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Carbon and oxygen isotope constraints on the origin of magnesite deposits, North Evia (Greece)

by *Efthimios Gartzos*[1]

Abstract

The origin and temperature of formation of the cryptocrystalline magnesite deposits of North Evia have been studied from an isotopic point of view. Magnesites and dolomites have $\delta^{18}O_{(SMOW)}$ compositions ranging from 25.45‰ to 29.85‰ and $\delta^{13}C_{(PDB)}$ compositions ranging from –8.63‰ to –13.31‰. The isotopic compositions indicate a common origin for all types of magnesite deposits. The variations in isotopic compositions can be related to different generations of magnesite and reflect different temperatures of precipitation as well. Based on analogies with the Red Mountain magnesite district, a process is proposed in which the formation of magnesite results from mixing of ascending CO_2-rich fluids with descending meteoric water. Temperatures of magnesite formation, inferred from oxygen isotope data, are less than 60 °C.

Keywords: Magnesite deposit, fluid, carbon isotopes, oxygen isotopes, North Evia, Greece.

Introduction

North Evia is the major magnesite producing area of Greece. There have been numerous studies on the magnesite deposits of Evia and similar deposits all over the world; however, the majority of the previous work on magnesite deposits in ultramafic rocks has been essentially descriptive (e.g. FAUST and CALLAGHAN, 1948; BONDELOS, 1949; Petrascheck, 1964; CAPEDRI and ROSSI, 1973; DABITZIAS, 1980). These studies reveal a general controversy on the origin of magnesite, persisting even today, in which weathering versus hydrothermal origin is debated. Two independant studies on the magnesite deposits of Vavdos (Chalkidiki peninsula, northern Greece) were recently published by DABITZIAS (1981) and BURGATH et al. (1981). They suggested two different origins for the same magnesite deposits, as hydrothermal and weathering products, respectively. The magnesite problem becomes more difficult as some workers suggest that lens-like bodies and medium- to large-sized veins of magnesite which occur at deeper levels are hydrothermal; while isolated, near-surface nodules and sub-spherical bodies of magnesite are products of weathering (ILLIC, 1968). Suggested temperatures for the precipitation of magnesite range from 10 °C to 400 °C,

In the present study, the conditions of magnesite formation and the origin of the magnesite deposits in Northern Evia are investigated from a stable isotope point of view.

Geological situation

The entire northern portion of Evia is highly faulted due to extentional tectonics prevailing in the area during the last 13 million years (LE PICHON and ANGELIER, 1979). The magnesite deposits occur in ultramafic rocks (Fig. 1) and are closely associated with these faults. The moste important deposits are hosted by non or partly serpentinized rocks (dunites and harzburgites) which usually have been altered to "brown serpentinite" (= a rock composed mainly of carbonates, quartz, limonite, and serpentinite) at the sites of intense mineralization or towards the contacts of some veins (GARTZOS, 1986). The

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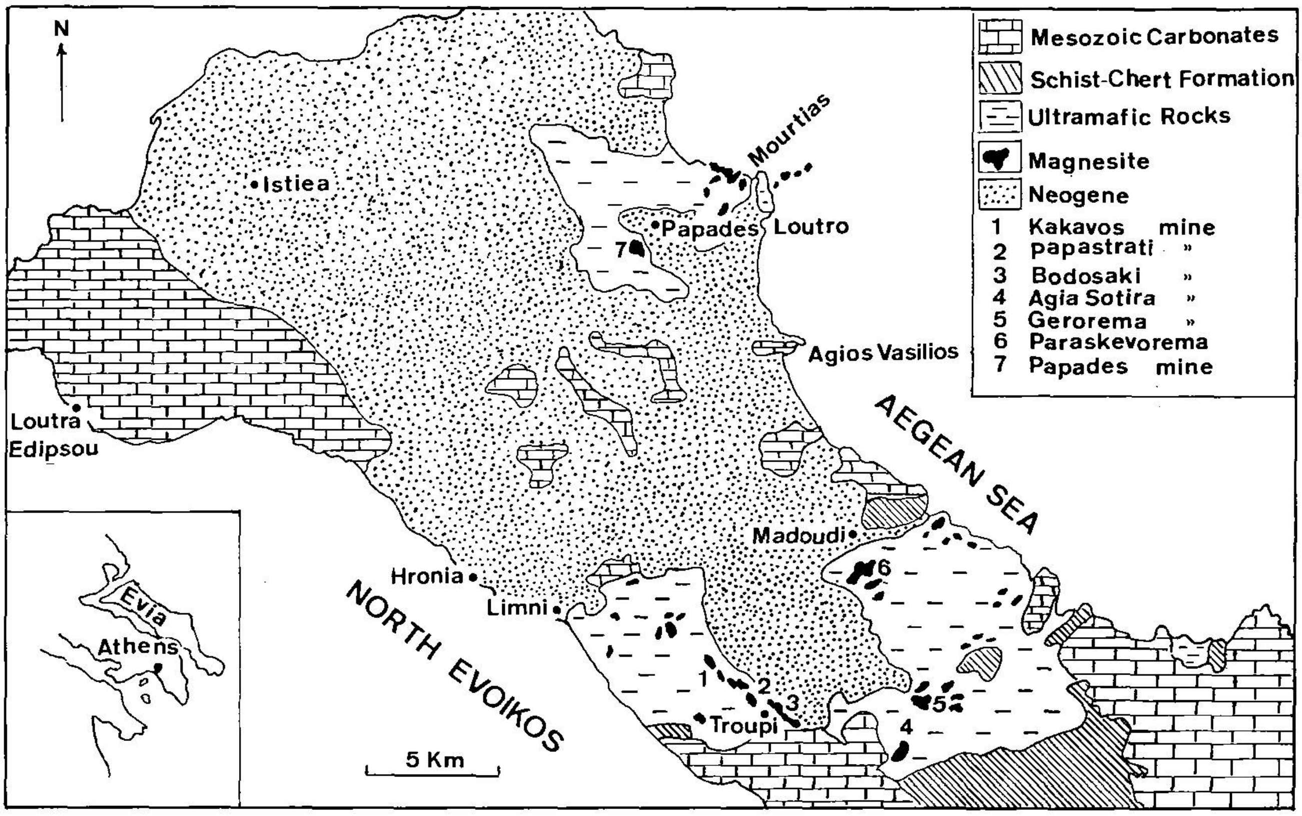

Fig. 1 Geological map of North Evia.

known deposits are restricted to shallow depths (maximum depth is about 200 meters) and the majority of veins are in a zone which roughly parallels the surface, thus indicating that a general zone of deposition prevailed during their formation.

Style of mineralization

Magnesite is cryptocrystalline with crystals 1–5 microns large. It is usually snow-white, shows conchoidal fracture, and resembles unglazed porcelain. On the basis of the style of mineralization three main types of magnesite deposits are distinguished:

a. Nodular aggregates of magnesite replacing the host rock. Very often, coalesced nodules form irregular to roughly subspherical bodies of magnesite, varying from a few cm to a few meters in diameter. They usually occur at higher levels in the mines (near-surface).

b. Fracture-filling magnesite which occurs as veins along fault or fracture surfaces. The veins which occur at the upper parts of the deposits (near-surface) are thin and usually form dense networks (stockwork-type deposits). Medium-sized veins (5–25 cm) and larger ones (25–100 cm) occur at deeper levels of the deposits. The majority of the veins have nodular structure.

c. Lens-like bodies of magnesite (1 to 4 meters wide and 5 to 12 meters long) formed by coalescence of nodules in dilatant zones of pinch-and-swell structures. They are located at the deeper levels in the mines.

Studied material and analytical procedure

Magnesite and dolomite associated with the ultramafic rocks and serpentinites of North Evia were sampled and analyzed for their ^{13}C- and ^{18}O-isotopic compositions. The modes of occurrence of the carbonate minerals include: 1. isolated nodules of magnesite (a-type in Table 1); 2. near-surface stockwork type deposits, medium size veins and thick veins of magnesite occurring at the deeper levels in the mines (b-type); 3. massive lens-like deposits (c-type); 4. fragments and nodules of magnesite occurring in the Neogene conglomerates, which are erosion products of magnesite deposits; and 5. dolomite formed by replacement of magnesite and serpentine.

All samples were reacted with phosphoric acid at 50 °C. The isotope ratios were determined on a VG Micromass 903 triple collector mass spectrometer at the stable isotopes laboratory of the ETH in Zürich. The samples were measured against the Carrara Marble laboratory

Tab. 1 Carbon and oxygen isotopic compositions of magnesites and dolomites from North Evia.

Nr.	Sample	Phase	Type of deposit	$\delta^{18}O_{PDB}$	$\delta^{18}O_{SMOW}$	$\delta^{13}C_{PDB}$
1	SOT.1.MG*	Magn.	C-medium size vein	-3.09	27.67	-10.57
2	SOT.1.MG**	Magn.	C-medium size vein	-3.09	27.67	-10.57
3	SOT.1B.MG	Magn.	C-thin vein	-1.69	29.12	-10.43
4	KAK.4.MG	Magn.	B	-4.05	26.42	-10.56
5	KAK.53.MG	Magn.	C-thick vein	-2.60	28.18	-11.07
6	KAK.2A.MG	Magn.	B	-5.29	25.40	-10.83
7	PARS.20MG	Magn.	A-nodular aggregate	-2.33	28.46	-9.98
8	PARS.23MG	Magn.	A-nodular aggregate	-0.98	29.85	-9.85
9	PARS.22.C	Magn.	A-nodule	-0.73	30.11	-9.87
10	PARS.21MG	Magn.	A-nodular aggregate	-1.03	29.80	-9.67
11	GER.11.MG	Magn.	C-medium size vein	-3.02	27.75	-11.50
12	PAP.6.MG	Magn.	A-nodule	-2.04	28.76	-12.35
13	PINK.MG	Magn.	A-nodule	-2.06	28.74	-13.31
14	MG	Magn.	C	-3.59	27.16	-9.87
15	MG^+	Magn.	C	-2.15	28.64	-10.90
16	MG^{++}	Magn.	C	-3.62	27.13	-9.29
17	LIMNI	Magn.	A	-3.33	27.43	-8.63
18	KAK.30.MG	Magn.	A-Neogene nodule	-7.27	23.37	-8.93
19	KAK.53.11x	Dol.	C	-5.08	25.62	-12.18
20	TR.6/4x	Magn.	B	-4.01	26.73	-11.93
21	TR7/3x	Dol.	B	-4.33	26.40	-10.64

A : Isolated nodules or nodular aggregates of magnesite.
B : Lens-like bodies of magnesite.
C : Fracture filling magnesite which occurs as veins along faults and fractures.

standard. Carbon isotope ratios of the carbonates are reported in per mil deviations relative to the Chicago PDB standard; whereas oxygen isotope ratios are given relative to SMOW.

The oxygen and carbon isotope compositions of the analyzed carbonates are presented in Table 1 and are shown graphically in Figure 2. Identical results were obtained from samples SOT.1.MG* and SOT.1.MG**, which represent two independent analyses of powder prepared from hand specimen SOT.1.MG and reacted separately.

Isotopic compositions of carbonates from North Evia

With the exception of one sample (No. 18, Table 1), the oxygen isotope compositions of the magnesites and dolomites range from 25.4 to 29.85‰, and carbon isotope compositions vary between –8.63 and –13.31‰. These compositions correspond to magnesite values which O'Neil and Barnes (1971) consider to represent isotopic equilibrium with their formation waters. Small isotopic variations in the North Evia carbonates occur over small distances and can be correlated with different generations of deposition. For example, a difference of 1.5‰ in both $\delta^{18}O$ and $\delta^{13}C$ is observed between the three samples MG, MG^+ and MG^{++} (Nos. 14–16 in Table 1) collected from the same outcrop over a distance of a few tens of centimeters. Multiple generations of magnesite formation is also substantiated by structural evidence in the field. However, larger isotopic variations occur on a regional scale and can be correlated with different types of magnesite deposits (Fig. 2).

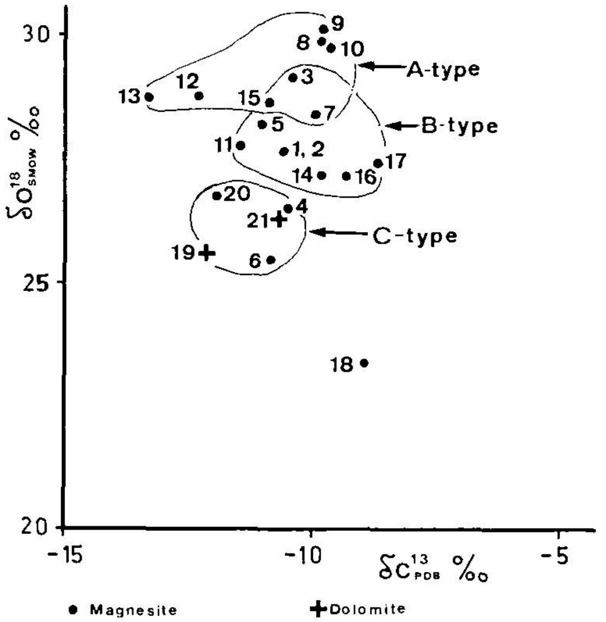

Fig. 2 Plot of $\delta^{18}O$ vs. $\delta^{13}C$ for the carbonates of this study.
A-type: Isolated nodules or nodular aggregates of magnesite occurring at the upper parts of the mines (near-surface). B-type: Fracture-filling magnesite which occurs as veins. C-type: Lens-like bodies of magnesite located at the deeper parts in the mines.

Sample KAK.30.MG (No. 18 in Table 1) is the most depleted in ^{18}O and the least depleted in ^{13}C. This sample is a magnesite nodule which was found in the overlying conglomerates at Kakavos mine. Many similar magnesite nodules and fragments have been replaced by opal and indicate interaction with fluids (weathering fluids) which have probably changed the isotopic composition of the magnesite nodules occurring in the overlying conglomerates.

The scatter in isotopic compositions of the North Evia carbonates (Fig. 2) contradicts the presence of a large, underlying, isotopically homogeneous fluid reservoir which could feed all tectonically-related channelways through the ultramafic host rocks. Relevant to the observed variation in the carbonates is the study of the chemistry and isotopic composition of waters occurring in North Evia and other areas with magnesite bearing ultramafic rocks (Gartzos, 1986).

Water chemistry studies (Gartzos, 1986) reveal that the area in which magnesite occurs is an extensive tectonically-controlled mixing site of fluids with different chemical and isotopic compositions (Papastamataki and Leonis, 1982). At these sites, descending dilute aqueous fluids (local meteoric waters), driven by gravity, are mixed with ascending fluids driven by deep-seated heat sources. The ascending fluids include gases very rich in CO_2 and aqueous solutions more or less charged with various aqueous species which have chemical and isotopic composition similar to that of seawater. Similar mixing processes have been reported from the Red Mountain magnesite district in the Western United States, where present-day magnesite deposition is observed (Barnes et al., 1973). However, no direct precipitation of magnesite has been observed at the North Evia area.

Comparison between North Evia and the Red Mountain area

A number of comparisons can be drawn between North Evia and the Red Mountain magnesite district in the Western United States. North Evia and Red Mountain belong to similar geotectonic environments with compareable main rock units. The vein mineralogy, wall rock alteration, style of mineralization, as well as the oxygen and carbon isotope compositions of the magnesite deposites of the Red Mountain magnesite district are identical to those of North Evia (e.g. Bondelos, 1949; Gartzos, 1986). Many of the ultramafic rocks occurring in the Western USA have suffered the characteristic "silica-carbonate" alteration found in North Evia. In many places these altered rocks are the host rocks of mercury and magnesite deposits. In addition, the isotopic compositions of the local meteoric waters in these two areas are similar, as they have the same latitude and proximity to sea.

Magnesite deposition as a result of fluid mixing in the North Evia area is comparable with present-day carbonate deposition in ultramafic rocks of the Western USA (Barnes and O'Neil, 1969, 1971; Barnes et al., 1967, 1972, 1973, 1978). Barnes et al. (1973) have shown that the most interesting waters associated with magnesite formation are those high in CO_2 with Mg^{++} as the dominant cation. On the basis of the chemical and isotopic composition of these waters, Barnes et al. (1973) argue that metamorphic CO_2 was added to the local meteoric water.

Some speculations of the temperatures of precipitation of magnesite and dolomite in the area of Red Mountain and North Evia

If the $MgCO_3$–H_2O isotopic relations were known, the temperatures at which magnesite was deposited at North Evia and the equilibrium $\delta^{18}O_{H_2O}$-compositions could be estimated. Unfortunately experimental data are lacking; however, the ^{18}O-fractionation between hydromagnesite and water at 0 °C and 25 °C, determined by O'Neil and Barnes (1971), can serve as a crude guide for the magnesite-water system. $\delta^{18}O$-values for water (Fig. 3) in equilibrium with the North Evia magnesites at various temperatures have been estimated using the relationship:

$$10^3 \ln\left(\frac{1000 + \delta M}{1000 + \delta W}\right) = 2.73\,(10^6\,T^{-2}) + 0.44$$

where δM is the δ-value of hydromagnesite and δW is the δ-value of water (O'Neil and Barnes, 1971).

Local meteoric water from North Evia has a $\delta^{18}O$-composition of approximately –8‰ (Papastamataki and Leonis, 1982). The temperature of isotopic equilibrium between such water and magnesite would be lower than 15 °C (Fig. 3). Waters issuing from hot springs occurring nearby have chemical composition close to that of sea water and $\delta^{18}O$-values from approximately –2.0 to 0.0‰ (Gartzos, 1986; Papastamataki and Leonis, 1982). These latter waters give magnesite formation temperatures from 25 to 60 °C. Higher temperatures can only be inferred if a hypothectical metamorphic water of $\delta^{18}O_{H_2O}$ = 7‰ is considered (Fig. 3). Thus, assuming that the above approximation is correct and depending on the fluid (meteoric water vs. altered marine water), the isotopic data indicate that North Evia magnesite deposits were formed at temperature between 5 to 120 °C. Probably lower than 60 °C. Similar precipitation temperatures (lower than 100 °C) were inferred by O'Neil and Barnes (1971) for the formation of the Red Mountain magnesite deposits.

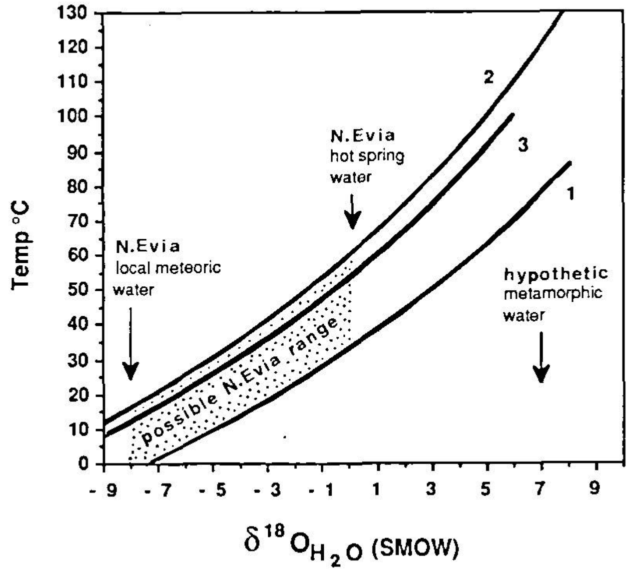

Fig. 3 Equilibrium T vs. $\delta^{18}O_{water}$ for carbonates from North Evia.
Curves (1) and (2): Water in equilibrium with magnesite having the highest (= 30.10) and the lowest (= 25.4) $\delta^{18}O$ value respectively. Curve (3): Water in equilibrium with dolomite (δ^{18} = dolomite = 26‰). Water compositions were estimated by extending the Dolomite-Water fractionation curve to lower temperature (Friedman and O'Neil, 1977) and by using the equation of O'Neil and Barnes (1971).

The oxygen isotope composition of water in equilibrium with dolomite at various temperatures can be estimated by using the compiled 1000 ln α vs. T curves for the fractionation of ^{18}O between alkaline earth carbonates and water (Friedman and O'Neil, 1977) and by extending the dolomite-water curve to lower temperatures. This is justified by the fact that oxygen isotope fractionation in other carbonate-water systems ($BaCO_3$–, $SrCO_3$–, and $CaCO_3$–H_2O) has been experimentally determined down to low temperatures, and all show parallel trends. Thus, by applying this relationship, the equilibrium temperatures for the precipitation of dolomite in North Evia have been determined for various water compositions (Fig. 3). For local meteoric water with $\delta^{18}O$ = –8‰, the equilibrium temperature is approximately 12 °C; whereas for hot spring water with $\delta^{18}O$ = 0‰, the temperature is about 53 °C (Fig. 3).

A temperature of approximately 50 °C is in agreement with the fact that dolomite is commonly associated with quartz at the North Evia area. All magnesite veins which show replacement of magnesite by dolomite are always associated with vugs lined by quartz. In contrast, at lower temperatures (during weathering), opal replaces magnesite clasts in the overlying Neogene conglomerates. This is analogeous to quartz deposition in active hydrothermal fields and in hydrothermal energy exploitation plants, where quartz precipitates at temperatures higher than at least 50 °C and opal at lower temperatures (e.g. Henley et al., 1984; Ellis and Mahon, 1977).

Summary and conclusions

Small isotopic variations in the North Evia carbonates occur over small distances and can be correlated with different generations of deposition. Multiple generations of magnesite formation is also substantiated by structural evidence in the field. Larger isotopic variations occur on a regional scale and can be correlated with the three types of magnesite deposits occurring at various depths. Isotopic fractionation increases from c-type to a-type deposit which is the most enriched in ^{18}O whereas their depth of occurrence in the mines increases from a-type to c-type. There is a partial overlap between a-type and b-type in both $\delta^{18}O$ values and depth of occurrence. The above relationship is interpreted to reflect increasing temperatures of precipitation with increasing depth of deposition. Consequently, all three types of magnesite deposits have a common origin. The variations in isotopic compositions can be related to different generations of magnesite and differences in temperature (depth) of precipitation.

One sample of redeposited nodular magnesite occurring in the Neogene conglomerates which shows a depletion in ^{18}O, but not in Carbon, is interpreted as a result of oxygen re-equilibration during weathering.

The type of magnesite occurrence, geotectonic environment, and isotopic composition of carbonates and meteoric water, as well as the water chemistries in North Evia are identical to those of the Red Mountain magnesite district of the Western USA. Thus, in analogy, a similar process is proposed for the North Evia deposits, in which the formation of magnesite results from mixing of ascending CO_2-rich fluids with descending meteoric water.

Precipitation temperatures depend on the isotopic composition of the fluid. Temperatures inferred for precipitation from fluids with isotopic compositions similar to local meteoric water are lower than those inferred for fluids enriched in ^{18}O. However, in any case they are lower than 120 °C, probably lower than 60 °C.

References

Barnes, I. and O'Neil, J.R. (1969): The relationship between fluids in some fresh Alpine type ultramafics and possible modern serpentinization. Western United States. Geol. Soc. Am. Bull. 80, 1947–1960.

Barnes, I. and O'Neil, J.R. (1971): Calcium-magnesium carbonate solid solutions from Holocene conglomerate cements and traver-tines in the Coast Range of California. G.C.A., 35, 699–718.

Barnes, I., Marche, Jr. and Himmelberg, G. (1967): Geochemical evidence of present day serpentinization. Science, 156, 830–832.

Barnes, I., Rapp, J. and O'Neil, J. (1972): Metamorphic assemblages and the direction of flow of metamorphic fluids in four instances of serpentinization. Contr. Min. Petr. 35, 263–276.

Barnes, I., O'Neil, J.R., Rapp, J. and White, D. (1973): Silica carbonate alteration of serpentine: wall rock alteration in mercury deposits of the Coast Ranges of California. Econ. Geol., 68, 388–398.

Barnes, I., O'Neil, J.R. and Trescases, J. (1978): Present day serpentinization in New Caledonia, Oman and Yugoslavia. G.C.A., 42, 144–145.

Bondelos, A.J. (1949): Geology of the Red Mountain magnesite district. Santa Clara and Stanislaus counties, California. Cal. Jour. Mines and Geology, 46, 223–278.

Burgath, K., Grissemann, C., Johannes, W., Jung, D., Knolke, H., Kockel, F., Makris, J., Mohr, M., Mussalam, K. and Raschka, H. (1981): On the genesis of magnesite deposits in Northern Greece. In: Proceedings of a Unesco International Symposium on Metallogeny of mafic and ultramafic complexes: The Eastern Mediterranean. Western Asia area and its comparison with similar metallogenic environments in the world. 3, 226–239.

Capedri, S. and Rossi, A. (1973): Conditions governing the formation of ophicalcites and listwanites (Central Evia, Greece). Bull. Geol. Soc. of Greece, v. 10, No. 2, 278–297.

Dabitzias, S. (1980): Petrology and genesis of the Vavdos cryptocrystalline magnesite deposits, Chalkidiki peninsula, Northern Greece. Econ. Geol., 75, 1138–1151.

Dabitzias, S. (1981): Additional evidence and a synopsis on the origin of the magnesite deposits in the Vavdos district, Northern Greece. In: Proc. of Unesco Int. Symp. (project 169), 3, 269–283.

Ellis, A.J. and Mahon, W.A. (1977): Chemistry and Geothermal Systems, Academic Press, 392 p.

Faust, G.T. and Callaghan, E. (1948): Mineralogy and petrology of the currant Creek magnesite deposits and associated rocks of Nevada. Geol. Soc. Am., Bull., 59, 11–74.

Friedman, I. and O'Neil, J.R. (1977): Data of Geochemistry, sixth ed., chapter KK: Compilation of Stable Isotope Fractionation Factors of Geochem. Inter., Geol. Sur., prof. paper 440–KK. Washington 1977.

Gartzos, E. (1986): On the genesis of cryptocrystalline magnesite deposits in the ultramafic rocks of North Evia. Ph. D. thesis. ETH Zurich.

Henley, R.W., Trusdell, A.H. and Barton, P. Jr. (1984): Fluid mineral equilibria in hydrothermal systems. Reviews in Econ. Geol., v., l., Society of Econ. Geol.

Illic, M. (1968): Problems of the genesis and genetic classification of magnesite deposits. Geologica Carpathica XIX, 1, Bratislava, 1968.

Le Pichon, X. and Angelier, J. (1979): The Hellenic arc and trench system: A key to the neotectonic evolution of the eastern Mediterranean area. Tectonophysics. 60, 1–42.

O'Neil, J.R. and Barnes, I. (1971): ^{13}C, ^{18}O compositions in some fresh-water carbonates associated with ultramafic rocks and serpentinites: W. U.S.A., G.C.A, 35, 687–697.

Papastamataki, A. and Leonis, K. (1982): Reports on geochemical exploration of geothermal fields: III. Area of Edipsos., I.G.M.E., Athens, Greece.

Petrascheck, W.E. (1964): Weitere Erkenntnisse über die Bildung der Lagerstätten des dichten Magnesits und des Meerschaums. Radex-Rdsch, 2, 103–108. 1964, Radenthein.

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