

# HUNTITE DEPOSITS IN THE NEOGENE LACUSTRINE SEDIMENTS OF THE ÇAMELİ BASIN, DENİZLİ, SW TURKEY

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**ABSTRACT:** Extremely white huntite having friable, earthy character occurs in the Çameli basin which was downthrown along reverse faults during neotectonic activity. The basement comprises dolomitic limestone and peridotite which were the main sources of Mg for huntite formation. These units are overlain unconformably by conglomerate, sandstone, and mudstone of a fan-delta environment and, locally, by swampy facies, and by dolomite-dolomitic marl-huntite and karstic limestone which represent mud-flat and open-lake sediments, respectively. The huntite occurs as 0.5-3-m-thick massive deposits as well as fillings of fenestral dissolution voids and as sheet cracks in dolomitic marl, dolomite and limestone which are evidence of arid to semi-arid climatic conditions. Massive huntite with dolomite and/or hydromagnesite/magnesite probably formed by diagenetic processes in light of the gradational contact of huntite with dolomite in the Suçatı huntite deposit. While discoidal and fenestral huntite formed by direct precipitation of Mg-rich pore waters in shallow coastal sediments of a mud-flat environment, the huntite flocculated during the precipitation of karstic limestone, probably in a pluvial climatic regime.

## INTRODUCTION

Huntite,  $\text{CaMg}_3(\text{CO}_3)_4$ , was first found and described by Faust (1953) in cavities of magnesite and dolomite which formed as a result of reaction between meteoric water and host rocks. Since then, there has been limited study of this scarce mineral in nature. Huntite forms principally in karstic limestone, dolomite and ultrabasic rocks by infiltration and precipitation of Mg-rich waters derived from ultrabasic and dolomitic rocks (Faust 1953; Baron et al. 1957; Skinner 1958; Wetzenstein 1975; Shayan 1984; Zachmann 1989; Stanger and Neal 1994), as early diagenetic products of Mg-rich solutions in pore waters of sabkha-supratidal environments (Kinsman 1967), by the activity of methanogene and sulfate bacteria on lagoonal sediments (Perthuisot et al. 1990), and by diagenetic transformation of calcite, aragonite, dolomite and hydromagnesite in alkaline lakes (Irion and Müller 1968;

Müller et al. 1972; Popov and Sadykov 1986; Calvo et al. 1995b; Mutlu et al. 1999).

The Çameli Neogene carbonate facies contain three huntite deposits, namely, in the Suçatı, Sarnıç and Yaylacık sections (Figs. 1 and 2). Huntite in some of these deposits is associated with small amounts of hydromagnesite, magnesite and dolomite (Table 1). The Çameli huntite is characterized by extreme whiteness, occurring as friable intervals in carbonate units. However, huntite also occurs as laminae, lumps and fenestral dissolution void-fillings in dolomite and limestone. The purpose of this paper is to elucidate the depositional environment and conditions of huntite formation. The genesis of the huntite also will be discussed in light of field observations, mineralogical associations and textural relationships.

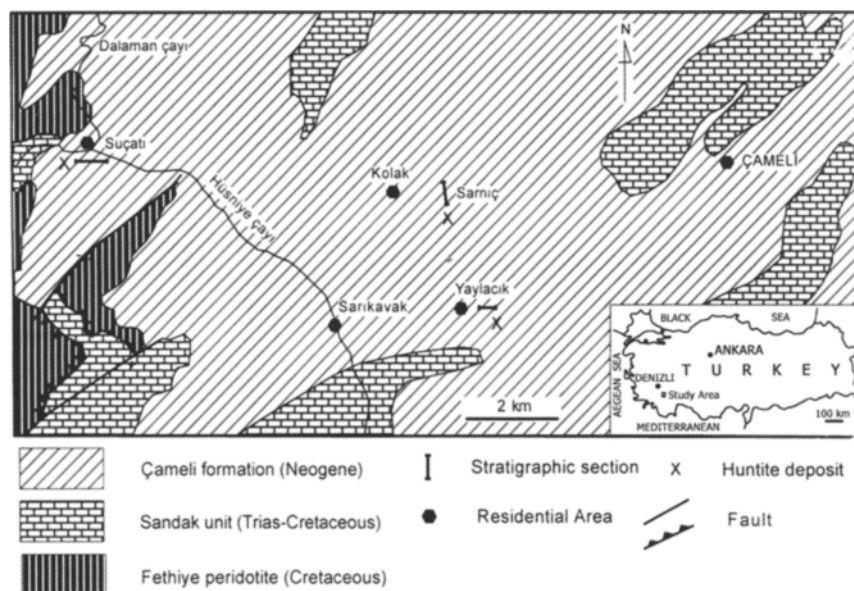


Figure 1. Geological map of the Çameli basin (revised from Erakman et al. 1982).

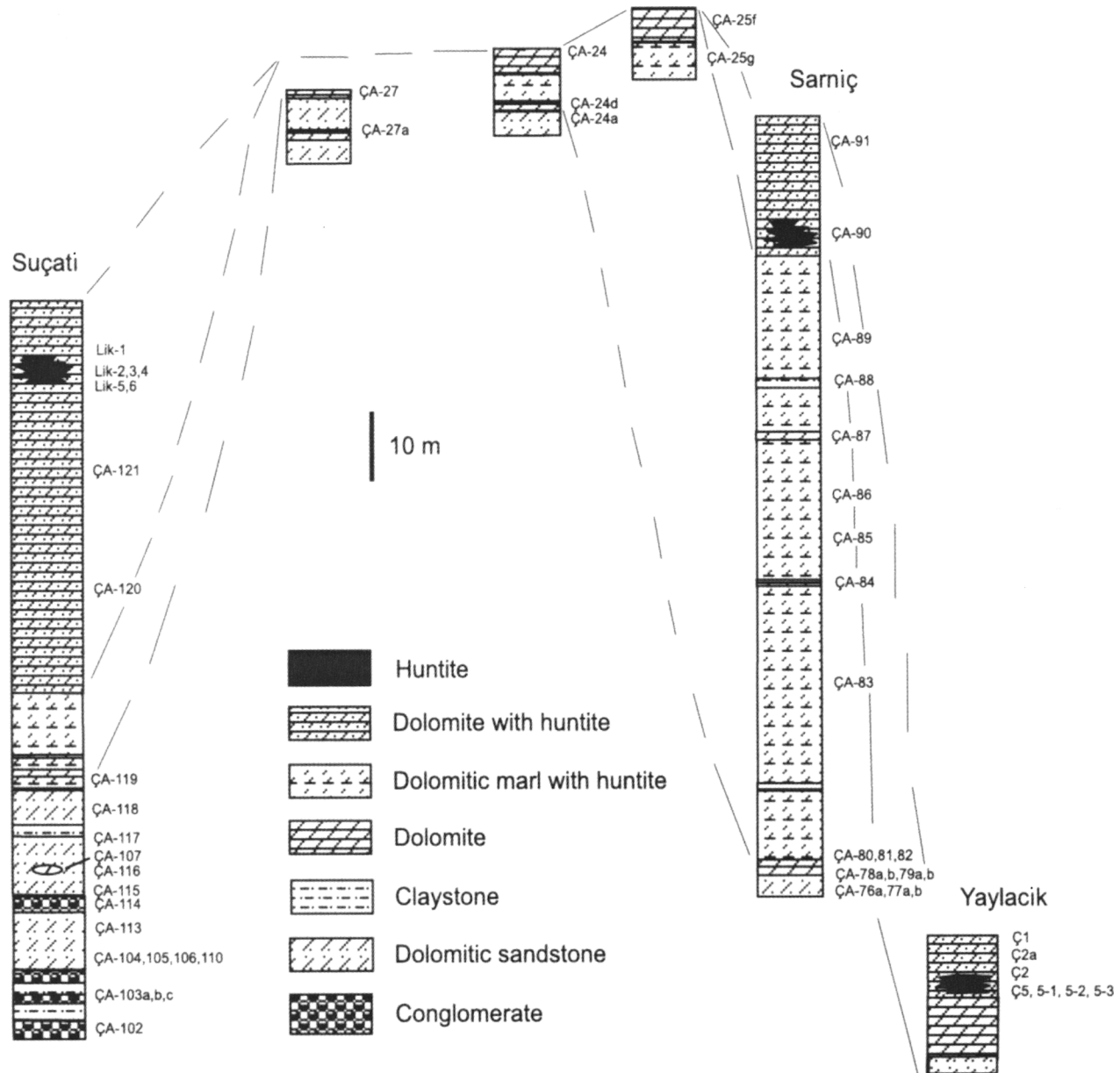


Figure 2. Distribution of the principal lithologies of the Çameli Neogene basin.

## METHODS

Carbonate-dominated facies in the Çameli Neogene basin were studied on the basis of the 1/100,000-scale N22 and O22 geological maps of previous workers (Erakman et al. 1982). In the present study, 1/25,000-scale geological mapping of the huntite-rich carbonate facies was completed, and several stratigraphic sections were measured and pits were dug in order to identify the vertical and lateral distribution of huntite (Figs. 1 and 2).

One hundred samples were collected from various facies, including huntite-rich ones. The mineralogical characteristics of the samples were determined by X-ray powder

diffraction (XRD) (Rigaku-Geigerflex), differential thermal analysis-thermogravimetry (DTA-TG) (Rigaku TAS 100, E model) and scanning electron microscopy (SEM-EDX) (Jeol JSM 6400–Noran instruments Series II). For petrographic studies, 30 thin sections were prepared from the samples. The mineralogical compositions of the samples were examined by XRD using CuK $\alpha$  radiation with a scanning speed of 1°2 $\theta$ /min. For determination of bulk mineralogy, unoriented mounts of powdered whole-rock samples were analyzed using an X-ray powder diffractometer. Semi-quantitative estimates of rock-forming minerals were calculated using the external standard method of Brindley (1980).

DTA-TG curves were recorded using 10 mg of powdered

Table 1. Mineralogy of Çameli basin lithologies.

Sample No	Hunt	Dol	Mag	Hmag	Cal	Serp	Amph	Feld	Qz	Smc	Chl
ÇA-104		+++				+		+			
ÇA-106		+++				+	+				
ÇA-107		++++				+				ac	
ÇA-110	++	+++			ac	ac			ac		
Lik-6	++++	+									
Lik-5	++	++		+							
Lik-4	++++	+									
Lik-3	+	++++									
Lik-2	+++	++									
ÇA-25g	++++	+									
ÇA-24a	++	+++				ac					
ÇA-27a	+	++++			ac						
ÇA-76a		+++++									
ÇA-77a, b		+++++									
ÇA-83		+++	+			+	ac				
ÇA-84		+++	+			+				ac	
ÇA-85	++++	+				ac					
ÇA-86		+++				+			ac	+	
ÇA-88		+++							ac	++	
ÇA-89	++	+	++			ac					
ÇA-90	++	+	++			ac					
ÇA-91		++	+		++						
Ç1	+++++										
Ç2	+++++										
Ç2a			+++++								
Ç5	++++				+						
Ç5-1	+++++										
Ç5-2	++++				+						
Ç5-2*					+++++						
Ç5-3	++		++		+						
ÇE-56*	+++			++							
ÇE-62*	++	++			ac	ac					+
ÇK-3*	+++	+		+							
ÇK-4*	++++			+		ac					
ÇY-11*	+++++				ac	ac					
ÇY-12*	++	+	+		+						
ÇY-13*	+++++										

Hunt: Huntite, Dol: Dolomite, Mag: Magnesite, Hmag: Hydromagnesite, Cal: Calcite, Serp: Serpentine, Amph: Amphibole, Feld: Feldspar, Qz: Quartz, Smc: Smedite, Chl: Chlorite, \*: Host rock of Ç5-2 \*: Point sample, +: Relative abundance of mineral, ac: Accessory

sample in a Pt sample holder at an average heating rate of 10°C/min with an alumina reference.

Three representative huntite-dominated samples were selected for SEM-EDX analyses; fresh, broken surfaces of the samples were affixed onto aluminum sample holders with double-sided tape and then coated with a thin film of gold using a Giko IB.3 ion coater.

Five representative samples of huntite and huntite-dominated dolomitic-marl host rock were chemically analyzed for major oxides by XRF (Rigaku X-ray Spectrometer RIX 3000).

### GEOLOGY AND HUNTITE FACIES OF THE ÇAMELI BASIN

The basement and periphery of the Çameli basin are composed of dolomitic limestone of the Triassic-Cretaceous Sandak unit and the Fethiye peridotite (Erakman et al. 1982; Fig. 1). The western part of the basin was downthrown along reverse faults during a period of neotectonic activity (Kaya 1982). The consequent depression was filled with detrital and lacustrine

carbonate sediments. These detrital sediments chiefly comprise conglomerate, sandstone and mudstone, and carbonate units consisting of marl and limestone. Medium- to thin-bedded marl and medium-thick-layered limestones contain scarce plant-stem imprints and, locally; gastropod and ostracod shells. The Upper Miocene-Lower Pliocene continental and lacustrine sediments have been assigned to the Çameli formation (Erakman 1982; Senel et al. 1989; Bilgin et al. 1990).

The lower part of Çameli formation, which has a thickness of ~ 600 m, consists of detrital facies, while the middle and upper parts are dominated by carbonate facies (Fig. 2). Conglomerate, sandstone and mudstone materials of a fan-delta environment (Allen and Collinson 1986; Changsong et al. 1991) and locally swamp facies (Normati and Salomon 1989; Szulz and Cwizewicz 1989) crop out on the margins of the Çameli basin (Figs. 1 and 2). Carbonate sediments of the basin are comprised mainly of dolomite, dolomitic marl, huntite and small amounts of limestone. Mg-rich carbonate units in the upper part of the basin show evidence of drought to arid/semi-arid climatic conditions in comparison to swamp

and fan-delta sediments in the lower part.

Mg-rich carbonate sediments in the marginal and central parts of the basin are closely related to the tectonic uplift of Triassic-Cretaceous dolomitic limestone and peridotite (Fig. 1). Mg-dominant carbonates formed in close proximity to the ultrabasic rocks in the southwestern part of the basin. Therefore, huntite probably precipitated from Mg-rich lake water. Huntite associated with small amounts of hydromagnesite/magnesite may have formed diagenetically from dolomite and dolomitic marl (Table 1). Huntite is the dominant carbonate mineral in the Suçati, Sarnıç and Yaylacık sections of the basin. Huntite is present as 0.5-3 m massive deposits and also as fenestral dissolution void-fillings, and as sheet cracks in dolomitic marl, dolomite and limestone (Fig. 3).

The Suçati mine is one of the most important huntite mines in operation, with a huntite thickness of ~ 5 m and a lateral extent of ~ 50 m (Fig. 3a). Huntite occurs in fenestral dolomite in the uppermost intervals. The huntite intervals are extremely white and have a friable, earthy character.

#### **Suçati Huntite Deposit**

The lower part of the Suçati section is composed mainly of fan-delta sediments characterized by peridotite pebbles intercalated with scarce, thin, friable sandstone and mudstone layers having scarce convolute structures. These sediments are overlain by sandy dolomitic marl of a mud-flat environment. The deposit crops out in the upper part of the dolomite-intercalated dolomitic marl that has a thickness of ~ 100 m (Fig. 2). These units are overlain by silicified dolomite and locally, by karstic limestone, and in the levels contains massive huntite deposits. Thick, laminated, whitish to cream-colored dolomitic marl contains huntite-filled cavities. Thin- to medium-layered, beige to cream-colored dolomite is silicified, and contains huntite-filled cavities. Massive huntite occurs as a lenticular bed having a thickness of 1.5-3 m and a length of up to 50 m, and also is observed in karstic limestones as huntite fillings of dissolution voids. These levels also enclose dull-white dolomite relicts, and scarce occurrences of hydromagnesite and magnesite. In addition, these levels have lateral and vertical transitions with discoidal huntite in dolomite and irregular huntite fillings in karstic limestones.

Huntite formed from Mg-rich waters as discoidal masses and/or as cavity fillings under arid to semi-arid climatic conditions. Dolomite and massive huntite precipitated in Mg-rich, shallow open-lake waters (Irion and Müller 1968; Müller et al. 1972).

#### **Sarnıç Huntite Deposit**

The lower part of Sarnıç section is composed of beige-brown dolomitic limestone containing gastropod shells, plant stems, and sandy clay and conglomerate which locally contain thin

lignite beds. The floor of dolomitic limestone is silicified as an inverse carbonate cone coated with plant stems and lignite particles, indicating a swamp and carbonate-rich environments existed for limited periods (Normati and Salomon 1989; Szulc and Cwizewicz 1989). The middle part of the sequence consists of dolomitic marl with thin dolomite and lenticular huntite intercalations (Figs. 2 and 3b). The dolomitic marl is white, massive to thickly layered in places, and generally includes fenestral structures and sheet cracks. These cavities are filled with discoidal and lenticular huntite (Fig. 3c). These sediments represent a mud-flat environment (Janaway and Parnell 1989; Calvo et al. 1995a). The upper part of the sequence is mainly composed of dolomitic marl, dolomitic limestone and dolarenite-calcarenite debris which contain several 0.5-1m-thick huntite intercalations. Magnesitic huntite is extremely white, massive, and thickly laminated, and contains scarce, earthy and friable, lenticular calcarenite-dolarenite. The calcarenite and dolarenite were probably transported from the upper beach rocks by waves and coastal flow. The Sarnıç huntite is free of dolomite and, therefore, probably formed by direct precipitation. In any case, the huntite may have precipitated when the lake water had a high Mg/Ca ratio due to strong evaporative conditions (Müller et al. 1972). The dolarenite-calcarenite exhibits the planar and thorough cross-stratification of beach rocks (Gischler and Lomando 1997). These units are overlain by beige-cream, porous, scarcely silicified, thin- to medium-layered dolomitic limestone and by white-cream karstic limestones having larger cavities in its uppermost intervals (Fig. 3d). Huntite in the karstic cavities has generally been leached by meteoric waters. These limestones may have formed by fresh-water influx which resulted in precipitation of  $\text{CaCO}_3$  under pluvial climatic conditions.

#### **Yaylacık Huntite Deposit**

The Yaylacık huntite crops out along the fault contact of Triassic-Cretaceous dolomite and dolomitic limestone and has a thickness of ~ 2 m and a lateral extent of ~ 50 m (Figs. 1 and 2). White-cream, white to greenish beige, massive, earthy and friable huntite is intercalated with thin claystone laminations and cauliflower-type magnesite lumps. Moreover, it contains scarce, nearly imperceptible calcite. There are lateral transitions to dolomite, and conglomerate-sandstone-claystone alternations are intercalated thin huntite laminations. Prominent dissolution voids in karstic limestone occur in the upper levels. Huntite relicts are preserved in cavities of the karstic limestone (Fig. 3d). These cavities have lenticular structures with irregular borders and diameters of 1-100 mm. The contact of the huntite with the host rocks is sharp. Moreover, this huntite encloses scarce calcite, indicating that calcite was precipitated in the last stage of sedimentation during huntite flocculation.

### **MINERALOGY AND CHEMISTRY**

In this study, carbonate minerals, including huntite, dolomite,

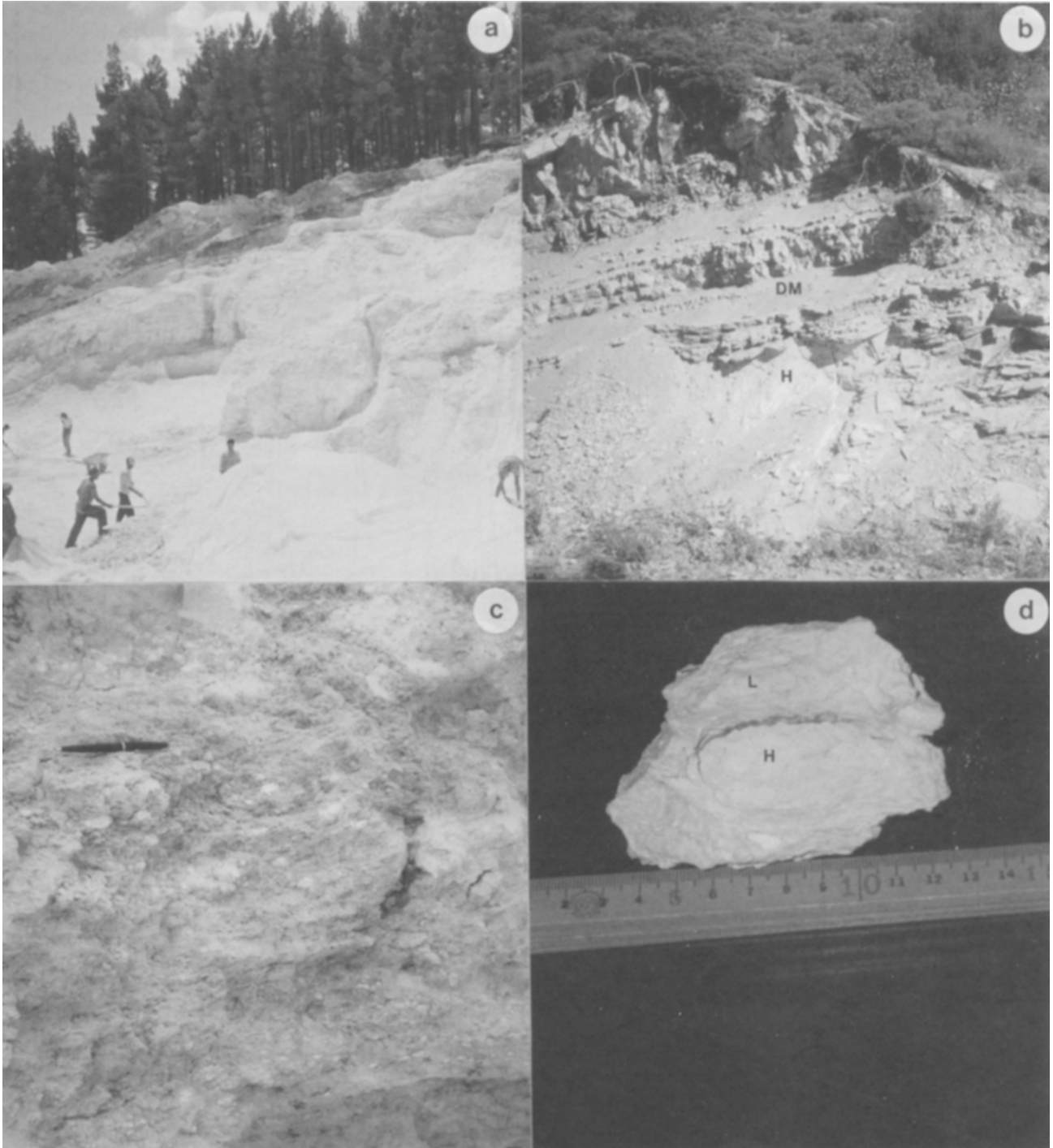


Figure 3. (a.) View of the Suçati huntite mine; (b.) Relationship of huntite layer (H) to dolomitic marl (DM); (c.) Huntite (white spot) in fenestral dissolution voids of dolomitic marl; (d.) Relict huntite (H) in irregular dissolution voids of limestone (L).

magnesite, hydromagnesite and calcite, were identified in bulk samples by X-ray diffractometry (Table 1). Huntite and dolomite generally coexist in the samples. Huntite is typically the predominant carbonate mineral in the dolomite, and dolomitic marl, on the other hand, occurs as a pure huntite facies (Fig. 2, Table 1). Apart from carbonate minerals, small amounts of serpentine and quartz were also detected. The huntite was determined from basal reflections at 5.67, 3.64,

2.89, 2.83, 2.74, 2.60, 2.43, 2.38, 2.28, 2.19, 2.10, 1.99, 1.97, 1.84, 1.77, 1.70, 1.58, and 1.48 Å (Fig. 4).

The DTA curve for the Çameli huntite has two endothermic peaks at 559°C (weight loss 23%) and 752°C (weight loss 8.8%) due to the decomposition of  $\text{MgCO}_3$  and  $\text{CaCO}_3$ , respectively (Fig. 5). The results of the DTA analyses of the Çameli huntite are in agreement with those reported by Shayan

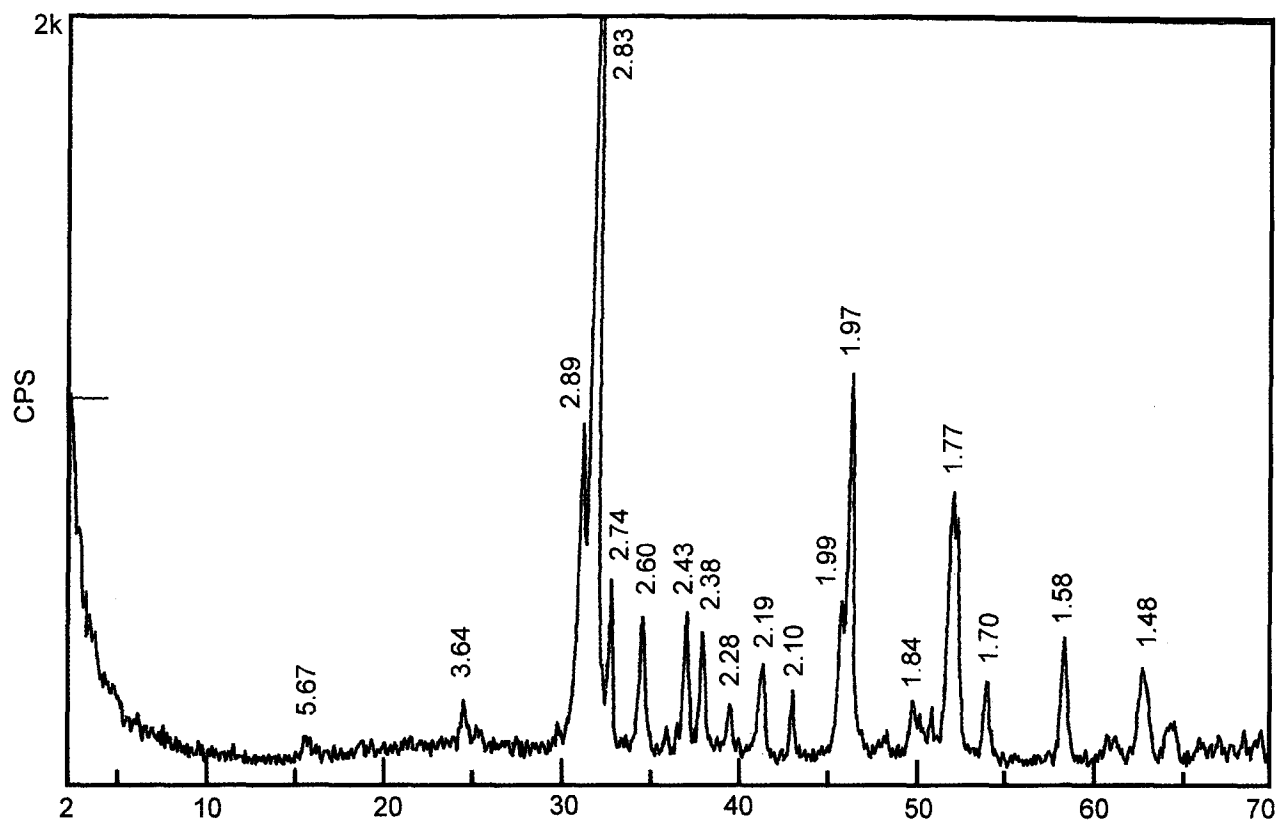


Figure 4. X-ray diffraction pattern of unoriented pure Çameli huntite (C2).

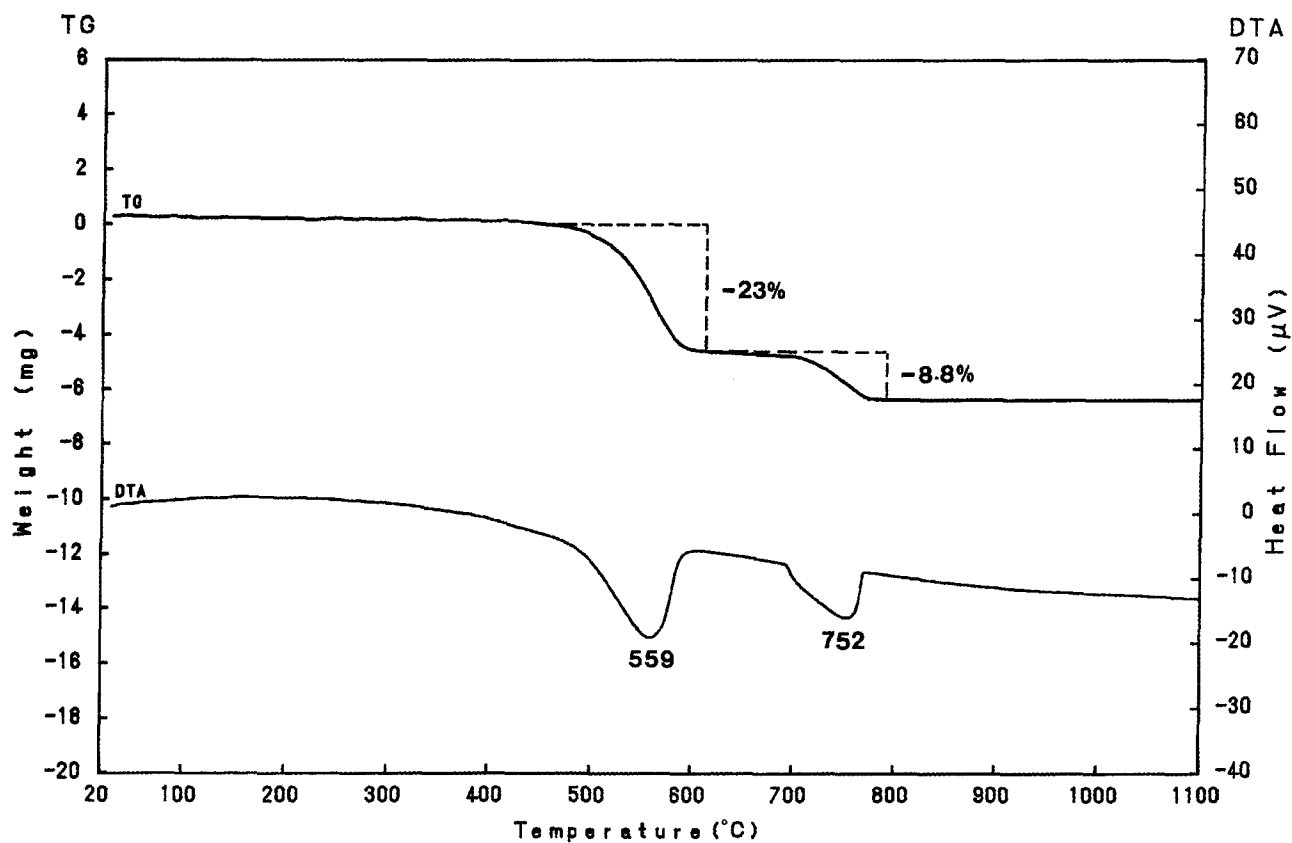


Figure 5. DTA-TG curves for pure Çameli huntite (C2).

(1984), but the temperatures are lower than those reported by Faust (1953), Koblencz and Nemecz (1953), Skinner (1958), Zhang and Zhang (1975), Ozao and Otsuka (1985), Popov and Sadykov (1987), and Stanger and Neal (1994). This difference may be related to the extremely fine grain size of the Çameli huntite.

The Çameli huntite occurs as irregular plates ( $<2\mu\text{m}$ ) that have mutual sub-parallel orientation (Fig. 6a). Huntite crystals enclose completely to partially corroded dolomite (Fig. 6b).

Moreover, huntite growth on/around dolomite and a close micromorphological relationship were also observed. The EDX analysis of the huntite plates show large peaks for Mg and smaller peaks for Ca and minor amounts of Si (Fig. 6c). Conversely, dolomite relicts yield strong peaks for Mg and Ca and minor amounts of Si. Therefore, the huntite and dolomite have similar compositions, but Mg in huntite is higher and Ca lower than in dolomite.

The Çameli huntite is composed mainly of high MgO,  $\text{CO}_2$ , and

*Figure 6. Scanning electron microscope (SEM-EDX) analyses. (a.) Irregular huntite plates showing mutual sub-parallel orientation; (b.) Relationship of huntite (H) to enclosed dolomite relict (D); (c.) EDX analyses of huntite and enclosed dolomite relict.*

# HUNTITE DEPOSITS IN THE NEOGENE LACUSTRINE SEDIMENTS OF THE ÇAMELI BASIN

Table 2. Chemical analyses of huntite and adjacent carbonate units (see Table 1).

	Ç1	Ç2	Ç5-1	Ç5-2	Ç5-3	1	2	3	4
MgO	38.5	34.05	34.6	26.5	43.45	33.2	33	33.49	34.09
CaO	12.2	15.29	15.4	25.88	6.4	15.6	15	13.71	15.42
SiO <sub>2</sub>	2.4	1.33	0.7	0.1	0.3				
Al <sub>2</sub> O <sub>3</sub>	0.1	0.2	0.1	0.1	0.1				
Fe <sub>2</sub> O <sub>3</sub>	0.1	0.1	0.1	0.1	0.1				
MnO	0.1	0.1	0.1	0.1	0.1				
K <sub>2</sub> O	0.1	0.1	0.1	0.1	0.1				
TiO <sub>2</sub>	0.1	0.1	0.1	0.1	0.1				
P <sub>2</sub> O <sub>5</sub>	0.1		0.1	0.1	0.1				
CO <sub>2</sub>	46.3	48.53	48.7	46.8	49.24	48.9	47.8	43.98	48.85
Total	100	99.80	100	99.94	99.99				

1 : Huntite, Tea Tree Gully, South Australia (Skinner, 1958);

2 : Huntite, Deer Park, Victoria, Australia (Shayan, 1984);

3 : Huntite, Geelong, Victoria, Australia (Koblencz and Nemezc, 1953);

4 : Huntite, Ala-Mar, Nye County, Currant Creek, Nevada (Faust, 1953).

low CaO (Table 2). However, MgO and CaO have variable molar ratios due to the presence of dolomite, magnesite, hydromagnesite and calcite associated with huntite. Pure Çameli huntite has compositions similar to those reported by Faust (1953), Koblencz and Nemezc (1953), Skinner (1958), and Shayan (1984).

## CONCLUSION AND DISCUSSION

The Çameli Neogene basin is rich in Mg which was supplied by ultrabasic and dolomitic rocks of the basement. Three types of huntite facies are observed in the basin: 1. massive huntite with dolomite and/or hydromagnesite/magnesite; 2. discoidal and/or fenestral huntite; and 3. irregular bulky huntite.

1. Massive huntite occurs as several-meter-thick intervals in dolomite of the upper part of the basin. It formed diagenetically along the gradational contact with enclosed carbonate relicts (Figs. 3a and 3b). Dolomite clasts are aggregated locally in dissolution voids. Moreover, SEM studies demonstrate a close micromorphological relationship between huntite plates and dolomite relicts (Fig. 6b). On the other hand, the Suçati huntite facies contains scarce hydromagnesite and magnesite indicating that these minerals formed diagenetically from huntite. Calvo et al. (1995b) described the formation of massive huntite by early diagenesis of dolomite in the Kozani basin of Greece. A similar mode of formation was also reported by Irion and Müller (1968), Müller et al. (1972), and Mutlu et al. (1999). Diagenetic huntite in the Çameli basin probably followed the order of formation dolomite-huntite-magnesite, similar to that reported by Müller et al. (1972). However, Zachmann (1989) described the formation of hydromagnesite in Greece by direct precipitation from Mg-rich lake water. The same writer also reported the formation

of diagenetic huntite by the reaction of karstic water with magnesite following a period of late-diagenetic transformation of hydromagnesite to magnesite. This mode of formation seems inapplicable to the Suçati massive huntite because the Suçati deposit contains only about 5% hydromagnesite and magnesite, probably due to Mg concentrations insufficient for their formation. The Sarnıç and Yaylacık massive huntite intervals do not contain dolomites relicts, probably due to their direct precipitation from Mg-rich lake water. Similar modes of formation for huntite were also reported by Calvo et al. (1995b). Hydromagnesite lumps in the Sarnıç and Yaylacık huntite deposits probably formed by the late diagenetic transformation of huntite via the leaking of CO<sub>3</sub>-rich meteoric waters through huntite intervals. In such cases, the concentration of CO<sub>3</sub> in the environment must exceed that of Mg<sup>2+</sup> (Lippmann 1973).

2. Discoidal and/or fenestral huntite occurs in dolomitic marl containing dissolution voids, as either regular discoidal or irregularly bordered lenticular structures filled by 0.1-3 cm huntite (Fig. 3c). This huntite probably formed by direct precipitation of Mg-rich pore waters in shallow coastal sediments of a mud-flat environment. The formation of huntite and magnesite in small cavities of ultrabasic rocks has also been reported by Stanger and Neal (1994).

3. Irregular massive huntite occurs in irregular dissolution voids (0.1-10 cm) which have been partly protected (Fig. 3d). Karstic limestone with dissolution voids is precipitated by high Ca and CO<sub>3</sub> ions supplied in a pluvial climatic regime. During this precipitation, huntite probably flocculated in bulk. Similar structures have been observed in Quaternary aragonite and magnesite of Uzbekistan, but those structures were described as diagenetic (Popov and

Sadykov 1986). Interpretation of these models is difficult due to the absence of any dolomite.

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