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PETROGRAPHY OF LACUSTRINE DOLOMITES IN SİVRİHİSAR NEOGENE BASIN AND INTERPRETATION OF THEIR DEPOSITIONAL ENVIRONMENT USING STABLE ISOTOPES ($d^{18}0;d^{13}C$)

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ABSTRACT.- The most common lithologies comprising the lacustrine deposits in the Sivrihisar Neogene (Upper Miocene-Pliocene) basin are dolomite, dolomite-bearing claystones, and gypsum. The scanning electron microscope (SEM) study of has revealed, microcrystalline dolomite (dolomicrite) different petrographical types such as euhedral, spheroidal, and sub-spheroidal. Stable $d^{18}O$ and $d^{13}C$ isotopes of above-mentioned dolomite types classify into 3 groups. 1) $8^{18}O$ between -1 and +4 %o; $d^{13}C$ between -4 and +0.5 %o; 2) $d^{18}O$ between 6 and -1 %o; $d^{13}C$ between -3 and -1 %o; 3) $d^{18}O$ between -5 and +2 %o;$d^{13}C$ between -1.5 and 0.0 %o. Petrographically different dolomite types and difference in their stable isotopes values may reflect the effect of climatological and hydrodynamic conditions in the Neogene lake-basin which controls the variation in temperature, salinity, and biological activity. Dolomites were formed in a lake environment where the water balance and salinity changes continuously Alkaline dolomite lake was transformed into ephemeral lake which has resulted in the deposition of magnesite and strontianite at the upper limit of evaporation. Salinity was extremely decreased when fresh water inflowed into the lake area or rise in groundwater level, that is supported by lighter $d^{18}O$ values. The local swamps, which has developed at these stages, provided the suitable conditions for the formation of sepiolites and dolomite-bearing sepiolites. The different petrographic types of dolomite crystals and their stable isotope values reflect the continuously changes temperature, salinity, and depth of the lake area The environmental conditions ranging from hipersaline to hyposaline indicate that Sivrihisar Neogene dolomites had been formed in a schizohaline environment as recorded in the geological literature.

INTRODUCTION

Dolomites and dolomitization are the result of a series of complex events during the early-and late-stages of diagenesis. Many different theories and models have been proposed for the origin of dolomites and dolomitization (Hardie, 1987). Among various dolomite types, particularly those of marine origin have been studied in more detail owing to their complex structure, variability, and economical potential. On the other hand, lacustrine dolomites has been drawn less interest than marine counterparts as they show very simple internal structure and homogeneous appearance in the field. It has been shown that majority of lacustrine dolomites were formed either in shallow lakes .under conditions of increasing evaporation, salinity, and Mg/Ca ratio or during early stages of diagenesis (Miiller. 1968; Muller and Irion, 1969; Irion, 1970). Recently, the formation of thick and uniform lacustrine dolomites have been observed in the modern lakes in which dolomite deposition occurs (Von Der Borch and Lock, 1979). The use of field and petrographical data are not adequate to examine the lacustrine dolomites which are very sensitive to all sorts of atmospheric conditions and seasonal changes. $d^{18}O$ and $d^{13}C$ stable isotopes particularly provide useful criteria to about the determine: The different climatological and hydrodynamic conditions affecting the fossil lakes; the salinity and biological changes in lake environments; and different steps, such as drying off , shrinkage and widening, in the general tectonic evolution of lakes (Talbot, 1990; Talbot and Kelts, 1990). Such lakes are recognized and known to be favorable places as economical mineral occurrences such as sepiolite, magnesite, bentonite, and strontianite (Bellance et at., 1992).

The wide-spread dolomite occurrence in Sivrihisar area provides suitable clues to understand the different factors upon the Neogene lake sedimentation (Fig. 1). In this study, all of data were used in determination of different climatological, hydrodynamic, and biological conditions controlling

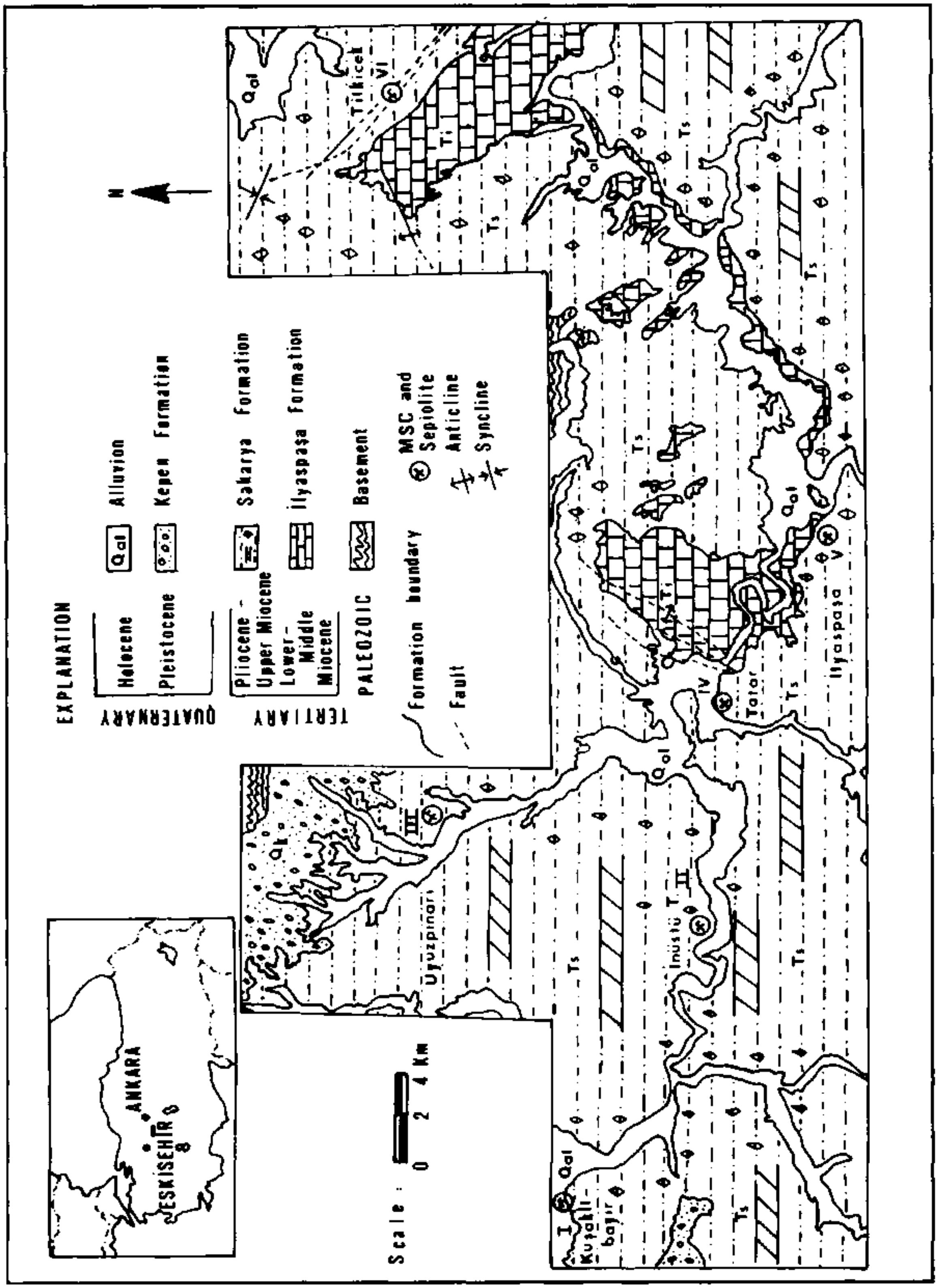

Fig. 1- Location and geological map of the study area.

the formation of these lacustrine dolomites and examination of the effect of these conditions over the environmental changes.

MATERIAL AND METHOD

Dolomites (40 samples) were collected for analysis through 6 different sections measured at Kuşaklıbayır, Inüstü, Uyuzpınarı, Tatar, İlyaspaşa and Tilkicek Yayla, the area covering about 1000 km^2 and lies 13 Km southeast of Sivrihisar (Fig. 1, 2).

In the field study, the lake dolomites were defined by microcrystalline texture, fracture pattern, white colour. Whole rock chemistry and mineralogical analysis provided by X-Ray (XRD). Dolomites were recognized, using their XRD graphy through their peaks at 2.89 A', 2.19 A', and 1.79 A'. This study was carried out using Philips PW 1140 model X-Ray difractometer. Electron microscope observations and micro -texture analyses were performed by means of Scanning Electron Microscope. Semi-quantitative spot analyses were performed using X-Ray spectrometer linked to the Trakor TN 5502 energy dispersive system fitted to a Jeol JSM 840 A type Scanning Electron Microscope. The measurement of stable isotopes ($d^{18}O$, $d^{13}C$) in the 20 selected samples were performed using special solutions through Varion Mat 250 type of mass-spectrometer. For this, the method proposed by Epstein et al., (1964) and Becker and Clayton (1972) were used.

STRATIGRAPHY

Dolomites are commonly present in Sakarya formation in association with gypsum, claystone, marl and limestones (Karakaş and Varol, 1993). The ostracod fossils of *Cyprinotus salinus* (Brady), *Candona neglecta* Sars, *Candona* cf. *compressa* (Koch), *Candona* cf. *angulata* Mueller, //yocypns cf. *gibba* (Ramdohr), *Cyprideis* cf. *torosa* (Jones), *Cyprideis* cf. *heterostigma* (Reuss), *Pseudocandona* sp., *Candonopsis* sp. were found in the marl levels in this formation. In addition, the pollens of *Compositae type pollen, Pityosporites* spp., *Tricolporopollenites* spp., *Monoporopollenites* sp., *Ovoidites* spp., *Monocolpopollenites trachycarpoides, Periporopollenites multiporatus* are generally predominant marly dolomite layers. In limestone samples gastropod fossils of *Coretus sulekianus* Brusina, *Gyraulus radmanesti* Fuchs, *Bulimus* sp., *Pisidium* sp., *Hydrobia sp., Valvata* sp. were recognized. This fossil associations of the formation indicate Upper Miocene-Pliocene time. The well-preserved gastropod fauna in the limestones, which conformably overlie dolomites in Tilkicek Yayla area, points to the age of Dacian (Lower Pliocene). Sakarya formation unconformably overlies the underlying Lower-Middle Miocene İlyaspaşa formation which is composed of limestone with chert, marl, claystone, and thin levels of peat and is unconformably overlain by the alluvial deposits of the Kepen formation (Karakaş and Varol, 1993) (Fig. 3).

Different lithologies in dolomite-dominated Sakarya formation display both lateral and vertical facies changes (Fig. 2). In particular, massive and bedded gypsum in Kuşaklıbayır area exhibits an interfingering with the gypsiferous dolomites in Inustu Tepe area. Similar relationship is also encountered between gypsiferous and clayey dolomites.

FACIES PROPERTIES OF DOLOMITIC UNITS

The diagnostic features of the dolomites are their with colour, thin-to medium-thick- bedding, calcarecous appearance, conchoidal fractures, and their highly cracked structures. The other rocks associated with dolomites help to identify the different facies among the uniform dolomite. Such as gypsiferous, clayey and calcarecous dolomites.

1- Gypsiferous dolomites: A great portion of dolomites falling into this group are characterized by their discoidal gypsum crystals, gypsum rosette and swallow-tail twin, and brown-green colours (Fig. 4a). These structures were developed in the form of displacive grown scattered crystals or fracture-fillings in dolomites. The fracture-fillings are more common in dolomitic levels containing less amount of clay (10-15 %). Typical examples of these structures are observed at the bottom levels of Uyuzpınarı, Inüstü, and İlyaspaşa sections (Fig. 2).

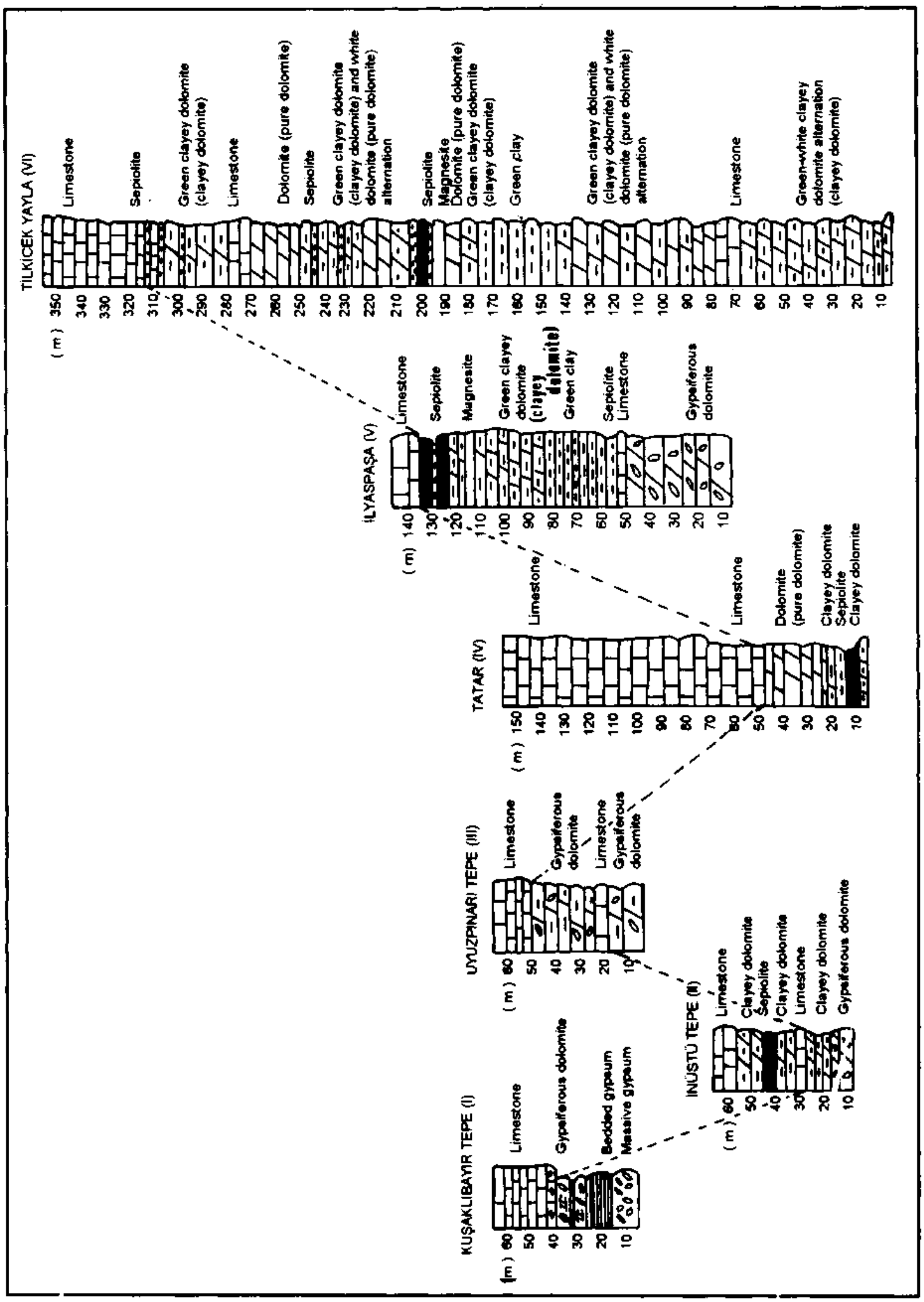

Fig. 2- Measured stratigraphical sections representing the different parts of the study area.

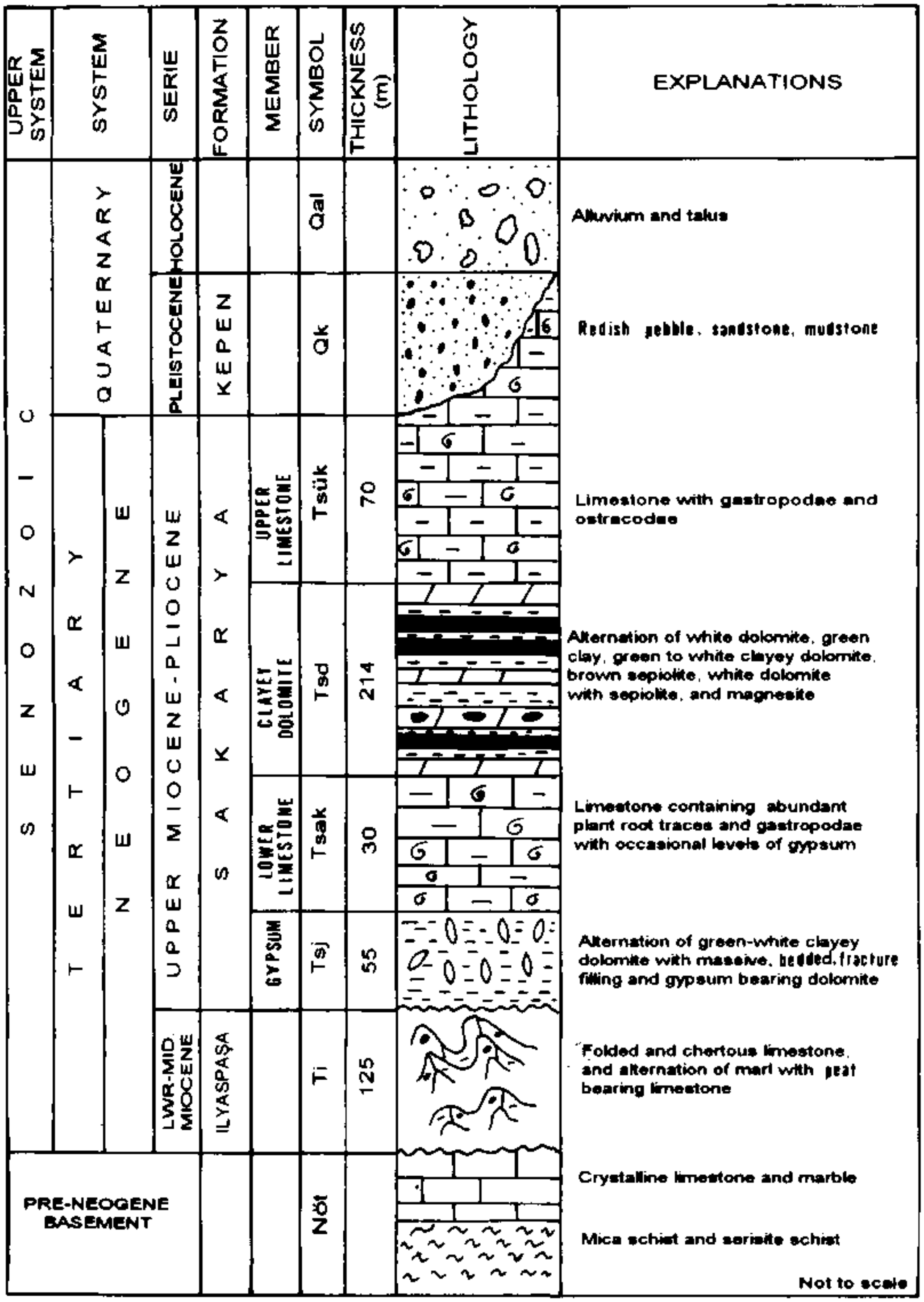

Fig. 3- Generalized columnar section of the Neogene units in the study area.

This facies also alternated with the bedded and massive gypsum levels which composed of white prismatic gypsum crystals. Reverse gradations, microparallel-and cross-laminations, and very weak ripple structures appear to be synsedimentary structures in this alternating section. The lower

Fig. 4a- Brown gypsum roses developed in dolomites in fracture-filling forms (Kuşaklıbayır Tepe).

most part of Kuşaklıbayır section is the only location exposed gypsiferous dolomites (Fig. 2). Towards eastward, the gypsiferous dolomites become thin and make up lateral facies change with the another gypsiferous dolomite beds composed of displacive gypsum crystals. In addition, fracture-filling gypsum with dolomite is observed at the Kuşaklıbayır section and grades into the gypsiferous limestones at the upper levels of this section (Fig. 2).

2- Clayey dolomites: Clay-bearing dolomites give a loose and soil-like appearance and have a minimum of 20 % clay in their composition. They are classified into two groups with respect to colour of the rock: such as green clays and white and brown clays. The green clays are characterized by the smectite-illite-chlorite group clay minerals and observed to be bentonites in İlyaspaşa and Tilkicek Yayla sections (Fig. 2). They also alternate with pure dolomite units. Individual limestone layers interbedded with green clays are also observed in the dolomite-bearing sections. Limestone beds of varying thicknesses are repeatedly encountered in Tilkicek Yayla section. The second group of clays in the same facies are the white coloured sepiolitic clays. These are observed either as pure clay levels or in mixed forms with dolomites which are highly fractured, occasionally brecciated nature, and filled by clays (sepiolite) in the root moulds. Brown clay is pure sepiolite in which organic matter is high but dolomite is very low (at about %5). As the dolomite content increases, the colour changes from black to white. The typical colour change in this facies depends on clay+dolomite+organic matter content, Inustu, Tatar, İlyaspaşa and Tilkicek Yayla locations exhibits these colour changes varying from brown clay (pure sepiolite) to white clay (dolomite-bearing sepiolite). In the last two locations, a few meter-thick lenticular magnesite formation is observed in association with the clayey dolomite facies (Fig. 4b).

3- Pure dolomites: These are uniform dolomites and lack of gypsum, clay, and any other matter. Plant moulds are commonly found in this dolomites. This facies display lateral facies change with the gypsiferous and clayey dolomite facies. In some areas, it is interfingering with limestones. Locally it

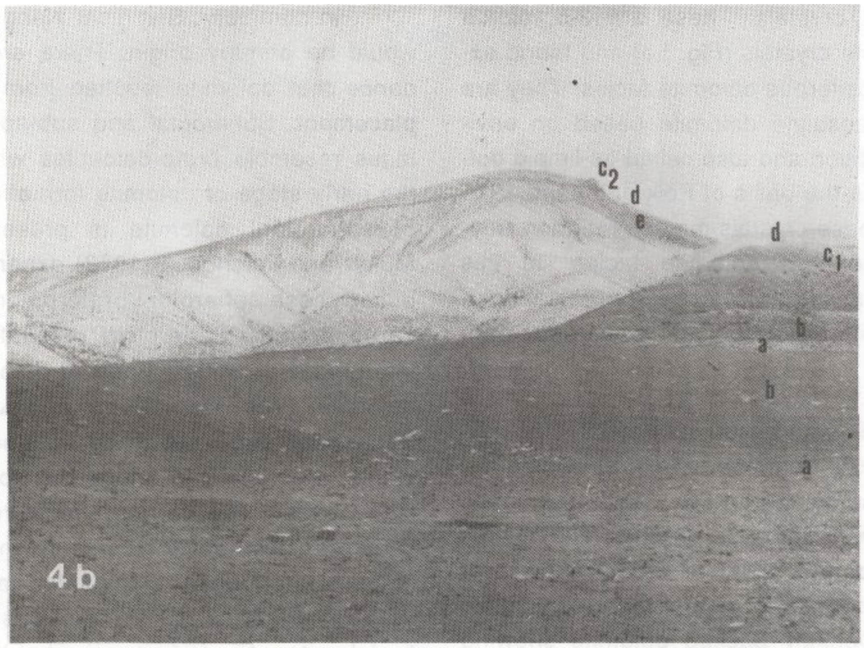

Fig. 4b- Alternation of clayey and pure dolomite (Tilkicek yayla). a) White clayey dolomite (clayey dolomite). b) Green clayey dolomite (clayey dolomite) c_1) Lower limestone. c_2) Upper limestone. d) Dolomite (pure dolomite). e) Sepiolite.

alternates with gypsifefous dolomite fades and some levels having conchoidal fractures show weak clay mineralization represented by sepiolite. Kuşaklıbayır section is typical area with the alternations of above facies types as shown in the Figure 2.

PETROGRAPHICAL TYPES

The samples collected from the above described facies present a dolorhicritic feature under polarizan microscope. In gypsiferous dolomite samples, individual gypsum crystals in dolomicritic matrix show displacive form. These crystals do not present any inclusions and irregular crystal boundary resulting from dolomite replacement. Dolomites usually encompass gypsum crystals. In these sorts of formations gypsum crystals develop in the displacive form in the soft dolomite mud formed related to the saline pore water (Masson, 1955; Arakel, 1980; Cody and Cody, 1988; Rosen and Warren, 1990; Magee, 1991). Various types of gypsum crystals Which are brown in colour, lack of bedding and fracture fillings are important features and indicate the rise of groundwater level enriched by earth elements due to the dehydration cracks in the slowly drying off dolomite lake (Cody and Cody, 1988). Anhydrite is rarely found in gypsiferous dolomites. It occurs in few mm thick crust forms in the alternating layers of thin dolomites and massive gypsum. Individual gypsum implacements in dolomites are often observed and indicates the fresh water leaching. Brecciations are found in clayey dolomites along the desiccation cracks and root tubes. Sepiolite infillings in these root tubes and brecciate are commonly. Present pure dolomites give generally homogeneous appearance. They are characterized by micro-concretion, soil formation, oxidation and rare algal traces.

Dolomites, which is petrographically describe as dolomicrite, described are classified into euhedral, sub-spheroidal and spheroidal crystals with respect to SEM examinations (Bellanca, et al., 1993).

Euhedral crystals: These are 2-5 micron rhombic dolomite crystals (Fig. 5a) and found extensively in gypsiferous dolomite facies. They are similar to schizosaline dolomite based on environmental condition and also called as limpid dolomite crystals in the basis of Folk and Land 1975 terminology. These crystals may be found in clayey (sepiolite-bearing) dolomite facies. In this case, they are mixed-up with the spheroidal dolomite crystals with the association of fibreous bundle of sepiolite.

Spheroidal and sub-spheroidal crystals: The nomenclature on these type of dolomites are based on the study of Von Der Borch and Jones (1976) and Amiri-Garroussi (1988). The typical rhombic and perfect crystals are gradually replaced with spheroidal or nearly-rounded crystals (Fig. 5b, 6). Densely packed dolomite showing plate type growing habit are also observed within the petrographic type. The spheroidal and sub-spheroidal dolomites are generally intercalated with euhedral dolomites. External dissolutions of the dolomite plate and vugs are associated with spheroidal and sub-spheroidal dolomite crystals. Inter-crystal pores are quite common and reflect ' dissolution activity (Fig. 5b, 6). Diatome shells- and remnants are often observed in the levels of spheroidal dolomites. Many researchers have reported that these spheroidal dolomites precipitated in the micropores of diatome shells or silicium gel (opal silicium) from dissolutions of diatomes involved in the spheroidal habit of dolomite crystal (Cook, 1973; Weaver and Beck, 1977). There are no clear evidence that diatomes invoked for the formation of spheroidal dolomite crystals. Nevertheless, the existence of this kind of crystals in the dolomitized diatome mud supports the above explained opinion. Sub-spheroidal and plate dolomite crystals are either products of marginal dissolution of rhombic crystals or they were formed through several-stages of dolomite crystalization that had been interrupted by non-dolomitization periods. They also covered sepiolite fibers in the micron-size length or precipitated within the open spaces of sepiolitic mass as shown in the Figure 5c.

In summary, Sivrihisar Neogene dolomites would be primary origin. There are no any evidence that dolomite resulted from aragonite replacement. Spheroidal and sub-spheroidal dolomites resemble proto-dolomites which represent the early stage of dolomite formation. The origin of spheroidal dolomite is presently debated. Muller and Fischbeck (1973) experimentally produced these spheroidal proto-dolomites from the carbonate-gel. Spheroidal dolomites were also interpreted as initial phase of dolomite or proto-dolomite (Von Der Borch and Jones, 1976). Spheroidal vugs could be related to diatome shells, which existed before the dolomitization in lake bottom. The porous shell structures would served as microenvironments in which spheroidal dolomite had been precipitated as pointed by Weaver and Beck, 1977. The transition from proto-dolomites to perfect euhedral-limpid crystals are very typical. It is very likely that this transition of the different dolomite crystals was controlled by the increase of magnesium content in the lake environment. In Figure 6, it is shown that decrease in magnesium content results in dissolution leading to pore development, and increase in magnesium content produces the perfect rhombic crystals shapes.

STABLE ISOTOPES

Stable isotope values obtained from the different petrographical types of dolomites have plotted in three different areas as shown in the Figure 7, 8. In these areas, a stable isotope values show a change from relatively small values (negative) to higher (positive). Among of them, the first group is $d^{18}O$: -1 to +4 %o and $d^{13}C$: -4 to +0.5 %o; the second group is $d^{18}O$: -6 and to -1 %o and $d^{13}C$: -3 to -1 %o; the third group is $d^{18}O$: -5 to +2 %o and $d^{13}C$: -1.5 to 0.0 %o (Fig. 7, 8). The variations observed in stable isotopes of dolomites are directly related to the changes of salinity and temperature of dolomitizing fluids through dolomitization periods (Folk and Land, 1975). In the Neogene lake area, rapld changes in the water chemistry of lake environments are quickly affected by atmospheric conditions and this involved in abrupt changes in the

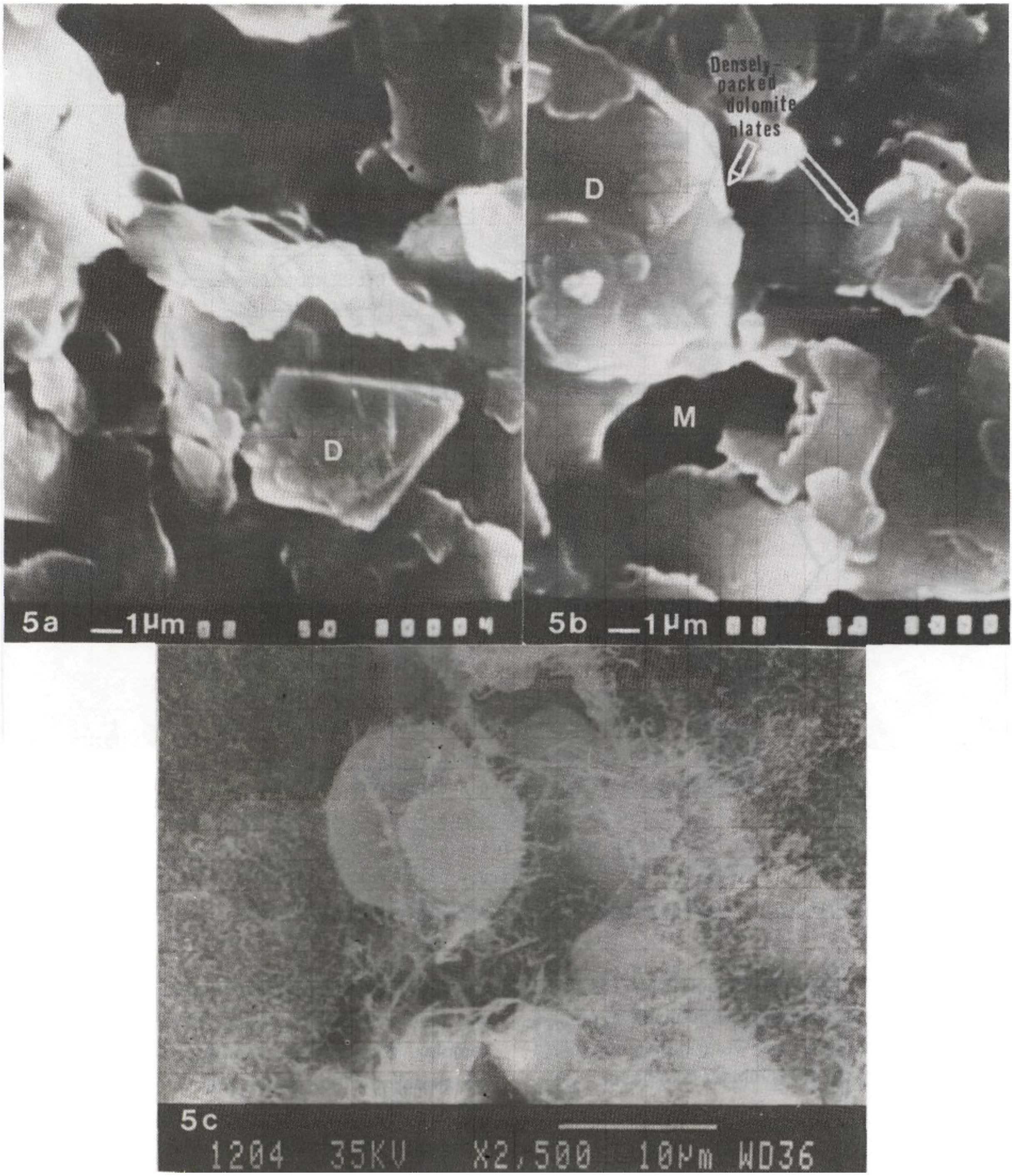

Fig. 5a- Euhedral dolomite (D) crystals developed in the gypsiferous dolomite fades.

Fig. 5b- Micropores (M) formed by external dissolution in the spheroidal dolomite crystals and densely packed dolomite plates (D).

Fig. 5c- Spheroidal and sub-spheroidal dolomite crystals in fibreous sepiolite bundles.

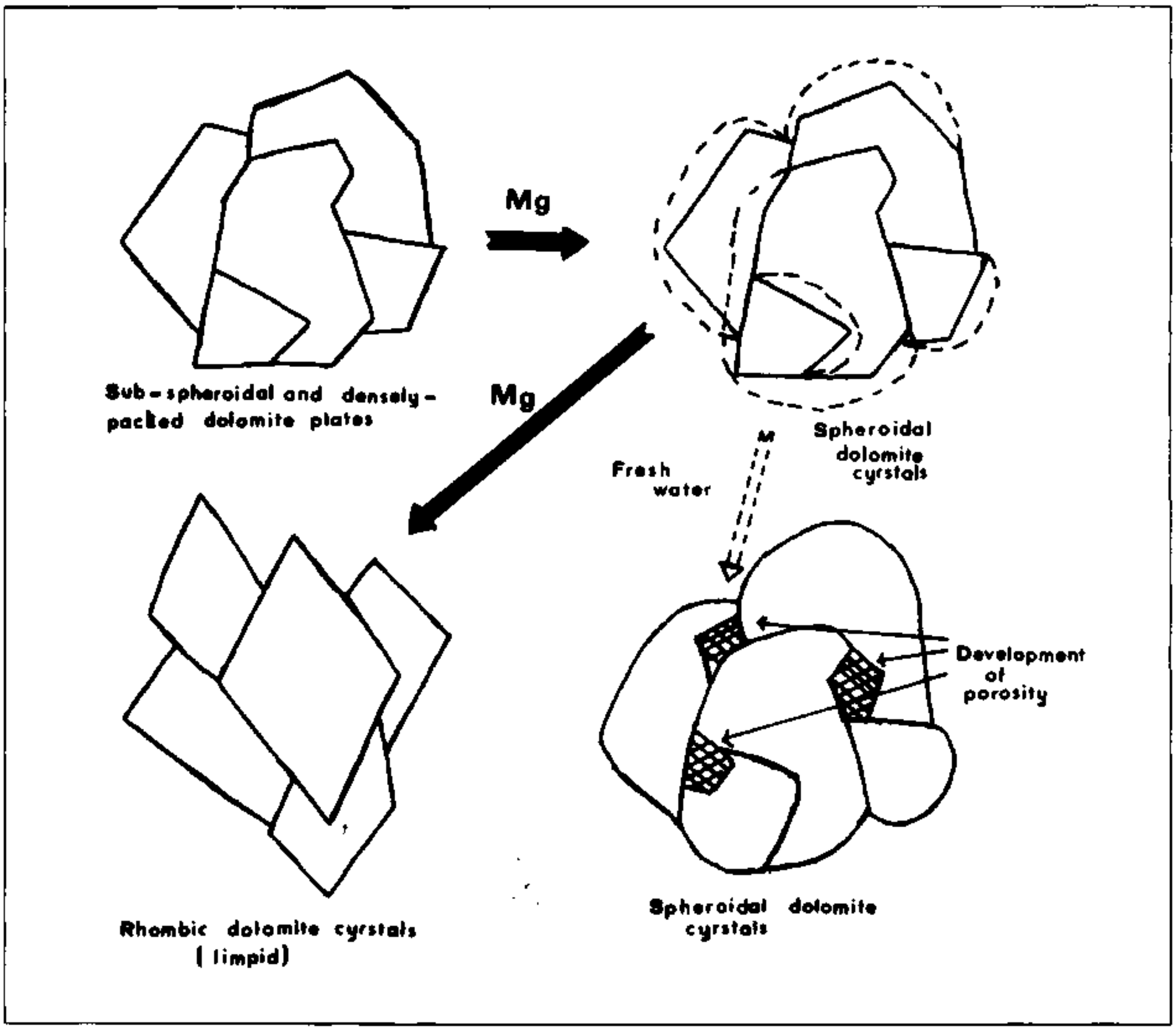

Fig. 6- Scheme showing the transition of different types of dolomites from one to another.

stable isotopes of dolomitizing solutions. These isotopic features are reflecting fluctuations of chemistry and temperature of lake water during dolomitization are very typical for Sivrihisar lake basin.

CONCLUSIONS AND DISCUSSION

Sivrihisar Neogene lacustrine dolomites present a fine-grained (dolomicrite) feature in the field and are similar to a number of lacustrine dolomites described in the literature (Muller, 1970; Von Der Borch and Jones, 1976). Lacustrine dolomites generally have simple appearance, but their internal structures, microscopic features, trace elements and stable isotope contents ($d^{18}O$; $d^{13}C$) are very complex. This provides important information about the modeling of the water chemistry and hydrology which of the lakes are heavily affected by the climatological changes. In particular, the variations in the oxygen isotope values ($d^{18}O$) provide important information about the isotopic composition and temperature of the lake water in which primary and early diagenetic lacustrine carbonate deposition takes place. The formation mechanism of $d^{18}O$ stable isotope values in lacustrine carbonates usually indi-

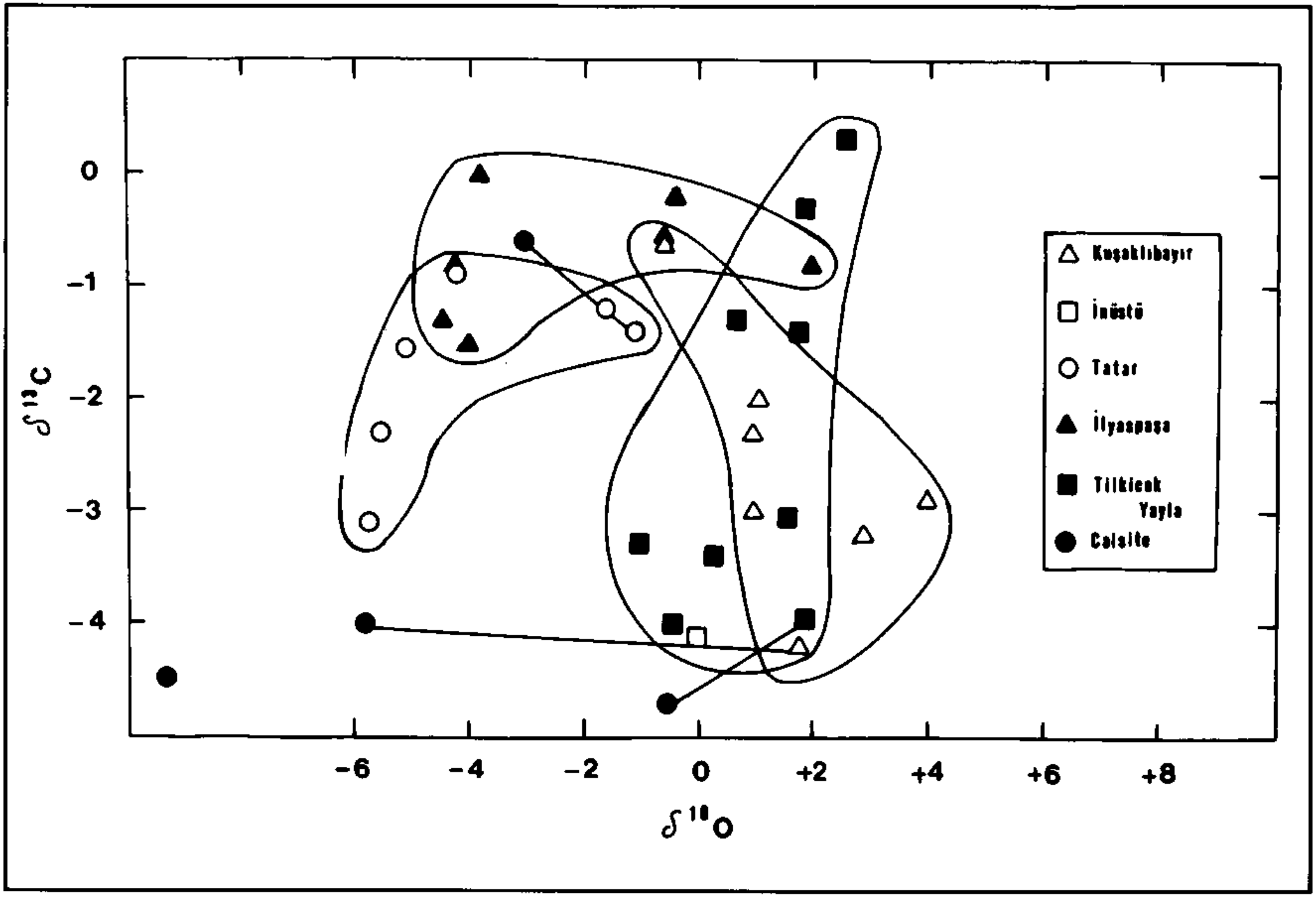

Fig. 7- Distribution table $\delta^{18}O$ and $\delta^{13}C$ stable isotopes of Sivrihisar Neogene dolomites according to the columnar sections (‰, PDB-1).

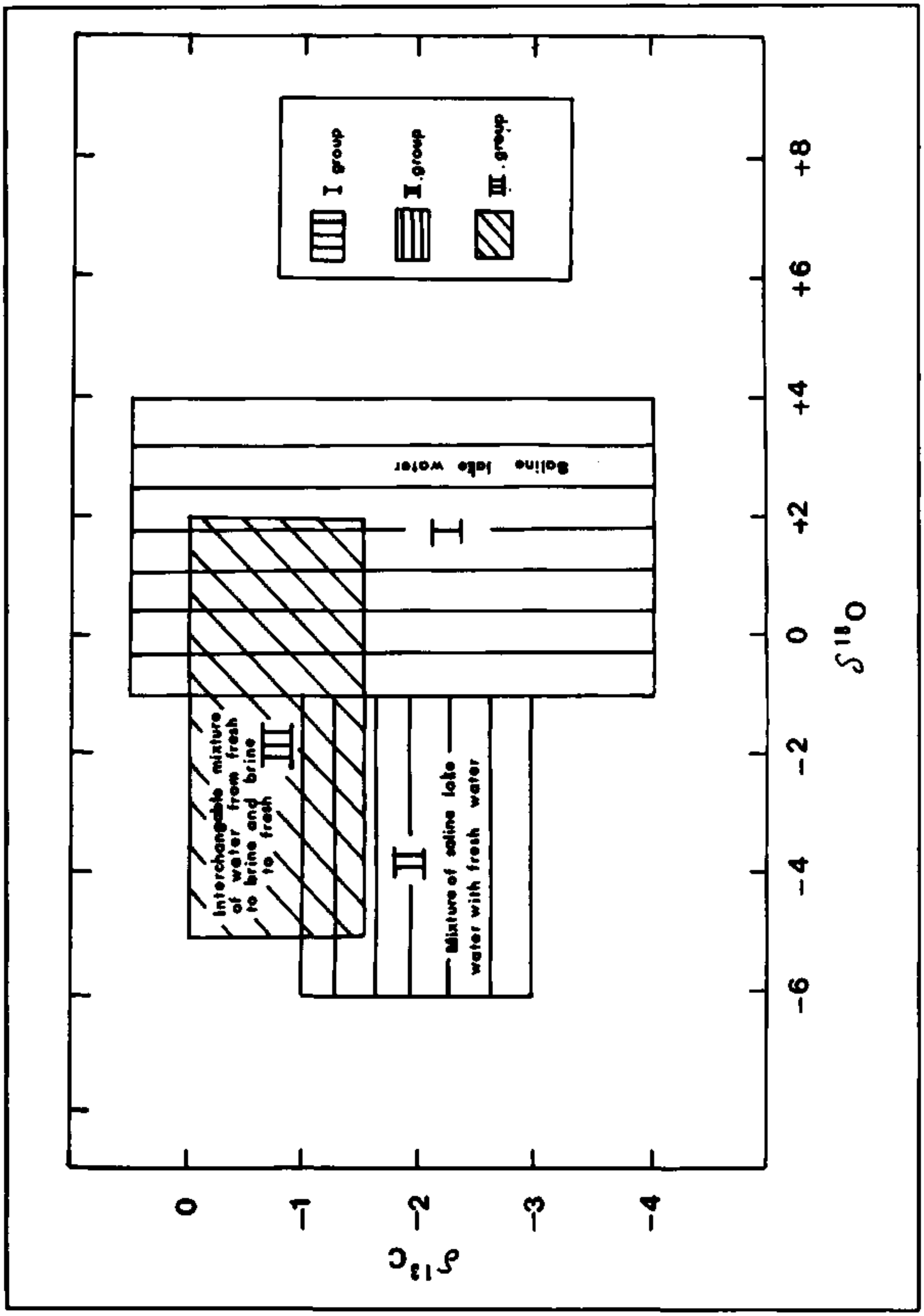

Fig. 8- Geochemical character of lake water according to $\delta^{18}O$ and $\delta^{13}C$ stable isotope groups of Sivrihisar Neogene dolomites.

cates that they are heavily affected by the evaporation during dry climate conditions (Gonfiantini, 1986; Gasse et al., 1987). Carbon isotope ($d^{13}C$) composition is controlled by many factors in lakes. The most important one is the derivation of CO_2, through photosynthesis from soil profile into the lake and causes great decrease in $5^{13}C$ values in lake areas (-10 to -28 %o) (Salomons and Mook, 1986). Decrease in $d^{13}C$ is rebalanced by the atmospheric sources (Gonfiantini, 1986; Hoefs, 1987). Another factor which cause decrease in $d^{13}C$ isotope is the microbiological destruction of the organic matter in the diagenesis environment.

Stable isotope of dolomites in the study area represent a variable character. Different isotope values which reflect variation in depth, salinity, and biogenic activity in the paleo-lake environment. The stable isotope data reveal different depositional and hydrologic periods of Neogene lake as follows:

Gypsiferous dolomites of the first facies and their typical crystals are limpid dolomites. These are placed in the first category and have values of $d^{18}O$: -1 to +4 %o and $d^{13}C$: -4 to +0.5 (Fig. 8) Positive values with the oxygen isotopes depends on increasing salinity due to excess evaporation. Under these environmental conditions, the enrichment of $d^{18}O$ isotope is the result of quick consumption of $d^{16}O$ which is lighter due to increasing ionization speed (kinetic isotope effect; Anderson and Arthur, 1983). The highest values of $d^{18}O$ in our samples indicate the decrease in water or negative water balance and even the complete dry-off of the lake. Low values of $d^{13}C$ in these samples indicate the effectiveness of the limited air circulation conditions (stagnant) in the lake. Thus, production of CO_2 is connected to the local biological sources (Talbot, 1990). $d^{18}O$ values in magnesite and strontianite occurrences are found considerably high. The deposition of strontianite is an indication of the limited biological activity in and around the lake environment. As the use of strontianite by fauna flora in areas of biological activity prevents the deposition of strontianite (Magee, 1991).

The second group consists of dolomites composed of spheroidal, dolomite crystals. Clayey dolomites are partially found in the second group. $d^{18}O$ values of this group are relatively low and between -6 to -1 %o (Fig. 8). Nevertheless, $d^{13}C$ isotope values are high and between -3 to -1 %o, which suggests that the fresh water partly mixed with saline lake water during dolomite deposition and the vicinity of the lake had a weak plant cover under the semi-arid climate conditions (Talbot, 1990).

The third group is composed of clayey dolomite and partially pure dolomite facies. It is a mixture of dolomite crystals of euhedral, and subspheroidal shapes. The samples in this group had isotope values of $d^{18}O$: -5 to +2; $d^{13}C$: -1.5 to 0.0 %o covering the two groups described above (Fig. 8). This indicates the rapid changes in short periods from fresh to saline and from saline to fresh water conditions. Overall, it reflects the climatological variations in short periods as humid-semiand-arid conditions.

Stable isotope values of $d^{18}O$ and $d^{13}C$ as explained above reflect changes from positive to negative in a certain interval (Fig. 7). According to the stable $d^{18}O$ isotope values, dolomites can be grouped into three accepting that the SMOW value for normal saline sea water environment is zero (Land, 1980) (Fig. 8). These different groups indicate the variations in the temperature and salinity of the lake water during the deposition of various types of dolomites deposited in the Sivrihisar lake basin of Neogene age. These variations might be due to climatological factors, geomorphological position of the lake as well as the tectonic activities. The type of dolomite was affected by the shrinkage, extension, and dry off of the fossil lake. The separation of the stable isotope fields shown in Figure 8 suggest that different hydrodynamic, tectonic, and seasonal changes existed in the Neogene lake basin. Stable isotope values of $d^{18}O$,and $d^{13}C$ are also affected by the short and long-term variations in salinity, temperature as well as biological activity. Neogene dolomite series make up a typical example of the dolomite depositions dependent upon the depositional environments of changing salinity conditions (schizohaline dolomite; Folk and Land, 1975). At the stages-of excess fresh water inout into the lake area, dolomite deposition ceases and transforms into dolomite dissolution. This is the event controlling the external dissolutions and pore development (Fig. 6). Similarly, interruption of the source of magnesium as a result of short-period variations in salinity caused densely-packed plates type of several-stage, sub-spheroidal shaped crystal growth. Peryt and Magaritz (1990) describe these dolomites as formed in sabkha environments open to the entries of fresh water. From the standpoint of depositional environment conditions, dolomites of the study area show a great similarity to ephemeral lake varying from hipersaline to hyposaline.

The resulting stable isotope values show that even under the most saline conditions leading to the dolomite deposition in the Sivrihisar lake basin, the depositional environment never had the character of a playa lake. This is because $d^{18}O$ values measured in gypsiferous dolomite facies in which the evaporation may have been the greatest are lower 4-6 %o than Coorong dolomites (Warren, 1990), typical for the highly saline lacustrine lagoons. The results also indicate that evaporitic dolomite deposition environments representing Sivrihisar Neogene basin were open to fresh water flush.

The stable isotope values of Sivrihisar Neogene basin show that the fossil lake had no stability with respect to either its salinity or areal extension. Short and long period seasonal changes controlling this character of the lakes provided new sources for the ionic enrichment of the lake water. For instance, in addition to the renewed magnesium sources due to fresh water inflows, magnesium and silicium enrichments dissolved through the lake sediments (dolomite-diatome) lead to the mineralizations increasing the economic value of the lake. The best example of these occurrence for the region is the formations of sepiolite and sepiolite bearing dolomite.

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