Available online at www.sciencedirect.com
ScienceDirect

Russian Geology and Geophysics 52 (2011) 1474–1490

RUSSIAN GEOLOGY AND GEOPHYSICS

www.elsevier.com/locate/rgg

Fluid inclusion and stable C-O isotope constraints on the origin of metasomatic magnesite deposits of the Western Carpathians, Slovakia

V. Hurai [a,*], M. Huraiová [b], P. Koděra [c], W. Prochaska [d], A. Vozárová [b], I. Dianiška [e]

[a] *Geological Institute, Slovak Academy of Sciences, Dúbravská cesta 9, P.O. Box 109, 840 05 Bratislava, Slovakia*
[b] *Department of Mineralogy and Petrology, Comenius University, 842 15 Bratislava, Slovakia*
[c] *Department of Economic Geology, Comenius University, 842 15 Bratislava, Slovakia*
[d] *Institut für Geowissenschaften, Montanuniversität Leoben, 8700 Leoben, Austria*
[e] *Mierová 16, 048 01 Rožňava, Slovakia*

Received 17 February 2011; accepted 5 April 2011

Abstract

Primary fluid inclusions in metasomatic magnesite deposits hosted in Palaeozoic basement of the Western Carpathians are filled with of low-to-moderately saline aqueous solutions, with locally increased CO_2 concentrations (up to 34 mol.%). Brine inclusions with up to 42 wt.% of dissolved salts are less frequent. K/Na ratios in the fluid inclusion leachates indicate formation temperatures between 180–310 °C in the Gemeric unit and 230–300 °C in the Veporic tectonic unit.

Carbon isotopes in metasomatic magnesite and dolomite show larger spread than those of oxygen. In some deposits, the $\delta^{18}O$ values are almost fixed in various generations of the metasomatic Mg-carbonates, while $\delta^{13}C$ values vary within several ‰. The C, O-isotope covariation reflects low concentrations of CO_2 (less than several mol.%) in the aqueous fluid precipitating the Mg-carbonates in an open hydrothermal system and high fluid/rock ratios ($w/r > 5$). Calculated $\delta^{18}O_{fluid}$ values between 2 and 10‰ (V-SMOW) indicate isotopic exchange of the carbonate-precipitating fluid with crustal silicate rocks and/or marine carbonates at increased temperatures. Calculated $\delta^{13}C_{fluid}$ values between –5 and 3‰ are thought to reflect dissolution of the metasomatised carbonate as well as the escape of lighter carbon isotope during the CO_2 degassing.

Mg-carbonate-precipitating fluids typically contain increased Br-concentrations resembling the halite-fractionated residual brines originated by seawater evaporation. However, extent of the Br-enrichment substantially exceeds the buffering capacity of the seawater evaporation and it is even greater than that in the spatially associated siderite vein- and replacement-type deposits. Apart from the seawater evaporation, superimposed leaching of the organic matter from marine sediments probably played important role. This mechanism has, however, little effect in open hydrothermal systems. Hence, mechanism of the aditional Br-enrichment of the magnesite-forming fluids remains unknown.

The observed stable isotope record is a result of Alpine hydrothermal processes as evidenced by coarse-grained dolomite with alpine-type mineral assemblage (rutile, apatite, zircon, muscovite-phengite) identified also in the spatially associated siderite vein- and replacement-type deposits. Another evidence for the Alpine origin are frequently observed primary CO_2-rich aqueous inclusions, up to 50 μm in diameter, which could not survive the Early Cretaceous Alpine metamorphic overprint, as well as different covariation of stable isotopes in siderite deposits, where larger oxygen isotope fluctuations are accompanied by less extensive carbon isotope fractionation. This indicates different precipitation mechanisms, i.e., CO_2-devolatilization in open system during Mg-metasomatism and devolatilization-absent precipitation of the siderite in a closed system triggered by rising temperature. The associated magnesite and siderite deposits may be co-sanguineous with respect to the presence of the evaporated seawater component in the ore-forming fluid, but they cannot be coeval owing to different composition of primary fluid inclusions, hydrologic regimes (open versus closed hydrothermal system) and precipitation mechanisms. The fluid inclusion and stable isotope evidence does not definitely discard genetic models, linking the Mg-metasomatism with infiltration of bitter brines along faults during Permo-Triassic rifting, but this process must have been entirely obliterated by the late Alpine (Cretaceous) hydrothermal activity along shear zones formed during middle-to-late Cretaceous transtension-extension of the orogenic wedge. The Permo-Triassic rift-related origin of the magnesite must cope with the problem of complete loss of pristine isotopic signature of the metasomatic Mg-carbonates during the superimposed Alpine hydrothermal activity, contrasting with none or negligible Alpine metamorphic/hydrothermal overprint of the spatially associated Fe-carbonate vein- and replacement-type deposits.

Keywords: fluid inclusions; magnesite deposits; Slovakia

* Corresponding author.
E-mail address: vratislav.hurai@savba.sk (V. Hurai)

1068-7971/$ - see front matter © 2011, V.S. Sobolev IGM, Siberian Branch of the RAS. Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.rgg.2011.10.015

Introduction

The Palaeozoic basement of the Western Carpathians contains numerous medium-sized deposits of coarse-grained (sparry) magnesite, which has become one of the most important mineral resources of Slovakia during the second half of 20th century. Average annual production of raw magnesite attained 1.2–1.6 million metric tones (Mt) in the period 1991–2003. Potential economic reserves are around 350 Mt and a total of 1600 Mt of raw magnesite was produced since the beginning of its exploitation at the outset of 20th century (Csikósová et al., 2000; Grecula et al., 2000).

Origin of the Carpathian magnesite deposits remains unresolved. Kužvart (1954), Trdlička (1959), Varček (1968), Varga (1970), Abonyi (1971), Abonyi and Abonyiová (1981) favoured a hydrothermal-metasomatic origin. Most authors invoked metasomatic Mg-rich fluids associated with magmatic intrusions (Kužvart, 1954; Trdlička, 1959; Varček, 1967) or metamorphic processes (Ilavský, 1957; Varček, 1968). The Mg-metasomatism was correlated either with Variscan (Ilavský, 1957; Kužvart, 1954) or Alpine processes (Abonyi, 1971; Slávik, 1967; Trdlička, 1959; Varček, 1968).

Ilavský et al. (1975, 1991), Turan and Vančová (1976, 1979), Turanová et al. (1996) proposed a syn-sedimentary chemogenic precipitation of magnesite during seawater evaporation. A sedimentary-exhalative deposition connected with submarine basic volcanism was also considered (Ilavský, 1979; Zorkovský, 1955). Some models assumed initially synsedimentary (chemogenic or sedimentary-exhalative) precipitation followed by reworking and metasomatism during superimposed metamorphism (Grecula et al., 1995; Ilavský et al., 1991; Turan and Vančová, 1979). Most recently, the Mg-metasomatism is attributed to hydrothermal-metasomatic replacement of marine reef carbonates by oxidizing brines, infiltrating the crystalline basement along rifts during Permian and Triassic times (Radvanec and Prochaska, 2001; Radvanec et al., 2004a,b).

Metasomatic magnesite of the Carpathian basement is believed to be cogenetic and coeval with spatially associated vein and metasomatic siderite and Fe-dolomite deposits (Radvanec et al., 2004a). The existing genetic model is identical with that proposed for the magnesite deposits of Eastern Alps, where an influx of ore-forming basinal brines is thought to be coincidental with the Late Permian–Early Triassic rifting (Ebner et al., 1999; Prochaska, 1999, 2001). Published fluid inclusion and stable isotope data on the Carpathian magnesite deposits (Huraiová et al., 2002; Koděra and Radvanec, 2002; Radvanec et al., 2004a,b; Vozárová et al., 1995) indicate strong metamorphogenic affinity of the ore-forming fluids, presence of various fluid types, including high-salinity brines and CO_2-rich low-salinity aqueous fluids.

This paper is aimed to provide review of fluid inclusion and stable isotope data published elsewhere (Huraiová et al., 2002; Koděra and Radvanec, 2002; Radvanec et al., 2004a,b; Vozárová et al., 1995), but new crush-leach and stable isotope analyses are also included. Temperature estimates based on fluid inclusion and cationic exchange thermometry will be presented. Halogen and alkali metal contents will be used to reveal possible sources of the ore-forming fluids. Thermometric and stable isotope data will be combined to calculate isotope composition of the magnesite-forming fluid and to correlate it with that precipitating spatially associated vein- and replacement-type siderite.

Geological background

The largest magnesite deposits of the Western Carpathians are aligned along the paleo-Alpine thrust boundary between the Gemeric and Veporic tectonic superunits (Fig. 1). Most important Gemeric magnesite deposits are hosted in the Upper Turnaisian–Viséan (Bajaník and Planderová, 1985; Planderová, 1982) Hrádok Formation, and the Upper Viséan–Serpukhovian (Kozur et al., 1976) Lubeník Formation. Lower Palaeozoic rocks of the Gelnica Group contain the second productive horizon of the Gemeric unit with the Gemerská Poloma talc–magnesite deposit (also called Dlhá Dolina) and smaller occurrences near Henclová, Vlachovo and Mníšek nad Hnilcom villages. Mg-carbonates occur here in volcanic-sedimentary complexes composed of black shales, chlorite–sericite schists, metarhyolites, basic pyroclastics and porphyroids of the Bystrý Potok and Vlachovo Formations (Grecula et al., 1995; Tréger et al., 2004). Structural characteristics, geological environment and reserves of some important Carpathian magnesite deposits mentioned in this paper are summarised in Table 1.

The Gemeric magnesite deposits are usually composed of fine-grained layers of black, graphite-pigmented diagenetic dolomite I in outer parts of carbonate lenses embedded within black shales and basic volcanoclastics (Fig. 2). The dolomite I encloses relics of unaltered limestone or dolostone. Metasomatic, coarse-grained dolomite II occurs together with metasomatic magnesite. The dolomite II occasionally forms euhedral crystals in open cavities. The metasomatic dolomite II is crosscut by dolomite III veins. Rhombohedral crystals of dolomite IV (also called horse-teeth) are interpreted as infillings of contraction vugs during metasomatic replacement. Veins of dolomite V sometimes associated with quartz fill NNE–SSW-oriented cracks. Transparent, pink and red drusy dolomite VI grows in cavities of the dolomite V as the last carbonate generation. In some deposits, veins of dolomite III crosscutting the dolomite II and IV types exhibit signs of antitaxial growth, with columnar crystals oriented perpendicularly to the vein direction (Fig. 3, *a*). Euhedral pinolitic crystals and crystalline aggregates embedded in the diagenetic dolomite I represent the earliest magnesite generation. Coarse- and medium-grained metasomatic (sparry) magnesite II forms euhedral crystals in some open cavities. Veins of magnesite III are composed of columnar and elongated grains oriented perpendicularly to the vein direction (Abonyi and Abonyiová, 1981; Trdlička, 1959).

Except for quartz, minerals other than Mg-carbonates are rare. Quartz occurs as discrete lenses and anhedral grains enclosed in Mg-carbonates, or veins intersecting the “sparry”,