

## P-T-X PARAMETERS AND C,O-ISOTOPE COMPOSITION OF MAGNESITE- AND SIDERITE-FORMING FLUIDS IN HYDROTHERMAL DEPOSITS OF THE WESTERN CARPATHIANS

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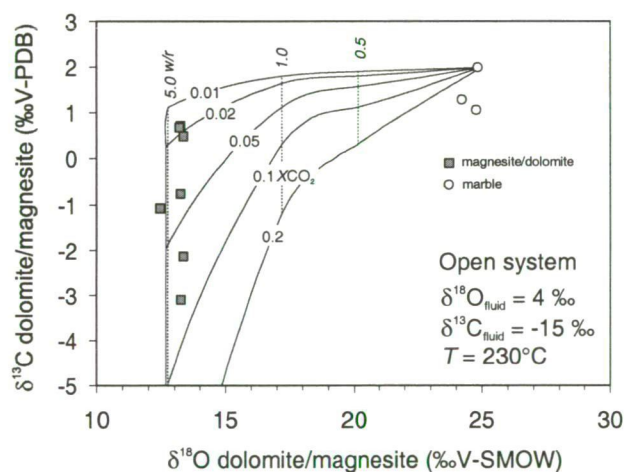
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Metasomatic and vein deposits of Fe-Mg carbonates belong to economically most important raw materials in the Western Carpathians. The hydrothermal deposits occur predominantly in the Carboniferous and Lower Palaeozoic low-to-medium grade metasediments of the Gemericum and Veporicum tectonic units. Average annual production of coarse-grained (sparry) magnesite is recently around 0.8-0.9 million metric tonnes (Mt) of concentrate (Grecula et al., 2000; Csikósová et al., 2000) and total assumed resources correspond to ~103 Mt (Grecula, 1995). A total of 683 siderite veins and metasomatic bodies has been mined continuously since stone and bronze ages (Chovan et al., 1994; Grecula, 1995), but the exploitation is now ceasing for economical reasons.

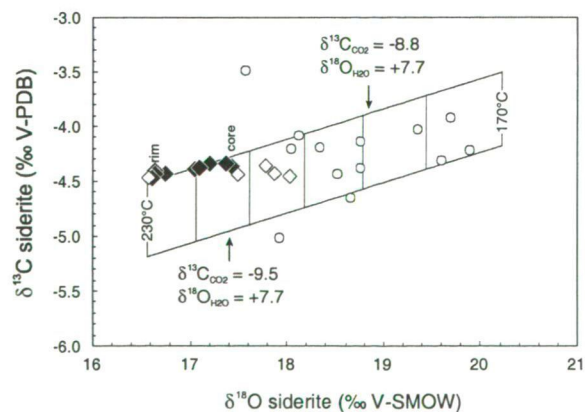
Origin of the magnesite and siderite deposits has been revisited using new fluid inclusion and stable isotope data. Primary fluid inclusions in metasomatic Mg-carbonates (dolomite, magnesite) contain low-to-moderately saline aqueous solutions (1-8 wt. %), with locally increased and variable CO<sub>2</sub> contents (<32 mole %). Fluid inclusions with the variable ratios of water- and CO<sub>2</sub>-rich phases trapped an immiscible fluid at 230-240°C and ~50 MPa. In contrast, siderite contains medium-to-high saline (17-35 wt. %) aqueous solutions and CO<sub>2</sub> contents are considerably lower, reaching up to 1.8 mol. % CO<sub>2</sub>. Crystallisation temperatures range between 145-290°C. Fluid pressures have tended to increase from ~50 MPa during crystallisation of siderite veins up to 2 kbars during the precipitation of siderite crystals in drusy cavities.



**Fig. 1.** Alteration model (Zheng, Hoefs, 1993) applied to the Burda magnesite deposit.

Covariations of stable isotopes are suggestive of different precipitation mechanisms for the magnesite and siderite deposits. Metasomatic Mg-carbonates show large carbon isotope variations accompanied with less extensive changes in oxygen isotope ratios (Fig. 1). The covariation was interpreted as reflecting high fluid/rock ratio and low concentration of CO<sub>2</sub> (several mole %) in the aqueous fluid. Assuming similar fluid parameters for all deposits, the temperatures of 190-240°C and 330-380°C have been estimated for the deposits hosted in Lower Carboniferous strata of the Gemericum unit and those located in the Lower Palaeozoic sediments of the adjoining Veporicum unit, respectively. The temperatures are consistent with those derived from Na/K ratio in fluid inclusion leachates, indicating that the fluids have been equilibrated with feldspar-bearing rocks prior to the Mg-

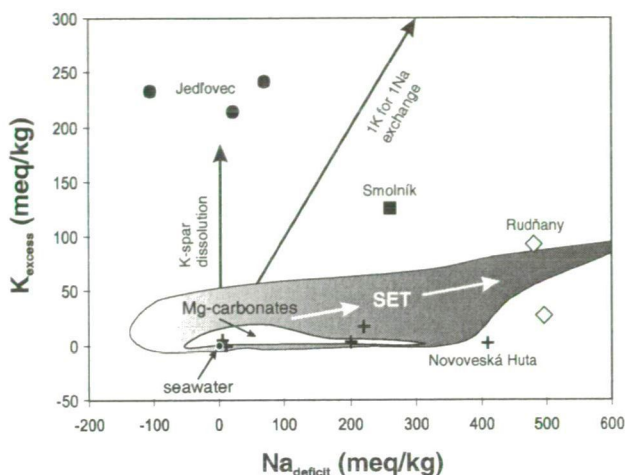
metasomatism.



**Fig. 2.** Isotope composition of siderite-forming fluid in the Rudnany ore field derived from the model of devolatilisation-absent Rayleigh precipitation (Zheng, 1990), with H<sub>2</sub>CO<sub>3</sub> as the dissolved carbonic compound in the aqueous solution, and temperatures constrained by fluid inclusions. Open circles – veiny siderite from the whole Rudňany ore field, open and solid diamonds – drusy siderites from cavities in the veiny siderite.

Contrasting with the magnesite deposits are large variations in δ<sup>18</sup>O accompanied with almost fixed δ<sup>13</sup>C in the siderite veins (Fig. 2). The trend has been interpreted to reflect increasing temperature, absence of CO<sub>2</sub> devolatilisation and low fluid/rock ratio (Hurai et al., 2002). Temperatures derived from K/Na ratios in leachates are consistent with those indicated by fluid inclusions.

Solute chemistry data on fluid inclusion leachates from the magnesite and siderite have revealed large enrichment in Br (Cl/Br molar = 77-416) compared to seawater (Cl/Br molar ~ 650), which is recently in geological literature attributed to residual brine originating in evaporated marine basins. Variable Na<sup>+</sup> contents compared with negligible K<sup>+</sup> variations in the magnesite-forming fluids are consistent with the seawater evaporation trendline (SET). The data for siderite, however, plot close to and above the SET, most likely due to more extensive interaction and cationic exchange reactions with country rocks at lower fluid/rock ratio (Fig. 3). Enrichment in Ca of the siderite-forming fluids might be due to dissolution of carbonate cement in the surrounding rocks.



**Fig. 3.** K/Na excess/deficit plot for fluid inclusion leachates from hydrothermal Fe-Mg carbonates of the Gemeric unit. Shaded area – seawater evaporation trend (SET), crosses – the Novoveska Huta siderite deposits.

According to the alteration model (Fig. 1),  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values of the fluid parental to metasomatic Mg-carbonates are between 4-5 ‰ V-SMOW. The model does not allow recalculation of the  $\delta^{13}\text{C}_{\text{CO}_2}$  values, which, however, must have been lower than -3 ‰ V-PDB. The fluid/rock ratios have been greater than 4 in open or closed systems.

Isotopic composition of the siderite-forming fluid has been inferred using precipitation model (Fig. 2). The  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values are almost uniform, ranging  $8 \pm 0.6$  ‰ V-SMOW in the whole Gemeric unit, except for the Novoveská Huta deposit, where the value of  $4.3 \pm 0.2$  ‰ has been estimated.

The  $\delta^{13}\text{C}_{\text{CO}_2}$  values tend to decrease from -8 ‰ in the north to -12 ‰ V-PDB in the southern part of the Gemeric unit. The calculated  $\delta^{18}\text{O}_{\text{fluid}}$  values are attributed to formation water enriched in  $^{18}\text{O}$  during isotopic exchange with crustal rocks at low fluid/rock ratios. The  $\delta^{13}\text{C}_{\text{fluid}}$  values probably correspond to a mixture of  $\text{CO}_2$  from dissolved matrix carbonates and that liberated by thermal decarboxylation of organic acids (acetates), which normally occur in formation waters (Hurái et al., 2002).

High pressures of the siderite-forming fluids (up to 2 kbars) must be linked with a deep circulation (at least ~4-8 km) of the basal brines derived primarily from marine water, but significantly modified by interaction with low-to-medium grade Palaeozoic rocks at low fluid/rock ratios. An anti-clockwise crystallisation *PT* path inferred from fluid inclusion and stable isotope data is inconsistent with the extensional tectonic regime during Permo-Triassic rifting. More likely, the progressively increasing fluid pressures and temperatures could be attributed to a compression and crustal thickening during Jurassic subduction.

The magnesite predates crystallisation of siderite, as evidenced by field observations, documenting intersection of the metasomatic Mg-carbonate bodies by siderite veinlets. However, siderite veins at Novoveska Huta, penetrating the Permo-Triassic sediments in the northern Gemericum, might be contemporaneous with the Mg-metasomatism in the underlying Carboniferous sequences, because of similar  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values (4-5 ‰) of the parental fluid for both mineralisations. This would constrain also a post-Triassic age of the sparry magnesite deposits in the Western Carpathians.

## References

- CHOVAN, M., HABER, M., JELEN, S., ROJKOVIC, I. (1994) Ore textures in the Western Carpathians. Slovak Academic Press, Bratislava, 219 p.
- CSIKÓSOVÁ, A., NOVEK, Z., KAMENÍKOVÁ, K. (2000) Position of the Slovak magnesite on world market. *Mineralia Slovaca*, **32**, 530-532.
- GRECULA, P. (1995) Deposits of mineral resources of the Slovenské rudohorie Mts. *Mineralia Slovaca – Monograph, Geocomplex*, Bratislava, 829 p.
- GRECULA, P., RADVANEC, M., NÉMETH, Z. (2000) Magnesite and talc mineralization in Slovakia. *Mineralia Slovaca*, **32**, 533-542.
- HURAI, V., HARCOVA, E., HURAIKOVA, M., OZDIN, D., PROCHASKA, W., WIEGEROVA, V. (2002): Origin of siderite veins in the Western Carpathians I. P-T-X- $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$  relations in ore-forming brines of the Rudnany deposits. *Ore Geology Reviews*, **21**, 67-101.
- ZHENG, Y. F. (1990) Carbon-oxygen isotopic covariation in hydrothermal calcite during degassing of  $\text{CO}_2$ . *Mineralium Deposita*, **25**, 246-250.
- ZHENG, Y. F., HOEFS, J. (1993) Carbon and oxygen isotope covariations in hydrothermal calcites. Theoretical modelling on mixing processes and application to Pb-Zn deposits in the Harz Mountains, Germany. *Mineralium Deposita*, **28**, 79-89.