Genesis of Vein Stockwork and Sedimentary Magnesite and Hydromagnesite Deposits in the Ultramafic Terranes of Southwestern Turkey: A Stable Isotope Study

VEYSEL ZEDER,* MICHAEL J. RUSSELL,† ANTHONY E. FALLICK,
Isotope Geosciences Unit, Scottish Universities Research and Reactor Centre, East Kilbride, Glasgow G75 OQF, Scotland

AND ALLAN J. HALL
Department of Archaeology, University of Glasgow, Glasgow G12 8QQ, Scotland

Abstract

Vein stockworks and lacustrine developments of cryptocrystalline magnesium carbonates of Neogene and Quaternary age occur within the partially serpentinitized, discontinuous ultramafic belts of southwestern Turkey. They are comparable to the Neogene cryptocrystalline magnesite bodies elsewhere in the Alpine orogen to the northwest and southeast. Our previous work (Fallick et al., 1991) suggested that cool (≤100°C) modified meteoric water was the mineralizer, that ultramafic rock was the source of the magnesite, but that there were three separate sources of the (bi)carbonate. These sources were distinguishable by their stable isotope composition as follows: (1) low-temperature carbonate with δ18O(SMOW) values of ~36 per mil and δ13C(PDB) values of ~4 per mil, derived from atmospheric CO2; (2) moderate-temperature carbonate with δ18O(SMOW) values of +28 per mil and δ13C(PDB) values of ~15 per mil, derived by decarboxylation of organic-rich sediments; and (3) higher temperature carbonate with δ18O(SMOW) values of ~19 per mil and δ13C(PDB) values of ~3 per mil, assumed to have been generated by thermal contact metamorphism of Paleozoic marine limestone at depth. In general these magnesite deposits were found to fall into two groups, comprising carbonate generated on two mixing lines. The first group spanned the putative mixing line from the "atmospheric" source (1) to "organically derived" source of CO2 (2). The second group extended between atmospheric source (1) and the "thermal" source (3), although there were concentrations either around the atmospheric end, or precisely at the contact metamorphic end of the line.

In the present study we found that large stockwork deposits at Helvacıbaba and Koyakçı Tepe have δ18O(SMOW) and δ13C(PDB) values averaging ~12 and ~+27 per mil, respectively, indicating a derivation mainly by oxidation of organic-rich metasediments perhaps underthrust at depth (end-member 2), with some involvement of atmospheric carbon dioxide as bicarbonate in the circulating, hot, and modified meteoric water (end-member 1). Calcite veinlets in a meta-argillite of the Cambro-Ordovician Seydisehir Formation, most likely to have been underthrust beneath the stockworks, yielded δ18O(CPD) values of ~20 per mil, consistent with, though not proving, oxidized organic carbon being one of the sources of carbonate. The δ18O(SMOW) values of these same veinlet carbonates are also rather low (22‰), indicating precipitation from heated ground water, though their age is unknown.

The major stratiform magnesite deposit at Hırsızdere in the center of the Menderes graben has δ18O(CPD) and δ18O(SMOW) values averaging ~3 and ~25 per mil, respectively, and thus appears to be an example of the hydrothermal-sedimentary (i.e., exhalative) type (Ilich, 1968). In contrast, the hydromagnesite stromatolites presently growing in Salda Gölü (Lake Salda) are apparently developing at cool ground-water seepages. The gross morphology of the Salda Gölü stromatolites and the hydromagnesite sediments derived therefrom is reminiscent of that revealed in the Bela Stena magnesite pit in Serbia. These lacustrine deposits have mean δ18O(CPD) values of ~4 and ~2 per mil and mean δ18O(SMOW) values of ~36 and ~33 per mil, respectively, i.e., they both plot broadly over the atmospheric CO2-meteorite water field (end-member 1), consistent with microbially mediated precipitation at cool ground-water seepages in enclosed evaporating lakes.

Introduction

A number of explanations have been mooted for the genesis of vein, stockwork, and sedimentary developments of cryptocrystalline magnesite in ultramafic terranes. Although it is generally agreed that the source of the magnesite is the ultramafic rocks themselves (e.g., Barnes and O’Neil, 1969; Barnes et al., 1973, 1978; Dabitzias 1980, 1981; Burgath et al., 1981), the sources of the carbonate are disputed. The following various origins have been suggested: (1) atmospheric carbon dioxide (O’Neill and Barnes, 1971; Fallick et al., 1991), (2) decarboxylation of organic-rich sediments (Fallick et al., 1991; Brydie et al., 1993), (3) thermal decarbonation of limestone (Fallick et al., 1991), (4) soil-derived decomposition of plant material and surface weathering (Petrov, 1967; Lesko, 1972; Zachmann and Johannes, 1989), (5) regional metamorphic reactions at >300°C (Abu-Jaber and Kimberley, 1992), (6) volcanogenic sources (Ilich, 1968), (7) a deep-seated source (cf. Kreulen, 1980); or combinations of the above.

In our own previous contributions to the cryptocrystalline magnesite problem we concluded tentatively that combinations of three dominant sources of carbonate (1–3) could explain the isotopic make-up of the various massive cryptocrystalline magnesite deposits in Serbia, Bosnia, and Cyprus (Fallick et al., 1991; Brydie et al., 1993).

The present study of magnesite bodies in southwestern Turkey gives us the opportunity to extend our knowledge of
the types of cryptocrystalline magnesites characteristic of Alpine-type ultramafic complexes and to assess our models for their origin. As in our earlier studies we find that, on a plot of δ¹³C_PDB vs. δ¹⁸O_SMOW, each deposit occupies a restricted field. In general the hypotheses survive the tests, though oxidation of organic carbon in underthrust metasediments may be an important mechanism of carbon dioxide generation (Shock, 1988) rather than decarboxylation. Moreover, CO₂ volatilization, evaporation, and cyanobacterial depletion of ¹²C are complicating factors.

Geologic Environment

The Turkish magnesite deposits are hosted by extensive Alpine-type ultramafic rock outcrops and subcrops that comprise major ophiolite complexes. These Mesozoic peridotites and serpentinites are associated with pillow lavas, Upper Cretaceous radiolarian cherts and limestones, Cenozoic limestones, and recent alluvium (Sarp, 1976, Ketin, 1983). The ultramafic rocks were extensively disturbed by Alpine orogenic movements (Gedik, 1988). According to Erdem (1974), Sen-gör and Yılmaz (1983), and Collins and Robertson (1998), the ultramafic rocks were episodically emplaced in their present-day juxtapositions during the mid- and Late Cretaceous to the late Miocene. The obduction was a consequence of the partial closure of the Tethys ocean. Serpentinization of the ultramafic rocks in fault zones and along contacts with country rocks may have taken place before, during, and/or following emplacement by thrusting over Paleozoic and Mesozoic formations.

Extensional stresses have been operating in western Turkey since the Oligocene (Köçyigit 1984). These stresses resulted in the development of several rifts, such as the Büyük Menderes and Gediz grabens (Fig. 1; Cohen et al., 1995), and encouraged volcanism (Seyitoglu and Scott, 1991). Kissel et al. (1993) reported that part of western Turkey (the Isparta region) has been rotated clockwise up to 40° since the Oligocene. Western Turkey is still seismically active (Jackson and McKenzie, 1984; Köçyigit, 1984; Livermore and Smith, 1985; Udías, 1985).

Neotectonic activity results in the development of many springs, both cool and hot. Percolating water in a continent will generally have a meteoric origin (Garven, 1995). Large chemically deposited fresh-water carbonate deposits clearly require a meteoric water recharge (Fallick et al., 1991). The drive for the aqueous flow can be either artesian or thermal. In the latter case, heating of meteoric water takes place by interaction with hot rocks at depth, by exothermic reactions (Haack and Zimmermann 1996), and/or magmatic intrusions. In such a tectonically active area as western Turkey, the geothermal gradient would be expected to approach 35° to 40°C/km in places (Tezcan, 1979), that is, higher than the usual 25° to 30°C/km.
Cryptocrystalline magnesium carbonate deposits are especially concentrated in southwestern Turkey where late Cenozoic extensional tectonic regimes dominate (Fig. 1). They fall into the following two categories: vein stockwork and lacustrine deposits.

**Descriptions**

**Vein stockwork deposits**

The largest of the cryptocrystalline magnesite deposits is the presently exploited Helvacıbaba stockwork. It occurs in the serpentinitized Çayırbağ ophiolite in the Konya district (Figs. 2 and 3, Table 1; Ozcan et al., 1988, Güleç, 1991). Several magnesite pebbles were discovered in the conglomerate at the base of the lacustrine sequence overlying the stockwork. Above this conglomerate dolomite beds occur in what are otherwise calcareous Neogene lake sediments in this region (Fig. 3).

![Fig. 2. Geologic map of the Meram-Çayırbağ area, Konya (Altunel, 1963; Zedef, 1994).](image)

**Table 1. Cryptocrystalline Vein Stockworks**

<table>
<thead>
<tr>
<th>Deposit</th>
<th>Host</th>
<th>Style</th>
<th>Alteration</th>
<th>Tonnage (Mt)</th>
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<td>Helvacıbaba</td>
<td>Serpentinite</td>
<td>Stockwork</td>
<td>Carbonate and silica</td>
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</tr>
<tr>
<td>Koyakcı Tepe</td>
<td>Serpentinite</td>
<td>Vein stockwork</td>
<td>Carbonate</td>
<td>~40</td>
</tr>
<tr>
<td>Arapöner</td>
<td>Serpentinite</td>
<td>Vein stockwork</td>
<td>Carbonate and silica</td>
<td>~0.1 ?</td>
</tr>
</tbody>
</table>

**Fig. 2.** Geologic map of the Meram-Çayırbağ area, Konya (Altunel, 1963; Zedef, 1994).
The Koyakçı Tepe stockwork, 10 km to the south-southwest of Helvacıbaba, is almost as large (Fig. 2). Although both stockworks comprise a myriad of centimeter-sized veins and veinlets, in the latter some individual west-northwest veins reach a width of 4 m. The host rocks are carbonated around, and silicified above, both deposits.

Lacustrine deposits

Cryptocrystalline lacustrine deposits comprise the remainder of the magnesite or hydromagnesite resources. The largest of these is Hırsızdere, which lies in the Büyük Menderes rift, 7 km southwest of Bozkurt (Ilich 1974; Figs. 1 and 4). It is a working deposit comprising five magnesite beds in Pliocene lacustrine sediments. The thickest and purest magnesite bed lies directly upon carbonated serpentinites and incorporates pebbles of this footwall at its base.

The other large lacustrine deposit is still forming in Salda Gölü (Sarp, 1976; Kastens, 1991). This is a suitable environment for the development of both artesian flow and thermally driven hydrothermal convection. Although the area with the largest geothermal energy potential in Turkey is situated on the north side of the Menderes graben, at Kızıldere, ~90 km northwest of Salda Gölü, and there is evidence of Plio-Pleistocene hydrothermal activity just 10 km north-northwest as well as 20 km north of Salda Gölü, there are no signs of recent hot-spring activity within the immediate surroundings of the lake. The only veins we found consisted of lizardite. Thus, we favor the topographic drive of meteoric water through ultramafic coarse alluvium as an explanation for the Salda Gölü hydromagnesite deposit, as suggested by Braithwaite and Zedef (1994, 1996b; cf. Lur’ye and Gablina 1972). A geochemical model is outlined below.

Cool (~10°C) meteoric fluids, presumably charged with atmospheric and soil-generated CO2, flow along the base of the Salda River (Karakova Dere) and other smaller channels. There they react with lizardite (our X-ray diffraction analyses; eq 1) and harzburgite (eq 2) to dissolve Mg++ (Lesko, 1972):

\[ \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{H}_2\text{O} + 6\text{CO}_2 \rightarrow 3\text{Mg}^{2+} + 2\text{SiO}_2 + 6\text{HCO}_3^- \]  
(1)

\[ 10(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4 + 16\text{H}_2\text{O} + 32\text{CO}_2 + \text{O}_2 \rightarrow 16\text{Mg}^{2+} + 10\text{SiO}_2 + 2\text{Fe}_2\text{O}_3 + 32\text{HCO}_3^- \]  
(2)

The springs, bearing an average of 60 ppm Mg, emanate just from below the waterline. Presumably the springs also bear nutrients to the cyanobacteria colonizing the mixing zone. There are no visible outlets and the water level of the lake drops a meter or so over the summer. It has dropped several meters in living memory (Ahmet Koç, pers. commun., 1992) and about 30 m since deposition of the first hydromagnesite beach deposits mentioned above (Russell et al., 1999). As the lake lies at the head of the regional watershed, some loss through subsurface drainage channels, particularly through the Upper Cretaceous limestones comprising a sector of the east shore and bottom of the lake, is likely. Nevertheless, the forty-fold enrichment of Na (200 ppm), compared to the contributing cool springs (5 ppm), attests to the importance of evaporation (Russell et al., 1999). Also, evaporation of the lake water has enriched the magnesium content beyond the saturation point of both magnesite and hydromagnesite. Yet the Mg in the lake has only increased by a factor of five or so, from 60 to 300 ppm (Russell et al., 1999; fig. 10b). The missing Mg has been precipitated in hydromagnesite. The precipitation of the supersaturated hydromagnesite

This exposure, now filled in, lies approximately 30 m above the present lake level and about 2.5 km west-southwest of the living microbialites (Fig. 4). Although best developed at Koçaalda Burnu, the fossil to subfossil hydromagnesite microbialites occur discontinuously all around the lake (Fig. 5a, e, f). The largest growths are developed where valleys, dry in summer months, meet the shore.

As the presently forming hydromagnesite in Salda Gölü may provide the key to understanding some ancient lacustrine magnesite deposits, we examined the mechanism of generation and deposition in some detail.

Salda Gölü is in a region of tectonic extension (Sarp, 1976; Kastens, 1991). This is a suitable environment for the development of both artesian flow and thermally driven hydrothermal convection. Although the area with the largest geothermal energy potential in Turkey is situated on the north side of the Menderes graben, at Kızıldere, ~90 km northwest of Salda Gölü, and there is evidence of Plio-Pleistocene hydrothermal activity just 10 km north-northwest as well as 20 km north of Salda Gölü, there are no signs of recent hot-spring activity within the immediate surroundings of the lake.

The submerged portions of the otherwise white microbial hydromagnesite mounds are covered with light green, slimy cyanobacterial filaments (see underwater photographs in Beköz et al., 1997). An extensive outcrop (>200 × 100 × 1 m thick) of what appears to be beach deposits of hydromagnesite with layers of lizardite pebbles, trenched by the side of the road in 1997, leads into Salda Village from the southeast.

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The other large lacustrine deposit is still forming in Salda Gölü (Sarp, 1976; Çoban et al., 1995). It is composed of hydromagnesite. Although evaporation increases concentration to supersaturation, precipitation is brought about by microbes (Russell, 1993; Braithwaite and Zedef, 1994, 1996a, b; pace Schmid, 1987; Figs. 4 and 5). Fine particles derived from the erosion of the mounds are deposited between them to comprise fine, water-saturated muds (Fig. 6a).

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is brought about by cyanobacteria (Russell, 1993) and diatoms (Braithwaite and Zedef, 1994, 1996b), perhaps aided by associated anaerobic heterotrophs deeper in the mounds. Riding (1992) notes that cyanobacteria prefer alkaline conditions and that they precipitate carbonate in warm freshwater environments. Deposition is linked with the photosynthetic fixation of carbon from bicarbonate by the cyanobacteria (Burne and Moore, 1987) and the emission of hydroxyl (Thompson and Ferris, 1990):

\[ \text{hv} \]
\[ \text{HCO}_3^- + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2 + \text{OH}^- \]  

where \( \text{hv} \) represents a solar photon which energizes the reaction. The magnesium ion is both small and highly charged, i.e., it has high ionic potential. It is, therefore, strongly hydrated (Christ and Hostetler, 1970; Lippmann, 1973). This hydration not only allows supersaturation in aqueous bicarbonate fluids, it also leads to the precipitation of hydromagnesite rather than magnesite at low to medium temperatures (Sayles and Fyfe 1973), unless carbonate far exceeds magnesium concentration. In the latter case the \( \text{CO}_3^{2-} \) might displace the water dipoles at the crystal surface to become directly bonded to \( \text{Mg}^{2+} \), effecting the direct precipitation of magnesite (Lippmann, 1973). But at normal atmospheric pressure

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**Fig. 4.** Simplified geologic map of the area around Salda Lake. Karakova Dere (stream) drains into Salda Lake from the southwest. Surface flow takes place only after rain. Note that the Arapömer Deresi deposit lies in a separate watershed that drains to the north. Also shown is the small development of hydromagnesite in Akgöl and the present and past (Pamukkale and Kocabas) travertines developed on the northern margin of the Menderes graben.
Fig. 5. Hydromagnesite developments in Salda Gölü. a. Northwesterly prospect across the lake showing hydromagnesite developments on the beaches which otherwise comprise lizardite and harzburgite pebbles. b. View from east-southeast across Kocaadalar Burnu (peninsular) comprised of earlier hydromagnesite developments, beyond is the Karakova Dere estuary, and then the ultramafic surroundings; to the north of the peninsular are the presently growing microbial mounds. c. Residual hydromagnesite stromatolites on Kocaadalar Burnu having the appearance of dunes. d. Recently exposed hydromagnesite microbialites on the islands pictured in (b). The cauliflower-like structures pictured here are rising 3 m above the lake surface. e. Looking down on recently emergent microbialites (note centimeter scale). f. Close-up view of partially eroded stromatolites.
hydromagnesite precipitates from supersaturated solutions, thus:

\[ 5\text{Mg}^{2+} + 4\text{CO}_3^{2-} + 2\text{OH}^{-} + 4\text{H}_2\text{O} \rightarrow \text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}. \]  (4)

The carboxylate groups embodied in the polysaccharide sheaths of the cyanobacteria could provide the initial epitaxial nucleation sites for the precipitation of the magnesium ions in the waters seeping through the mounds (cf. Pentecost, 1978, 1995; Thompson and Ferris, 1990; Mann et al., 1993; and see Möller, 1989). In this case Mg\(^{2+}\) acts as the bridging cation from the carboxyl to the carbonate, the counter anion, in the mucilaginous exterior of the cyanobacterial mounds:

\[ \text{R.CO}O^{-} + \text{Mg}^{2+} + \text{HCO}_3^{-} \rightarrow \text{R.COOMgHCO}_3. \]  (5)

Following nucleation, continued deposition is encouraged by the increase in pH in the periplasm (eqs 3 and 4).

The Geochemist’s Workbench program REACT (Bethke, 1996) was used to examine the relationship between magnesium concentration and magnesite supersaturation (Fig. 7). When water is in equilibrium with atmospheric CO\(_2\), oversaturated in magnesite, and precipitating hydromagnesite, the computed pH is about 9 and the concentration of Mg\(^{2+}\) is only about 80 ppm. Higher concentrations require lower pH values at higher CO\(_2\) fugacities unless the solutions are supersaturated. Salda Gölü contains nearly four times this concentration of magnesium, yet has a pH of around 9 (Russell et al., 1999). Thus the lake water is also supersaturated in hydromagnesite. As we have seen, the reason for this is the polar bonding between the small, doubly charged Mg\(^{2+}\) ion with water molecules (Christ and Hostetler, 1970). The Mg/Ca ratio, at over 100 (Russell et al., 1999), is particularly high, an added impetus to the precipitation of hydromagnesite rather than magnesite (Müller et al., 1972).

Given the association between ultramafic rocks, Mg-rich springs, and lacustrine hydromagnesite demonstrated at Salda Gölü, we analyzed springs draining into Akgöl, an enclosed dry lake 15 km north-northeast, and of Salda (Fig. 4). These springs carried up to 170 mg/l Mg\(^{2+}\) and about 10 mg/l Na\(^+\) (Russell et al. 1999). The bed of this lake also proved to
Hydromagnesite is not a common mineral and, previous to these discoveries, unknown in large concentrations. O’Neil and Barnes (1971) hypothesize that hydromagnesite occurs as a result of Brucite weathering and Barnes (1971) hypothesize that hydromagnesite occurs as a product of serpentinite and brucite.

Idria and Red Mountain, United States, is the weathering product of serpentinite and brucite.

Travertine

Whereas the Salda Gölü magnesian carbonate deposits were, and are being, generated over cool seepages (Braithwaite and Zedef, 1994, 1996b), the travertine (calcite) deposits at Pamukkale, north of Denizli, are developed at hot springs (~60°C, Ford and Pedley, 1996) about 100 m above the Büyük Menderes rift floor on its northern scarp (Altunel and Hancock, 1993). We investigated and analyzed these deposits, as well as some Pleistocene travertines at nearby Koçağlı and Hancock, 1993). We investigated and analyzed these deposits, as well as some Pleistocene travertines at nearby Koçoğlu, to allow us to compare and contrast the stable isotope ratios of carbonates from this well-characterized system with Mg carbonates where genesis is not so clear.

Analytical Procedures

One hundred and twenty-two samples, representing five major carbonate deposits, several small associated developments, and six possible carbonate source rocks, were analyzed for their \( \delta^{13}C_{\text{PDB}} \) and \( \delta^{18}O_{\text{SMOW}} \) isotope values. Mineralogical compositions were determined by X-ray diffraction. Powdered samples (100 mesh) were reacted under vacuum with 5 ml 103 percent H\(_3\)PO\(_4\) (specific gravity 1.92) at 100°C, for magnesite, hydromagnesite, and dolomite, and at 25°C for calcite. Eighteen hours were allowed for the reaction. The CO\(_2\) was then purified in the extraction line by the standard procedure of McCrea (1950) and the yield was measured by an attached digital manometer. The ratios of \( ^{18}O/^{16}O \) and \( ^{13}C/^{12}C \) of the samples were analyzed on a mass spectrometer (ISOGAS, SIRA-10).

Results

The tabulated results (Table 2), plotted in Figure 8, are compared with the Yugoslavian trend (Fallick et al., 1991). The four calcite samples from veinlets in the Seydisehir argillites have the lowest \( \delta^{13}C_{\text{PDB}} \) values, ranging between –19.3 to –20.0 per mil and the \( \delta^{18}O_{\text{SMOW}} \) values of these calcites are extremely low (~21.7‰). Salda Gölü hydromagnesites represent the heaviest values (3.9–4.7‰ for \( \delta^{13}C_{\text{PDB}} \) and 30.0–36.8‰ for \( \delta^{18}O_{\text{SMOW}} \)), with the recently denatured samples being at the heaviest end of the range. The average \( \delta^{13}C_{\text{PDB}} \) and \( \delta^{18}O_{\text{SMOW}} \) values of two hydromagnesite samples from the dry surface of Akgöl are 0.4 and 28.0 per mil, respectively. The Hırsızdere sedimentary magnesite deposits have \( \delta^{13}C_{\text{PDB}} \) values of –0.3 to +4.4 per mil but unexpectedly light \( \delta^{18}O_{\text{SMOW}} \) values, between 21.6 and 26.5 per mil. The results of 11 magnesite samples of the Koyakçı Tepe vein- and stockwork-type magnesite deposits, near Helvacıbaba, are –11.8 to –14.3 and 25.9 to 27.7 per mil for \( \delta^{13}C_{\text{PDB}} \) and \( \delta^{18}O_{\text{SMOW}} \) values, respectively. Isotopically, these are the lightest values of the magnesite samples we analyzed from western Turkey, though they are similar to ratios found in vein magnesites from North Evia, Greece, and in Serbia (Gartzos, 1990; Fallick et al., 1991). Magnesite samples from the Helvacıbaba cryptocrystalline stockwork magnesite deposit itself have \( \delta^{13}C_{\text{PDB}} \) values ranging from –10.1 to –13.8 per mil and \( \delta^{18}O_{\text{SMOW}} \) values of 26.4 to 27.6 per mil. Three magnesite samples of pebbles from the conglomerate lying unconformably above the Helvacıbaba stockwork magnesites have significantly higher \( \delta^{13}C_{\text{PDB}} \) (–7.5 to –8.2‰) and slightly lower \( \delta^{18}O_{\text{SMOW}} \) (24.9–25.3‰) values with respect to Helvacıbaba stockwork magnesites. The isotopic values of the three samples collected from the bedded dolomites of probable Neogene age, which in turn overlie the conglomerates, have values similar to the magnesite pebbles (\( \delta^{13}C_{\text{PDB}} \) of –7.0 to –7.9‰ and \( \delta^{18}O_{\text{SMOW}} \) of 25.3–27.0‰).
<table>
<thead>
<tr>
<th>Sample no.</th>
<th>$\delta^{13}C_{\text{PDB}}$ (‰)</th>
<th>$\delta^{18}O_{\text{SMOW}}$ (‰)</th>
<th>Description</th>
<th>Sample no.</th>
<th>$\delta^{13}C_{\text{PDB}}$ (‰)</th>
<th>$\delta^{18}O_{\text{SMOW}}$ (‰)</th>
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<td>25.3</td>
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<td>36.0</td>
<td>Living microbialite</td>
<td>VZ48</td>
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<td>4.5</td>
<td>31.1</td>
<td>Mudstone (SW)</td>
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<td>33.8</td>
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<td>15 m terrace (SW)</td>
<td>VZ55</td>
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<td>33.6</td>
<td>30 m terrace (SW)</td>
<td>VZ56</td>
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<td>26.5</td>
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**Akgöl hydromagnesite**

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>$\delta^{13}C_{\text{PDB}}$ (‰)</th>
<th>$\delta^{18}O_{\text{SMOW}}$ (‰)</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>MV19</td>
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<td>Dry lake sediment</td>
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<tr>
<td>MV19</td>
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<td>Dry lake sediment</td>
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**Pammukale**

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<tr>
<th>Sample no.</th>
<th>$\delta^{13}C_{\text{PDB}}$ (‰)</th>
<th>$\delta^{18}O_{\text{SMOW}}$ (‰)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>VZ92-57</td>
<td>5.8</td>
<td>19.7</td>
<td>Travertine calcite</td>
</tr>
<tr>
<td>VZ92-56</td>
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<td>VZ92-58</td>
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<tr>
<td>VZ92-59</td>
<td>5.3</td>
<td>19.9</td>
<td>Travertine calcite</td>
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**Kocabas**

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>$\delta^{13}C_{\text{PDB}}$ (‰)</th>
<th>$\delta^{18}O_{\text{SMOW}}$ (‰)</th>
<th>Description</th>
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<tr>
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<td>MV24</td>
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<td>VZ33</td>
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<td>Bedded dolomite</td>
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<td>24.9</td>
<td>Bedded magnesite</td>
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<td>VZ45</td>
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</table>
Arapömer Deresi cryptocrystalline stockwork magnesite deposits have isotopic values that contrast strongly with the other cryptocrystalline vein stockwork deposits. Here $\delta^{13}C_{\text{PDB}}$ values are −0.4 to +1.4 per mil and $\delta^{18}O_{\text{SMOW}}$ values are 27.0 to 27.7 per mil. The calcite samples of Pamukkale travertines have the lowest $\delta^{18}O_{\text{SMOW}}$ (−20.7‰) and highest $\delta^{13}C_{\text{PDB}}$ (−6.1‰) values. Two calcium carbonate samples of Cretaceous limestone comprising the southeastern shoreline to Salda Gölü have 1.6 to 2.4 per mil $\delta^{13}C_{\text{PDB}}$ and 29.8 to 30.9 per mil $\delta^{18}O_{\text{SMOW}}$ values. The water samples of Salda Gölü have $\delta^{18}O_{\text{SMOW}}$ values of 2.8 per mil and $\delta D$ values of −3.5 per mil (Fig. 9).

Fluid Temperatures

In order to calculate the isotopic composition of the mineralizing fluids and hence their temperatures, the equation:

$$10^3 \ln \alpha = \delta^{18}O_m - \delta^{18}O_w = A(10^6T^2) + B$$  \hspace{1cm} (6)

(Aharon, 1988) is used where 103 ln is the per mil fractionation between mineral (m) and water (w). Temperature (T) is in Kelvin, and A and B are the constants appropriate to each particular carbonate (Table 3). Temperatures of the mineralizing solutions are calculated on the assumption that they are generally derived from meteoric water with a $\delta^{18}O_{\text{SMOW}}$ value of −5 per mil. On the other hand, the temperature of deposition of hydromagnesite in Salda Gölü is calculated using the analyzed value of the (evaporated) lake water of 2 per mil (Table 4).

Interpretation and Models

Status of the three hypothetical carbonate sources

In our previous studies of cryptocrystalline magnesite deposits in ophiolites we suggested that three main sources of carbonate variously contributed to the deposits (Falllick et al., 1991). These were (1) atmospheric carbon dioxide (O’Neil and Barnes, 1971; Falllick et al., 1991), (2) carboxyl from organic-rich sediments (Falllick et al., 1991; Brydie et al., 1993), and (3) carbon dioxide driven off limestone during contact metamorphism (Falllick et al., 1991). The $\delta^{13}C_{\text{PDB}}$ vs. $\delta^{18}O_{\text{SMOW}}$ values of the three supposed dominant sources or end members established for the Yugoslavian magnesite deposits were −4 and −36 per mil (end-member 1), −15 and +28 per mil (end-member 2), and +3 and +19 per mil (end-member 3). A regression line between 1 and 2 was given by:

$$\delta^{18}O = 0.5083\delta^{13}C + 32.3$$  \hspace{1cm} (7)

significant at the 99 percent confidence level (Falllick et al., 1991).

How these putative end members relate or otherwise to the main hypothetical sources of the Turkish deposits, and the waters from which the carbonates were precipitated, is discussed below.

Salda Gölü hydromagnesite (end-member 1): The $\delta^{13}C_{\text{PDB}}$ value of atmospheric CO$_2$ is −7.0 per mil. The $\delta^{13}C_{\text{PDB}}$ value of carbon in carbonate precipitated in lakes at around 20°C is expected to be about 4 per mil or a little more, a fractionation of around 11 per mil (O’Neil and Barnes, 1971). Meteoric water in the area has a $\delta^{18}O_{\text{SMOW}}$ value of −5 per mil though the lake water sampled from Salda Gölü is +2 per mil. Therefore, hydromagnesite precipitated at 20°C would be expected to have a $\delta^{18}O_{\text{SMOW}}$ value of around 35 per mil (Fig. 8a). (Were magnesite to have been precipitated from the same fluid then its $\delta^{18}O_{\text{SMOW}}$ value would have been about 40‰). With a mean $\delta^{13}C_{\text{PDB}}$ value of 4.4 per mil (excluding one value of 0.2‰) and a mean $\delta^{18}O_{\text{SMOW}}$ value of 35.9 per mil (excluding values from older developments well above the present lake) the isotopic values of the Salda Gölü hydromagnesite samples are as expected from our model. The isotopic values are also broadly comparable with those of cryptocrystalline sedimentary magnesite deposits such as Bela Stena, Serbia (Falllick et al., 1991), the huntite-hydromagnesite-magnesite deposits of Servia, Macedonia (Kralik et al., 1989), the evaporitic stromatolitic magnesite and dolomite developments in the Coorong lagoon, South Australia (Walter et al., 1973; Botz and von der Borch, 1984), and even one cryptocrystalline stockwork, the Miokovachi Beli Kamen deposit in Serbia (Falllick et al., 1991).

The isotopic results are best interpreted as indicating precipitation from the supersaturated surface waters of Salda Lake (end-member 1; Fig. 10a). The fact that the range of $\delta^{13}C$ values is so restricted can be taken to indicate minimal direct cyanobacterial involvement in precipitation (Guo et al., 1996), though the bacteria do bring about the nucleation of hydromagnesite (eqs. 3–5). We estimate, given the volume of the lake from the rate of evaporation, that a million tons or more of hydromagnesite could be generated well within 5,000 yr (Russell et al., 1999). Our conclusion is supported by the
Fig. 8. a. The plot of $\delta^{13}C_{\text{PDB}}$ vs. $\delta^{18}O_{\text{SMOW}}$ for the Turkish magnesite and hydromagnesite and associated carbonate deposits in relation to the regression lines from magnesite deposits in the former Yugoslavia, reported by Fallick et al. (1991). As with the Yugoslavian data, populations of isotopic ratios for each deposit are relatively distinct; thus symbols contrast only where fields overlap. b. Plot of $\delta^{13}C_{\text{PDB}}$ vs. $\delta^{18}O_{\text{SMOW}}$, for possible carbonate source rocks. Also shown are the putative end members EMY1 and EMT1 (theoretical low-temperature atmospheric-meteoric magnesite-hydromagnesite for the Yugoslavian and Turkish fields, respectively) as well as EMT2 (theoretical hot, organically derived $CO_2$ in ground water). Abbreviations: A = Ardlici Limestone of Perm–Jurassic age, B = Bozkir Limestone of Jurassic age, C = Caltepe Limestone at Seydisehr of Cambrian age, L = Loras Limestone of Cretaceous–Jurassic age, M = Midos Limestone of Cretaceous age, S = Cretaceous Limestone from the east shore of Salda Gölü.
The Mediterranean meteoric water line is from Sheppard (1986). The average meteoric water for this region is estimated on the basis of rainfall as δD ~ −20 per mil. The δ18O(SMOW) of two water samples from Lake Salda is −20.4‰ and −20.5‰, respectively. Extrapolating back to a pure end member would give δ13C(PDB) and δ18O(SMOW) values of −20 and +22 per mil, respectively (Fig. 8a).

Phyllites with vestigial organic carbon (now graphite and/or kerogen) comprise members of the Seydisehir Formation that crops out about 80 km to the southwest of Konya. This Cambro-Ordovician unit, metamorphosed to lower greenschist facies (Öncel 1995), looks to have been underthrust beneath the serpentinites hosting the giant stockwork deposits near Konya (Figs. 1–3). It took our interest as a possible contributor of hydrothermal carbonate via oxidation of inorganic carbon because it does contain veins of carbonate. Clearly in the case of the Seydisehir meta-argillite and other Paleozoic strata, carboxyl groups could not have survived the metamorphism. Thus, if carbonate were to have been partially derived from this and similar sources it could only have been by oxidation (e.g., Shook, 1988).

Isotopic ratios of calcites from the Seydisehir Formation (~19.4‰ δ13C(PDB) and +22.2‰ δ18O(SMOW)), whereas much lower than the δ13C(PDB) and δ18O(SMOW) values of either vein or stockwork magnesites, do lie on the extrapolation of the line drawn by Fallick et al. (1991: eq 7 and Fig. 8) for Serbian magnesite deposits. Thus, they could represent a contributor to the isotopically light δ13C(PDB) and δ18O(SMOW) end-member 2, i.e., the putative underthrust source of carbonate in the vein stockwork deposits of the Konya region. Organic carbon generally incorporates very light carbon (δ13C(PDB) around —25‰), whereas carboxyl group carbon normally plots around —20 per mil (Irwin et al., 1977). Again the results plot approximately as expected (Fig. 8a), though given the metamorphic grade of the Seydisehir Formation, we cannot consider this a definitive result. Indeed, we might have expected the isotopically lighter values typical of oxidation of organic carbon. In any case, it may be that these veinlets formed in the Variscan, and further work is required to substantiate, or otherwise, this hypothesis.

Limestones (end-member 3): Because contact thermal metamorphism of limestone could release CO2, to contribute one possible source of the carbonate in magnesite (Fallick et al., 1991), all the formations close to magnesite deposits were analyzed. In the Konya area these are the Midos Limestone (Upper Cretaceous), the Loras Limestone (Upper Jurassic to Upper Cretaceous), the Bozkir Limestone (Jurassic), and the Ardili Limestone (Permian to Lower Jurassic: Fig. 2). Also, the Çaltepe Limestone (Cambro-Ordovician), which crops out 80 km southwest of Konya (mentioned above), was analyzed as a possible deep source. The Cretaceous Limestone, which crops out on the eastern shore of Salda Gölü, was analyzed because it impinges on the lake itself. Marine carbonates generally have a δ13C(PDB) value of 0 ± 4 per mil (Field and Fifarek, 1985; Salomons and Mook, 1986; Emery and Robinson, 1993). The marine limestones that crop out in the region generally follow the evolutionary oxygen isotope path systematically backward, period by period, of ever heavier

**Table 3. Values of Constants A and B Used in Equation 6**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>A</th>
<th>B</th>
<th>References</th>
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</thead>
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<tr>
<td>Hydromagnesite</td>
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<td>O’Neil and Barnes (1971) Friedman and O’Neil (1977)</td>
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<td>Magnesite</td>
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<tr>
<td>Calcite</td>
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<td>O’Neil et al. (1969) Friedman and O’Neil (1977)</td>
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<tr>
<td>Dolomite</td>
<td>3.23</td>
<td>3.29</td>
<td>Sheppard and Schwarz (1970)</td>
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**Table 4. Calculated and Measured Temperatures of Deposition**

<table>
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<tr>
<th>Deposit</th>
<th>Calculated temperature (°C)</th>
<th>Measured temperature (°C)</th>
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<td>Arapömer Deresi stockwork</td>
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<td></td>
</tr>
<tr>
<td>Koyaki Tepe stockwork</td>
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<td>−100</td>
</tr>
<tr>
<td>Helvacababa stockwork</td>
<td>−50</td>
<td>−100</td>
</tr>
<tr>
<td>Helvacababa sedimentary dolomites</td>
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<td>−100</td>
</tr>
<tr>
<td>Salda Gölü</td>
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<td>20</td>
</tr>
<tr>
<td>Hırszdere exhalative deposit</td>
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<td></td>
</tr>
<tr>
<td>Pamukkale and Kocabas travertines</td>
<td>−40</td>
<td>40–60</td>
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</table>
oxygen, from the Cretaceous to the Cambrian, presumably a reflection of progressive diagenesis (Fig. 8b; Keith and Weber, 1964; Faure, 1986). The one exception is the Cretaceous Loras Limestone with low values for both $\delta^{18}O$ (SMOW) and $\delta^{13}C$ (PDB), averaging $+21$ and $-4$ per mil, respectively. It is inappropriate for us to make an interpretation on just two data points, though it is possible that the samples represent a small pocket of the limestone that has reacted with basin fluids bearing some petroleum.

Deposits lying on the putative mixing line 1–2

Helvacıbaba and Koyakçı Tepe deposits: The isotopic results from these vein stockwork deposits are in concert with expectation. We have previously suggested (Fallick et al., 1991, Brydie et al., 1993) that the $\delta^{13}C$ (PDB) values between $-10$ and $-15$ per mil indicate a contribution of carbonate from decarbonation of organic-rich sediments, which may be underthrust beneath the ultramafic host and source rocks (Karamata, 1974; Smith and Spray, 1984; Brydie et al., 1993), with the remainder derived from surface CO$_2$. According to Curtis (1978) and Emery and Robinson (1993), the decarbonation of organic-rich sediments begins at temperatures of around 70° to 75°C. This process results in fractionations such that a range of $\delta^{13}C$ (PDB) values from $-10$ to $-20$ per mil for carbon dioxide (as bicarbonate) are realized (Irwin et al., 1977). However, Shock (1988, 1994) has argued from thermodynamic considerations that organic acids are oxidized directly to carbon dioxide. If so, $\delta^{13}C$ (PDB) values found in carbonates might be expected to range between $-20$ and $-25$ per mil. This is not the case in our analyses. Nevertheless, Shock (1988) goes on to speculate that oxidation can be mediated by bacteria, a complicating factor in isotopic fractionation (and see Pedersen, 1997). The simplest explanation of the $\delta^{13}C$ (PDB) values ranging from $-15$ to $-10$ per mil in the magnesites might be that a proportion of the carbonate is derived by the decarbonation of organic-rich sequences underthrust beneath the ultramafic host rocks (and see Jedrysek and Halas, 1990; Abu-Jaber and Kimberley, 1992; Brydie et al., 1993). However, the Seydisehir veinlet carbonates (see above) are isotopically a little too heavy to be considered as derived from light carbon from R groups (i.e., about $-25\%o$, as expected by Shock 1988). Certainly the metamorphic grade of these meta-argillitic phylmites (Öncel 1995) would preclude a carboxyl source. It could be that the somewhat sparse accumulations of organic carbon in these meta-argillites underthrust beneath the Çayırbagı ophiolite were oxidized and provided a portion of the carbonate, though as stated above, it could just as well be argued that the veinlets were formed during an earlier metamorphic event. Alternatively, the source could be an unknown Mesozoic organic-rich formation underthrust beneath the same ophiolite. Either way, precipitation would be brought about by the sudden release of carbon dioxide as fluids saturated in magnesite neared the surface (Ilich 1974).

The alternative explanation of Petrov (1967) and Lesko (1972) that such vein stockwork deposits are generated by surface weathering (see Zachmann and Johannes 1989) is rejected on mass-balance grounds. Moreover the “equilibrium field” of O’Neil and Barnes (1971, fig.1) presumed for their surface weathering model does not have the positive correlation between $\delta^{13}C$ (PDB) and $\delta^{18}O$ (SMOW) values revealed in this study (Fig. 8).

Arapömer Deresi deposit: The isotopic data from the Arapömer Deresi cryptocrystalline stockwork magnesite deposits reveal high $\delta^{13}C$ (PDB) values (ranging from $-0.4$ to $+1.4\%o$) with respect to other stockwork deposits. Cryptocrystalline magnesites in ultramafic complexes are more often represented

by isotopically lighter $\delta^{13}C_{(PDB)}$ values ($-6$ to $-18\%$; Králik et al., 1989), though Miokovčevići, in Serbia, is even heavier (Fallick et al., 1991). The carbon isotope signature of the Arapömer Deresi magnesite can be explained by a marine carbonate source though some contribution from magmatic CO$_2$ is also likely. When ground water convects at depth through marine limestones or marbles it could pick up CO$_2$ either by decarbonation or dissolution of limestone (e.g., as at Kızıldere 65 km to the northwest; Ten Dam and Erentöz, 1970). If so, isotopic reequilibration could be established between mineralizing fluid and the marine limestone source ($\delta^{13}C_{(PDB)}$ from $-2$ to $+2\%$). Moreover the oxygen isotope values are comparable with those from Mesozoic limestones. Decarbonation of such limestones at depth as a source of carbonate becomes more attractive when the Neogene to Recent andesitic-basaltic volcanics cropping out at centers 10 and 20 km to the west are taken into account. We previously explained the genesis of the Oshve vein in Bosnia in the same way. Here the magnesite was interpreted to have precipitated at around 105°C, the highest temperature calculated in all the deposits analyzed from the former Yugoslavia (Fallick et al., 1991). Nevertheless, the coincidence of the isotopic ratios with those of the hydromagnesite lake sediments in Akgöl does permit a per descendent model to be considered for this small deposit. Magnesite (originally hydromagnesite) could have been precipitated in an evaporating lake (any evidence for which has been eroded) as well as in fractures beneath.

**Hırsızdere sedimentary deposits:** The isotopic results of carbonate samples from the Hırsızdere (Denizli) sedimentary magnesite deposits plot between the fields generally occupied by thermal decarbonation of marine limestones through to atmospheric values (Fig. 8). The $\delta^{18}O_{(SMOW)}$ values are lower than is usual for sedimentary magnesites, although the $\delta^{13}C_{(PDB)}$ values are comparable with the well-defined sedimentary and volcanic-related vein-type deposits. The deposit itself is associated with Neogene volcanic rocks judging from the 1:2,000,000 geologic map of Turkey and lies in the center of the Büyük Menderes graben (Figs. 1 and 4).

High $\delta^{13}C_{(PDB)}$ values indicate that the carbon dioxide could have an atmospheric origin. Alternatively some carbon dioxide could have evolved during contact metamorphism of marine limestone thrust beneath the serpentinite (cf. Arapömer Deresi). Yet another possible interpretation is that these values resulted from fractionation during evaporation of the lighter carbon isotope. The unusually low oxygen isotope ratio ($-25\%$) could be explained by depositional temperatures, at or close to the boiling point. Hydrothermal solutions feeding the deposit could have risen up a boundary-parallel fault in the middle of Neogene Lake Aşıklı, gaining magnesium as water rises from the depths (Fallick et al., 1990) for a similar association in North Evia, Greece.

The isotopic results of the sedimentary dolomites overlying the stockwork are comparable with the magnesite pebbles, if the different oxygen isotope fractionation of $-2$ per mil between magnesite and dolomite is taken into account. But the carbon isotope ratios are also about 4 per mil higher than the stockwork. The data permit the interpretation that the dolomites are sedimentary-exhalative (cf. Ilich, 1968), the isotope shift being explained by degassing of CO$_2$. If so, it is likely that the hydrothermal fluids generated the stockwork before escaping into the coeval Neogene lake.

**Pamukkale and Kocabas:** Of all the Neogene-Quaternary carbonates analyzed, the present-day, hot-spring travertine (calcite) deposits at Pamukkale have the highest $\delta^{13}C_{(PDB)}$ values (avg 6.1\%) and the isotopically lightest $\delta^{18}O_{(SMOW)}$ values ($-20\%$). The Pleistocene travertines at Kocabas are similar though their $\delta^{18}O_{(SMOW)}$ values rise to 24.7 per mil. The $\delta^{13}C_{(PDB)}$ results could be attributed to carbonate derived from Paleozoic marbles beneath the travertines as suggested by Altunel and Hancock (1993), although the $\delta^{18}O_{(SMOW)}$ values are also typical of heated ground waters. Indeed, if we assume for the moment calcite to have been precipitated from local meteoric water with a $\delta^{18}O_{(SMOW)}$ value of $-5$ per mil, then the calculated temperature for a $\delta^{18}O$ value of 25 per mil turns out to give the expected temperature of $\sim 40°C$ (cooled from the original $60°C$). Yet an atmospheric source of carbon (in CO$_2$) from carbonate at $40°C$ would be expected to afford a lighter $\delta^{13}C_{(PDB)}$ value ($-2\%$). Against this, degassing would enrich the hot water in the heavier isotope. As another additional explanation of the high $\delta^{13}C_{(PDB)}$ value, Guo et al. (1996) have shown that cyanobacterial growth tends to fix $^{12}CO_2$ from the hot-spring waters leaving more $^{13}CO_2$ as a source for the carbonate precipitates, although more of a spread of $\delta^{18}C$ values might be expected in such a case (Ammundson and Kelly, 1987).

**Comparisons**

The isotopic values of the Salda Gölü hydromagnesites and the Koyakci Tepe magnesites fall into the same heavy and light isotopic end-member fields as those of the Bosnian and Serbian magnesites (Fallick et al., 1991). The Salda Gölü association of hydromagnesite microbialites with the derived hydromagnesite sediments and beach deposits is a good candidate for precursors to massive irregular magnesite deposits found in lacustrine sediments. The Bela Stena deposit in Serbia is so far the only possible fossil example known to us. Given the similarity in gross morphology and stable isotope ratios between the Salda Gölü hydromagnesite microbialite mounds and the lacustrine Bela Stena magnesite deposit (Fallick et al., 1991; Russell et al., 1999), it is possible that the carbonate at Bela Stena was originally precipitated as hydromagnesite. According to Sayles and Fyfe (1973) hydromagnesite can start converting into magnesite about 55°C at an
enhanced CO₂ pressure (about 1 bar). These conditions are likely to have occurred at Bela Stena during diagenesis:

$$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O} + \text{CO}_2 \rightarrow 5\text{MgCO}_3 + 5\text{H}_2\text{O}.$$ (8)

In some contrast to the Bela Stena deposit, judging from the isotopic ratios ($\delta^{13}$C$_{\text{PDB}}$ and $\delta^{18}$O$_{\text{SMOW}}$ avg 7.2 and 34.2‰, respectively), the huntite-hydromagnesite-magnesite deposits in the Servia intermontane basin, Macedonia (Wetzenstein, 1975; Kralik et al., 1989; Stamatakis, 1995), could have developed over methane-rich seepages derived from lidentity seams beneath (Kralik et al., 1989; and see Hovland, 1990). Here magnesite occurs in massive bodies close to faults. Nevertheless, Wetzenstein (1975, p. 129) has suggested that the magnesium in these huge deposits was "received...through fluvial transport," whereas Stamatakis (1995) argues that the magnesium (and minor calcium) was delivered as bicarbonate from springs emanating from the basement, final enrichment being caused by evaporation.

Conclusions and Predictions

The following factors favor the generation of large (hydro) magnesite deposits in obducted ophiolites: an underthrust organic source of carbonate or atmospheric carbon dioxide, extensional stress, igneous intrusion, moderate relief, a long-lived low-temperature artesian system, wet winters, and hot dry summers. Nevertheless, a direct demonstration of an underthrust and oxidizing organic source is still wanting. From the research reported here and with reference to our models for the generation of cryptocrystalline magnesite deposits in ultramafic terranes, we make the following predictions:

1. Giant stockwork and vein complex magnesite deposits will generally be found in ultramafic bodies only where an underthrust organic-rich sediments, capable of sourcing the carbonate, exist at depth. Helvacıbaba and Koyakçı Tepe are the main examples in western Turkey. In Serbia, the main vein deposits are Golešë, Brezack, Dragica, and Liska, and the main stockwork is Mrămor-Razhana (Fallick et al., 1991). Values of $\delta^{13}$C$_{\text{PDB}}$ and $\delta^{18}$O$_{\text{SMOW}}$ generally plot along a line from −15 to +25 to −9 and +28 per mil, respectively, implying a deep organic source of CO₂ and fluid temperatures around 50°C. But in one exceptional case, Miokovachi Beli Kamen, the $\delta^{13}$C$_{\text{PDB}}$ and $\delta^{18}$O$_{\text{SMOW}}$ trend extends to 4 and 36 per mil, respectively (Fallick et al., 1991, fig. 6), which is consistent with a surface-derived origin of CO₂ and a low depositional temperature, conditions possibly met beneath a shallow evaporating lake.

2. More rarely, vein deposits can occur where limestone, underthrust beneath the ultramafic body, has supplied carbon dioxide to ground waters through decarbonation by an igneous intrusion. The type example is Oslive, in Bosnia, where $\delta^{13}$C$_{\text{PDB}}$ and $\delta^{18}$O$_{\text{SMOW}}$ values approximate −3.1 and 19 per mil, respectively. The Arapçevo Deresi cryptocrystalline stockwork magnesite deposit in western Turkey could also have had such an origin ($\delta^{13}$C$_{\text{PDB}}$ and $\delta^{18}$O$_{\text{SMOW}}$ avg 0.3 and 27.5‰, respectively). The temperature of the mineralizing fluids would have been between 70° and 100°C.

3. Massive strata-bound hydromagnesite stromatolites comprising cyanobacteria and diatoms (Salda Gölü, western Turkey), as well as their diagenetically equivalent magnesite bodies (Bela Stena, Serbia), will be found developed in sediments in enclosed lacustrine basins above river delta slopes in ultramafic terranes. We should think of them as microbially mediated (nucleated) evaporite deposits. Their $\delta^{13}$C$_{\text{PDB}}$ and $\delta^{18}$O$_{\text{SMOW}}$ values will be those expected of fractionations from atmospheric-meteoric values at ambient temperatures. In the southern Alpine terranes these values will approach 4 and 36 per mil, respectively. This type of deposit, not requiring a source of carbonate at depth, could develop (perhaps in association with huntite; Stamatakis, 1995) in lakes or lagoons subject to strong evaporation, in any ultramafic terrane, not only on Earth but also Mars (Russell et al., 1999). Such a deposit could be awaiting discovery beneath the surface hydromagnesite crusts near the southwestern margin of Akgöl, 15 km north-northeast of Salda Gölü.

4. Massive stratiform magnesite beds of hydrothermal exhalative origin will be found to occur above ultramafic bodies near contemporaneous faults in extensional terranes marked by local volcanism as predicted by Ilich (1988; and see Ilich, 1952). An example is Hurszidere, which lies within Pliocene lacustrine sediments of what was a more extensive Lake Açıqöl, in the middle of the Büyük Menderes graben. Shilopaj-Nevade is the main example of this type in Serbia (Ilich, 1976; Fallick et al., 1991). Carbonate (augmented by atmospheric carbon dioxide) can be derived either from limestones or carbonaceous rocks traversed by convecting thermal waters, perhaps augmented by magmatic carbon dioxide. The oxygen isotope values will reflect the relatively high temperatures of the mineralizing fluids (≤100°C). In Serbia, Bosnia, Greece, and Turkey, the $\delta^{18}$O$_{\text{SMOW}}$ values are expected to range between 20 and 30 per mil. The $\delta^{13}$C$_{\text{PDB}}$ values can range across the whole spectrum from about −10 to +7 per mil.

5. Further isotopic analyses of cryptocrystalline magnesite deposits in Alpine terranes will plot on the two mixing lines hypothesized to explain the genesis of the various deposits in the former Yugoslavia. The $\delta^{13}$C$_{\text{PDB}}$ vs. $\delta^{18}$O$_{\text{SMOW}}$ plot first revealing these lines (Fallick et al., 1991) is generally reinforced by analyses of the Turkish deposits.

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REFERENCES
