

SEMA TETIKER¹

Geochemistry of the Cretaceous-Tertiary (K/T) Transition Clays in the Southeastern Turkey

Introduction

The widely discussed Cretaceous/Tertiary boundary (K/T) event 65 million year (My) ago led to a mass extinction at the end of the Cretaceous and associated geochemical anomalies in sediments deposited at this time (Smit and Hertogen 1980; Alvarez et al. 1980). Important evidence has been obtained regarding the transition in clayey rock levels that were deposited in abundance during the K/T period (Ortega-Huertas et al. 1995; Debrabant et al. 1999; Martinez-Ruiz et al. 2001; Madhavaraju et al. 2002). Paleo-oceanographic changes during this period were marked by a sharp decrease in notation sea levels and carbonate sedimentation at the K/T boundary, accompanied by an increase in clay mineral contents due to a decrease in biological productivity (Chamley 1989). The clay minerals deposited at the K/T boundary have been studied in different areas of the world (Rampino and Reynolds 1983; Jehanno et al. 1987; Vannucci et al. 1990; Robert and Chamley 1990; Elliott 1993; Ortega-Huertas et al. 1995, 1998; Abboud 2016). In general, metal and other platinum group elements are always enriched in these boundary clays (Signor and Lipps 1982; Graup and

✉ Corresponding Author: Sema Tetiker; e-mail: sema.tetiker@batman.edu.tr

¹ Batman University, Turkey; ORCID iD: 0000-0001-5158-7364; e-mail: sema.tetiker@batman.edu.tr



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Spettel 1989; Robin et al. 1993; Kerr 1996; KYTE 1998; Shukolyukov and Lugmair 1998; Kiessling and Claeys 2001; Kusky 2011; Pal et al. 2015).

The Germav Formation member rocks in the Batman and Mardin regions of southeastern Turkey provide a unique opportunity to study the clay mineralogical associations and geochemical data at the K/T transition. By analyzing major, trace, and rare elements, we can gain insights into the sources of the clays present during this critical geological period. This research aims to contribute to our understanding of the sources and geological processes that occurred during the K/T transition in this region.

1. Geological setting

A marine environment that started to deposit 66 My ago in the north of the Arabian Plate is home to the Southeast Anatolian geographic belt. The Southeast Anatolian geographic belt thus serves as a valuable geological record, providing insights into the past marine environments and the dynamic processes that shaped the region. Within this belt, the Arabian plate emerges as an Alpine tectonic-stratigraphic unit. The Bitlis-Pütürge Crystalline Complex (Bitlis Belt) and the Southeastern Anatolian Autochthonous (SEAA) rocks comprise the majority of this platform (Göncüoğlu et al. 1997). In southeast Turkey, the Bitlis Belt, sometimes called the Telbesmi Formation, is part of the Precambrian Basement Complex (Şenalp and Tetiker 2020). The earliest known formation in Turkey, the Telbesmi Formation was initially identified by Moses in the village of Derik (Mardin) in 1934. Overlying this Late Neoproterozoic igneous basement complex are Cambrian-era continental fluvial sandstones. SEAA rocks in the north-northeast of the Arabian plate and the Taurus Belt in the north-northwest are units of the Bitlis and Southeast Anatolian Ophiolite Belts (Figure 1a). The study areas are represented on the geologic map (MTA 2008) and cover the Upper Cretaceous and Lower Paleocene (Maxon 1936) age Germav Formation (Figure 1b). This unit's lower member is from the higher Cretaceous, and its higher member is from the Lower Paleocene.

2. Materials and methods

A total of 77 samples were collected along the point and measured stratigraphic sections from the rocks (pelitic, sandstone and carbonate) of the Batman and Mardin areas. The XRD analyses employed a $\text{CuK}\alpha$ anode (1.541871 Å), Ni filter, 35 kV voltage, current of 15 mA, goniometer speed of 1 or paper speed of 2°/min., time constant of 1 sec, slits of 1° 0.15 µm, and paper spacing of 2° = 5–35° and 4–30°. The whole rock and clay-sized components (<2 µm) of the samples were defined and their semi-quantitative result were calculated based on the external standard method (Brindley 1980; Yalçın and Bozkaya 2002). Following dispersion, clay minerals (<2 µm) were sorted by centrifugation. In order to keep

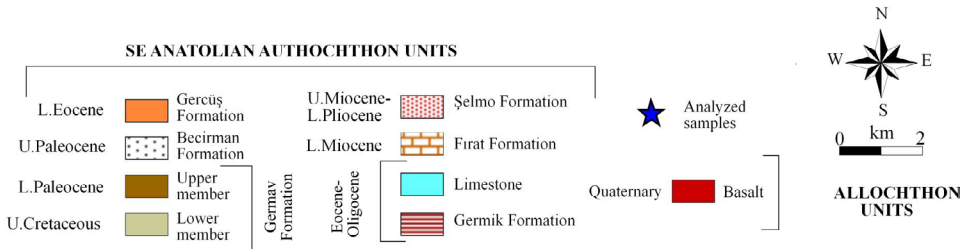
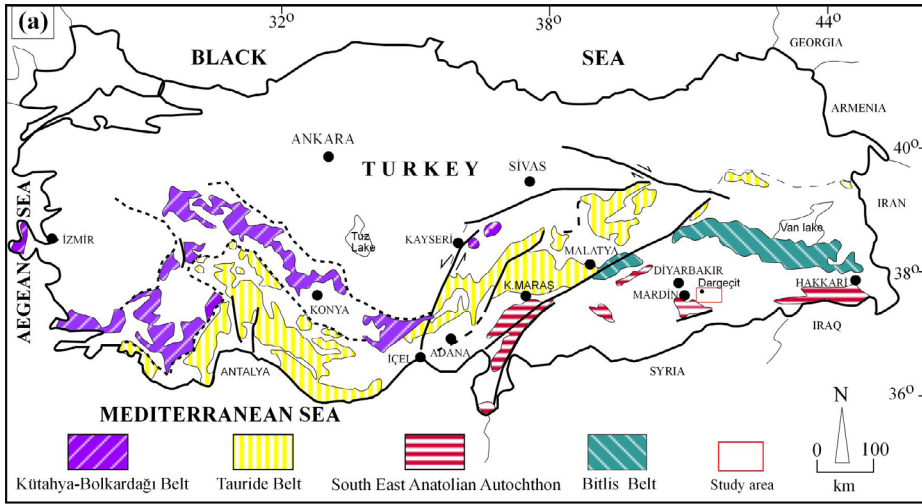


Fig. 1. a) Tectonic units of Southern Anatolia and location of study area (simplified from Göncüoğlu et al. 1997), b) Simplified geology map of northern Mardin and sample areas (1/100:000 scaled M47 sheet: MTA 2008)

Rys. 1. a) Jednostki tektoniczne południowej Anatolii i lokalizacja obszaru badań, b) Uproszczona mapa geologiczna północnego Mardin i przykładowe obszary (arkusz M47 w skali 1/100:000: MTA 2008)

non-clay materials out of the clay sized fraction, high clay-bearing rocks, particularly shale, were finely ground before the clay was extracted. The identification of clay minerals (001) was made according to their basal reflections.

For the purpose of the study, pure and nearly pure clay/phylosilicate fractions from samples with different stratigraphic ages and lithology were analyzed to determine their chemical compositions (Tables 1 and 2), mixed with a flux of lithium metaborate/tetraborate, and fused in an induction furnace at the Acme Laboratory, Ltd. in Canada. ICP-MS (inductively coupled plasma-mass spectrometry) was used for the trace and REE analysis. Details of the analytical methods and instrumental detection limits are presented on the company's website (<http://www.acmelab.com/>).

3. X-ray Mineralogy

Whole-rock (WR) and clay fraction (CF) X-ray diffraction (XRD) studies were carried out on claystone and clayey-carbonate rocks. The XRD-WR analysis revealed the presence of minerals with an alteration/weathering (phylosilicate), magmatic (feldspar, pyroxene, amphibole, serpentine), and chemical and/or diagenetic (quartz, dolomite, analcime, goethite, pyrite) origin. Upper Cretaceous and Lower Paleocene rocks had a similar mineral paragenesis, as shown by XRD-WR, while Lower Paleocene samples showed more dolomite. In the XRD-CF analyses of illite, chlorite, serpentine (Srp), vermiculite (V), and smectite (S), phyllosilicate/clay minerals were found; the mixed layers included C-S (chlorite-smectite), C-V (chlorite-vermiculite), I-C (illite-chlorite), and I-V (illite-vermiculite). Mineral paragenesis is similar in Upper Cretaceous and Lower Paleocene rocks. The XRD-CF results showed that illite and C-S represented the dominant paragenesis during the Upper Cretaceous, while vermiculite and C-V dominated during the Lower Paleocene. (Figure 2).

4. Geochemistry

Clay samples were analyzed and their major and trace element compositions are presented in Tables 1 and 2. The samples' most prevalent component, silica, ranged in weight percentage from 41.20 to 49.40 (average: 46.08 wt.%). The oxide that was next most prevalent was MgO (12.17–18.15 wt.%, average: 15.23 wt.%), followed by Al₂O₃ (7.93–14.74 wt.%, average: 11.30 wt.%), Fe₂O₃ (9.86–15.41 wt.%, average: 12.00 wt.%).

By normalizing the phyllosilicate/clay minerals to chondrite values (Sun and McDonough 1989), the trace element distributions were examined (Figure 3). Furthermore, an attempt was made to compare these values with the following sources: the Neoproterozoic Basement rocks of SEAA (Tetiker 2012), the Archaean-Proterozoic-Phanerozoic Cratonic Sandstones (A-Pr-Ph-CS; Condie 1993), the North American Shale Composite (NASC), and Cambrian Sandstones from the Amanos area (Bozkaya et al. 2011).

Table 1. Major element chemical compositions of phyllosilicate/clay minerals of Upper Cretaceous and Lower Paleocene members

Tabela 1. Skład chemiczny głównych pierwiastków minerałów krzemianów warstwowych/ilastych przedstawicieli górnej kredy i dolnego paleocenu

Age	Upper Cretaceous				Lower Paleocene											
	BBG-34	BBG-36	BBG-1c	C-S	BBG-3c	BBG-5c	BBG-13c	S	BBG-14c	Chl	MKP-12	MKP-19	MKP-22	MKP-30	MKP-32	MKP-35
SiO ₂	47.27	48.63	47.24	48.94	48.94	49.40	46.77	47.59	47.15	43.07	42.57	43.07	42.57	45.84	41.20	43.38
TiO ₂	0.57	0.68	0.89	1.03	0.95	0.95	0.44	0.54	0.70	0.72	0.98	0.72	0.98	0.68	0.62	0.78
Al ₂ O ₃	12.56	12.27	13.81	14.74	13.10	13.10	8.59	9.43	11.58	9.42	11.35	9.42	11.35	7.93	9.39	12.72
Fe ₂ O ₃	10.81	9.86	12.83	12.72	10.47	10.47	14.51	15.41	10.69	11.20	12.07	11.20	12.07	10.11	13.68	11.69
MnO	0.04	0.04	0.04	0.05	0.04	0.04	0.02	0.02	0.05	0.08	0.04	0.08	0.04	0.03	0.07	0.04
MgO	16.82	14.76	13.40	12.67	13.23	13.23	16.43	14.87	12.17	15.88	18.15	15.88	18.15	17.79	17.37	14.56
CaO	0.39	0.48	0.66	0.48	0.36	0.36	0.33	0.23	0.75	1.30	0.32	1.30	0.32	0.83	0.34	0.86
Na ₂ O	0.10	0.15	0.49	0.18	0.22	0.22	0.16	0.24	0.54	1.68	1.37	1.68	1.37	0.47	3.30	0.90
K ₂ O	1.07	1.41	1.79	2.09	1.74	1.74	0.39	0.61	1.40	0.42	0.85	0.42	0.85	0.36	0.58	0.61
Cr ₂ O	0.073	0.064	0.060	0.086	0.079	0.079	0.082	0.068	0.074	0.142	0.100	0.142	0.100	0.150	0.165	0.100
P ₂ O ₅	0.02	0.02	0.23	0.13	0.04	0.04	0.08	0.24	0.10	0.18	0.17	0.18	0.17	0.04	0.79	0.17
LOI	9.35	10.30	7.40	6.20	9.50	9.50	10.80	9.65	14.4	15.4	11.5	15.4	11.5	15.3	12.03	13.7
Total	99.00	98.60	98.78	99.23	99.05	99.05	98.52	98.89	99.73	99.66	99.62	99.66	99.62	99.65	99.72	99.66
Al ₂ O ₃ /TiO ₂	22.04	18.04	15.52	14.31	13.79	13.79	19.52	17.46	16.54	13.08	11.58	13.08	11.58	11.66	15.15	16.31

Fe₂O₃: Total iron, LOI: Loss on ignition, C-S = Mixed-layered chlorite-smectite, S = Smectite, Chl = Chlorite, I-C = Mixed-layered illite-vermiculite, V = vermiculite, C-V = Mixed-layered chlorite-vermiculite

Table 2. Trace element chemical compositions of phyllosilicate / clay minerals of Upper Cretaceous and Lower Paleocene members
 Tabela 2. Skład chemiczny pierwiastków śladowych minerałów krzemianów warstwowych/ilastych przedstawicieli górnej kredy i dolnego paleocenu

Age	Lower Paleocene											Upper Cretaceous		
	BBG-1c	BBG-3c	BBG-5c	BBG-13c	BBG-14c	MKP-12	MKP-19	MKP-22	MKP-30	MKP-32	MKP-35	BBG-34	BBG-36	
Clay	C-S	C-S	S	S	Chl	I-C	C-S	V	C-V	C-S	C-S	C-S	C-S	
Cr	411	588	541	561	465	506	972	684	1026	1129	684	500	438	
Ni	730	752	694	819	843	848	1018	980	1216	1202	849	915	799	
Co	31.4	39.2	26.2	31.7	46.8	37.2	48.8	50.1	45.9	42.5	49.4	39.4	32.1	
Sc	30	24	26	27	26	17	37	21	20	33	31	23	23	
V	199	250	199	226	223	184	224	196	207	315	293	173	165	
Cu	64.8	I.S.	29.5	53.2	I.S.	48.3	50.0	55.4	28.6	I.S.	134.2	I.S.	50.3	
Pb	2.9	I.S.	3.9	3.0	I.S.	2.3	2.0	3.1	2.6	I.S.	4.2	I.S.	4.5	
Zn	95	I.S.	85	84	I.S.	79	97	91	94	I.S.	161	I.S.	200	
Bi	<0.1	I.S.	<0.1	<0.1	I.S.	<0.1	<0.1	<0.1	<0.1	I.S.	<0.1	I.S.	<0.1	
Cd	0.3	I.S.	<0.1	<0.1	I.S.	1	<1	1	<1	<1	<1	I.S.	<0.1	
Sn	2	2	2	1	1	3.3	2.7	6.5	3.1	<1	5.0	2	1	
W	16.0	7.0	17.8	39.6	27.2	0.2	<0.1	0.1	0.1	3.3	0.1	43.6	12.4	
Mo	0.4	I.S.	0.3	0.8	I.S.	3.0	2.4	1.0	0.6	I.S.	1.3	I.S.	0.2	
As	3.8	I.S.	2.8	5.7	I.S.	<0.1	<0.1	<0.1	<0.1	I.S.	0.1	I.S.	1.9	
Se	<0.5	I.S.	<0.5	<0.5	I.S.	1	<1	<1	2	I.S.	<1	I.S.	<0.5	
Sb	0.2	I.S.	0.2	0.1	I.S.	<0.1	<0.1	<0.1	<0.1	I.S.	<0.1	I.S.	0.2	
Be	<1	<1	<1	<1	4	46.4	12.4	27.0	11.8	<1	19.7	<1	1	
Ag	<0.1	I.S.	<0.1	<0.1	I.S.	2.3	1.0	1.0	1.1	I.S.	1.3	I.S.	<0.1	
Au	1.9	I.S.	<0.5	1.1	I.S.	54	31	45	14	I.S.	44	I.S.	6.0	
Hg	0.02	I.S.	0.01	<0.01	I.S.	29.5	23.0	17.5	20.0	I.S.	25.9	I.S.	0.04	
Rb	61.5	68.2	58.4	12.8	20.6	<0.1	<0.1	<0.1	<0.1	16.5	<0.1	48.0	58.9	
Cs	2.9	3.7	2.8	0.6	0.8	14.8	12.3	15.1	9.4	1.2	13.5	3.6	4.2	
Ba	65	59	51	21	34	0.9	0.6	1.2	0.5	34	0.7	40	57	

Age	Lower Paleocene											Upper Cretaceous	
	Trace element (ppm)	BBG-1c	BBG-3c	BBG-5c	BBG-13c	BBG-14c	MKP-12	MKP-19	MKP-22	MKP-30	MKP-32	MKP-35	BBG-34
Clay	C-S			S			Chl	I-C	C-S	V		C-S	
Sr	24.5	21.3	19.5	10.4	10.0	13.8	11.9	21.1	7.8	25.9	11.3	19.7	27.7
Tl	<0.1	I.S.	<0.1	0.1	I.S.	2.6	1.7	2.6	1.2	I.S.	2.1	I.S.	0.2
Ga	18.2	18.0	15.8	11.0	12.7	110.6	71.0	121.4	48.3	9.7	72.8	13.1	13.6
Ta	1.4	1.4	1.3	0.6	0.7	12.7	9.7	8.4	4.4	0.6	7.3	0.6	0.8
Nb	21.0	22.2	19.0	10.4	11.7	2.7	1.5	2.7	1.0	10.3	2.0	9.9	12.1
Hf	4.0	4.3	3.5	2.4	2.6	0.6	0.3	0.6	0.2	1.9	0.6	2.1	2.6
Zr	166.1	157.4	132.7	72.4	110.6	13.9	7.5	4.6	3.4	73.0	5.6	81.9	94.2
Y	15.0	10.2	9.7	7.6	12.7	21.6	13.5	8.9	6.1	6.1	10.9	7.7	9.6
Th	5.4	4.1	3.6	2.0	2.6	2.45	1.73	0.91	0.73	2.0	1.31	3.2	3.6
U	1.1	1.3	1.0	0.4	0.9	9.2	7.2	3.5	3.2	0.6	5.3	1.2	1.5
La	17.5	10.5	7.9	10.9	12.1	1.93	1.57	0.72	0.71	6.3	1.07	4.8	6.6
Ce	36.5	18.2	14.1	22.6	22.8	0.54	0.48	0.27	0.21	9.2	0.33	8.5	11.3
Pr	3.74	1.83	1.53	2.25	2.29	1.95	1.65	0.89	0.71	1.17	1.21	0.92	1.09
Nd	14.1	7.3	5.2	7.7	8.5	0.30	0.26	0.19	0.11	4.8	0.19	3.8	4.2
Sm	2.61	1.38	1.05	1.57	1.48	1.84	1.66	1.38	0.71	0.79	1.18	0.75	0.89
Eu	0.72	0.40	0.31	0.42	0.46	0.43	0.35	0.30	0.16	0.27	0.27	0.20	0.22
Gd	2.58	1.61	1.24	1.44	1.70	1.36	1.05	0.99	0.50	0.92	0.85	0.77	0.94
Tb	0.71	0.28	0.24	0.32	0.15	0.19	0.15	0.16	0.08	0.17	0.13	0.17	0.32
Dy	2.83	1.70	1.56	1.52	2.15	1.29	0.89	1.07	0.54	1.18	0.85	1.21	1.15
Ho	0.61	0.41	0.38	0.33	0.48	0.19	0.14	0.16	0.08	0.23	0.14	0.28	0.30
Er	1.82	1.39	1.10	1.02	1.63	0.9	1.0	2.3	<0.5	0.64	4.0	0.91	1.04
Tm	0.27	0.22	0.18	0.15	0.24	<0.01	0.01	0.02	0.02	0.12	0.04	0.17	0.16
Yb	1.94	1.56	1.25	1.04	1.56	<0.5	<0.5	<0.5	<0.5	0.78	0.8	1.10	1.21
Lu	0.27	0.23	0.22	0.16	0.24	<0.1	<0.1	<0.1	<0.1	0.11	0.1	0.16	0.19
ΣREE	86.2	47.01	36.26	51.42	55.78	57.17	38.13	24.04	17.24	26.68	29.33	23.74	29.61

C-S = Mixed-layered chlorite-smectite, S = Smectite, Chl = Chlorite, I-C = Mixed-layered illite-vermiculite, V = vermiculite, C-V = Mixed-layered chlorite-vermiculite, I.S = insufficient sample

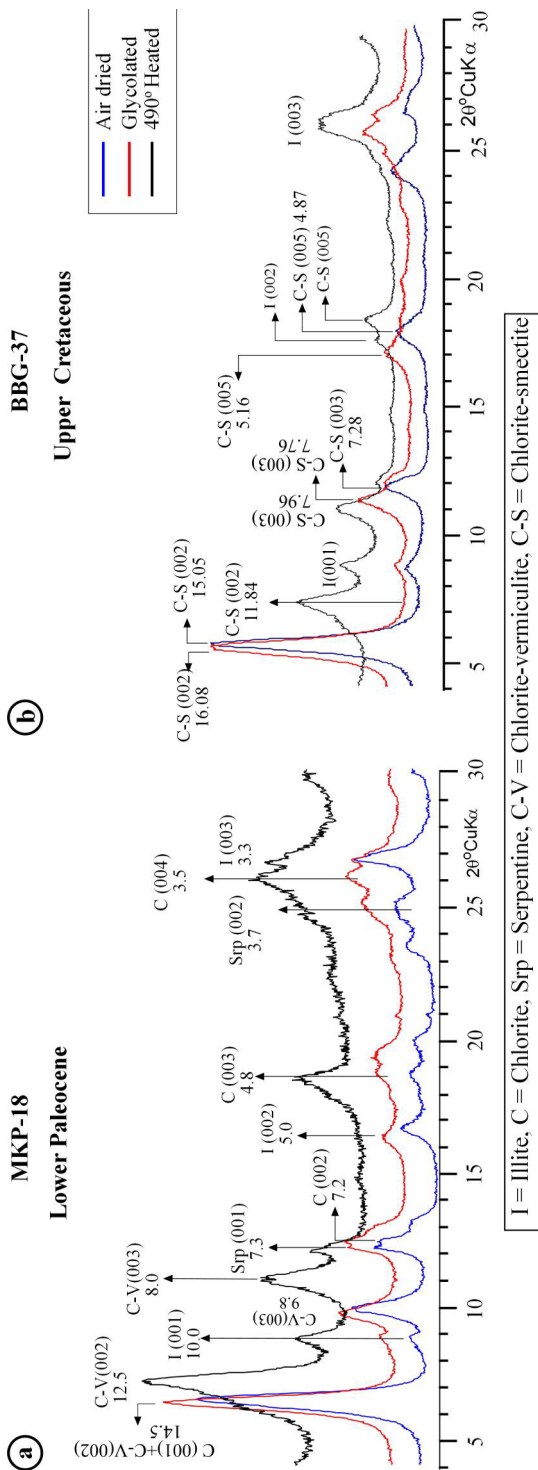


Fig. 2. XRD patterns of the clay fraction of Upper Cretaceous-Lower Paleocene Germav Formation Members

Rys. 2. Dyfrakcja rentgenowska XRD frakcji ilastej górnej kredy i dolnego paleocenu przedstawiciela formacji Germav

In the Batman region, the Upper Cretaceous clays showed 188-fold enrichment in U and two-fold depletion in P. For the Lower Paleocene clays, a 93-fold enrichment was observed for Th. Furthermore, the clays showed positive anomalies for Ta, Gd, Nd, Zr, and Ti, and negative anomalies for K, P, Sr, and Eu (Figure 3a, b). With the exception of Nb and Ti values, the clays had lower concentrations of every element than the NASC. The trace

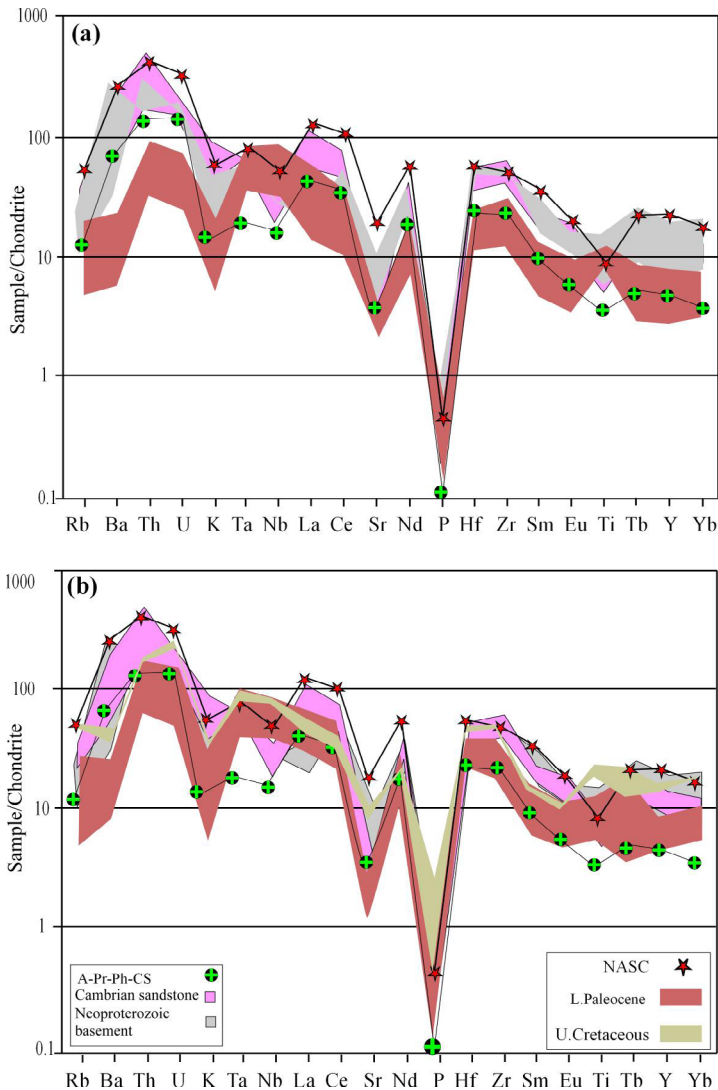


Fig. 3. Chondrite-normalized trace element patterns of phyllosilicate/clay minerals in Upper Cretaceous-Lower Paleocene rocks (Chondrite: Sun and McDonough 1989; Nb and Y for NASC: Condie 1993; other elements: Gromet et al. 1984) a) Mardin area, b) Batman area

Rys. 3. Znormalizowane chondrytem wzory pierwiastków śladowych w krzemianach warstwowych/minerałach ilastych skał górnej kredy i dolnego paleocenu: a) obszar Mardin, b) obszar Batman

element contents of the members and basement rocks of distinct ages in the study area showed a similar trend. The trace element patterns of the Upper Cretaceous clays were similar to those of the Neoproterozoic and Cambrian rocks, while those of the Lower Paleocene clays resembled the patterns of cratonic sandstones.

According to Sun and McDonough (1989), the elemental concentrations of the REE values of the phyllosilicate/clay minerals in the Mardin and Batman regions were compared and normalized to chondritic abundance. (Figure 4a, b). Also the element values were then

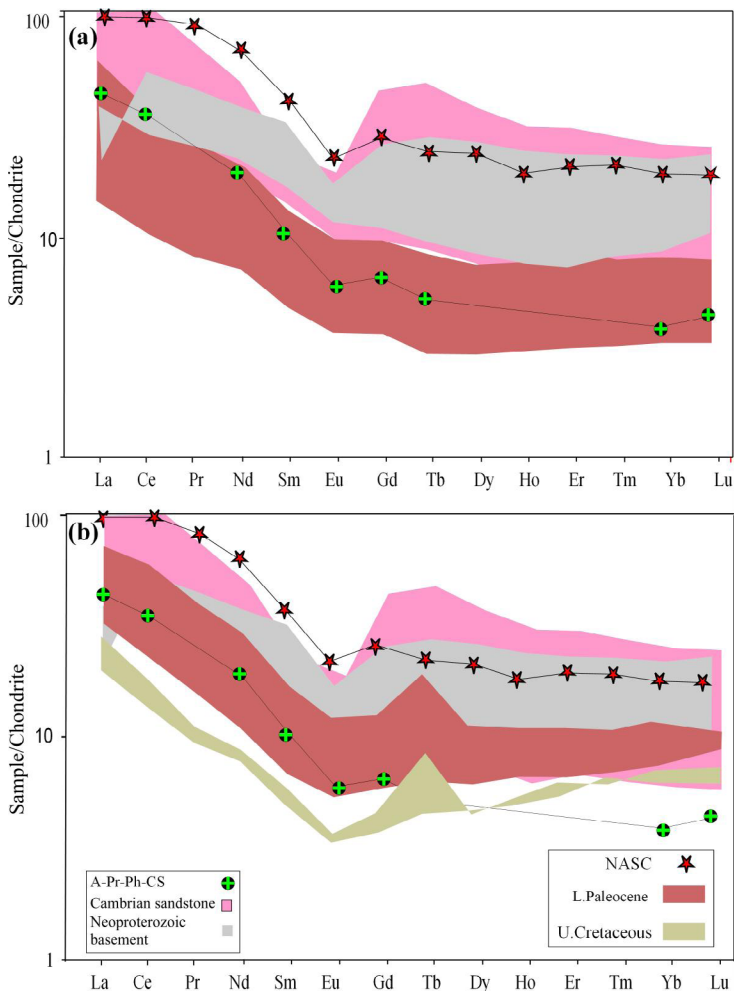


Fig. 4. Chondrite-normalized REE element patterns of phyllosilicate/clay minerals in Upper Cretaceous-Lower Paleogene rocks (Chondrite: Sun and McDonough 1989; Nb and Y for NASC: Condie 1993; Ho and Tm for NASC: Haskin et al. 1968; other elements: Gromet et al. 1984; A-PR-CH-CS: Condie 1993)
a) Mardin area, b) Batman area

Rys. 4. Znormalizowane chondrytem wzory pierwiastków REE w krzemianach warstwowych/minerałach ilastych skał górnej kredy i dolnego paleocenu: a) obszar Mardin, b) obszar Batman

compared with those of the NASC, A-Pr-Ph-CS, and Neoproterozoic (Tetiker 2012) and Cambrian basement rocks (Bozkaya et al. 2011) in Figure 4. The REE contents of all clays were lower than those of the NASC but were higher than the chondritic values. The total REE concentrations were lowest in the Lower Paleocene vermiculite minerals (17 ppm) and highest in the C-S minerals (86 ppm) (Table 2). The total REE concentrations of the Lower Paleocene clays were between 51.42 and 55.78 ppm (average: 53.60 ppm) for smectite, 57.17 ppm for chlorite, 38.13 ppm for I-C, and 29.33 ppm for C-V. Total REE concentrations were found to be 23.74–29.61 ppm (average 26.68 ppm) in Upper Cretaceous C-S minerals. In addition, the light REE (LREE) abundances of the clays were lower than the heavy REE (HREE) ones. Negative Eu anomalies were found in the NASC and all other samples. Positive Tb anomalies were observed in the Upper Cretaceous and Lower Paleocene C-S minerals from the Batman region. The REE patterns of the Lower Paleocene clays were relatively similar to those of the cratonic sandstones, while those of the Upper Cretaceous clays were entirely distinctive.

The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios and SiO_2 concentrations of the sedimentary rocks provided information about their origin (He et al. 2010; Dai et al. 2015). $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios in igneous rocks typically fall into three categories: felsic (21–70), intermediate (8–21), and mafic (3–8). The majority of the clays had $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios between 12 and 22 (average: 16), which suggests that intermediate igneous rocks were the source rocks of these deposits. This study confirmed the findings of Feng and Kerrich (1990) that ferromagnesian trace elements (Cr and V) exhibit high levels of fractionation. Specifically, the claystone had higher values of Cr (411.00–1129.00 ppm, average: 654 ppm) and V (165.00–315.00 ppm, average: 220 ppm), suggesting that a basic (ophiolitic) rather than felsic igneous source region contributed to the sample (Table 2). According to McLennan et al. (1983), ratios of less than 8 indicate felsic sources, whereas ratios greater than 8 indicate mafic sources. Trace element ratios, such as Cr/V, can be used to consistently distinguish between mafic and felsic sources. In this study, the Lower Paleocene Cr/V ratios ranged from 2.07 to 4.96 (average: 3.01) and the Upper Cretaceous rocks exhibited a Cr/V ratio of 2.77 (between 2.65 to 2.89), therefore indicating a felsic provenance source for the Upper Cretaceous sediments. Clays usually have Y/Ni ratios between 0.1 to 0.8, which indicates the benefit of a silicic and felsic provenance.

The Y/Ni ratios fall in mafic sources due to their increased ferromagnesian abundance (Hiscott 1984; McLennan et al. 1983). The average Cr/Ni ratios of the clays from members were 0.75 for Lower Paleocene and 0.55 for Upper Cretaceous, respectively. Additionally, the members' clays have Cr/Ni ratios ranging from 0.5 to 1.0; values of 0.1 or above would indicate a mafic/ultramafic provenance (Jaques et al. 1983; Garver et al. 1996).

5. Discussion

The C-S and smectite minerals likely originated from volcanic or pedogenic sources (Chamley 1989). The development of pedogenic smectite and mixed layer clays in sandstones and shales are common features of rocks formed during the Upper Cretaceous and Paleocene (Chengfa et al. 1986; Pollastro and Barker 1986; Madhavaraju et al. 2002). Conversion of smectite to chlorite minerals usually forms in the corrensite interphase (Brigatti and Poppi 1984; Inoue 1987; Inoue and Utada 1991), and corrensite minerals are mostly known in basic or intermediate volcanoclastic rocks. Interlayers chlorite/vermiculite (C-V) and illite-chlorite (I-C) develop as a result of alteration of mica (biotite, muscovite) minerals (Noack and Collin 1986). In addition, studies conducted in the region have shown that degradation/decomposition and diagenetic processes were also effective during these K/T times (Tetiker et al. 2016, 2017). For instance, in several of the levels where the concentrations of smectite and analcime increased, feldspar and/or pyroxene minerals were discovered. The presence of the former also demonstrates that the analcime and smectite formed from volcanic glass independently of the weathering or alteration of dark-colored minerals (such as biotite, pyroxene, and amphibole) (Renaut 1993).

In the Permian–Triassic period, the basin began to expand up inside the Neotethys Ocean to the north of the Arabian Plate. The Neotethys ocean's remnants were represented by the basin, which closed during the Upper Cretaceous (Şengör and Yılmaz 1981; Robertson et al. 2007). The study's clastic origin materials that were brought to the basin show the sequence of geotectonic events that occurred in the SEA Ophiolite Belt.

The members' clays revealed that the main oxides in the rocks under study, namely Al_2O_3 , Fe_2O_3 , and MgO , had comparable abundances. Higher MgO , Al_2O_3 , and Fe_2O_3 concentrations in the clays were associated with the development of mixed layers (C-S, I-C, and C-V) that contained chlorite and phyllosilicate structures that were similar to each other. Similar $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios were seen in the Lower Paleocene and Upper Cretaceous clays, suggesting that the feldspar concentrations of these rocks were similarly comparable. It is possible that the samples were composed of hydrated siliceous aluminosilicate clays that resulted from the full weathering of feldspars.

By normalizing the total trace element contents of the phyllosilicate/clay minerals to the chondrite values (total trace element: 2229.6 ppm) from clay, vermiculite had the largest change (normalizing total trace element: 227 ppm) and C-S had the least change (normalizing total trace element: 919 ppm). In other words, vermiculite allowed for more substitutions within its crystal structure than chlorite and chlorite-containing mixed-layer minerals. Pronounced negative K, Sr, and P and positive Th and Nd anomalies were recorded. The Ni and Cr contents of siliciclastic sediments are commonly considered as a usually indicates about provenance.

Higher concentrations of Ni and Cr and low ratios of Cr/Ni usually indicate an ultramafic source (Garver et al. 1996). The clays had higher of mean of Ni and Cr contents (Cr = 654.23 ppm, Ni = 897.31 ppm) than typical ultramafic source rocks. Furthermore, additional proof that their host basin was supplied with Upper Cretaceous ophiolitic rocks

came from the high Cr and Ni concentrations of the clays, which were corroborated by additional petrographic and mineralogical data.

Clay minerals, as products of weathering of magmatic minerals, tend to inherit and average the REE distributions of their sources (Henderson 1984). The REE contents of the Upper Cretaceous clays were approximately average 27 ppm (23.74–29.61 ppm) while the Lower Paleocene clays contained around 44 ppm of REE on average (17.24–86.20 ppm). The examined clays had a negative Eu anomaly and were richer in LREE with comparatively little variation from HREE. Highly illitization sediments were described as having a change in REE patterns where HREE was depleted relative to LREE in a sedimentary sequence that was subjected to illite diagenetic transformation of smectite (Bozkaya and Yalçın 2010; Furquim et al. 2008). In comparison to LREE, high weathering rates facilitate the release of HREE from the solid phase (Yusoff et al. 2013; Lara et al. 2018). Moreover, negative Eu anomalies in sedimentary environments are commonly thought to suggest reducing (i.e., oxygen deficient) conditions (Constantopoulos 1988; Henderson 1984).

In other words, REE content of clays increased from detrital to phyllosilicate/clay minerals of chemical/diagenetic/neoformation origin during the Lower Paleocene. Indicated that a history of clay phases controls the availability of trace elements mainly by adsorption (Roaldset 1973; Courtois and Chamley 1978; Elderfield et al. 1990; Condie 1991). The leaching and enrichment of REEs in weathered materials causes migration over short distances and accumulation in sedimentary basins (He et al. 2003). As the intensity of weathering increases, the degree of formation of clays increases, leading to the formation of clay-siltstone sedimentary layers that are extremely rich in REE (Zhang et al. 2016). REE-rich clay layers may be associated with sedimentary processes in geotectonic environments where transport of weathered materials of older rocks is active, which can form a new type of sedimentary layer controlling REE deposits.

Conclusions

1. The differences in mineral associations observed in sections, as well as the clay mineralogy of the Upper Cretaceous and Lower Paleocene of the formation were interpreted as having improved as a result of the basin being fed from varied source and provenance during the Cretaceous and Tertiary periods. The clay mineral associations were interpreted as neoformation / transformation developing in particular as a result of the volcanic glass and sea water interaction, and authigenic products.
2. The Mg-bearing minerals observed in the Paleocene rocks were interpreted as having developed due to the possible tectonic emplacement of ophiolites during the Cretaceous period.
3. According to analytic methods (XRD and ICP-MS), the illite/mica minerals observed in the rocks of the Germav Formation members are likely of detrital and/or volcanic origin and derived from Neoproterozoic and Cambrian basement rocks.

4. The clay sedimentation process and differences in provenance from the Upper Cretaceous and Lower Paleocene sections along the K/T boundary were largely controlled by local or regional geodynamic and diagenetic events.

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**GEOCHEMISTRY OF THE CRETACEOUS-TERTIARY (K/T) TRANSITION
CLAYS IN THE SOUTHEASTERN TURKEY****Keywords**

Arabian Plate, clay minerals, Germav Formation, source, REE

Abstract

The mineralogy and chemistry of Upper Cretaceous–Lower Paleocene claystone sediments from Mardin and Batman, southeastern Turkey, were analyzed. The main mineral paragenesis in the Upper Cretaceous member formed chlorite-smectite (C-S) and illite, while the Lower Paleocene member occurred of chlorite-vermiculite (C-V) and vermiculite minerals. The clays were silica-poor but indicated high values of Al, Fe, Mg, Cr, Ni, V, and Zr. Lower contents of the alkali elements (Na, Ca, Mg, K) of the clayey sediments suggests a relatively denser weathering of the source area. The mineralogical compositions, major element ratios, trace, and rare earth element (REE) contents of the sediments show that the Upper Cretaceous member consists of materials with a mainly felsic source lithology, while relatively contributions from basic sources are found in the Lower Paleocene unit. A comparison of the major and trace element contents of the phyllosilicate/clay minerals with the members revealed that the patterns of the clays were different from each other, although the enrichments/decreases varied depending on the origin (basement rocks or detrital) of the derived rocks, minerals, and elements. REE content of clays increased from detrital to phyllosilicate/clay minerals of chemical/diagenetic/neoformation origin during the Lower Paleocene. During the Cretaceous and Tertiary periods, local or regional geodynamic and diagenetic events largely governed the rock sedimentation processes and provenance variations amongst Germav Formation members.

**GEOCHEMIA ILÓW PRZEJŚCIOWYCH KREDE I TRZECIORZĘDU (K/T)
W POŁUDNIOWO-WSCHODNIEJ TURCJI****Słowa kluczowe:**

płyta arabska, minerały ilaste, formacja Germav, źródło, REE

Streszczenie

W artykule przeanalizowano mineralogię i skład chemiczny osadów ilowców górnej kredy i dolnego paleocenu z Mardin i Batman w południowo-wschodniej Turcji. Główną paragenezą minerałów w elemencie górnej kredy były minerały chloryt-smektyt (C-S) i illit, natomiast w elemencie dolnego paleocenu występowały minerały chloryt-wermikulit (C-V) i wermikulit. Gliny były ubogie w krzemionkę, ale wykazywały wysoką zawartość Al, Fe, Mg, Cr, Ni, V i Zr. Niższa zawartość pierwiastków alkalicznych (Na, Ca, Mg, K) w osadach ilastych sugeruje stosunkowo intensywne zwietrzenie obszaru źródłowego. Skład mineralogiczny, proporcje głównych pierwiastków, zawartość pierwiastków śladowych i pierwiastków ziem rzadkich (REE) w osadach pokazują, że element górnej kredy składa

się z materiałów o litologii źródeł felsowych, podczas gdy stosunkowo udział źródeł podstawowych występuje w jednostce dolnego paleocenu. Porównanie zawartości pierwiastków głównych i śladowych w minerałach krzemianów warstwowych/ilastych z członami ujawniło, że układy glin różniły się od siebie, chociaż wzbogacenia/ubytki były odmienne w zależności od pochodzenia (skały bazowe lub detrytyczne) skał pochodnych, minerałów i pierwiastków. W dolnym paleocenie zawartość REE w łałach wzrosła z minerałów detrytycznych do krzemianów warstwowych/ilastych pochodzenia chemicznego/diagenetycznego/neoformacyjnego. W okresie kredy i trzeciorzędu lokalne lub regionalne zdarzenia geodynamiczne i diagenetyczne w dużej mierze wpływały na procesy sedymentacji skał i różnice w pochodzeniu wśród przedstawicieli formacji Germav.

