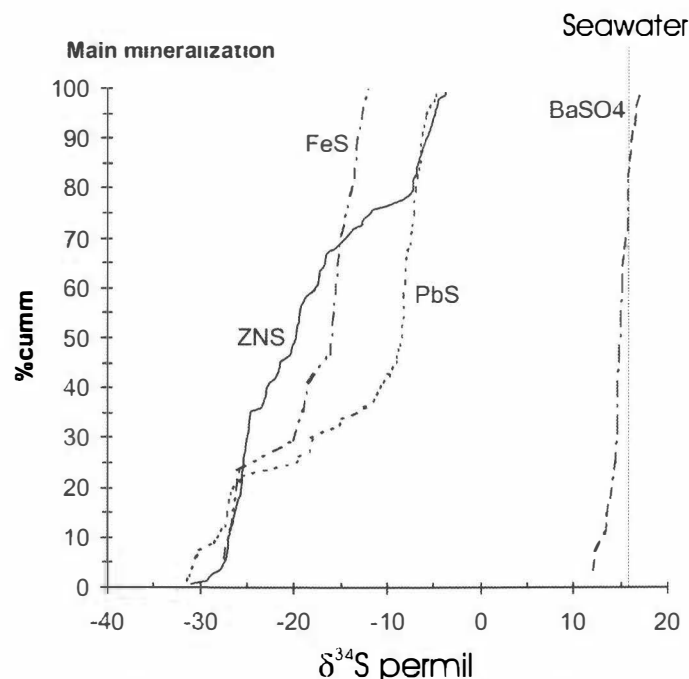


Figure 1. Sulfur isotope distribution in the Bleiberg deposit.

The  $\delta^{34}\text{S}$ -values of barite indicate precipitation of sulphate sulphur from the coeval seawater and evaporates of the Carnian stage (16‰). Main source of sulfidic sulfur is the coeval seawater produced by bacterial activity (Kucha et al 2002). Stratiform mineralizations show highly depleted sulphur (~-25‰) corresponding with the difference  $\Delta\delta^{34}\text{S}\%$  (sphalerite) –  $\Delta\delta^{34}\text{S}\%$  (seawater) of ~-41‰ and with bacterial sulphate reduction (BSR) in an open system.

The bacterial activity is confirmed by optical and instrumental methods (Kucha et al. 2001). The lightest sulphur (-31.6‰) is reported from late stage stalactitic botryoidally sphalerite. The origin of the sulfur isotope population which is characterized by a broad peak at -17‰ is multimodal: BSR, of pre-existing sedimentary iron sulphide or ore sulphide, mixing with hydrothermal sulphur (<-10‰) dominate in discordant ore structures. The hydrothermal sulfur probably originates from sedimentary iron sulphides of the basement or its cover. Sulphur isotope patterns of other carbonate-hosted Pb-Zn deposits in the Alps and anywhere support this assumption.

The detection of bacteriogenic activities during syndiagenetic sedimentary processes in sulphides from the most important ore horizons at Bleiberg deposit excludes the MVT-model, and confirms the model of Mid-Triassic age. The proposed model for the Bleiberg deposit corresponds with the interpretation of sulfur isotopes of the (Irish type) Lower Carboniferous giant lead-zinc deposit Navan in Ireland (Fallick et al. 2001).

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## New applications of hydrogen isotopes in geo- and biochemistry

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In spite of the enormous hydrogen isotope fractionations that occur in nature, the applications of hydrogen isotope geochemistry have been limited, in part due to the difficulty in making the isotopic analyses. However, new continuous flow analytical techniques, developed in the last several years, have made analyses vastly easier and less time consuming than those in the past. Much smaller amounts of material can be analyzed with a minimum of sample preparation. As a result, large number of analyses can be made in a relatively short time. In this communication, I present a number of varied applications of hydrogen isotope geochemistry, archaeology and ecology in order to illustrate the types of problems that can be addressed.