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Yer Bilimleri ve Mühendisliği Konuları

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İÇİNDEKİLER

CHEMOSTRATIGRAPHY OF SAYTEPE LIMESTONE (UPPER CRETACEOUS) (HADİM, KONYA, TÜRKİYE)

Ali Müjdat ÖZKAN[1]

1. INTRODUCTION

As emphasized by Hayashi et al. (1997), sediments are reliable records of changes in physical, chemical, and biological conditions before, during, and after their deposition, and the changes are expressed through mineralogical and geochemical compositions. Chemostratigraphy is a discipline that enables the stratigraphy of the sequences to be revealed based on the elemental changes of geochemical analysis values obtained from sedimentary rocks. Its applicability to sediments of any lithology found in any place and deposited in any environment is an important advantage of chemostratigraphy.

Chemostratigraphy can be divided into two parts: elemental and isotope chemostratigraphy.

Individual sedimentation events create more or less homogeneous bulk chemistry of sediments at varying temporal and spatial scales. This is emerging as a reliable stratigraphic method for determining homogeneities and classifying stratigraphic records and correlating layers at varying spatial-temporal scales, and is called "chemical stratigraphy" (Ramkumar, 2015). Therefore, this method is quite useful in providing stratigraphic correlation in cases where other formal

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stratigraphic methods have limitations or do not reach the required spatiotemporal resolution. The study of geochemical changes in stratigraphic context has gained importance since the 1980s. In chemostratigraphy studies, a systematic order is classified as zones, subzones, sections, subsections, units, and subunits.

The high field strength elements Zr, Hf, Nb, Ta, Th, Ti, Y, Cr, and HREE are considered to be the most useful in chemostratigraphic studies as they are highly immobile, largely unaffected by post-depositional weathering/diagenesis and concentrated almost exclusively in detrital heavy minerals (Craigie, 2015; Ramkumar, 2015). Additionally, U and P elements are also used in chemostratigraphy studies.

In the paleoredox determination studies, the use of elements such as Mo, Cu, Co, Ni, Zn, Cr, U, and V is quite common. In chemostratigraphic studies of sedimentary rocks, it is recommended to use elemental ratios such as Zr/Nb, Zr/Th, Th/Nb, Ti/Ta, and Cr/Nb to classify chemozones, as well as elemental ratios such as Zr/P, Ti/P, Ta/P, Y/P, Yb/P, Th/P, P/U, Zr/U, Ti/U, Ta/U, Y/U, Yb/U, Th/U, Gd/Zr, Gd/Ti, Gd/Y, Gd/Ta, Gd/Yb, Gd/Th, Gd/U, Gd/P, Na/K, Na/Sc, K/Sc in determining provenance, depositional environment, and weathering or diagenetic changes (e.g. Ramkumar, 2015; Craigie, 2015).

While most chemostratigraphic schemes are based on elements and ratios that correlate with changes in provenance, it is equally important to consider parameters that reflect the severity of atmospheric weathering, as weathering surfaces often lie immediately beneath unconformities that may be correlated at local, subregional, or regional scales (Craigie, 2015; Ramkumar, 2015).

The aim of this study is to establish a chemostratigraphic framework for the Upper Cretaceous Saytepe formation

limestones around Hadim district, located in the southwest of Konya Province (Turkey) (Figure 1). As emphasized by Delpomdor and Préat (2013), a very important issue in any study on clastic/carbonate chemostratigraphy is whether the primary depositional indicator is preserved or not. The Saytepe limestones in this study exhibit very insignificant change (Mn/Sr ratios range from 0.21 to 0.54) and are suitable for accurate results in chemostratigraphic studies.
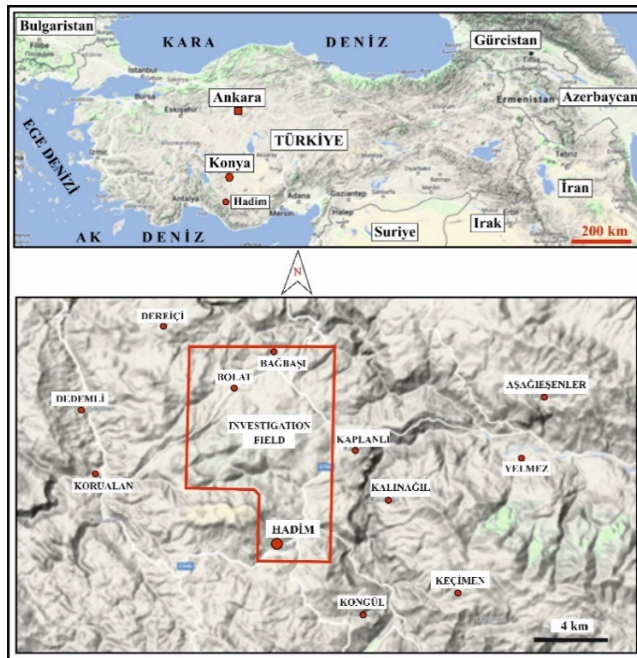

Figure 1. Location map of investigation field (Google Maps)

2. RESULTS AND DISCUSSION

The conglomerates forming the base of the formation are red, purple in color, contain sandstone and mudstone interlayers, and show lens-like geometries. These medium-thick layered conglomerates show a transition laterally to gray-colored, carbonate-cemented conglomerates that show the same grain

characteristics but lack red material (Turan 1990). The pebbles of the conglomerates with a maximum grain diameter of 7 cm were taken entirely from the carbonates of the Hacıalabaz Formation (Turan 1990).

After the conglomerates in the type locality, the formation passes into gray-colored, medium-thick limestone layers containing rudist shells and ends with medium-thick gray-colored, slightly crystallized limestones containing abundant rudist residues at the upper levels (Turan, 1990). The light gray-colored limestones that constitute the dominant lithology of the formation are observed in some levels as thin-medium bedded, laminated, burgundy-colored, and heavily crushed laminated levels, mostly in sections where synsedimentary deformation is effective, and frequently show micro-scale imbrications within the formation (Turan, 1990). Again, chert nodules and intra-formation conglomerates are encountered in some levels of the formation (Turan, 1990).

Saytepe Formation limestones are formed as crystalline calcitic dolostone, packstone, wackestone-packstone, packstone, wackestone, mudstone, wackestone, mudstone, and wackestone microfacies from bottom to top (Figure 2).

The microfacies characteristics of the carbonates of the Saytepe Formation and the benthic foraminifera it contains indicate that it was deposited in a shallow and open marine (carbonate shelf) environment.

Figure 2. Measured stratigraphic section of Saytepe Formation

The geochemical results of Saytepe limestones are given in Tables 1-3. The measurable element values in some of the limestone samples that are very low or below the limit values may be due to the adsorption of these elements to clay minerals. In addition, some of the samples have low Na/K ratios, as stated by Kuchenbecker et al. (2016), indicating a relationship with clay mineralogy (Table 4). In Table 1, Mn values are below the limit values in all samples, and Na, K, Ti, P, and Cr are below the limit values in most samples. In Table 2, Ga, Ta, and Sc are below the limit values in all samples, and Rb, V, Th, Mo, Nb and, Co are below the limit values in most samples. In Table 3, Tm is below the limit value in all samples, and Pr, Nd, Sm, Eu, Gd, Tb, Ho, Yb, and Lu are observed below the limit values in most samples.

Elements below the limit value were used in this study by taking their limit values.

Table 1. Major oxide (%) concentrations of Saytepe Formation carbonates (*calcitic dolostone)

Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3
B-80	0.15	0.021	0.063	0.713	55.11	0.01	0.01	0.01	0.01	0.01	0.002
B-68	0.21	0.041	0.112	1.462	53.52	0.01	0.01	0.01	0.01	0.01	0.002
B-55	0.21	0.041	0.132	18.07	34.41	0.02	0.01	0.01	0.01	0.01	0.002
B-49	0.30	0.152	0.043	0.553	54.62	0.01	0.06	0.01	0.02	0.01	0.002
B-43	0.39	0.191	0.082	0.612	54.35	0.01	0.05	0.01	0.02	0.01	0.002
B-30	0.15	0.011	0.051	0.393	55.34	0.01	0.01	0.01	0.01	0.01	0.002
B-19	0.11	0.010	0.043	0.323	55.64	0.01	0.01	0.01	0.01	0.01	0.002
B-15	0.19	0.010	0.042	0.362	55.43	0.01	0.01	0.01	0.01	0.01	0.002
B-10	0.15	0.011	0.071	0.413	55.25	0.01	0.01	0.01	0.01	0.01	0.002
B-6	0.18	0.031	0.113	0.545	55.13	0.01	0.01	0.01	0.01	0.01	0.002
B-1*	1.02	0.452	0.482	16.37	34.76	0.04	0.13	0.03	0.01	0.01	0.002

Table 2. Trace element (ppm) concentrations of Saytepe formation carbonates (*calcitic dolostone)

Sample	Ba	Rb	Sr	Zr	U	V	Th	Mo	Cu	Ni	Ti
B-80	12	0.1	263	5.7	1.4	8	0.2	0.1	1.4	3.7	0.00599
B-68	15	0.4	357	4.5	2.3	21	0.2	0.1	1.6	4.5	0.00599
B-55	8	0.1	179	6.1	2.3	15	0.2	0.2	2.3	4.3	0.00599
B-49	11	1.3	311	8.2	0.4	8	0.2	0.1	1.4	3.3	0.00599
B-43	6	1.8	240	6.3	0.5	8	0.2	0.1	1.6	4.2	0.00599
B-30	5	0.1	307	5.3	1.2	8	0.2	0.1	1.3	3.5	0.00599
B-19	4	0.1	321	3.7	0.6	8	0.2	0.1	0.8	3.4	0.00599
B-15	5	0.1	268	6.5	0.5	8	0.2	0.1	1.2	3.2	0.00599
B-10	8	0.1	367	3.4	0.7	8	0.2	0.1	1.1	2.6	0.00599
B-6	8	0.3	212	4.3	0.8	8	0.2	0.3	1.6	2.6	0.00599
B-1*	6	4.3	143	5.5	3.3	23	0.4	9.1	3.7	9.0	0.01199

Table 2. Continued (*calcitic dolostone)

Sample	Ga	Hf	Nb	Ta	Cd	Pb	Zn	Sc	Co	Cs
B-80	0.5	0.11	0.1	0.1	0.4	2.4	3	1	0.2	0.1
B-68	0.5	0.11	0.1	0.1	0.3	2.4	4	1	0.3	0.1
B-55	0.5	0.21	0.1	0.1	0.5	2.2	11	1	0.4	0.1
B-49	0.5	0.12	0.1	0.1	0.7	1.5	5	1	0.2	0.1
B-43	0.5	0.21	0.1	0.1	0.5	1.7	3	1	0.2	0.1
B-30	0.5	0.11	0.1	0.1	0.4	2.1	4	1	0.2	0.1
B-19	0.5	0.10	0.1	0.1	0.2	2.8	4	1	0.2	0.1
B-15	0.5	0.21	0.1	0.1	0.4	2.1	3	1	0.2	0.1
B-10	0.5	0.10	0.1	0.1	0.3	2.2	5	1	0.2	0.1
B-6	0.5	0.10	0.3	0.1	0.6	10.5	12	1	0.2	0.1
B-1*	0.5	0.11	0.2	0.1	0.3	12.4	22	1	0.6	0.1

Table 3. Rare earth element (ppm) concentrations of Saytepe formation carbonates (*calcitic dolostone)

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y
B-80	0.1	0.2	0.02	0.3	0.05	0.02	0.05	0.01	0.05	0.3
B-68	0.5	0.5	0.06	0.5	0.08	0.02	0.11	0.01	0.11	1.6
B-55	0.2	0.3	0.02	0.3	0.05	0.02	0.05	0.01	0.05	0.4
B-49	0.4	0.7	0.08	0.5	0.06	0.02	0.07	0.01	0.06	0.3
B-43	0.5	1.2	0.12	0.7	0.11	0.02	0.05	0.01	0.08	0.5
B-30	0.3	0.3	0.02	0.3	0.05	0.02	0.05	0.01	0.05	0.6
B-19	0.2	0.3	0.02	0.3	0.05	0.02	0.05	0.01	0.07	0.6
B-15	0.2	0.4	0.02	0.3	0.05	0.02	0.05	0.01	0.05	0.5
B-10	0.4	0.3	0.06	0.3	0.05	0.02	0.05	0.01	0.06	0.9
B-6	0.3	0.6	0.03	0.4	0.05	0.04	0.09	0.01	0.08	1.2
B-1*	0.8	1.8	0.17	0.9	0.15	0.02	0.15	0.01	0.07	0.8

Table 3. Continued (*calcitic dolostone)

Sample	Ho	Er	Tm	Yb	Lu	LREE	MREE	HREE	TREE
B-80	0.02	0.03	0.01	0.05	0.01	0.68	0.14	0.13	0.93
B-68	0.02	0.09	0.01	0.05	0.01	1.83	0.22	0.16	2.23
B-55	0.02	0.03	0.01	0.05	0.01	0.66	0.14	0.13	0.93
B-49	0.02	0.05	0.01	0.05	0.01	1.73	0.15	0.14	2.02
B-43	0.02	0.04	0.01	0.05	0.01	2.51	0.17	0.15	2.82
B-30	0.02	0.04	0.01	0.05	0.01	0.78	0.12	0.13	1.03
B-19	0.02	0.03	0.01	0.05	0.01	0.78	0.15	0.11	1.04
B-15	0.02	0.05	0.01	0.05	0.01	0.78	0.12	0.12	1.02
B-10	0.02	0.02	0.01	0.05	0.01	0.91	0.13	0.13	1.15
B-6	0.02	0.07	0.01	0.05	0.03	1.26	0.21	0.17	1.68
B-1*	0.02	0.08	0.01	0.07	0.01	3.93	0.26	0.18	4.32

Table 4. Redox sensitivity trace element concentrations and geochemical ratios of Saytepe Formation limestone samples (*calcitic dolostone)

Sample	Mo/U	V/Cr	Ni/Co	U/Th	V/(V+Ni)	Mn/Sr	K/Rb	Si/Al	Al/Ti	Cu+Mo/Zn
B-80	0.08	0.57	19.4	7.4	0.68	0.28	0.084	7.04	1.78	0.532
B-68	0.05	1.45	23.6	11	0.82	0.23	0.027	4.86	3.54	0.601
B-55	0.08	1.18	11.2	12	0.79	0.44	0.084	4.41	3.52	0.216
B-49	0.34	0.57	16.1	1.4	0.73	0.26	0.028	1.89	13.3	0.261
B-43	0.15	0.59	20.4	3.1	0.65	0.33	0.025	1.85	16.6	0.401
B-30	0.08	0.59	18.2	5.4	0.68	0.24	0.084	14.2	0.89	0.374
B-19	0.21	0.57	16.6	2,6	0.73	0.25	0.082	8.83	0.89	0.334
B-15	0.17	0.59	15.4	3.1	0.71	0.28	0.084	17.7	0.89	0.468
B-10	0.15	0.57	13.6	3.2	0.74	0.22	0.081	14.2	0.89	0.274
B-6	0.23	0.59	13.6	4.4	0.76	0.38	0.043	5.57	2.64	0.155
B-1*	2.73	1.76	15.3	8.6	0.74	0.53	0.023	2.03	19.7	0.624

Table 4. Continued (*calcitic dolostone)

Sample	Rb/Sr	Sr/Ba	Sr/Rb	Ga/Rb	Sr/Cu	Mg/Ca	Fe$_T$/Al	K/Na	Th/U
B-80	0.0005	25	2632	5.1	174	0.012	3.95	1.13	0.12
B-68	0.0009	23	1191	1.6	211	0.024	3.64	1.13	0.09
B-55	0.0007	24	1786	5.2	73	0.441	4.28	0.55	0.08
B-49	0.0046	32	223	0.3	258	0.009	0.34	5.61	0.68
B-43	0.0078	49	125	0.4	161	0.008	0.57	6.71	0.32
B-30	0.0002	78	3076	5.1	221	0.007	6.61	1.12	0.17
B-19	0.0004	63	3208	5.2	355	0.006	5.27	1.11	0.41
B-15	0.0003	46	2682	5.2	207	0.005	5.27	1.12	0.34
B-10	0.0004	51	3677	5.1	367	0.007	9.23	1.11	0.34
B-6	0.0008	22	1059	2.4	142	0.009	4.85	1.11	0.23
B-1*	0.0292	21	35	0.2	37	0.395	1.42	4.51	0.13

Four chemozones, C1, C2, C3, and C4 were distinguished from the Saytepe limestones from bottom to top (Figure 3).
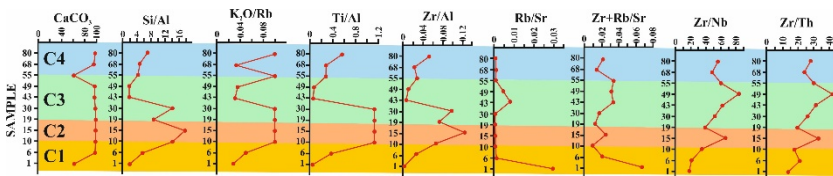
Figure 3. Showing chemozones with some major and element ratios for Saytepe limestones.

In chemozone C1, increase in CaCO$_3$, Si/Al, K$_2$O/Rb, Zr/Nb, and Zr/Th; decrease in Rb/Sr and Zr+Rb/Sr is observed. In chemozone C2, stability in CaCO$_3$ and K$_2$O/Rb, Ti/Al, Rb/Sr, increase and decrease in Si/Al, Zr/Al, Zr+Rb/Sr, Zr/Nb and Zr/Th is observed (Figure 3). In chemozone C3, stability and increase in CaCO$_3$, increase and decrease in Si/Al, Rb/Sr, Zr/Nb and Zr/Th,

decrease and increase in K_2O/Rb and Ti/Al, increase-decrease and increase in Zr/Al, and increase in $Zr+Rb/Sr$ is observed. In chemozone C4, increases in $CaCO_3$, Si/Al, Ti/Al and Zr/Al, decreases and increases in K_2O/Rb, $Zr+Rb/Sr$, Zr/Nb and Zr/Th, and low stability in Rb/Sr were observed (Figure 3). This situation observed in chemozones reflects the changes in the sedimentation rate within the basin and the terrigenous input rate outside the basin.

For example, in the SiO_2 versus Zr diagram in Figure 4, we can say that the silica coming to the basin is provided by terrigenous input and there is no biogenic and/or hydrothermal (Figure 5) contribution.

It was observed that the terrigenous input source in Saytepe limestones was taken entirely from felsic rocks (Figure 6A). It was determined that the Late Cretaceous paleoclimate was arid-semiarid (Figure 6B). Again, the depositional environment of Saytepe limestones indicates deposition in a completely saltwater (marine) environment (Figure 7A) and in a continental margin and open sea (shelf) environment (Figure 7B).
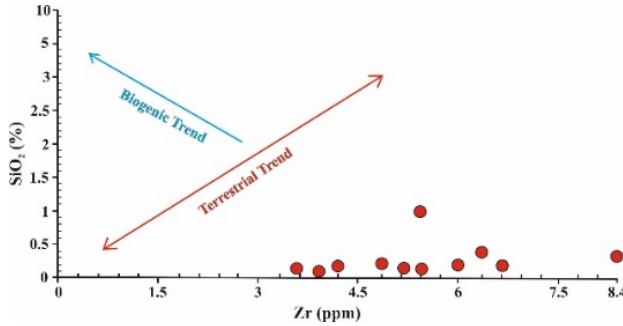

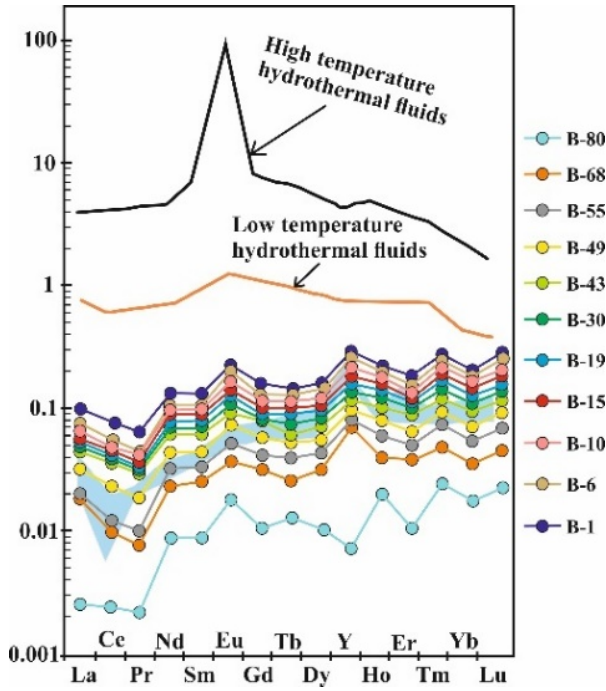**Figure 4. SiO_2 versus Zr diagram**

Figure 5. Shale-normalized (PAAS; Haskin et al., 1968) REE+Y diagram of Saytepe limestone samples. The blue area is present-day seawater
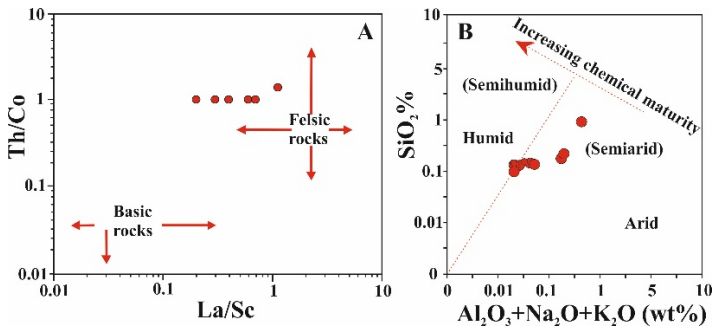
Figure 6. Th/Co versus La/Sc diagram (A) and SiO$_2$ versus Al$_2$O$_3$+Na$_2$O+K$_2$O diagram (B) of Saytepe limestone
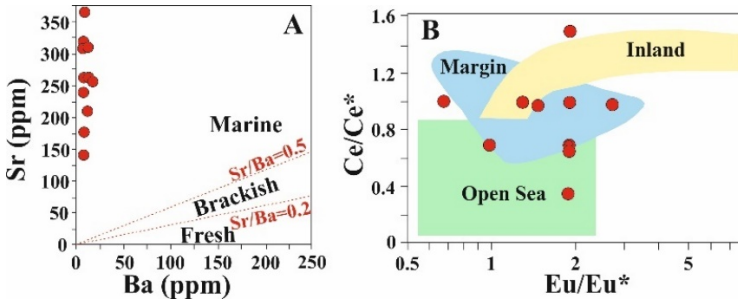
Figure 7. Diagrams showing the depositional environment of Saytepe limestones. A) Sr versus Ba diagram, B) Ce/Ce* anomaly versus Eu/Eu* anomaly diagram

All V/Cr (0.58-1.75) values of Saytepe limestones are <2, indicating oxic environmental conditions (Tables 4 and 5). Ni/Co values of the examined limestones vary between 11-23.5 (Tables 4 and 5). Since all samples are >7, they represent anoxic environmental conditions. U/Th values of Saytepe limestone samples vary between 1.5-12 and are >1.25, indicating anoxic environmental conditions. V/(V+Ni) values of the examined samples vary between 0.66-0.81 and are all samples >0.6, indicating anoxic environmental conditions (Tables 4 and 5). Again, Fe$_T$/Al ratios vary between 0.35-9.24 (Table 4), one sample is <0.5, indicating an oxic environment, and all other samples are >0.5, indicating anoxic environmental conditions. In addition, Hallberg (1976) emphasized that the Cu+Mo/Zn ratio can also be used in determining redox conditions (Table 5). Cu+Mo/Zn values of Saytepe limestone samples vary between 0.15-0.62 and indicate oxic environmental conditions since they are <2 (Tables 4 and 5). Therefore, Saytepe Formation limestones indicate deposition in oxic and anoxic environmental conditions.

Table 5. Some element concentrations used to evaluate paleo-redox conditions

Element ratio	Oxic	Suboxic	Anoxic	Euxinic	Writers
Ni/Co	<5	5-7	>7	-	Jones ve Manning (1994)
V/Cr	<2	2-4.5	>4.5	-	
U/Th	<0.75	0.75-1.25	>1.25	-	
V/(V+Ni)	<0.46	0.46-0.60	0.54-0.82	>0.84	Hatch ve Leventhal (1992)
Fe_T/Al	<0.5	-	>0.5	-	Taylor ve McLennan (1985)
(Cu+Mo)/Zn	<2	-	>2	-	Hallberg (1976)

The very strong positive correlation between SiO_2 and Al_2O_3 (r=0.98), Fe_2O_3 (r=0.93), MgO (r=0.59), Na_2O (r=0.78), K_2O (0.96), TiO_2 (r=0.95) indicates that these major oxides were taken from a similar source, probably aluminosilicates (clay).

CaO exhibits a strong positive correlation only with Sr (r=0.74) and very strong negative correlations with SiO_2 (r=-0.63), Al_2O_3 (r=-0.58), Fe_2O_3 (r=-0.76), MgO (r=-0.99), Na_2O (r=-0.93), TiO_2 (r=-0.66), Cu (r=-0.88), Zn (r=-0.84), Co (r=-0.93) and Ni (r=-0.75), indicating that it was taken from carbonates (calcite and dolomite).

The observation of a very strong positive correlation between Al_2O_3 and Fe_2O_3 (r=0.86), Na_2O (r=0.78), K_2O (0.99), TiO_2 (r=0.89), Th (r=0.89), Mo (r=0.89), Cu (r=0.80), Ni (r=0.87), Zn (r=0.74), Co (r=0.78) and Nb (r=0.76) indicates that the minerals were taken from aluminosilicates (clay) from a similar source.

The strong positive correlation observed with Zr only with P_2O_5 (r=0.67) and negative correlations with other elements indicates that zircon was taken from the heavy mineral zircon. The fact that Ba did not show a positive correlation with any element indicates that barium was probably taken from barite.

MgO must have been taken from dolomite and clay (especially chlorite) minerals. Na_2O must have been taken mainly from plagioclase feldspar and/or clay minerals (smectite).

Elements such as Ti, Nb, Zn, Ni, Mo, Co, and Cu must have been taken from Fe-oxyhydroxides and/or clay minerals.

3. CONCLUSIONS

Four chemozones were distinguished from the Saytepe limestones. All the silica observed in the limestones provided terrigenous contribution. No hydrothermal effect was observed in the limestone samples. The terrigenous input source found in the Saytepe limestones shows that it was taken entirely from felsic rocks. The Saytepe limestones were deposited in the continental margin and open sea (carbonate shelf) environment. The Saytepe Formation limestones indicate deposition in oxic and anoxic environmental conditions. It was determined that the Saytepe limestones were affected by disintegration and diagenesis to a minor extent. The paleoclimate was observed to be arid-semiarid.

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CHEMOSTRISTIGRAPHY OF KIZILÖREN FORMATION LIMESTONES IN THE WEST OF AKYOKUŞ (KONYA, Türkiye)

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1. INTRODUCTION

As emphasized by Hayashi et al. (1997), sediments are reliable records of changes in physical, chemical, and biological conditions before, during, and after their deposition, and they express these changes through mineralogical composition and geochemical composition. Chemostratigraphy can be defined as a correlation technique involving the application of inorganic geochemical data, and is expressed as "the study of chemical variations within sedimentary sequences to determine stratigraphic relationships" (Ramkumar, 2015). The applicability to sediments of any lithology found in any place and deposited in any environment is an important advantage of chemostratigraphy.

The subject of chemostratigraphy can be broadly divided into isotope and elemental chemostratigraphy (Ramkumar, 2015), and just as biostratigraphy can be divided into the subfields of palynology, micropaleontology, and nanopaleontology, it has been thought that chemostratigraphy can be divided into two distinct subcategories: elemental and isotope chemostratigraphy (Ramkumar 2015).

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While most chemostratigraphic schemes are based on elements and ratios that correlate with changes in provenance, it is equally important to consider parameters that reflect the severity of atmospheric weathering, as weathering surfaces often lie immediately beneath unconformities that may be correlated at local, subregional, or regional scales (Craigie, 2015).

The aim of this study is to determine the chemostratigraphic properties of the Late Triassic-Early Jurassic Kızılören Formation limestones in and around Akyokuş Mevkii, located in the west of Konya Province (Türkiye) (Figure 1). As emphasized by some researchers (e.g. Delpomdor and Préat, 2013), a very important issue in any study on clastic or carbonate rock chemostratigraphy is whether primary depositional indicators are preserved.

The Kızılören Formation consists of dark grey-black limestones (Figure 2). The Kızılören Formation conformably overlies the Aladağ Formation from below and is conformably covered by the Lorasdağı Formation from above (Figure 2).

Figure 1. Location map of investigation field (Google Maps)

Figure 2. Geological map of the study area (modified from Karakoç, 1996).

A measured stratigraphic section (type section) representing the Kızılören Formation from bottom to top was taken from the study area (Figure 3) and 10 clean (unweathered) samples were collected from certain levels suitable for the purpose. Major oxide, trace element and rare earth element analyses were performed on the collected samples. From these analysis data, the environmental conditions (anoxic-oxic) in which the limestones of the Kızılören Formation were deposited, whether there was a terrigenous detrital input into the basin during the deposition process, whether there was a hydrothermal effect in the basin, whether the primary characteristics of the carbonate phase were preserved, the source rock types (felsic, mafic or mixed) of terrigenous inputs, the degree of impact of the limestone samples during the diagenesis process, whether there was a metamorphic effect on the samples and the changes in paleoclimate conditions in the Late Triassic-Early Jurassic time interval were determined.
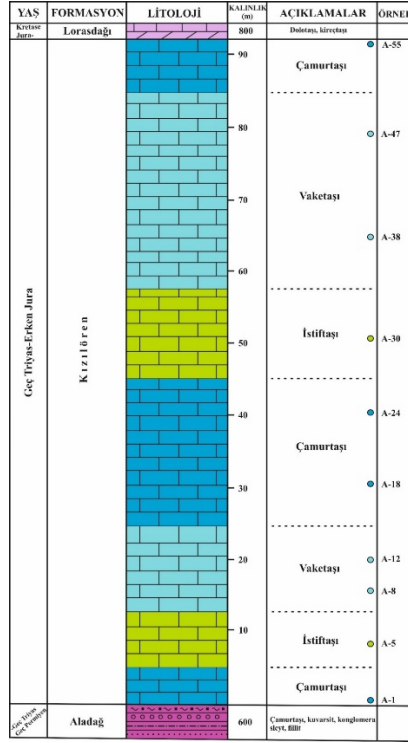
Figure 3. Measured stratigraphic section of Kızılören limestones.

2. RESULTS AND DISCUSSION

Kızılören Formation is observed as dark gray, gray colored, thin-thick bedded, abundantly fractured and calcite veined, brecciated in some levels and laminated in some levels. In the thin section examination, limestones were named as mudstone, wackestone and packstone according to Dunham (1962) classification (Figure 3). Kızılören limestones in this study exhibit very insignificant change (Mn/Sr ratios are between 0.054-0.974) and, naturally, they give correct results in chemostratigraphic study. Again, no hydrothermal effect was observed in our samples in the rare earth element graph of Kızılören limestones (Figure 4A) and Ce anomaly values mostly exhibit true negative values (Figure 4B). Geochemical (major

oxide, trace, and rare earth element) analysis results of Kızılören limestone samples are given in Tables 1-3, and in this study, values below the limit value and not measured were used as limit values.
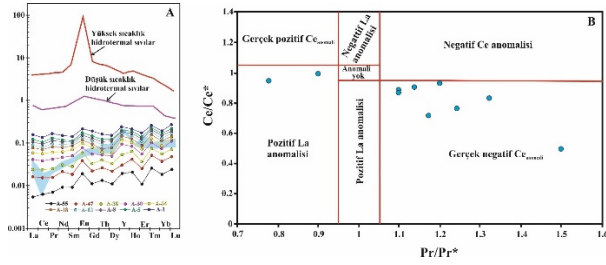
Figure 4. A) Shale-normalized (PAAS; Haskin et al., 1968) REE+Y diagram of Kızılören limestone samples. The blue area is present-day seawater. B) Diagram showing the relationship between Ce/Ce* and Pr/Pr* for Kızılören limestone samples.
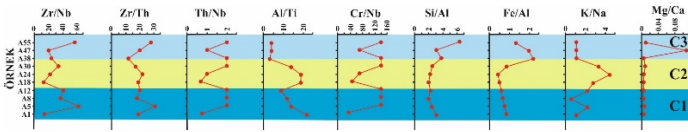
Figure 5. Geochemical profile of Kızılören limestone samples based on some element ratios.

Table 1. Major oxide (%) values of Kızılören limestones

Örnek	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	CaO	Na$_2$O	K$_2$O	TiO$_2$	P$_2$O$_5$	MnO	Cr$_2$O$_3$	LOI	SUM
Limit	**0.01**	**0.01**	**0.04**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.002**	**-5.1**	**-**
A-55	0.29	0.04	0.04	0.63	54.80	0.01	0.01	0.01	0.01	0.01	0.002	44.1	99.90
A-47	0.14	0.04	0.06	6.26	48.77	0.01	0.01	0.01	0.01	0.01	0.002	44.6	99.88
A-38	0.13	0.03	0.05	0.32	55.29	0.01	0.01	0.01	0.01	0.01	0.002	44.1	99.90
A-30	0.40	0.14	0.09	0.54	54.61	0.01	0.03	0.01	0.01	0.01	0.002	44.1	99.94
A-24	0.48	0.19	0.06	0.31	54.93	0.01	0.04	0.01	0.01	0.01	0.002	43.8	99.87
A-18	0.43	0.19	0.07	0.34	54.90	0.02	0.05	0.01	0.01	0.01	0.002	43.9	99.87
A-12	0.23	0.09	0.04	0.30	55.17	0.01	0.02	0.01	0.01	0.01	0.002	44.0	99.82
A-8	0.27	0.12	0.06	0.28	55.02	0.02	0.01	0.01	0.01	0.01	0.002	44.1	99.90
A-5	0.39	0.14	0.08	0.41	54.62	0.01	0.02	0.01	0.01	0.01	0.002	44.2	99.90
A-1	0.77	0.22	0.14	0.32	54.81	0.01	0.01	0.01	0.01	0.01	0.002	43.6	99.86

Table 2. Trace element (ppm) values of Kızılören limestones

Örnek	Ba	Rb	Sr	Zr	U	V	Th	Mo	Cu	Ni	Pb	Zn	Sc	Co	Cs	Ga	Hf	Nb	Ta	Cd
Limit	0.1	0.1	0.5	0.1	0.1	8	0.2	0.1	0.1	0.1	0.1	1	1	0.2	0.1	0.5	0.1	0.1	0.1	0.1
A-55	0.1	2	676	5.7	2.7	8	0.2	0.3	0.9	2.1	0.8	3	1	0.2	0.1	0.5	0.1	0.1	0.1	0.1
A-47	0.5	1	79	4.1	0.9	8	0.2	0.2	0.9	2.0	0.7	4	1	0.2	0.1	0.5	0.1	0.2	0.1	0.1
A-38	0.6	2	713	2.4	2.1	8	0.2	0.1	1.1	1.8	0.8	1	1	0.2	0.1	0.5	0.1	0.1	0.1	0.1
A-30	1.6	2	352	3.4	2.4	8	0.2	0.1	1.2	2.1	1.2	2	1	0.2	0.1	0.5	0.1	0.1	0.1	0.1
A-24	1.5	4	1008	4.4	2.6	8	0.2	0.2	1.2	2.3	1.2	1	1	0.2	0.1	0.5	0.1	0.2	0.1	0.1
A-18	1.5	7	966	3.9	2.4	8	0.2	0.1	1.1	0.7	1.3	2	1	0.2	0.2	0.5	0.1	0.3	0.1	0.1
A-12	0.3	6	1409	4.1	2.3	8	0.2	0.1	0.9	1.3	1.1	2	1	0.2	0.1	0.5	0.1	0.1	0.1	0.1
A-8	0.5	1	797	3.7	2.0	8	0.2	0.1	1.8	1.3	1.6	2	1	0.2	0.1	0.5	0.1	0.1	0.1	0.1
A-5	0.6	6	709	6.3	1.8	8	0.2	0.1	2.1	2.1	2.0	3	1	0.2	0.1	0.5	0.2	0.1	0.1	0.1
A-1	0.5	1	1101	5.7	1.2	8	0.3	0.1	3.1	1.6	2.6	2	1	0.2	0.1	0.5	0.1	0.4	0.1	0.1

Table 3. Rare earth element (ppm) values of Kızılören limestones

Örnek	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	TREE
Limit	0.1	0.1	0.02	0.3	0.05	0.02	0.05	0.01	0.05	0.1	0.02	0.03	0.01	0.05	0.01	-
A-55	0.2	0.5	0.06	0.3	0.05	0.02	0.05	0.01	0.05	0.5	0.02	0.03	0.01	0.05	0.01	1.36
A-47	0.4	0.7	0.07	0.4	0.05	0.02	0.05	0.01	0.05	0.3	0.02	0.04	0.01	0.05	0.01	1.88
A-38	0.3	0.6	0.08	0.3	0.05	0.02	0.05	0.01	0.05	0.6	0.02	0.03	0.01	0.05	0.01	1.58
A-30	0.6	1.1	0.14	0.5	0.11	0.02	0.10	0.01	0.07	1.0	0.02	0.05	0.01	0.05	0.01	2.79
A-24	0.7	1.4	0.17	0.5	0.11	0.02	0.10	0.01	0.08	0.7	0.02	0.05	0.01	0.05	0.01	3.23
A-18	0.7	1.2	0.18	0.6	0.09	0.02	0.08	0.01	0.08	0.5	0.02	0.03	0.01	0.05	0.01	3.08
A-12	0.4	0.5	0.12	0.4	0.05	0.02	0.08	0.01	0.05	0.7	0.02	0.05	0.01	0.05	0.01	1.77
A-8	0.6	1.2	0.15	0.5	0.05	0.02	0.06	0.01	0.08	0.4	0.02	0.05	0.01	0.05	0.01	2.81
A-5	0.6	1.1	0.15	0.4	0.05	0.02	0.09	0.01	0.06	0.5	0.02	0.04	0.01	0.05	0.01	2.61
A-1	1.2	1.8	0.27	1.0	0.14	0.04	0.19	0.03	0.10	1.0	0.02	0.10	0.01	0.06	0.02	4.98

Trace elements and rare earth elements have been accepted as highly reliable indicators of chemical functions to determine the development of carbonate systems (e.g., Özyurt et al., 2020). One of the ways to display geochemical data of clastic or carbonate rocks is by using geochemical profile diagrams (Figure 5) created by plotting element concentrations against sample depth. In Figure 5, three chemozones (C1, C2, C3) were determined depending on the vertical change of elemental ratios. In chemozone C1, Zr/Nb, Zr/Th and K/Na ratios show increase-decrease and increase, Th/Nb, Cr/Nb ratios increase-stable, Al/Ti and Fe/Al ratios continuously decrease, Si/Al ratio decrease-increase, Mg/Ca ratio almost stable (Figure 4). In Chemozone C2, Zr/Nb, Zr/Th, Al/Ti, K/Na ratios show increase-decrease, Th/Nb, Cr/Nb ratios decrease-increase-stable status, Si/Al slightly decrease-continuous increase, Fe/Al ratio decrease-increase, Mg/Ca ratio is stable-slightly increase-decrease. In Chemozone

C3, Zr/Nb, Th/Nb, Cr/Nb, Si/Al ratios show decrease-increase, Zr/Th ratio continuously increase, Al/Ti ratio slightly increase and stable status, Fe/Al ratio continuously decrease, K/Na slightly continuous increase, Mg/Ca ratio increase-decrease. The vertical change of these elemental ratios indicates the increase and decrease in terrigenous input to the basin where carbonate precipitation continues. Therefore, it can be said that there was a high rate of terrestrial input (fluvial and/or eolian) in some stages and a low rate of terrestrial input in some stages (Figure 5).

The correlations of major oxides and some trace elements of limestone samples from the Kızılören Formation are given in Table 4. Because, as emphasized by Craigie (2015), interpretation of statistical data with binary diagrams is quite important and widely used in chemostratigraphy and geochemical studies. When we look at Table 4, TiO_2, P_2O_5, and MnO major oxides do not exhibit any relationship with any other components. This situation must be due to the fact that the analysis values of these three major oxides were below the limit values and could not be measured and were used by us after taking the limit values.

In Table 4, very strong positive correlations are observed between SiO_2, and Al_2O_3 and, Fe_2O_3 and between Th, Cu, Pb, and TREE, and the lack of correlation with CaO indicates that silica is supplied from terrestrial sources (especially quartz and clay minerals). Very strong positive correlations of Al_2O_3 with SiO_2, strong with Fe_2O_3, very strong with Pb and TREE, moderate positive correlations with K_2O, Rb, and Cu, and no correlation with CaO indicate that Al_2O_3 is also supplied from terrestrial sources (especially clays). Again, very strong positive correlations are observed between Fe_2O_3 and SiO_2, strong with Al_2O_3, and very strong positive correlations between Th, Cu, Pb, and TREE, indicating that Fe_2O_3 is also supplied from terrestrial sources (clays, silicates, Fe-oxyhydroxides, and heavy minerals). The very strong negative correlation observed between MgO and

CaO indicates that MgO is not taken from carbonates, while the strong correlation only with Zn indicates that MgO is provided from clay minerals. The moderate positive correlation of CaO with Sr and U and the very strong negative correlation with MgO and Zn indicate that CaO is provided from carbonates (especially calcite and dolomite) and has an intra-basin source.

Table 4. Major oxide (%) and some minor element (ppm) correlations of Kızılören limestone samples (Green: very strong positive, Blue: strong positive, and Red: strong-very strong negative values)

	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	CaO	Na$_2$O	K$_2$O	TiO$_2$	P$_2$O$_5$	MnO	Ba	Rb	Sr	Zr	U	Th	Mo	Cu	Ni	Pb	Zn	TREE
SiO$_2$	1																					
Al$_2$O$_3$	0.83	1																				
Fe$_2$O$_3$	0.83	0.70	1																			
MgO	-0.44	-0.43	-0.11	1																		
CaO	0.03	0.36	0.05	0.40	1																	
Na$_2$O	-0.01	0.27	-0.07	0.19	0.18	1																
K$_2$O	0.28	0.58	0	-0.27	0.24	0.33	1															
TiO$_2$	0	0	0	0	0	0	0	1														
P$_2$O$_5$	0	0	0	0	0	0	0	0	1													
MnO	0	0	0	0	0	0	0	0	0	1												
Ba	0.13	0.34	0.45	0.04	-0.08	0.10	0.21	0	0	0	1											
Rb	0.26	0.55	-0.01	0.30	0.27	0.24	0.62	0	0	0	0.22	1										
Sr	0.38	0.43	0.03	0.66	0.69	0.13	0.23	0	0	0	0.26	0.19	1									
Zr	0.52	0.29	0.34	0.07	0	0.25	0.13	0	0	0	0.33	0.16	0.15	1								
U	0.08	0.02	0.49	0.67	0.14	0	0	0	0	0.55	0.36	0.41	0.17	1								
Th	0.51	0.64	0.12	0.9	0.17	0.27	0	0	0	0.07	0.34	0.50	1									
Mo	0.18	0.39	0.41	0.34	0.31	0.30	0.15	0	0	0	0.12	0.59	0.20	0.20	1							
Cu	0.8	0.01	0.5	0.28	0.2	0.01	0.2	0	0	0	0.33	0.25	0.47	0.41	1							
Ni	0.04	0.24	0.01	0.22	0.23	0.26	0	0	0	0.33	0.45	0.53	0	1								
Pb	0.26	0.55	0.39	0.33	0.11	0.04	0	0	0	0.31	0.35	0.53	0.49	0.44	0.1	1						
Zn	0.35	0.03	0.78	0.11	0.34	0	0	0	0.26	0.57	0.43	0.37	0.68	0.36	0.05	0.09	1					
TREE	0.66	0.50	0.32	0.26	0.07	0.24	0	0	0	0.37	0.21	0.33	0.27	0.24	0.41	0.13	0.32	1				

The fact that Na$_2$O does not show a positive correlation with any element and only exhibits a very strong negative correlation with Ni indicates that Na$_2$O is provided from plagioclase feldspars. The moderate positive correlation observed between K$_2$O and Al$_2$O$_3$ and the very strong positive correlation

observed with Rb indicates that K_2O is provided from alkali feldspars and clay minerals (especially illite). TiO_2 has been stated in many studies (e.g., Ramkumar 2015; Sial et al., 2015; Craigie, 2015) to be provided from sources such as titanomagnetite, magnetite, ilmenite, rutile, anatase, and/or sphenene. It has been stated that P_2O_5 is mainly provided from biogenic phosphate and/or P-bearing heavy minerals such as apatite and monazite (Ramkumar, 2015). It has been stated that MnO is provided from various clay and carbonate minerals.

Ba is probably supplied from barite minerals, as it shows a strong negative correlation only with Mo. Rb is moderately positively correlated with U and Al_2O_3 and strongly positively correlated with K_2O, indicating that it was supplied from alkali feldspars and clay minerals. Sr is probably supplied from intra-basinal carbonates, as it shows a strong positive correlation only with CaO and a very strong negative correlation with MgO. Zr is probably supplied from zircon minerals, as it shows moderately positive correlation only with $SiO2$, Cu, and Pb.

We can say that other trace elements and rare earth elements in Table 4 are also provided from terrestrial sources (especially clays).

Source rock composition can be determined with Al_2O_3/TiO_2 ratios of clastic rocks (Hayashi et al., 1997). Because Hayashi et al. (1997) emphasized that Al_2O_3/TiO_2 ratios vary between 3 and 8 for mafic magmatic rocks, between 8 and 21 for neutral rocks, and between 21 and 70 for felsic magmatic rocks. Al_2O_3/TiO_2 ratios of Kızılören formation limestones vary between 3 and 22. Therefore, we can say that terrigenous material in Kızılören limestones is taken from mixed (mafic, neutral, and felsic) sources.

The V/Cr ratio of Kızılören limestones is 0.57 and <2, indicating oxic environmental conditions. Ni/Co values vary

between 3.5-11.5, one sample is <5, indicating oxic environmental conditions, two samples are 6.5, >5, and <7, indicating dioxic environmental conditions, seven samples are 8-11.5, >7, indicating anoxic environmental conditions. U/Th values vary between 4-13.5, indicating >1.25, indicating anoxic environmental conditions. V/(V+Ni) values vary between 0.77-0.92, seven samples are <0.84, indicating anoxic environmental conditions, 3 samples are >0.84, indicating euxinic environmental conditions. Again, Fe$_T$/Al ratios vary between 0.42-2.20, two samples are <0.5, indicating oxic environmental conditions, and eight samples are >0.5, indicating anoxic environmental conditions. Since the Cu+Mo/Zn ratios vary between 0.27-1.6 and are <2, it indicates oxic environmental conditions. As a result, the Kızılören Formation limestones indicate the development in oxic-anoxic environmental conditions (Tables 5 and 6).

Tablo 5. Paleoredoks şartlarını değerlendirmede kullanılan bazı element konsantrasyonları

Element ratio	Oxic	Suboxic	Anoxic	Euxinic	Writers
Ni/Co	<5	5-7	>7	-	
V/Cr	<2	2-4.5	>4.5	-	Jones ve Manning (1994)
U/Th	<0.75	0.75-1.25	>1.25	-	
V/(V+Ni)	<0.46	0.46-0.60	0.54-0.82	>0.84	Hatch ve Leventhal (1992)
Fe$_T$/Al	<0.5	-	>0.5	-	Taylor ve McLennan (1985)
(Cu+Mo)/Zn	<2	-	>2	-	Hallberg (1976)

Table 6. Some element ratios of Kızılören limestone samples.

Örnek	Mn/Sr	V/Cr	Ni/Co	U/Th	V/(V+Ni)	Fe$_T$/Al	Cu+Mo/Zn	Zr/Nb	Zr/Th	Th/Nb	Al/Ti	Cr/Nb	Si/Al	K/Na	Mg/Ca
A-55	0,114	0,571	10,5	13,5	0,792	1,32	0,4	57	28	2	4	140	6,391	1,12	0,0097
A-47	0,975	0,571	10	4,5	0,800	1,98	0,27	20	20	1	4	70	3,085	1,12	0,1083
A-38	0,108	0,571	9	10,5	0,816	2,20	1,2	24	12	2	3	140	3,818	1,12	0,0048
A-30	0,220	0,571	10,5	12	0,792	0,85	0,65	34	17	2	14	140	2,522	3,36	0,0082
A-24	0,076	0,571	11,5	13	0,776	0,42	1,4	22	22	2	19	70	2,231	4,49	0,0048
A-18	0,079	0,571	3,5	12	0,919	0,49	0,6	13	19	0,67	19	46,6	1,999	2,8	0,0051
A-12	0,054	0,571	6,5	11,5	0,860	0,59	0,5	41	20	2	9	140	2,256	2,24	0,0046
A-8	0,097	0,571	6,5	10	0,860	0,66	0,95	37	18	2	12	140	1,986	0,56	0,0043
A-5	0,109	0,571	10,5	9	0,792	0,75	0,73	63	31	2	14	140	2,459	2,24	0,0064
A-1	0,069	0,571	8	4	0,833	0,84	1,6	14	19	0,75	22	35	3,09	1,12	0,0048

3. CONCLUSIONS

Three chemozones (C1, C2, C3) were identified from the Kızılören Formation limestones. Depletion was observed in all rare earth elements studied. Two samples exhibit positive La anomaly and eight samples exhibit true negative Ce anomaly. No

hydrothermal effect was observed in the Kızılören limestones. The terrigenous input in the Kızılören limestones originated from mixed (mafic, neutral, and felsic) provenance. The SiO_2 source was provided entirely from the continental (non-basin) area. The Kızılören Formation limestones indicate deposition in oxic-anoxic environmental conditions. The Kızılören Formation was deposited in a shallow marine (carbonate shelf) environment. The calculated C-values of the Kızılören Formation samples vary between 0.000958-0.002734 (average 0.00148) indicating that the paleoclimate was in arid climate conditions. The Mn/Sr ratios (0.05-0.97) of the studied limestone samples being <<3 also indicate that diagenetic alteration is extremely insignificant.

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YER BİLİMLERİ VE MÜHENDİSLİĞİ KONULARI

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