

Genetic considerations for the L. Cambrian(?) Rubian magnesite deposit, Galicia, Spain

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ABSTRACT : The Rubian sparry magnesite deposit (NW Spain) consists of an up to 17 m-thick succession of alternating cm- to dm-thick sub-horizontal beds. The deposit is located within a thick sequence of Variscan (L. Cambrian) carbonate/siliciclastic metasedimentary rocks metamorphosed under low- to medium-grade conditions. Combined geochemical, mineralogical, textural and fluid inclusion evidence point towards formation of magnesite by hydrothermal/metasomatic replacement of pre-existing dolostone although this interpretation conflicts with stratigraphic and paleogeographic evidence, which could support a sedimentary/diagenetic formation model for the magnesite deposit. Fluid inclusion data point out to NaCl-CaCl₂(±MgCl₂) mineralising aqueous brines similar to evolved basinal brines, depositing magnesite at minimum temperatures 170±15°C.

1 INTRODUCTION

According to geological setting, magnesite deposits are classified in the following major groups (Pohl and Siegl 1986; Aharon 1988; Pohl 1989, 1990; Wedzestein 1989; Stamatakis 1995; Harben and Kuzvart 1997): I) Sparry magnesite hosted in carbonate rocks of Archean-Proterozoic and Palaeozoic age; II) Crypto crystalline magnesite hosted in ultramafic rocks; III) Fine-grained magnesite in Neogene to recent lacustrine sediments, sabkhas and playas.

Two main genetic theories exist for the origin of group I sparry magnesite deposits (Kralik et al. 1989; Ellmies et al. 1999; Melezhik et al. 2001; Lugli et al. 2000; 2002): (1) Diagenetic transformation of a Mg-rich protolith deposited under evaporitic conditions; (2) Replacement of carbonates due to interaction with metasomatic/hydrothermal fluids, occasionally related to metamorphic processes. This study deals with mineralogical and fluid inclusion data in an attempt to decipher the origin of the L. Cambrian sediment-hosted magnesite deposit of Rubian, Galicia, NW Spain, in relation to the present genetic theories.

2 GEOLOGICAL SETTING AND GENERAL FEATURES OF MAGNESITE

The Rubian magnesite deposit is located near Sarria in the south Galicia Region, NW Spain. It is included in the Variscan fold-belt in the Iberian Peninsula (Dallmeyer and Martínez García, 1990). The deposit is hosted within the "Caliza de Candana" which is part of a major sedimentary unit of L. Cambrian age (Walter 1968). The Rubian magnesite is hosted within hundred meters thick carbonate/siliciclastic metasedimentary sequence that has been deformed and metamorphosed under low- to medium-grade conditions (Suarez et al. 1990). The ore body consists of a series of alternating cm- to dm-thick sub-horizontal beds, up to 17 m thick; stylolite surfaces can be seen in magnesite beds. At the upper and lower limits, the magnesite rock gradually becomes dolomite-rich; and passes to micaschists and slates. Magnesite rock thickens eastwards passing to dolostone deposits displaying cross-stratification structures and laminated limestone marble with local slump beds. This lateral facies change conforms to a lithological zonation that has been suggested previously (Guillou, 1970) as representative of an initial carbonate ramp depositional framework.

3 RESULTS

3.1 Petrographic & SEM analysis

Based on colour variance and grain size, macroscopically, the magnesite ore-deposit is distinguished in four textural types: (1) Sparry yellowish-white magnesite; (2) Banded black/grey-white magnesite; (3) Banded rose-white magnesite; (4) Neo-formed transparent coarse-grained magnesite/ dolomite in veins.

Type 1 magnesite constitutes the major part of the deposit and is characterized by the presence of dolomite relics in magnesite crystals (Fig. 1). Magnesite crystals contain some CaO, and higher amounts of FeO than the dolomite relicts (Table 1). Sub microscopic lensoidal grains of evaporite minerals of Mg-Na-K-SO₄-Cl composition are also hosted in magnesite (Fig. 2). Late dolomite rhombs have been also observed in cleavage surfaces, at the expense of magnesite crystals. Type 2 is randomly developed throughout the deposit. The banded texture is defined by thin (< 1cm) rhythmically alternating of black/grey and white magnesite bands. Besides magnesite, dark bands contain Ba-mica, quartz and pyrite. Ba-mica occurs as dense aggregates of small tabular crystals lying parallel to banding. Type 3 is confined to maximum distance of ten meters from fault systems/surfaces. The rock is composed of subhedral to angular magnesite crystals that are variously replaced at sub-microscopic scale by neo formed quartz, ferroan dolomite and dolomite along micro-fissures, and grain margins. Quartz-filled sub microscopic fissures are also present. Subordinate

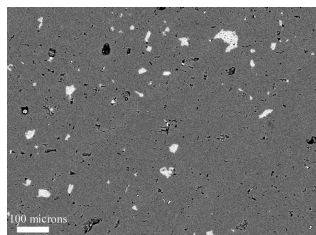


Figure 1. SEM image of unreplaced dolomite relics (white) within magnesite (dark).

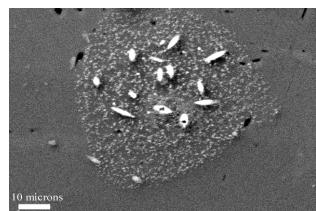


Figure 2. SEM image of solid inclusions of Mg-Na-K-SO₄-Cl evaporate minerals (white) within magnesite (dark).

pyrite -cubes and iron oxides occur either in dolomite or magnesite. Type 4 represents late dolomite/ magnesite formed in caves due to the action of groundwater.

3.2 Fluid inclusions

Magnesite Types 1 and 2 contain two types of fluid inclusions: (1) liquid-rich (<30% vapour) aqueous two-phase (L-V) inclusions, and (2) rare aqueous three- or multi-phase (L-V± S) inclusions, which contain one or two additional unidentified accidentally trapped solid(s). Sizes of the fluid inclusions range from 10 to 50 μm. The solid phases may be equant or sub-rounded, transparent prismatic (carbonate?) and, more rarely, opaque with metallic lustre (sulphides?). All-liquid inclusions were not found. Care was taken that all measured fluid inclusions conform to a primary origin. No differences in microthermometric measurements were observed between massive and banded magnesite and data are treated collectively.

First melting (T_{m1}) range widely between -42 °C and -65 °C with a clear peak centered on -60 °C and two minor peaks at -56 °C and -52 to -50 °C. Hydrohalite melting was the next observed phase change between -30 to -46.6 °C with a mean about -38±5 °C and a mode of -44 °C. Ice always melted after hydrohalite and was the last solid phase to melt. Final ice-melting temperature ($T_{m, ice}$) ranges from -1.9 to -42.9 °C.

Eutectic melting at -52±5 °C indicates that the inclusion fluids are CaCl₂-rich aqueous solutions (Goldstein and Reynolds, 1994). The ternary system CaCl₂-NaCl-H₂O has been chosen for all microthermometric data reduction as the best approach to the measured first melting temperatures.

Fluid inclusion bulk salinities (wt.% NaCl+CaCl₂ equiv.), NaCl (X_{NaCl}), CaCl₂ (X_{CaCl2}) and NaCl/(NaCl+CaCl₂) weight ratios were calculated in the ternary system CaCl₂-NaCl-H₂O from final ice-melting and final hydrohalite melting (Naden 1996). Bulk salinities range from 3.9 to 29.5 wt.% NaCl+CaCl₂. Moreover, fluid inclusions show variable NaCl/(NaCl+CaCl₂) ratios between 0.07 and 0.30. Calculated X_{NaCl} (range:0.6-7.8 wt.%; mean X_{NaCl} =2.3±1.2) versus X_{CaCl2} (range:2.90-27.4wt.%; mean X_{CaCl2} =16.5 ±8.7) data fall within a narrow range of X_{NaCl} (0.6 to <4 wt. %) and a highly variable range of X_{CaCl} values; the latter follow two branches, one higher- X_{CaCl2} (27.4 to ~15 wt. %) and one lower- X_{CaCl2} (3 to ~15 wt.%).

All studied fluid inclusions homogenised to the liquid at temperatures from 92 to 235 °C. However, all data with the exception of four homogenisation temperatures fall within a relatively narrow range between 135 and 175 °C. Bulk salinity versus homogenisation temperature data are presented in Figure 3.

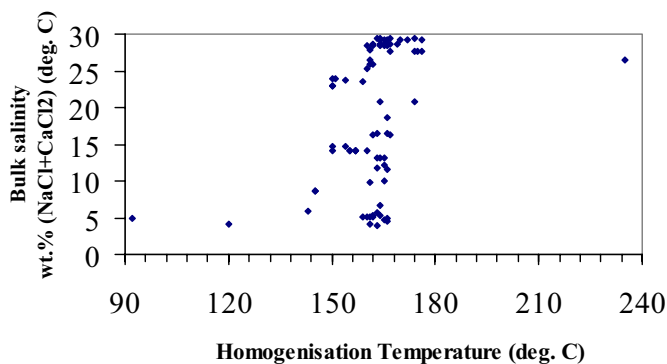


Figure 3. Fluid inclusion salinity vs. Th plot.

Table 1. Microprobe analyses of Rubian magnesite and dolostone samples, Galicia, NW Spain

| | RM1-1 | RM1-2 | RM1-3 | RM2-1 | RM2-2 | RM2-3 | RM3-1 | RM3-2 | RM3-3 | RM4-1 |
|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | MG | MG | MG | MG | MG | DOL | DOL | DOL | MG | DOL |
| FeO | 1.20 | 1.27 | 1.43 | 1.36 | 1.48 | 0.52 | 0.29 | 0.44 | 1.13 | 0.66 |
| CaO | 0.44 | 0.38 | 0.26 | ND | ND | 28.67 | 28.29 | 29.80 | ND | 27.09 |
| MgO | 45.91 | 45.26 | 44.88 | 44.92 | 43.89 | 19.66 | 19.97 | 19.95 | 44.02 | 18.51 |

Explanatory notes: RM1=black magnesite, RM2=yellow-white magnesite, RM3=rose magnesite, RM4= secondary dolomite formed in fissure fillings in magnesite. MG=magnesite, DOL=dolomite relics in magnesite

4 DISCUSSION

The presence of irregularly distributed dolomite relics within magnesite crystals seems to support that the formation of magnesite resulted from hydrothermal/metasomatic replacement of a dolostone precursor. All studied magnesites are richer in FeO than the dolomite relics (Table 1), suggesting that magnesite-forming fluids were carrying appreciable amounts of Mg and Fe.

In addition, magnesite occasionally host evaporitic micro-inclusions of K-Na-Cl-SO₄ composition, whereas these have not been detected in the dolomite relics and the spatially related dolostone, indicating that magnesite post-dates dolostone and probably regional metamorphism. The microthermometric features of the magnesite-forming fluids indicate that magnesite was deposited at minimum temperatures around 170+15°C from NaCl-CaCl₂(+MgCl₂) aqueous brines. The nearly vertical trend in the bulk salinity vs. homogenisation temperatures (Fig. 3) has been interpreted as representing mixing of CaCl₂-rich brines of high-salinity (25-30 wt.% NaCl+CaCl₂) CaCl₂-rich brines of low-salinity (<10 wt.% NaCl+CaCl₂) over a narrow temperature interval (Sangster et al., 1998). The high-salinity CaCl₂-rich brines may be compatible either with hot evolved basinal fluids identical to those responsible

for MVT-type deposits (e.g. Sangster et al., 1998), or external hot fluids that have interacted with evaporates (e.g. Xu, 2000). The origin of low-salinity fluids remains speculative at the moment; they could be caused by meteoric water interacting with evaporates (Crespo et al., 2002). Additional supportive evidence comes from the absence of all-liquid inclusions (indicative of initial low-T precipitation) associated with the two-phase inclusions; this coupled by the absence of any leakage and refilling trends (Goldstein and Reynolds 1994) in the salinity vs. homogenisation temperature plot (Fig. 3), argue against elevated temperature deep burial fluids being trapped in two-phase inclusions (Goldstein and Reynolds 1994). Consequently, homogenisation temperatures of fluid inclusions which can not be explained by a deep-burial origin could be thought to have been caused by rising hydrothermal fluids. In addition, variations in the NaCl/(NaCl+CaCl₂) (see above) of the fluid, coupled by variation of X_{NaCl} vs. X_{CaCl₂} (see above,) could be interpreted as a result of water/rock interaction and may be therefore consistent either with local dissolution and replacement of the host dolostone during magnesite mineralisation (Kontak and Sangster 1998) in accordance with mineralogical evidence, or fluid mixing.

Despite this line of evidence, the proposed model of replacement of carbonates by metasomatic/hydrothermal fluids does not clearly explain the

lithological zonation, i.e. banded magnesite – cross-stratified dolomite – laminated marble limestone, observed in the L. Cambrian carbonates of Rubian. Further investigation is needed to establish the best genetic model which, at the present state of knowledge, must be consistent with all of the geological facts and geochemical data (Schroll, 2002)

5 CONCLUSIONS

Combined mineralogical and fluid inclusion evidence point towards formation of magnesite by hydrothermal metasomatic/replacement of pre-existing dolostone from CaCl₂-bearing aqueous fluids expelled from sedimentary basins. However, the stratigraphic and paleogeographical evidence from the L. Cambrian carbonates in the region could suggest an alternative genetic model fitting the sedimentary/diagenetic origin of magnesite after a Mg-rich protolith. The study provides a new chance for progressing in the recurrent problem of the origin of sparry magnesite.

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