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Colour genesis of Upper Cretaceous pelagic red sediments within the Eastern Pontides, NE Turkey

Doğu Pontidlerdeki (KD Türkiye) Üst Kretase pelajik kırmızı çökellerin renginin kökeni

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ABSTRACT

In the Eastern Pontides (NE Turkey), Upper Cretaceous pelagic red sediments have a great lateral extent with remarkable colour, lithology and thickness of up to 45 m. Their geographical distribution represents two distinct zonations similar to the tectono-sedimentary division from north to south. In this study, characteristic samples of the pelagic red sediments from different parts of the Eastern Pontides were investigated by X-ray diffraction (XRD), X-ray fluorescence (XRF), and scanning electron microscopy coupled with energy dispersive analyses (SEM-EDAX). The red sediments are composed of limestone and muddy (silty and argillaceous) limestone, and characterized by abundant planktonic foraminifers. Hematite was detected in the all samples and its content ranges from 0.5 to 3.0 wt %. Electron microscope observations suggest that the hematite pigment has a diagenetic origin.The red color is due to the presence of hematite pigment, and indicates oxidizing conditions during early diagenesis in a relatively deep marine environment.

Key words: Color origin, diagenesis, pelagic red carbonates, Upper Cretaceous.

ÖZ

Doğu Pontidlerde (KD Türkiye), Üst Kretase pelajik kırmızı çökeller belirgin renk, litoloji ve 45 m' ye varan kalınlıklarıyla geniş bir yanal yayılıma sahiptirler. Bunların coğrafik dağılımı, kuzeyden güneye tektono-sedimanter bölümlendirmeye benzer şekilde, iki farklı zonlanma göstermektedir. Bu çalışmada, Doğu Pontidlerin değişik yörelerinden toplanan pelajik kırmızı çökellerin karekteristik örnekleri X-ışınları difraksiyonu (XRD), X-ışınları floresansı (XRF) ve taramalı elektron mikroskopu ve enerji dağılım (SEM-EDAX) yöntemleriyle incelenmiştir. Kırmızı çökeller, bol miktarda planktonik foraminifer içeren kireçtaşı ve çamurlu (siltli ve killi) kireçtaşından oluşur. Hematit tüm örneklerde saptanmış olup, içeriği ağırlık olarak % 0.5 ile 3.0 arasındadır. Elektron mikroskop gözlemleri hematit pigmentinin diyajenetik kökenli olduğunu göstermiştir. Kırmızı rengin nedeni hematit pigmentidir ve göreceli olarak derin deniz ortamında erken diyajenez sırasındaki oksitleyici koşulları gösterirmektedir.

Anahtar kelimeler: *Renk kökeni, diyajenez, pelajik kırmızı karbonatlar, Üst Kretase.*

INTRODUCTION

This study investigates the color origin of the Upper Cretaceous pelagic red carbonates which consist of limestone and muddy (silty and argillaceous) limestone within the Eastern Pontides, NE Turkey (Figure 1). The red beds have a great lateral extent with remarkable lithology and thickness of up to 45 m, and are characterized by abundant planktonic foraminifers. These beds are used as a stratigraphic marker horizon, and indicate an important change in tectono-sedimentary conditions (Görür et al., 1993; Bektaş et al., 1995).

The red color of these sedimentary rocks is due to the presence of finely dispersed hematite (Van Houten, 1973). There are two fundamentally different hypotheses to explain the origin of the hematite pigment (see the reviews of Turner, 1980; Pye, 1983; Friedman et al., 1992; Einsele, 1992). The first hypothesis suggests that the hematite is detritally derived from lateritic soils. According to the second hypothesis, the hematite forms authigenetically after deposition by alteration of iron- bearing detrital grains. Little detailed information is available on the origin of hematite pigment in the pelagic red sedimentary rocks (e.g. Franke and Paul, 1980), as most of the previous studies focus on clastic sedimentary rocks deposited in non-marine or high intertidal environments (Turner, 1980). The main content of this paper is summarized in a previous paper (Eren and Kadir, 1999).

REGIONAL AND STRATIGRAPHIC SETTINGS

The Eastern Pontides are located along the Alpine orogenic belt in the Eastern Black Sea region of Turkey, extending in E-W direction, and geologically subdivided into two zones roughly parallel to the axis of the mountain chain (Arni, 1939). The assumed boundary between the two zones is defined by the southern boundaries of the acidic-intrusive rock exposures of Mesozoic to Cenozoic age (see Figure 1). In general, the southern zone is dominated by sedimentary rocks which unconformably overly the Paleozoic basement comprised of metamorphic and granitic rocks (Figure 2), whereas in the northern zone, subduction -related volcanic and intrusive rocks are widespread (Bektaş et al., 1995; Figure 3). The volcanics including lavas and pyroclasts are intercalated with sedimentary rocks.

The geographical distribution of the Upper Cretaceous red beds within the Eastern Pontides represents two distinct zonations similar to the tectono-sedimentary division from north to south. In the northern zone, the pelagic red beds alternate with the Upper Cretaceous lavas and pyroclasts. In the Ardanuç (Artvin) area, red carbonates form the matrix of pillow-lavas (Özsayar et al., 1981a). In the southern zone, the pelagic red beds (Figure 4) generally occur together with yellow calcarenites at the base of the Upper Cretaceous turbiditic sequence composed of alternation of thin-bedded marl, pelagic biomicrite and sandstones (Tokel 1972; Pelin, 1977; Eren, 1983). The age of the pelagic red beds is assumed to be Campaian (Pelin et al., 1982).

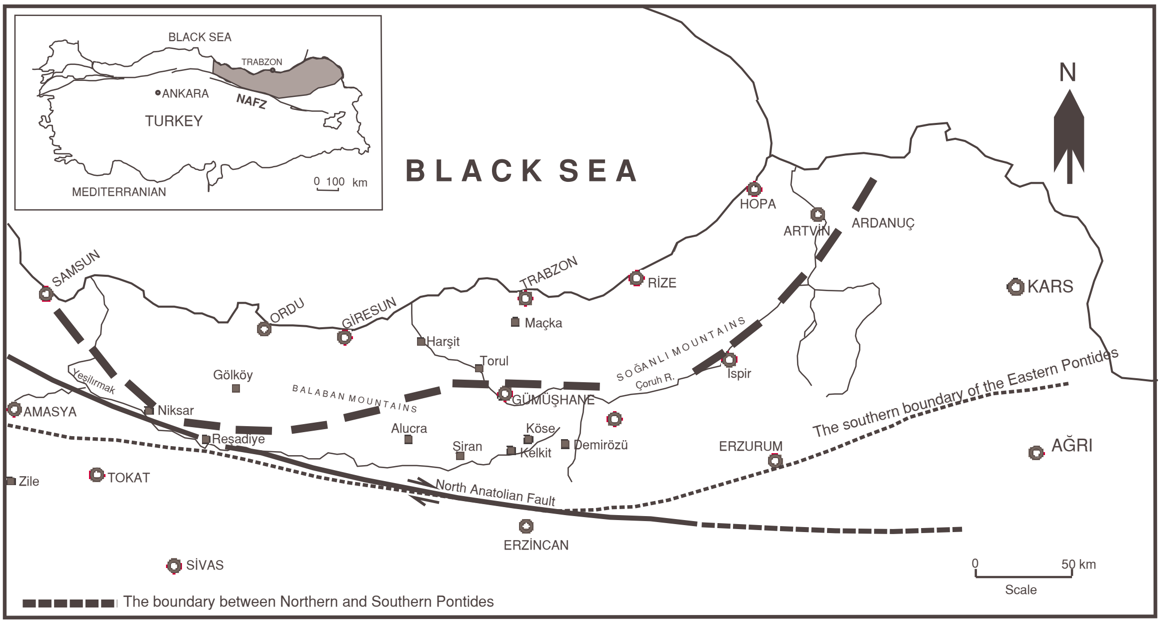

Figure 1. A schematic map illustrating northern and southern subdivisions of the Eastern Pontides (after Özsayar et al., 1981b).
Şekil 1. Doğu Pontidlerin kuzey ve güney alt bölümlerini gösteren şematik harita (Özsayar vd., 1981b' den).

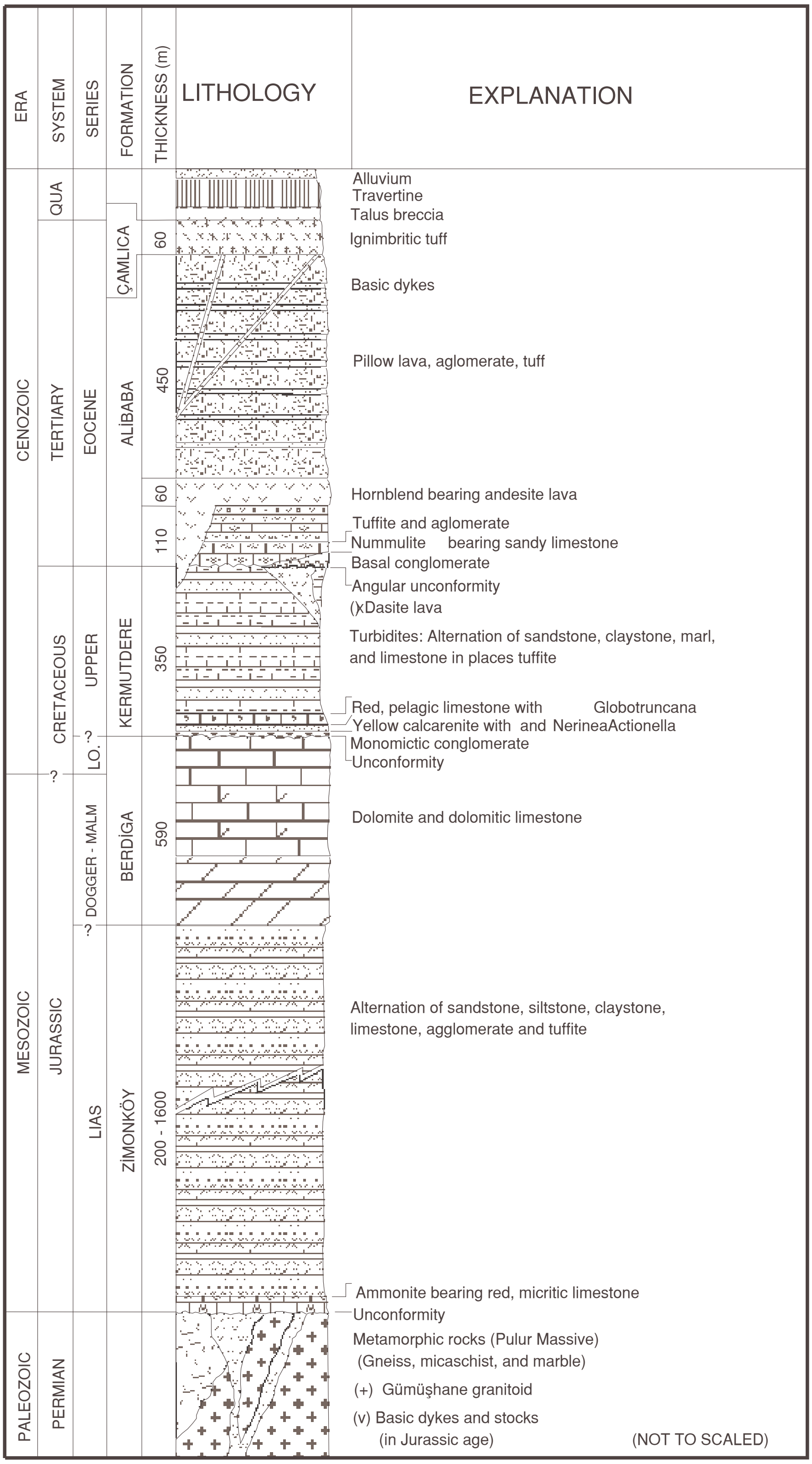

Figure 2. Generalized stratigraphic columnar section of the southern zone of the Eastern Pontides (modified partly from Eren, 1983).

Şekil 2. Doğu Pontid güney zonunun genelleştirilmiş dikme kesiti (Eren, 1983' den kısmen değiştirilerek).

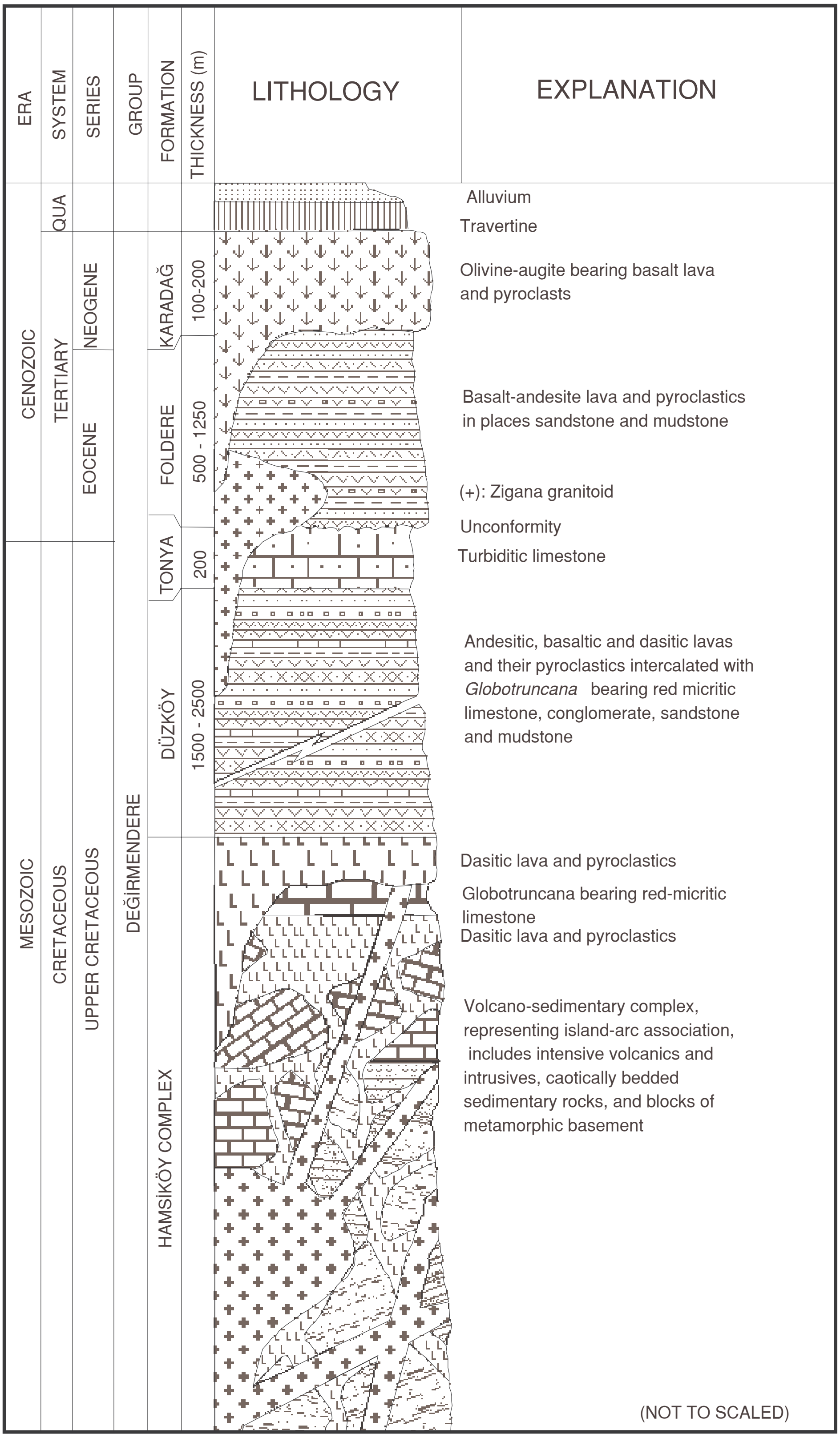

Figure 3. Generalized stratigraphic columnar section of the northern zone of the Eastern Pondites (after Gedik et al., 1996).

Şekil 3. Doğu Pontid kuzey zonunun genelleştirilmiş dikme kesiti (Gedik vd., 1996' den).

Figure 4. Field photograph of the pelagic red- muddy limestone (2) in the Kilop area (Kale, Gümüşhane), showing thin-bedding at the lower part and marly appearance at the upper part (1: shallow-water limestone of the Berdiga formation bounded by local hardground surface (see also Eren and Taslı, 1998); 3: Upper Cretaceous turbiditic sediments).

Şekil 4. Kilop (Kale, Gümüşhane) sahasında pelajik kırmızı-çamurlu kireçtaşının (2) arazi fotoğrafı, alt kısımda ince katmanlı, üst kısımda ise marn görünümlü (1: lokal sert zemin yüzeyi ile sınırlanan Berdiga formasyonunun sığ su kireçtaşı (Eren ve Taslı, 1998' e bakınız); 3: Üst Kratase türbidit çökelleri).

MATERIAL AND METHODS

During the field work, twenty-five characteristic outcrop samples of pelagic red beds were collected from outcrops at different parts of the Eastern Pontides, including Trabzon (Maçka), Gümüşhane (Torul, İkisu, Pirahmet, Kale), Giresun (Alucra, Harşit) and Artvin areas (see Figure 1). From each sample, thin-sections were prepared and examined under an optical microscope. Selected bulk samples and their impurities of some of them were determined by X-ray diffraction (XRD), X-ray fluorescence (XRF), and scanning electron microscopy coupled with energy dispersive analyses (SEM-EDAX). The impurities were seperated from carbonates by a mild acid treatment at pH = 5.0 using Na- acetate/ acetic acid mixture.

PELAGIC RED CARBONATES

Field Description

In the field, the red pelagic carbonates are identified by their characteristic colour. Their average thickness is approximately 30 meters. These rocks consist mainly of thin- to- medium- bedded limestone and muddy (silty and argillaceous) limestone (see Figure 4). In general, muddy limestones have appearance as marls. In some places, such as Mescitli (Gümüşhane) area, slump structures are associated with the red pelagic carbonates.

Sedimentary Petrography

The pelagic red carbonates in thin sections are represented mostly by biomicrite (Figure 5), rich in planktonic foraminifers with subordinate thin-shelled bivalve fragments, radiolaria, and echinoderm fragments. The planktonic foraminifers are mainly composed of Globotruncanidae, Globigerinidae, and Heterohelicidae, scattered into a micritic matrix. Small amounts of silt and sand-sized quartz grains are observed in some thin sections.

Depositional Environment

The red limestones and muddy limestones with abundant planktonic foraminifera represent basinal and lower slope environments (SMF type

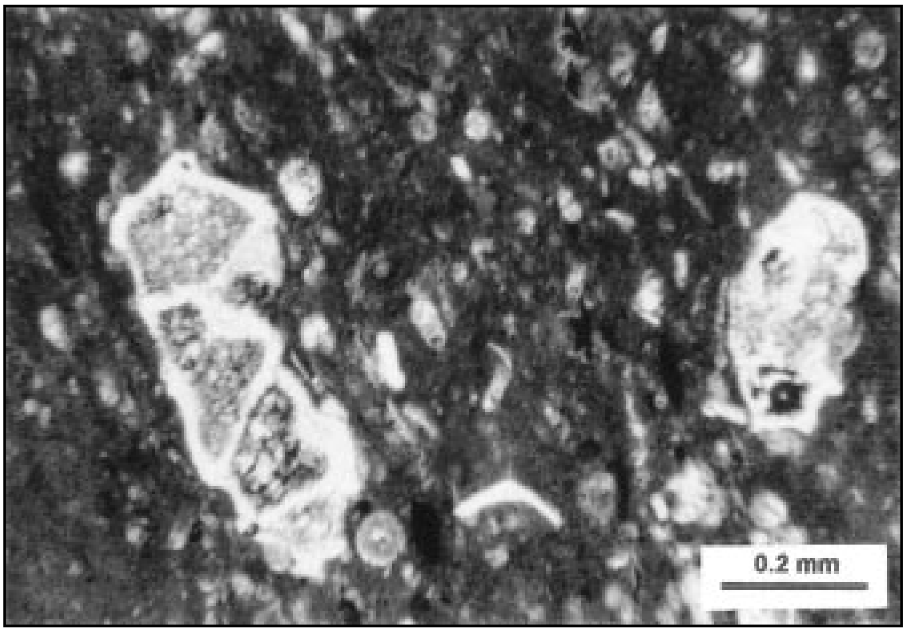

Figure 5. Photomicrograph of pelagic wackestone showing *Globotruncanids* scattered in a micritic matrix (from Kilop area (Kale, Gümüşhane)).
Şekil 5. Mikritik matriks içinde saçılmış Globotruncanid'leri gösterir pelajik vaketaşının fotomikrografı (Kilop (Kale, Gümüşhane) sahasından).

3, Wilson, 1975), and probably accumulated slowly within a pelagic settling (condensed sequence). Görür et al. (1993) proposed a depositional depth ranging from 500 to 1000 m for pelagic red carbonates.

Mineralogical and Geochemical Determinations

A series of X-ray analyses have been done to determine the precise composition of pelagic red sediments. Both XRD and XRF analyses indicate that calcite is a dominant mineral in all samples. The total calcium carbonate content ranges from 63 to 84 wt % as derived from CaO content and LOI (loss on ignition) values given in Table 1. Figure 6 is a cross-plot illustrating $CaCO_3$ content for each sample. In Figure 6, the 75 %- line represents a rough boundary between limestone and muddy limestone. Hematite content ranges from 0.5 to 3.0 wt %. In some samples, values of Al_2O_3, MgO, and K_2O are slightly higher than others because of higher clay content. Sr values are consistent with given values for pelagic sediments in the literature (Tucker and Wright, 1990; Tunoğlu and Temel, 1996).

The XRD patterns of acid residues show that quartz, illite and hematite are the main impurities, small amounts of chlorite, feldspar, kaolinite and anatase are also present. These estimations are semi-quantitative and shown in Table 2. It has to be considered that these estimations may have significant error range, and only show

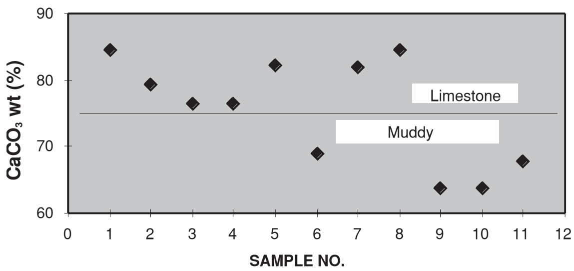

Figure 6. A cross-plot illustrating $CaCO_3$ content for each sample (the 75%- line indicates a rough boundary between limestone and muddy limestone. $CaCO_3$ values represent mean values derived from CaO and LOI values).
Şekil 6. Her örneğin $CaCO_3$ içeriğini gösterir grafik. (% 75 çizgisi kabaca kireçtaşı ve çamurlu kireçtaşı arasındaki sınırı göstermektedir. $CaCO_3$ değerleri CaO ve LOI değerlerinden elde edilmiş ortalama değerlerdir).

Table 1. The results from the chemical analysis of the pelagic red sediments.
Çizelge 1. Pelajik kırmızı çökellerin kimyasal analiz sonuçları.

Sample No.	1	2	3	4	5	6	7	8	9	10	11
SiO_2	13.2	12.8	19.9	16.1	12.8	21.5	15.5	11.7	23.0	25.0	23.0
TiO_2	≤ 0.1	0.1	0.1	0.2	0.1	0.3	0.1	0.1	0.4	0.2	0.2
$Al2O_3$	1.0	2.8	1.5	3.7	2.4	4.6	1.2	1.4	5.0	3.8	3.5
tFe_2O_3	0.6	2.9	1.1	1.9	1.3	2.9	0.9	0.8	3.5	2.8	2.8
FeO	0.1	0.25	≤ 0.05	0.35	0.1	0.2	≤ 0.05	0.2	0.7	1.3	0.55
MnO	0.2	0.6	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.3	0.2
MgO	0.5	0.8	0.4	1.1	0.6	0.5	0.2	0.7	1.6	1.4	0.8
CaO	47.0	44.0	42.4	42.0	45.6	38.0	45.5	46.1	35.5	36.5	38.0
Na_2O	≤ 0.1	0.3	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1	0.1	0.5	0.9	0.1
K_2O	0.2	0.5	0.3	0.8	0.4	1.3	0.2	0.3	1.2	0.8	1.0
P_2O_5	≤ 0.1	0.1	0.1	0.1	0.1	0.1	≤ 0.1	0.1	0.1	0.1	0.1
LOI	37.4	35.25	34.0	34.15	36.6	30.85	36.25	38.2	28.15	27.5	29.85
Total	≤100.4	100.15	≤100.1	≤101.25	≤100.2	≤101.25	≤100.25	99.6	99.15	99.3	99.55
H_2O^-	0.25	0.45	0.5	0.9	0.6	1.0	0.3	0.6	1.05	0.6	0.35
SO_3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01
Sr (ppm)	650	520	350	325	525	440	450	nd	nd	nd	nd

Oxides in wt %; tFe_2O_3 = total iron as ferric oxide; LOI = loss on ignition at 1050 ºC; nd = not detected.

Table 2. Semi-quantitative estimations of the impurities in the bulk samples.
Çizelge 2. Örneklerde, karbonatlı olmayan bileşenlerin yarı sayısal tahminleri.

Sample No.	Quartz	Feldspar	Illite	Himatite	Kaolinite	Anatase
1	3–	–	+	–	–	
3	71	–	2	–	–	
4	10	–	–	1	–	–
6	10	1	5	1	–	–
8	5–	–	1	–	–	
9	15	+	8	4	3	+

Impurities in wt %; –: not detectable with XRD; +: present but below 1% level

the relative abundance of the impurities in the bulk samples. A quantitative analysis would require the measurements of integrated intensities and preparation of synthetic mixtures of the above impurities. Hematite was detected in all samples and identified by its basal reflections at 3.68, 2.70, 2.52, 2.20, 1.84, 1.69, and 1.486 Å.

The bulk samples and their impurities were used for the SEM analyses. We were able to get good images of hematite pigment in the impurities because of their relative enrichment in iron-oxide. As seen under the SEM, the iron-oxide appears to grow epitaxially on the grains as dense platelets up to 1.0 micron in size (Figure 7a). The hexagonal shape of hematite platelets strongly suggest that the hematite pigment represents a diagenetic product. It patchily coats the grains. EDAX analyses were made of the areas of the particles. The iron values are distinctly different for Fe-rich and poor areas (Figure 7b and c). SEM analyses also show the existence of Fe-rich clay particles in the impurities which might be a significant Fe-source.

DISCUSSION AND CONCLUSIONS

As stated above, there is a debate on the origin of hematite pigments in the red sediments and on the iron-source. This study provides data which favour a diagenetic origin. But the iron-source and the timing of reddening still remain as a problem. Ferric iron can not be carried away by circulating water like dissolved ferrous iron because of its low mobility. Thus, intrastratal alteration of iron-bearing detrital grains (Walker, 1967) including Fe-rich clays appears to be a possible source of Fe. Franke and Paul (1980) suggested that ferric iron, from which hematite is formed during diagenesis, is provided by con-

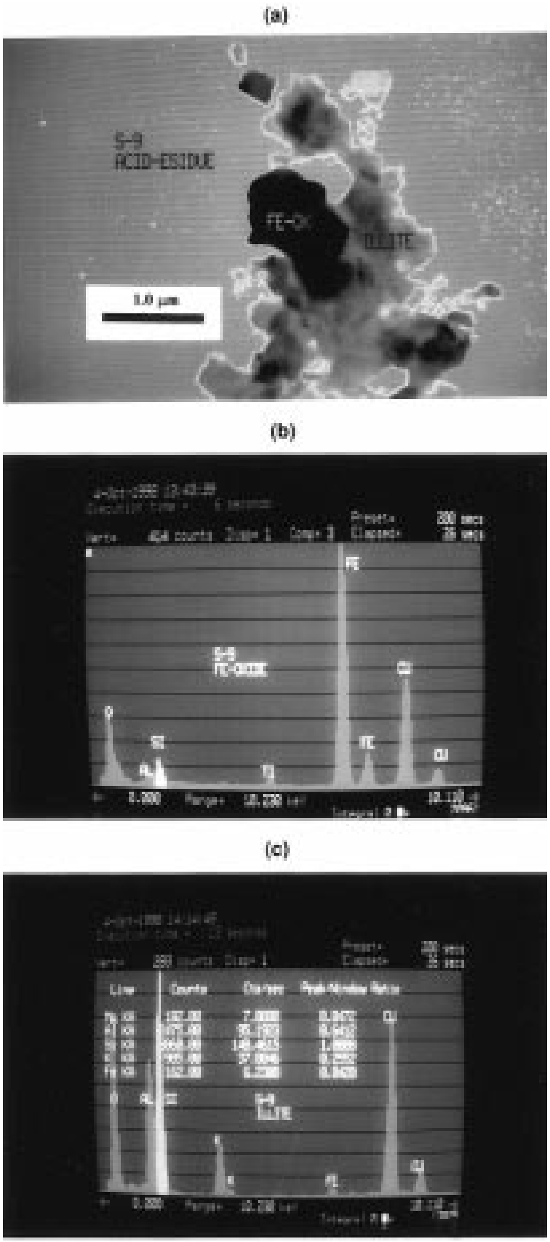

Figure 7. SEM micrograph and X-ray spectras: (a) typical occurrence of a dense iron oxide (hematite) crystallite on a mica (illite) substrate; (b) X-ray spectrum obtained from the dense crystallite; and (c) X-ray spectra obtained from the clean section of illite platelets (free of iron-oxide).
(Note: Cu-and Au lines in the spectras are belong to the sample holder and sample preparation).

Şekil 7. SEM mikrografı ve X-ışını spekrumları: (a) mika (illit) tabanı üzerinde yoğun demir oksit (hematit) kristalinin tipik oluşumu; (b) yoğun kristale ait X-ışını spekrumu; and (c) demir içermiyen illit plakasına ait X-ışını spekrumu (Not: Spekrumlarda Cu ve Au çizgileri örnek tutucusuna ve örnek hazırlamasına aittir)

tinental weathering and is mainly bound to the clay fraction, either as part of the clay structure or as an interlayer cation on the clay surface. Thus, it might be possible that additional iron has been supplied by submarine decomposition of iron-bearing mineral silicates (e.g. hornblend and biotite) in the adjacent volcanics.

The results of this study support the assumption that red colour alone is not directly diagnostic of a specific climate in the source area and depositional environment, but it is, however, an indicator of oxidizing conditions during early diagenesis (Walker, 1967). The widespread occurrence of the pelagic red sediments, their uniform coloration and low permeability for compacted forms suggest a coloration immediately after deposition. The oxidation took place in a relatively deep marine environment and was resulted by oxygene-rich bottom currents.

Most investigators (Tucker and Wright, 1990; Görür et al., 1993; Bektaş et al., 1995) assume that the formation of pelagic red carbonates is related to a world-wide drowning events which terminate the carbonate platform development The drowning of carbonate platforms results either from rising of sea-level or tectonic subsidence (Schlager, 1981). The drowning of the Pontide carbonate platform is related to tectonic subsidence as indicated by the presence of neptunian- dykes, syn-sedimentary faults, and local hardgrounds (Eren and Taslı, 1998; Bektaş et al., 1995). The pelagic red carbonates represent the first post-breakup sediments (Görür et al., 1993).

The red color of the pelagic carbonates of the Eastern Pontides is due to the presence of a hematite pigment whose content ranges from 0.5 to 3.0 wt %. SEM images of the hematite pigment suggest that it is an early diagenetic product which patchily coats the mineral grains. The red color indicates oxidizing conditions during early diagenesis in a marine environment.

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