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A comprehensive assessment of huntite ore formation

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ABSTRACT

The Çameli basin (Southwestern Turkey), economically important exploitable huntite ore deposits are located a basin. The huntite deposits in the basin are the largest known deposits in worldwide. In this study, new huntite outcrops were identified in northeastern of the basin and the samples from the outcrops were analyzed. The results of X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses were combined and comprehensive interpreted with literature studies. In the samples, average 70.4% huntite, 15.2% dolomite, and 14.4% larnite minerals were detected. Major element analysis showed an average of 28.62% MgO, 18.78% CaO, and 44.09% loss on ignition. Loss on ignition (LOI) values are 38.85-47.53%. CO_2 values are 44.77% and 45.14%. In literature, huntite mineral is theoretically predicted to contain 34.15% MgO and 15.88% CaO. In the samples, the MgO values are 26.00-31.77% and CaO values are 18.50-19.66%. SrO values are 0.11-0.30%. Sr concentration in huntite indicates that Ca-rich karst waters play a role in huntite ore formation. The low SrO contents sign that the formation of huntite in Çameli basin is a result of the mixture of Mg-rich saline waters and small amounts of Ca-rich karstic waters from the basement. The results of the analyses, when compared with previous studies on huntite minerals, it is understood that all values are quite close to each other. Therefore, Mg- and Ca-rich solutions that precipitated during huntite ore formation played a role in releasing Sr on aragonite, which then precipitated together with Ca and Mg. This suggests that huntite is a product of the late meteoric phase and the primary mineral is aragonite. The results of this study indicate that huntite are an ore by carbonization of the altered serpentine according to SiO_2-CaO-MgO contents.

Keywords: huntite ore; huntite mineralization; genesis of huntite ore; huntite ore occurrence; formation model.

INTRODUCTION

Huntite ore is used as a flame-retardant filler material in the industrial field. In the manufacturing of products made of combustible materials such as plastic, paper, wood, etc., it is aimed to minimize the loss of life and property in the event of a possible fire by including flame retardant or flame retardant fillers. As the number and quality of studies on the origin, development, and impact area of fire increases, the importance of flame-retardant fillers is better understood, and in parallel with this, their usage areas and quantities are increasing day by day. In economically exploitable huntite and hydromagnesite deposits, these two minerals are always observed together. Since both of them have flame-retardant properties, these minerals can be used as commercial products in a natural mixture without any separation. Thus, in addition to the flame-retardant properties of hydromagnesite due to its endothermic decomposition starting at 220 ºC, the fact that huntite does not decompose until about 400 ºC and then forms a resistant residue due to its sheet mineral form, serves as a thermally protected barrier and creates an additional flame-retardant property (Çakmakoğlu, 2016; Yücel and Gül, 2017).

Huntite, which does not give a broken surface, has white and lemon white colors, and has a hardness between 1 and 2 according to Mohs hardness level, is a very fragile mineral depending on its structure. Having a porous structure, huntite easily sticks to the tongue when touched to the tongue. With a specific gravity of 2.696 g/cm^3 at 4 ºC, huntite can be easily scratched with a fingernail, while it becomes porous when left in water. It can easily foam and dissolve in cold acids. Its luster is fluorescent; its transparency is earthy (matte) and its line color is white (Faust, 1953). Huntite mineral was first identified by Faust (1953) as a late meteoric stage mineral within the pores of rocks made of magnesite, dolomite, and deweylite minerals in Ala-Mar deposits in Current Creek Nevada. He states that hydrothermal solutions enriched in Mg and CO_2 along faults cutting the tuffs transformed the calcite-containing tuffs into dolomite.

With the impoverishment of calcium in the solution, magnesite and deweylite are formed. This replacement rock is hollow and finally, these voids are filled by huntite ore. Huntite is predicted to have been deposited in the late meteoric stage from cold surface waters enriched in magnesium while passing through local magnesite formations. However, in most of the studies conducted to date, huntite ores have either been treated individually based on recent examples or very different formation mechanisms and mineral transformations have been described for their coexistence. Huntite mineralizations have been identified in different locations (Figure 1).

The huntite ore occurrences in the Çameli Basin (Southwestern Turkey) are rare and economically important deposits due to their special formation conditions. A similar deposit is located in the Kozani Basin (Northern Greece). It is known that the production amount from the deposits in Greece, which is currently operated by Sibelco, is approximately 18,000 tons/year (Charalampides et al., 2014) and the reserve is around 4,000,000 tons when the data between 2008-2012 are averaged. The huntite-hydromagnesite deposits in the Çameli Basin are the

Figure 1. Known important localities of huntite ore mineralization in worldwide. 1. Turkey (Çameli basin and Lakes district), 2. Greece (Kozani basin, Sounion, Lavrion mining district, Lavreotiki, Attica), 3. United States (in Nevada, from the Ala-Mar deposit, Currant Creek district, and the Gabbs mine, Gabbs district, and the Nevada Magnesite and Snowball deposits; in the Chief Consolidated mine, Eureka, Utah; at the Kalkar quarry, Santa Cruz, California; in the Line Pit, Pennsylvania, Carlsbad Cavern, New Mexico), 4. Australia (from Tea Tree Gully, South Australia; at Katherine, Northern Territory; and from Deer Park and Geelong, Victoria), 5. Pakistan (Khuzdar area, Balochistan), 6. Uzbekistan (in the Kurgashinkan Pb-Zn deposit), 7. Italy (Cerchiara Mine, Borghetto di Vara, La Spezia Province, Liguria), 8. Spain (Montcada Hill Quarry, Montcada i Reixac, Vallès Occidental, Barcelona, Catalonia), 9. Canada (from Castleguard Cave, Columbia Icefields, Alberta), 10. Iran (Abarkurh district).

largest known deposits worldwide. It is stated that the total reserve in the quarries operated by Likya Minerals Co. Ltd. is over 20 million tons. Likya Minerals Co. Ltd. processes the huntite and hydromagnesite raw material obtained by the open pit method in its micronizing plant and offers it to the flame-retardant market under the trade name UltraCarb with various options below 20 microns (Çakmakoğlu, 2016).

In this study, new huntite outcrops were identified in northeastern of the Çameli basin and the outcrop samples were analyzed (the currently known and operated deposits are located in the western and southwestern of the basin). The results of the analyses were combined and comprehensive interpreted with literature studies. The results of the study indicate that huntite was formed by carbonization of the altered serpentine.

GEOLOGY OF THE ÇAMELI BASIN

In the Çameli basin (Figure 2), especially mud flat and lake sediments, industrial raw materials such as sepiolite, sepiolite clay, palygorskite, huntite, and magnesite are located. Almost all of these are diagenetic sedimentary deposits. Although marsh environment deposits including thin coal seams and bands are encountered in places, no significant coal deposits have been formed in the basin. Huntite and magnesite deposits are still operated by private-sector companies (Akbulut and Kadir, 2003). Huntite ore occurrences are encountered in the Çameli Basin, which is located on magnesium-rich basement rocks of the Lycian Nappes, which are widely distributed in southwestern Anatolia. The basin fill consists of the Upper Miocene-Lower Pleistocene Çameli Formation. Huntite formations are observed in the form of lenses in the limestone layer in the uppermost parts of the Değne member, which consists

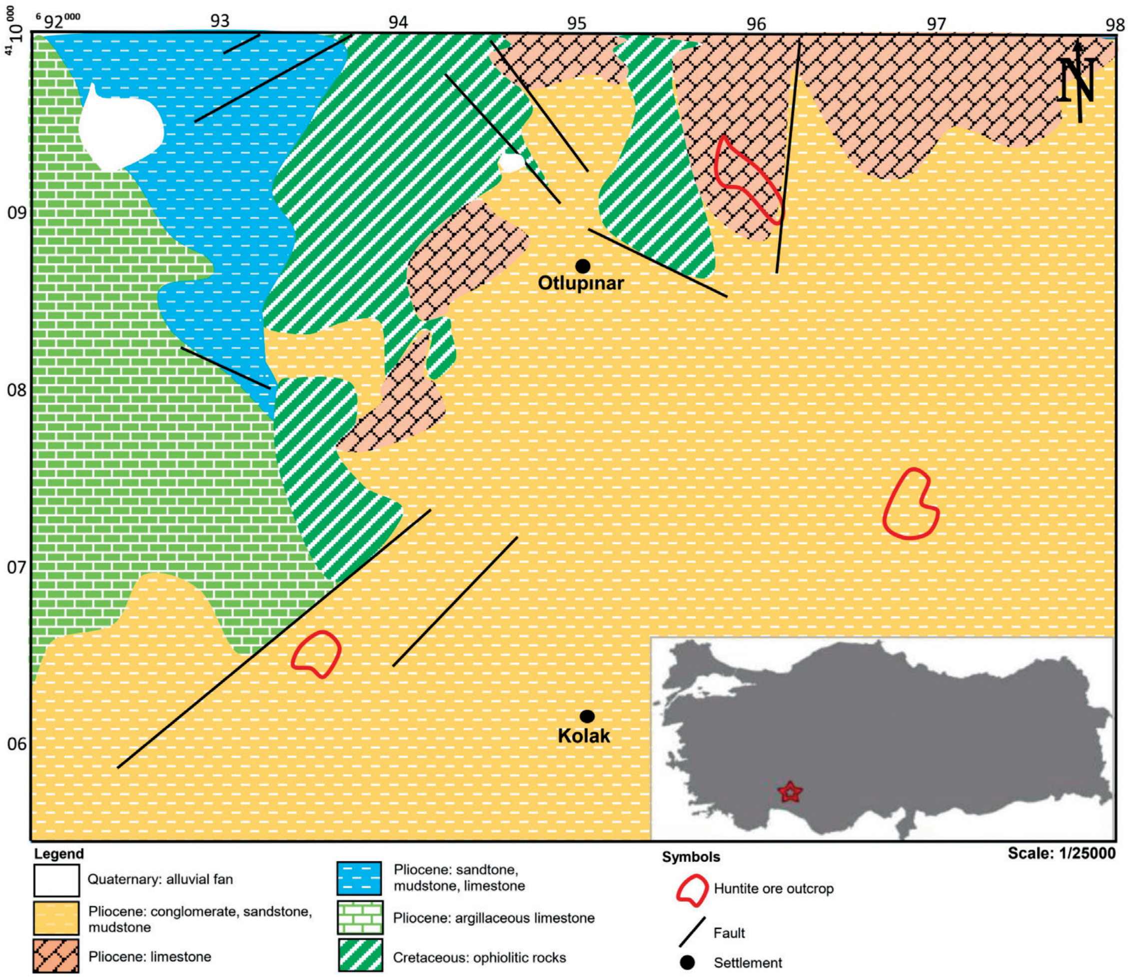

Figure 2. Geological map of northeastern of Çameli basin and new huntite ore outcrops determined in this study (prepared according to field observations from Alçiçek et al., 2004).

of the lacustrine deposits of the Çameli Formation. Changes in the Mg/Ca ratio of lake waters resulted in dolomitic limestone and huntite-hydromagnesite succession. Huntite fills the voids in hydromagnesite and is deposited in the shallow lake margins and temporary carbonate ponds (Çakmakoğlu, 2016).

The geological units outcropping in the Çameli Basin are divided into three categories (Figure 3): Pre-Miocene basement units, Upper Miocene-Upper Pliocene graben fill units, and Quaternary units. The basin is underlain by Mesozoic ultrabasic and carbonate rocks and Paleogene clastic and carbonates, which are defined by various researchers with different formations and unit names. Neogene sediments are defined under the name of Çameli Formation of Upper Miocene-Upper Pliocene. Although the Çameli Formation shows some differences in the north, middle, and south of the basin, it is generally dominated by pebble-sandstone-mudstone succession in the lower part, claystone-marn-clay limestone succession in the middle part, and limestone in the upper part. Pebble-sandstone-mudstone-mudstone alluvial fan; claystone-marn-clayey limestone succession is the lake shore mud flat and limestone is the lake environment sediments (Akbulut and Kadir, 2003). Quaternary alluvium covers all these units unconformably.

There are many different views regarding the extensional Neotectonic period in western Anatolia, in which the Çameli basin is located, which has been active until today. According to the tectonic escape model advocated by Dewey and Şengör (1979), the west-southwest movement of the Anatolian plate created an extension regime in western Anatolia after the collision of the Arabian-Eurasian plates along the Bitlis margin belt in southeastern Anatolia in the Late Cretaceous. The Anatolian plate responded to the compression following this collision by first thickening and then moving westward along the Northern Anatolian and Eastern Anatolian faults. This movement resulted in a E-W compression in the Aegean Sea and western Anatolia and a N-S extension (Şengör, 1979; Şengör and Yılmaz, 1981; Şengör et al., 1985). According to the spreading model proposed by Le Pichon and Angelier (1979), the northward subduction of the

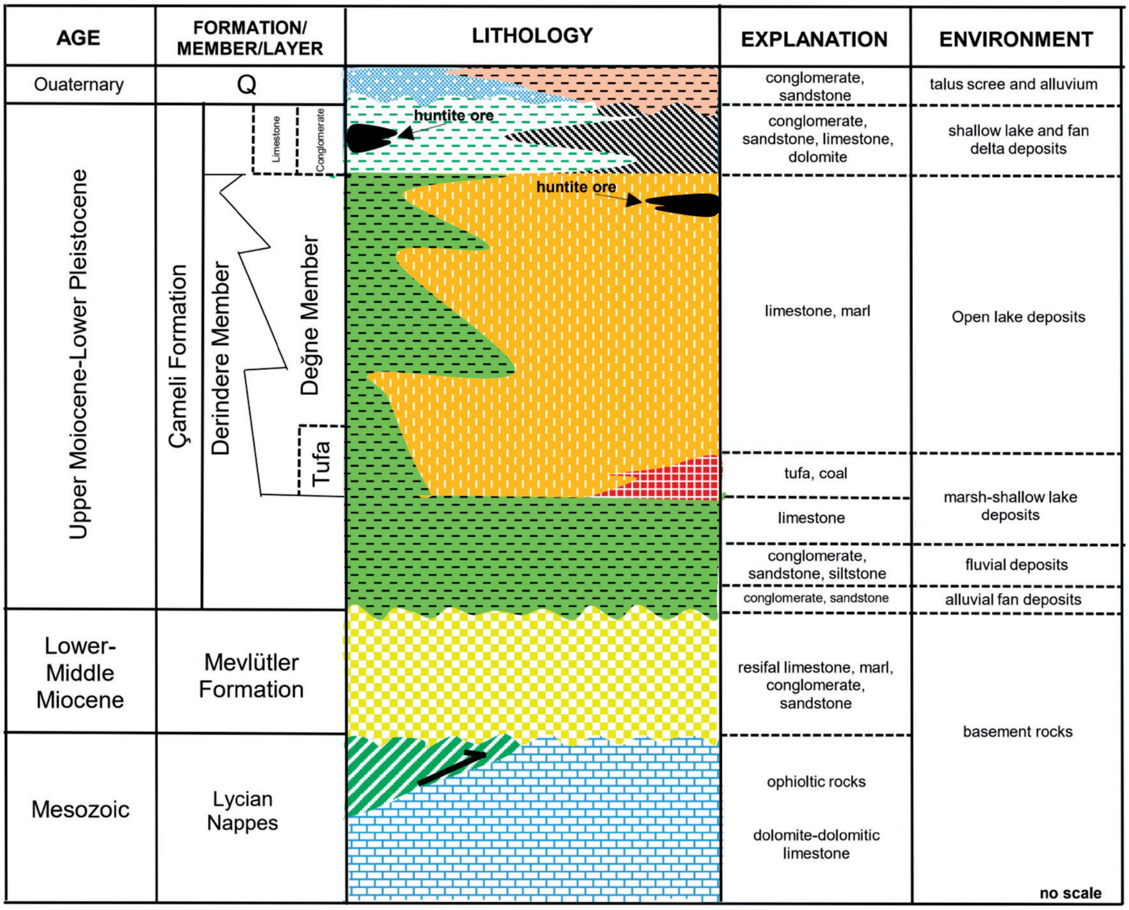

Figure 3. Generalized stratigraphic section of the Çameli basin (modified from Alçiçek et al., 2004 and Çakmakoğlu, 2016).

northern margin of the African plate along the Hellenic arc resulted in crustal stretching in the Aegean region starting in the Late Serravalian Tortonian. According to the orogenic subsidence model proposed by Seyitoğlu and Scott (1991), the expansionary neotectonic regime started as a result of the spreading of the overthickened crust. This event started in the Upper Oligocene-Lower Miocene following the Paleocene collision and the shortening and thickening of the Anatolian plate along the Izmir-Ankara-Erzincan Neotetis suture. Regardless of which of these regional models is accepted as valid, the findings indicate that the Çameli basin was opened in the Upper Miocene and tectonic control continued after the opening. Facies assemblages separated within the basin fill and their lateral and vertical relationships are direct and more reliable data on basin evolution (Alçiçek et al., 2004).

HUNTITE ORE OCCURRENCES IN THE ÇAMELI BASIN

The first study on huntite and hydromagnesite deposits in the Çameli Basin belongs to Akbulut and Kadir (2003). In the study; three types of huntite formations were defined as i) massive huntite, ii) discoidal and fenestral huntite, iii) irregular massive huntite. Massive huntite formations are predicted to be the diagenetic product of dolomite. It is said that the formation probably follows the dolomite-huntite-magnesite sequence. It is suggested that hydromagnesite and magnesite formations are observed at a rate of 5%. Hydromagnesite is said to be formed by the conversion of huntite in the late diagenetic stage under the influence of CO_3-rich meteoric waters passing through huntite intermediate formations. Discoidal or fenestral huntite is said to be formed by the direct precipitation of 0.1-3 cm huntite formations observed in dolomitic marls from Mg-rich pore waters in shallow coastal sediments in the mud-flat environment. Irregular massive huntite is reported to be formed in partially preserved (0.1-10 cm) irregular dissolution cavities. The dissolution void karst limestone is stayed to have been deposited from high Ca and CO_3 ions under pluvial climatic conditions and during this deposition, huntite was formed by flocculation in the form of masses.

The source of the dominant Mg-carbonate precipitation in Salda Lake is probably the washing of altered olivines in the basement rocks to reach the lake environment. Similarly, the huntite and hydromagnesite formations in the Çameli basin originate from the basement rocks in the harzburgite-dunite interval. For this reason, XRF analysis was performed on the petrographically analyzed sample and it was observed that the MgO value was 39.3%. In detailed petrographic and geochemical studies on the upper mantle peridotites within the Lycian Nappes, similarly, high MgO values have been obtained in the harzburgite and dunite dominant samples. According to XRD results, huntite and hydromagnesite minerals are mixed in the Çameli Basin with a ratio of at least 75%. In places, huntite-hydromagnesite deposits are accompanied by dolomite and magnesite minerals to a lesser extent. It has been observed that huntite can be found in different proportions at different levels, but hydromagnesite is not found above 70% at any level (Çakmakoğlu, 2016).

Huntite and hydromagnesite deposits in the Çameli basin are located in limited areas within the limestone layer in the upper parts of the Değne member, which reflects deposition in the lake environment. The formations observed in the marls at levels close to the limestone layer do not present a thickness to form a deposit but are spread throughout the basin (Çakmakoğlu, 2016). The geological basis of the Çameli (Denizli) deposits is the Mesozoic ophiolite series in the north and Ultrabasics in the south. The boundary of these two series is overlapping. In the inter-mountain basin developed as a result of the tectonic activities that probably occurred in the early Pliocene on the basement, the transport of clastic material from the land remained at a minimum level and the elements and oxides that were mostly melted and transported from the surrounding basement were deposited in the basin in the form of calcite, dolomite, magnesite, hydromagnesite, quartz and huntite mineralization according to the ambient conditions. Their abundance was determined by the local physicochemical conditions within the basin. In general, huntite formation was more dominant and dominant in the parts of the basin close to ultrabasics. The best example of this is the huntite field of Likya Minerals Co. Ltd., which is still in operation. Calcite-dolomite-magnesite-hydromagnesite is more common and dominant (Kangal and Güney, 2006).

Çameli Basin was opened within the Lycian Nappes due to the NW-SSE extension tectonics during the Late Miocene. The basin was filled with alluvial fan deposits defined as Derindere member along the marginal faults (Bozdağ and Dirmil faults). The fan deposits are mainly represented by divergent products. Towards the middle of the basin, fan delta deposits representing the transition to the lake environment and marsh levels symbolized by lignite bands are encountered. Alçiçek et al. (2004) obtained an early-middle Pliocene from mammal fossil samples taken from the backshore marsh environment of the lake. The marsh levels transition to the lacustrine deposits with limestone lenses and interlayers. The fact that the lacustrine stack is observed in limited areas and does not present much thickness indicates that the lake at this stage was temporary and shallow. In the vicinity of Sarıkavak, the lacustrine stack is observed to be overlain by the Tufa layer. It is stated that the Tufa formation developed due to faulting in the Early-Middle Pliocene and the basin was divided into two along the

Sarıkavak Fault, which resulted in this formation. With this faulting, the basin deepened and the open lake facies sediments represented by the Değne member started to be deposited. Deposition continues until the Middle-Late Pliocene, overriding the marginal faults, and shallow lake sediments are encountered. The shallow lake sediments composed of sandy limestone, dolomitic limestone, limestone, and locally observed tufa formations from bottom to top are defined as Limestone layers. Within the dolomitic limestones, huntite and hydromagnesite formations are encountered in three levels in the form of lenses (Figure 4). The basin is then quartered by the Kelekçi and Çameli faults. Early Pleistocene age was obtained from the sediments related to this faulting phase. The basin sediments are finally covered by Quaternary sediments (Çakmakoğlu, 2016).

The Late Pliocene-Early Pleistocene limestone layer starts with marl-sandy limestone succession and transitions to dolomitic limestones deposited due to the presence of microbialites in the marginal plains of the lake. The dolomitic limestones were probably formed as an aggregation of cyanobacteria through the contact of different clusters. It is thought that it was originally deposited as aragonite in the subaqueous environment and then transformed into dolomite in the early diagenetic stage. The relative rise of the water level in the shallow lake environment during rainy periods due to climatic changes allows the formation of dolomitic limestones. Both in parallel with the rhythmic changes in climatic conditions and depending on the Mg/Ca balance in the lake water, Ca and Mg carbonate succession begins. The abundantly porous, tufa-like structure of the dolomitic limestone indicates sudden crystallization. Along with the formation of dolomitic limestone, the rapid depletion of Ca^{2+} ions in the lake water allowed a sudden increase in the Mg/Ca ratio and the formation of huntite-hydromagnesite. Accordingly, during relatively dry climatic periods, huntite is precipitated on the lakeshore plain and in shallow ponds behind the shore, with the Mg/Ca ratio reaching around 30-40 as stated by Kinsman (1967) and Müller et al. (1972). The self-shaped crystals in the SEM images of the levels made entirely of huntite indicate that huntite can be deposited directly from lake waters as predicted by Calvo et al. (1995) (Çakmakoğlu, 2016).

While huntite was deposited in the marginal plains and local shallow ponds of the shallow lake environment, aragonite was deposited due to the presence of microbiality in the sections where it crossed into the open lake and transformed into hydromagnesite during the periods when it remained above the water table (subaerial environment) due to seasonal changes. As predicted by Calvo et al. (1995), facies made of huntite grains (reworking) locally scraped from the underlying huntite levels and transported to hydromagnesite zones over short distances are encountered. It is thought that the gaps in the hydromagnesite clusters were filled by the huntite mineral due to the advancing lake waters and that these huntite-filled areas were locally or bedded by dolomite in the late diagenetic stage. Dolomitic limestone is transitioned to dolomitic limestone by relatively deepening lake waters. Finally, the shallow lake environment deepens further and closes with limestone, the end product of the lake. At the transition levels from the open lake environment to the shallow lake environment, levels, where huntite is found as nodules in hydromagnesite mud, can be traced throughout the basin where the lacustrine deposits spread. Probably, this period of the lake indicates a short playa phase covering large areas (Çakmakoğlu, 2016).

Huntite-hydromagnesite deposits occur in a depositional environment that requires unique lacustrine conditions. The common feature of the deposits and recent formations is that they are found in alkaline and hydrologically closed lacustrine environments surrounded by Mg-rich rocks, with high pH values (>9) and microbialitic activity. Accordingly, it is predicted that huntite and hydromagnesite formations may be encountered in shallow lake facies within the lacustrine stacks of terrestrial basins opened in ophiolitic complexes (Çakmakoğlu, 2016).

In northeastern of the Çameli basin with this study, wide and long outcrops (some outcrops are more than 80 m wide and more than 2 m thick) were identified, indicating the possibility of significant new huntite ore mineralization areas (Figure 5). Huntite and hydromagnesite levels are characterized by their milky white color. The very thin laminated structure of the huntite mineral is distinctive due to its slab-like characteristics. Sometimes, it has a massive appearance and fractured structure.

In the Çameli basin, there are predominantly lacustrine sediments defined as Değne Member. The area is commonly represented by yellowish beige-grayish beige colored mudstone-claystone-marn, limestone at the upper levels, and conglomerate-travertine bands at the lower levels. Huntite mineralizations are located within the Değne member and tufa/travertines are dominant in the upper levels of mineralization. Beige-colored tufa/travertine formations with lateral and vertical transitions were observed within the huntite-hydromagnesite levels (Figure 5). It has a spongy texture with overlapping irregular and flat pores and it was observed that the laterally and vertically extending levels cut the huntite-hydromagnesite levels. However, it never cuts the overlying dolomitic limestones. Probably, these local formations are the products of the groundwater discharged into the lake along the fault zones during the huntite-hydromagnesite formation (Çakmakoğlu, 2016).

X-ray diffractometer (XRD) analyses were performed

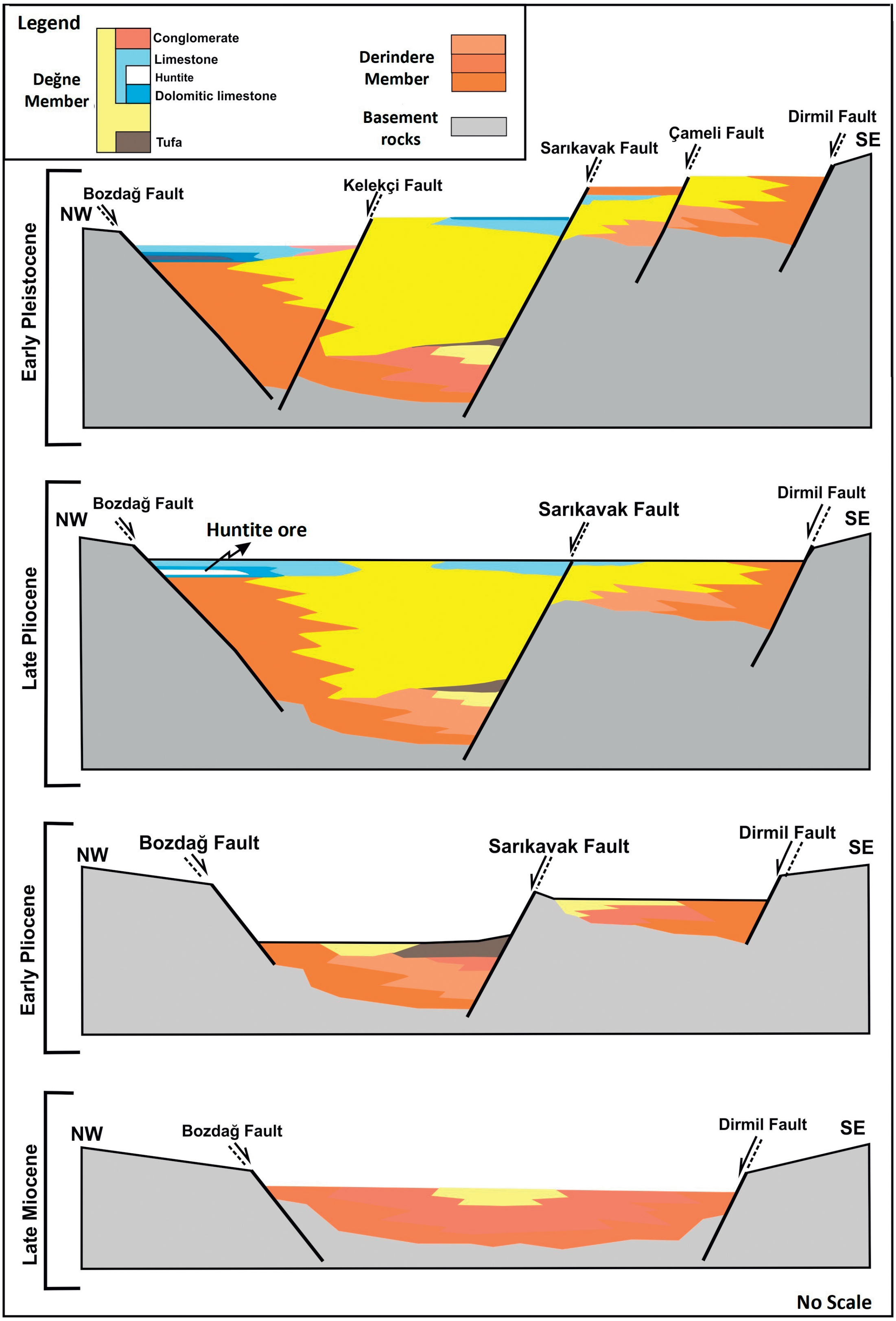

Figure 4. Location of huntite ore occurrence in the evolution of the Çameli Basin model cross-section (modified from Çakmakoğlu, 2016).

Figure 5. Views of huntite ore outcrops in northeastern of the Çameli basin.

on samples taken from outcrops in the northeastern of the Çameli basin with this study (Figure 2). In the samples, average 70.4% huntite, 15.2% dolomite, and 14.4% larnite minerals were detected. Major element analysis (X-ray fluorescence analysis) of the samples showed an average of 28.62% MgO, 18.78% CaO, and 44.09% loss on ignition (Table 1). Huntite mineral is theoretically predicted to contain 34.15% MgO and 15.88% CaO (Hollingbery, 2011). MgO values of the samples are 26.00-31.77% and CaO values are 18.50-19.66%. It is known that Shayan (1984) obtained a SrO value of 1.86% in the analysis values based on huntite samples taken from

Geelong-Victoria. He states that Sr content is most likely present in the structure of huntite and that Mg and Ca-rich solutions, which provide precipitation during huntite formation, play a role in releasing Sr on aragonite and then precipitate together with Ca and Mg. Here, huntite is thought to be a late meteoric phase product and the primordial mineral is aragonite.

SrO values in the samples are 0.11-0.30% (Table 1). Zachmann (1989) obtained high Sr values in huntite samples from the Kozani basin. He states that this high Sr concentration in huntite indicates that Ca-rich karst waters play an important role. Accordingly, it suggests that huntite was formed as a result of the mixture of karst waters from the basement and Mg-rich saline waters. The low SrO contents determined in the analysis results (Çakmakoğlu, 2016 and this study) sign that the formation of huntite in Çameli basin is a result of the mixture of Mg-rich saline waters and small amounts of Ca-rich karstic waters from the basement. Loss on ignition (LOI) values of the samples are 38.85-47.53%, CO_2 values are 44.77% and 45.14% (Table 1). When compared with previous studies on huntite minerals (Table 2), it is understood that all these values are quite close to each other.

DISCUSSION

The huntite ore occurrences in the Çameli Basin (Southwestern Turkey) and the Kozani Basin (Northern Greece) are stratiform deposits. The huntite ore deposits in the Kozani Basin have been studied by many researchers (Wetzenstein, 1975; Zachmann, 1989; Calvo et al., 1995). The Kozani Basin is a basin located in northern Greece near the Macedonian border, covering an area of approximately 400 km^2. It draws attention with its structural and lithologic features similar to the other one, Çameli Basin. The basin is located between the basins (Kozani, Florina, Ptolemais, Elassona) that were opened due to post-Alpine extension tectonics within the Pelagonian Zone (Metaxas et al., 2007). During the Late Miocene-Early Pliocene, it was filled by terrestrial clastic, fluvial, and lacustrine deposits. The basin sediments are

Table 1. Geochemical analysis results of the samples taken from outcrops.

Sample No	Coordinates		MgO (%)	CaO (%)	MgO/CaO	SiO_2 (%)	Fe_2O_3 (%)	SrO (%)	LOI (%)	CO_2 (%)
	X	Y								
Outcrop-1	4107278	696808	31.77	18.50	1.72	1.61	0.092	0.20	47.53	45.14
Outcrop-2	4108854	696088	28.10	19.66	1.43	13.16	1.930	0.11	38.85	-
Outcrop-3	4106484	693599	26.00	18.18	1.43	5.21	0.250	0.30	45.89	44.77

Table 2. Results of geochemical analyses for huntite ore.

Field/Basin	Kozani Basin	Current Greek (US)	Deer Park Victoria (Australia)		Geolong Victoria (Australia)		Tea Tree Gully (Australia)	Eğirdir (Turkey)	Yalvaç (Turkey)	Burdur (Turkey)	Western-Northwestern Çameli Basin (Turkey)	Northeastern Çameli Basin (Turkey)
Reference	Sibelco Hellas (2015)	Faust (1953)	Cole and Lancucki (1975)	Shayan (1984)	Shayan (1984)	Koblencz and Nemecz (1953)	Skinner (1958)	Kangal and Güney (2006)	Yavuz et al. (2006)	Parlak and Akgöz (2020)	Çakmakoğlu (2016)	This study (average)
MgO (%)	38.00	34.09	33.00	33.66	33.27	33.49	33.20	35.10	32.70	33.20	33.81	28.62
CaO (%)	9.50	15.42	15.00	14.00	13.24	13.71	15.60	12.48	13.84	13.70	15.05	18.78
SiO_2 (%)	0.20		0.20					2.43	6.18	3.90	1.13	6.66
Fe_2O_3 (%)	0.05		0.11					0.18	0.04	0.70	0.04	0.76
SrO (%)				1.82	1.86			2.43		0.05	0.17	0.20
LOI (%)	52.50							46.40	46.41	47.30	49.04	44.09
CO_2 (%)	43.40	48.85	47.80	47.80	48.18	43.98	50.40					44.96

divided into the Lower and the Upper Neogene Series. The Lower Neogene Series consists of limestone and marl deposits of freshwater environment containing lignite intercalations. The Upper Neogene Series consists of dolomitic marl, limestone, and sandstone deposits containing Mg-carbonate layers and lenses. The Upper Neogene Series also includes marly diatomites (Owen et al., 2010) and tuff levels made of volcanic ash debris (Hall and Stamatakis, 2000). Mg-carbonate formations contain huntite, hydromagnesite, magnesite, dolomite, and aragonite minerals (Zachmann, 1989).

Wetzenstein (1975) categorized the Mg-carbonate formations in the basin into four types. He mentions clayey-silty huntite magnesite as the most common type. The second type is hydromagnesite-huntite, the third type is nodular huntite in a clayey matrix and the fourth type is the less common magnesite along the cracks.

Zachmann (1989) observed hydromagnesite formations several hundred meters wide and 4-6 meters thick in the Kozani basin and suggested that hydromagnesite may be present in the lacustrine environment to form extensive sedimentary Mg-carbonate deposits. Based on the presence of aragonitic sinter observed with hydromagnesites, he predicted that hydromagnesite was deposited by the inclusion of karstic waters in Mg-rich surface waters. The surface waters are strongly enriched in Mg^{2+}. The karst waters trapped beneath the surface are saturated with Ca^{2+} and HCO_3^- and climb in separate periods from the base to the surface. High HCO_3^- and rising pH in the vicinity of aragonite sinter fields trigger hydromagnesite precipitation. Subsequently, hydromagnesite is transformed into magnesite under high pressure as a result of late diagenetic metamorphic functions. Huntite is another mineral found in significant quantities (several hundred thousand tons) in the basin, occurring with/along with magnesite or in uniform layers. Based on its paragenesis with magnesite and its rare element content (e.g. high Sr), a similar origin is predicted for both carbonate minerals. Huntite was formed in the subsurface under the influence of karst waters and fed to the surface. However, it has been suggested that huntite formed after magnesite with decreasing pressure.

Calvo et al. (1995) suggest that huntite in the Kozani basin was deposited in pockets in the coastal parts of the main lake system, either associated with hydromagnesite and magnesite or as a pure Mg carbonate phase. Unlike Zachmann (1989), they argue that huntite is a direct precipitation or early diagenetic product in these pockets under surface conditions. This is indicated by the observation of huntite grains in the clastic facies. The huntite probably started to form as a kind of gel-like mud, similar to the “yogurt” appearance described for dolomite in other evaporitic lakes, and then evolved into the more solidified massive huntite. The huntite formed on the coastal carbonate plains as the lake level decreased, and then during the rise of the water level, the huntite began to disintegrate with the flow formed on these plains and was transported towards the lakeshore deltaic complex. This detrital character of huntite is considered to be stable for a long time. Therefore, contrary to the views suggesting a late diagenetic origin, huntite is said to have formed by direct deposition or as a very early diagenetic product.

In addition, small amounts of huntite and/or hydromagnesite minerals can be found in evaporitic lakes (Kinsman, 1967; Müller et al., 1972) and magnesite deposits (Bashir et al., 2009; Topak et al., 2009). Kinsman (1967) observed huntite minerals in unlithified sediments in the Trucial coastal plain, 30 km southwest of Abu Dhabi. The mineral is in the form of irregular fringes and bubbles and is stated to be only 1 cm thick. The Mg/Ca ratio in marine lagoon waters is around 5.3-5.5. In marine-derived cavity fluids, it is stated that this ratio increases rapidly as a result of the loss of calcium due to the precipitation of gypsum and anhydrite, and huntite precipitation occurs when the Mg/Ca ratio reaches 10 (or even 30) values. The pH values taken from the solution in the cracks are in the range of 6.5-7.5. Other conditions required for precipitation are temperature in the range of 20-40 ºC and CO_2 pressure of 10^{-2}-$10^{-3.5}$.

Müller et al. (1972) determined aragonite, low and high Mg-calcite, dolomite, huntite, and magnesite minerals in their study conducted in modern lakes with different depths, salinity, and pH values. It says that low and high Mg-calcite, aragonite, hydromagnesite, and neskehönite minerals were formed primordially. Dolomite, huntite, and magnesite were formed secondarily under diagenetic conditions. Three main functions control primitive carbonate mineral precipitation. These are; i) CO_2 loss or export (as a result of change in pressure-temperature conditions, plant assimilation), ii) evaporation intensity, iii) a mixture of different water bodies (such as a mixture of river waters of normal composition rich in Ca and HCO_3 and a highly alkaline environment, as in most Anatolian lakes). It has been reported that low Mg-calcite is precipitated primordially in environments where the Mg/Ca ratio is less than 2, high Mg-calcite in the range of 2-12, and aragonite in environments with a Mg/Ca ratio greater than 12. It has been suggested that the first diagenetic carbonate mineral was dolomite and that it may have formed at a Mg/Ca ratio between 7 and 15 (probably closer to 7) based on investigations in some recent lake samples. However, if the primary mineral of lake sediments is aragonite, no trace of dolomite is found, no matter how high the Mg/Ca ratio is. Huntite and magnesite, the other diagenetic secondary carbonate minerals, require a higher Mg/Ca ratio. According to the increasing Mg/Ca ratio; high Mg-calcite, dolomite, huntite, magnesite respectively.

Bashir et al. (2009), in their study conducted in the Khuzdar lakes region of Pakistan, identified magnesite occurrences in the form of thick veins and stoichiometric settings within serpentinized harzburgites. It was stated that brucite mineral was first formed by the hydration of Mg ions, but it was only stable under low temperature, basic pH, and low CO_2 pressure. It is said to transform into hydromagnesite under higher partial CO_2 pressure. At higher temperatures, hydromagnesite turns into magnesite. With the presence of calcium ions coming into the system from meteoric waters and side rocks, huntite starts to crystallize. With the increase in carbonate ion concentration, huntite turns into dolomite, a more stable mineral. All these metastable minerals finally transform into magnesite with changes in temperature, CO_2 pressure, and water saturation level. Accordingly, the mineral trend is brucite, artinite, hydromagnesite, huntite, dolomite, and magnesite.

Topak et al. (2009) mentioned the mineral association of calcite, dolomite, calcite-magnesian, huntite, and magnesite in the sedimentary magnesite deposits in Lake Hoyran (Southwestern Anatolia), which they considered as Bela Stena type. They stated that the Mg required for magnesite formation comes from the alteration of ultramafics and carbon dioxide from the atmosphere and anaerobic fermentation in the underlying lignites. As calcite begins to precipitate in the lake water, accordingly, the Mg/Ca ratio increases respectively.

Huntite is formed as a result of superficial weathering or alteration of rocks containing dolomite or magnesite. It can be found in cavities of magnesite-bearing rocks, travertines, caves, and fault zones as precipitated as very fine grains from cold groundwater (Weber, 2000). Carbonate deposits containing hydromagnesite and aragonite were formed by the evaporation of salt-alkaline-based lakes that have survived from the Tertiary when the Mg/Ca ratio increased up to 30. They are evaporative deposits in origin. The deposits containing huntite, hydromagnesite, and magnesite are formed as a result of precipitation in lakes with Mg/Ca ratios up to 500 (Dead Sea Bromine Company, 1996). Indeed, laboratory studies show that hydromagnesite can precipitate directly from solutions rich in magnesium and sodium bicarbonate. Therefore, it is understood that huntite and hydromagnesite were formed either by direct precipitation or as alteration products of aragonite and/or hydromagnesite (Atay and Çelik, 2010). The first ophiolitic rocks were subjected to serpentinization. Mg, Ca, Fe and other elements from serpentinized rocks were transported by hydrothermal fluids, resulting in the carbonation of these ions, the formation of their hydroxides and the formation of carbonates of different compositions to form these sediments. Initially, at low temperature and under low partial pressure of carbon dioxide (P_{CO_2}), quasi-stable hydroxides and carbonates were formed, which gradually transformed into the stable magnesite phase. The scarcity of foreign minerals indicates relatively high temperature conditions and carbon dioxide pressure that transformed the semi-stable minerals into the magnesite phase (Figure 6). Huntite crystallizes in the trigonal system and its structure is similar to that of dolomite. Huntite formations contain different mineral types such as hydromagnesite, magnesite, aragonite and dolomite. Huntite can form in low-temperature surface or near-surface conditions, either by direct precipitation from Mg-rich solutions or by interaction of Mg-rich water with carbonate minerals. It can also be found as a fill in weathered serpentinite cracks just below the soil profile. It has been experimentally shown that huntite always precipitates before dolomite, depending on any increase in CO_2 concentration. Huntite precipitates before dolomite because its more open structure allows for enhanced Mg dehydration (Bashir et al., 2009).

According to Özden (2004), the high Sr, As and B contents in the carbonates indicate that the magnesium-rich solutions feeding the basin are of hydrothermal origin. In the study, it was stated that the depositional environment in the Yalvaç-Yarıkkaya Neogene basin in Turkey shows great similarities with the Kozani Basin in Greece. It was reported that the spring waters from ultrabasic and dolomitic rocks in the basin have alkaline pH and are rich in Mg^{2+} and HCO_3 ions. Therefore, serpentinized ultrabasic rocks, carbonates and volcanic activities are possible sources of some trace elements in the basin. During the alteration process of ultrabasic rocks, silica was released from serpentinized ultrabasic rocks and probably fixed by siliceous lacustrine organisms, leading to the amorphous silica phase. Three thermodynamic parameters can be said to play a major role during the precipitation of a carbonate phase in a lacustrine environment: alkalinity of the solution, partial pressure of carbon dioxide (P_{CO_2}) and the amount of Mg and Ca in the solution. If the Ca concentration in a magnesite-containing solution is high, aragonite precipitates first, followed by huntite and finally hydromagnesite (see the 1-2-3 pathway in Figure 7, orange colored circles). If the concentration of Mg and P_{CO_2} are both high, magnesite precipitates out of solution. Thus, depletion of Mg in solution causes precipitation of the mineral huntite in the carbonate precipitation environment. Under low conditions for a relatively low carbonate ion concentration and a constant Mg/Ca ratio, hydromagnesite can precipitate from lake water as a thin horizon with the formation of huntite (see the 4-5-6 pathway in Figure 7, orange colored circles).

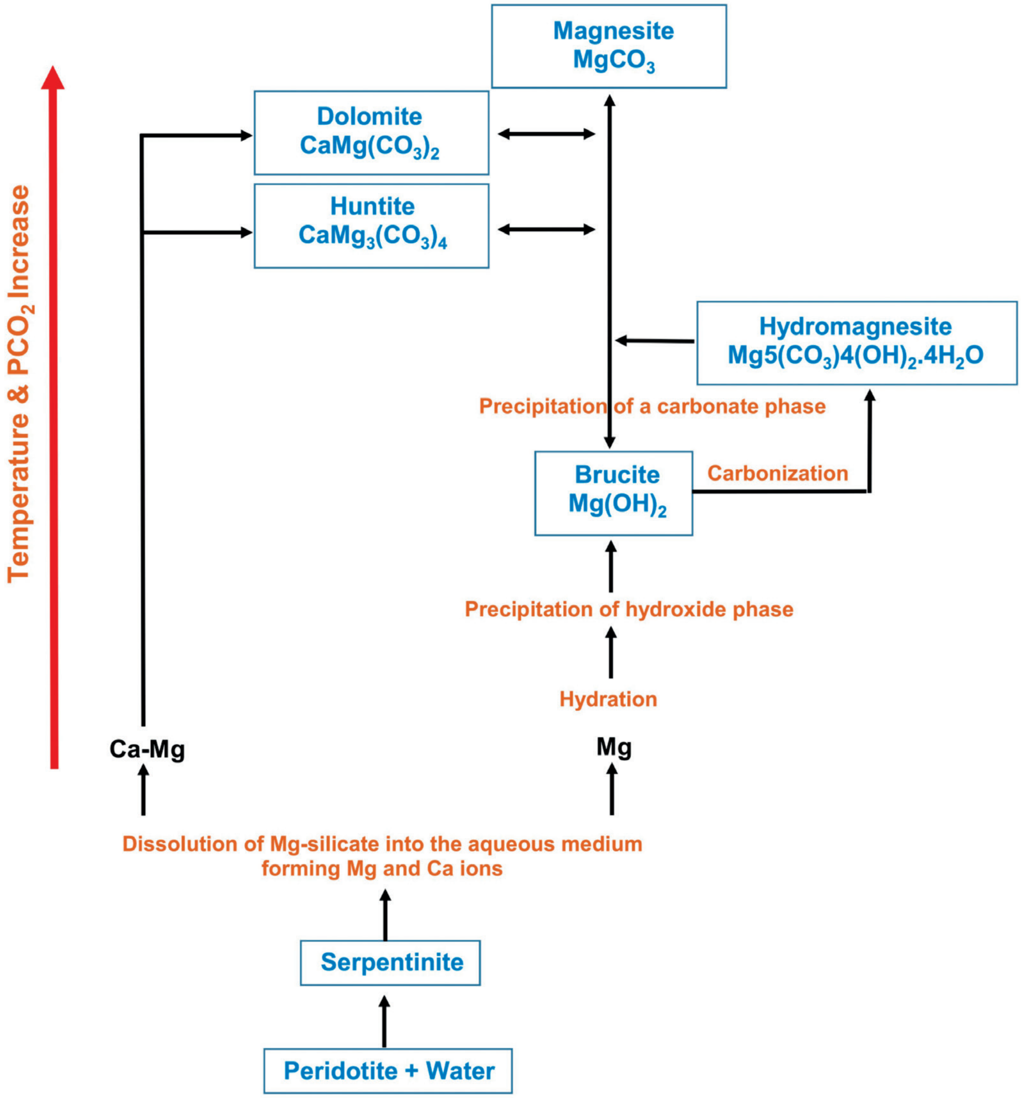

Figure 6. Schematic model of huntite ore formation (modified from Bashir et al., 2009).

In the Yalvaç-Yarıkkaya Basin, cyclic carbonate deposition was formed depending on the chemical composition of solution with respect to Mg and Ca ions. There exist carbonate rocks composed mainly of dolomite at the base (1 pathway in Figure 7, blue colored circles). Following the deposition of dolomite, relatively magnesium-rich lake water was deposited huntite at the suitable part of lacustrine environment (2 pathway in Figure 3, blue colored circles). The precipitation of huntite in turn removed sufficient calcium from the system and then lake water was saturated by more magnesium content than the initial stage of dolomite deposition. At this part of the deposition, magnesite was started to precipitate depending on the appropriate physicochemical condition of carbonates (3 pathway in Figure 7, blue colored circles). Removing high concentration of magnesium from the lake water may later precipitate huntite in the basin when sufficient magnesium and calcium in solution are able to crystallize huntite. Mg- and CO_2-rich surface and karst waters circulating in ultrabasic and dolomitic rocks may carry significant amounts of Mg^{2+} as well as Ca^{2+} and Sr^{2+} ions. The high As, B and Li contents in the carbonates analyzed may also indicate a possible magma chamber beneath the depositional environment. This possible source could be the cause of the high content of some trace elements during the circulation of the hydrothermal solution within the rocks (Özden, 2004).

Kuşçu et al. (2018) stated that huntite formations in

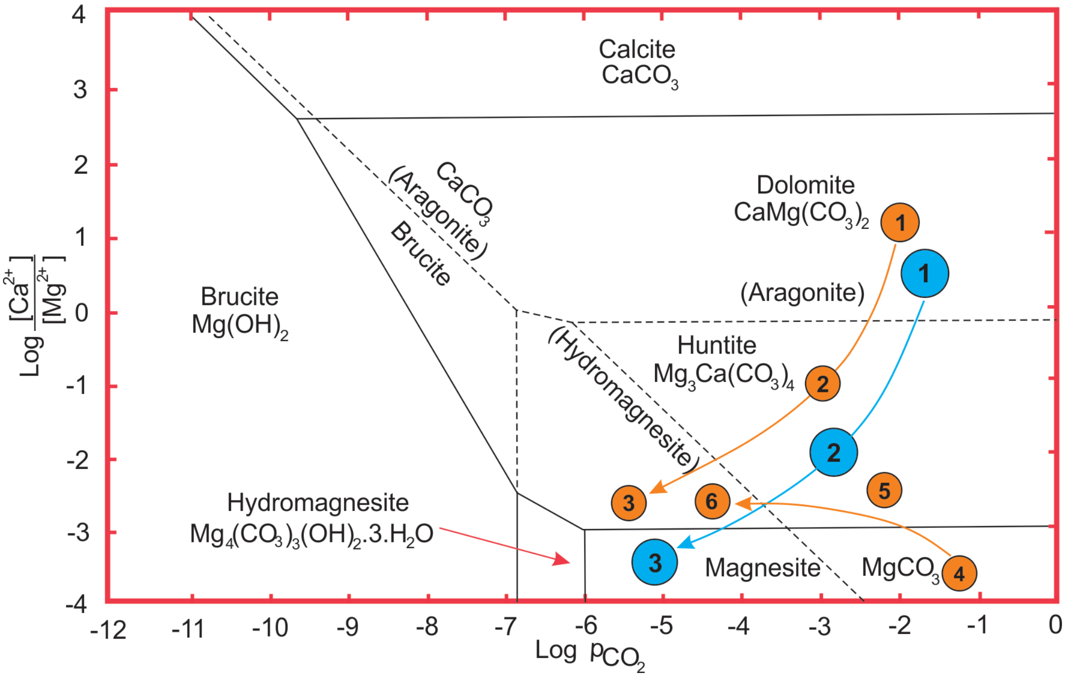

Figure 7. Precipitation pathways and stability relations of huntite ore occurrences in the Kozani basin in Greece (orange colored circles) (from Stamatakis, 1995) and Yalvaç-Yarıkkaya basins in Turkey (blue colored circles) (from Özden, 2004).

the Eğirdir-Hoyran Lake Basin (Southern Turkey) were deposited in shallow, alkaline (8.5-9.5 pH) and low temperature (approximately 25 °C) lake conditions. The Mg^{2+}, Ca^{2+} and Sr^{2+} ions required for huntite formation were derived from the surrounding rocks such as ultrabasic rocks, dolomite, dolomitic limestone and limestone in the basin. The required source of CO_2 is metamorphic CO_2, carbonate rocks, freshwater carbonates and groundwater. The source of oxygen can also be marine limestone, freshwater carbonates and meteoric water (Kuşçu et al., 2018).

As suggested by Calvo et al. (1995), a model of initial massive huntite formation in pockets on carbonate plains at the edge of the lake basin can be proposed for huntite mineralization in the western and northwestern of Çameli basin. During periods of arid climate, hydromagnesite and huntite are deposited at the lake margin. Spongy tuff clusters within the hydromagnesite levels were formed under the influence of groundwater opening into the shallow lake environment. Hydromagnesite was deposited by microbial processes at the lakeside (Kazmierczak et al., 2011). Huntite, on the other hand, precipitates by forming a gel-like level in local zones (temporary ponds and pockets) at the lake margin due to the sudden change in the Mg/Ca ratio (Calvo et al., 1995). It is also observed as a mineral filling the voids in hydromagnesite. The rise of the lake level over time and the flattening and widening of the lake margin must have caused the massive huntite ores to be wetted and dispersed, allowing the huntite crumbs to be carried by the rivers and deposited in the deltaic units along the lake margin (Figure 8). Even if the huntite is broken and dispersed, the probability of the huntite mineral remaining intact for a long time is much higher than expected (Calvo et al., 1995; Çakmakoğlu, 2016).

Yalcin and Bozkaya (2004) have shown the alteration trend of the sediment and ore minerals on a triangular diagram. This diagram is organized according to the SiO_2-CaO-MgO contents of serpentine, magnesite, and carbonates. This diagram reveals that serpentine minerals have similar compositions to peridotites and that Ca entered the alteration environment later. The position of huntite ores on the diagram (Figure 9) indicates that huntite was formed by carbonization of alterated serpentine. This result is in line with the studies of Calvo (1995), Özden (2004) and Bashir et al. (2009) (Figures 6 and 7).

CONCLUSION

The results of this study indicate that Sr content is most likely present in the structure of huntite and that Mg- and Ca-rich solutions that precipitated during huntite formation played a role in releasing Sr on aragonite, which then precipitated together with Ca and Mg. This suggests that huntite is a product of the late meteoric phase and the primary mineral is aragonite. The Sr concentration in

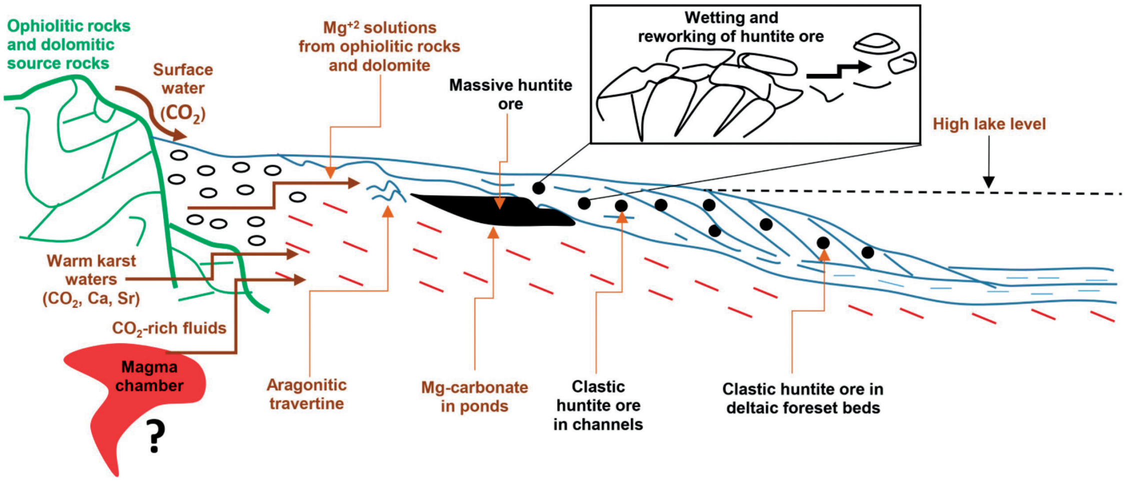

Figure 8. Proposed schematic model for the formation of huntite ore (complied from Calvo et al., 1995; Özden, 2004; Çakmakoğlu, 2016 and Kuşcu et al., 2018).

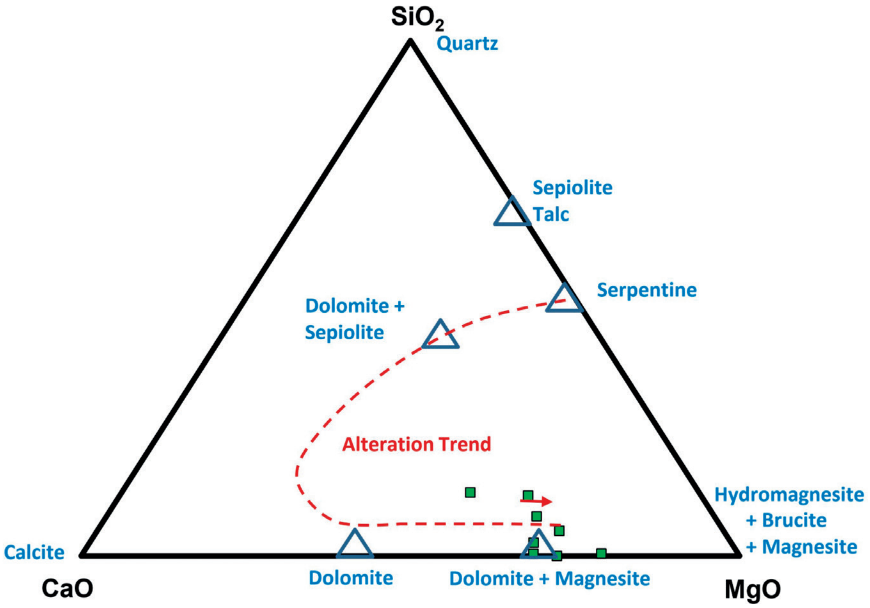

Figure 9. Triangular diagram showing that huntite ore is formed by carbonization of altered serpentine (the diagram: modified from Yalçın and Bozkaya, 2004). Green quadrangles: Huntite ores in Tables 1 and 2 (see Figures, 6-8).

huntite signs that Ca-rich karst waters played an role in the process. Accordingly, it is thought that huntite was formed as a result of the mixture of karst waters coming from the basement and Mg-rich saline waters. The positions of the huntite ores in the northeastern od Çameli basin and in the literature on the triangular diagram of the alteration trend indicate that the huntite ore was formed by carbonation of the serpentine.

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