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Editör: Dr.Öğr.Üyesi Seda ÇELLEK



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yayınları

**Yer Bilimleri ve Mühendisliği Alanında
Güncel Konular ve Akademik Değerlendirmeler**

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Dr.Öğr.Üyesi Seda ÇELLEK

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"Bu kitapta yer alan bölümlerde kullanılan kaynakların, görüşlerin, bulguların, sonuçların, tablo, şekil, resim ve her türlü içeriğin sorumluluğu yazar veya yazarlarına ait olup ulusal ve uluslararası telif haklarına konu olabilecek mali ve hukuki sorumluluk da yazarlara aittir."

PALEOENVIRONMENTAL RECONSTRUCTION OF THE UPPER CRETACEOUS SAYTEPE FORMATION LIMESTONE IN HADİM, KONYA, TÜRKİYE

Ali Müjdat ÖZKAN¹

1. INTRODUCTION

Sellwood and Valdes (2006) and Iqbal et al. (2019) stated that the Earth was 6 °C or slightly warmer than today's climate during the Mesozoic era. Therefore, according to the geological record, the climate of the Cretaceous period was significantly warmer than it is today (Deconto et al., 2000). Evidence indicating the warmth of the climate: The spread of heat-loving organisms to wide latitudes, dinosaur life expanding to the polar regions, the expansion of vegetal provinces to the polar regions, and the low temperature variation along the meridian on both land and ocean (Deconto et al., 2000). Extraordinarily high sea levels are the main reason for the mild climate conditions during this period. While average temperatures were 0-15 °C in the polar regions, they ranged from 15-40 °C near the equator (Deconto et al., 2000).

Located in the Alpine-Himalayan belt, Turkey acquired its current geological structure largely as a result of the closure of the northern and southern arms of the Neotethys Ocean during the Late Cretaceous to Cenozoic period and the collision of the

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Anatolian and Arabian plates in the Middle Miocene (Şengör and Yılmaz, 1981).

The enrichment of redox-sensitive elements reflects the depositional environment of ancient sedimentary rocks rich in organic carbon, and is therefore used to clarify the paleoceanographic conditions that influenced the formation of these sediments (Akinyemi et al., 2013). For this reason, Mo/U, U/Th, V/Cr, Ni/Co, V/(V+Ni), Fe_T/Al, Cu/Zn element ratios, and Ce/Ce* anomaly values were used to determine the redox conditions of the depositional environment of Saytepe limestones. Sr/Cu, FeO/MnO, Al₂O₃/MgO, and Mg/Ca values were used to determine the paleoclimatic conditions of Saytepe limestones, while Mn/Sr, Fe/Sr, Rb/Sr, Mg/Ca, Sr/Ca, Fe, and Sr element ratios were used to determine diagenetic weathering.

This study aims to determine the paleo-oceanographic and paleoclimatic changes that occurred during the deposition of the Late Cretaceous Saytepe Formation carbonates (mostly limestone, with a small amount of dolomitic limestone and calcitic dolostone) (Figure 2), located within the borders of Konya province in the Geyikdağı Unit of the Central Taurus Mountains in Turkey (Figure 1).

Two measured stratigraphic sections (Büyükkaratepe MSS [A] and Dedetepe MSS [B]) selected north of Hadim were sampled at appropriate intervals along their lines. Thin sections were prepared from these samples and examined under a polarizing microscope to determine their microfacies. However, due to budget constraints, only 11 samples from the Dedetepe (MSS-B; Figure 3) line were analyzed for major oxides, trace elements, and rare earth elements (Tables 1-3) to determine the geochemical characteristics of the Saytepe Formation carbonates.

Within this framework, studies have been conducted to determine the environmental conditions (oxic-anoxic) under

which the Saytepe carbonates were deposited, whether there was terrestrial clastic influx (stream and/or wind) into the basin during deposition, whether there were hydrothermal influxes into the basin, whether the original characteristics of the carbonate phase were preserved, to determine the type of source rock (felsic, intermediate, mafic or mixed) if there was terrestrial input, to determine the extent to which the carbonates were affected by diagenetic processes, whether they underwent metamorphism, and to determine the ancient climatic conditions.

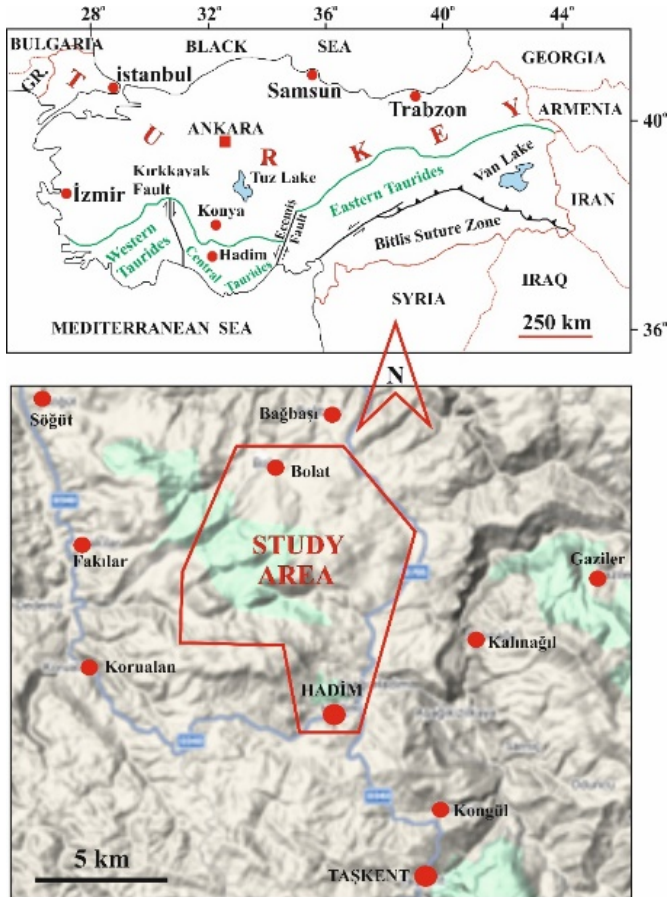


Figure 1. Location map of the study area (from Google Maps)

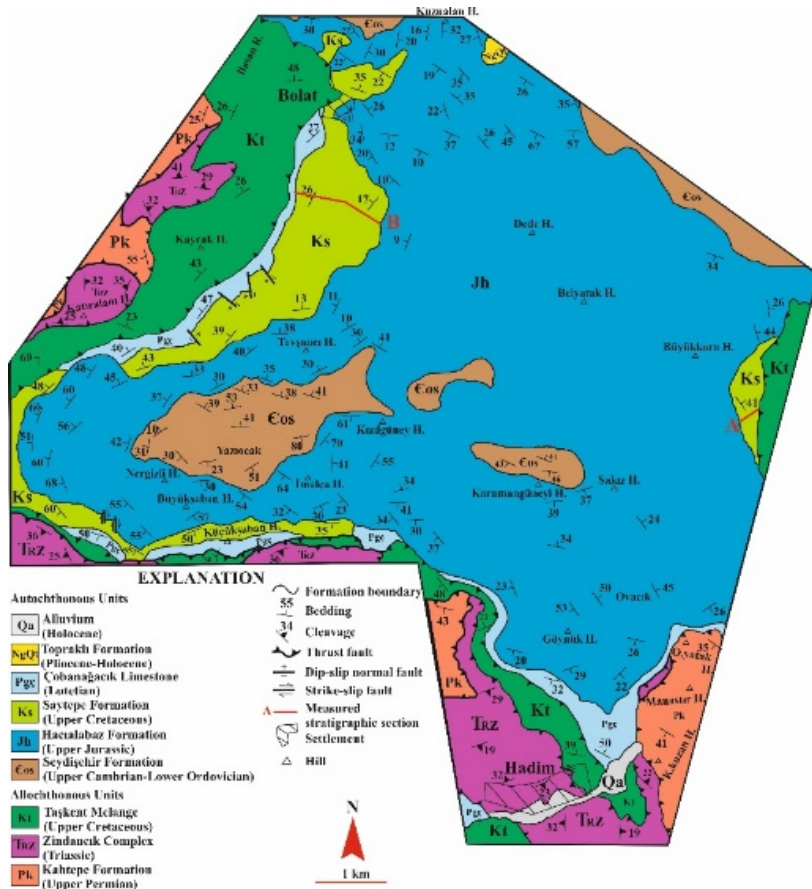


Figure 2. Geological map of the study area (modified from Özkan and Kırcan, 2023)

Table 2. Trace element (ppm) concentrations of carbonates from the Saytepe Formation (*calcite dolostone)

Sample	Ba	Rb	Sr	Zr	Cr	Ni	Cu	Zn	U	V	Th	Mo	Cd	Co
MDL	1	0.1	0.5	0.1	20	0.1	0.1	1	0.1	8	0.2	0.1	0.1	0.2
B-80	11	<0.1	263.3	5.6	13.68	3.9	1.5	3	1.5	<8	<0.2	<0.1	0.3	0.2
B-68	16	0.3	357.0	4.8	13.68	4.7	1.7	3	2.4	20	<0.2	0.1	0.4	0.2
B-55	7	<0.1	178.7	6.0	13.68	4.4	2.4	12	2.2	16	<0.2	0.2	0.4	0.4
B-49	10	1.4	311.2	8.4	13.68	3.2	1.2	5	0.3	<8	<0.2	<0.1	0.8	0.2
B-43	5	1.9	240.2	6.2	13.68	4.1	1.5	4	0.6	<8	0.2	<0.1	0.4	0.2
B-30	4	<0.1	307.5	5.2	13.68	3.6	1.4	4	1.1	8	<0.2	<0.1	0.3	0.2
B-19	5	<0.1	320.7	3.9	13.68	3.3	0.9	3	0.5	<8	<0.2	<0.1	0.3	0.2
B-15	6	<0.1	268.3	6.6	13.68	3.1	1.3	3	0.6	<8	<0.2	<0.1	0.3	0.2
B-10	7	<0.1	367.8	3.5	13.68	2.7	1	4	0.6	<8	<0.2	<0.1	0.2	0.2
B-6	9	0.2	211.6	4.2	13.68	2.7	1.5	11	0.9	<8	<0.2	0.2	0.7	0.2
B-1*	7	4.2	142.7	5.4	13.68	9.1	3.9	21	3.4	24	0.4	9.2	0.2	0.6

Table 3. Rare earth element (ppm) concentrations of Saytepe Formation carbonates (*calcite dolostone)

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	TRE
MDL	0.1	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	
B-80	<0.1	0.2	<0.0	<0.1	<0.0	<0.0	<0.0	<0.0	<0.0	0.1	<0.0	<0.0	<0.0	<0.0	<0.0	0.92
B-68	0.6	0.6	0.05	0.5	0.09	0.02	0.10	0.01	0.10	1.7	0.02	0.08	<0.0	<0.0	<0.0	2.24
B-55	0.1	0.2	<0.0	<0.1	<0.0	<0.0	<0.0	<0.0	<0.0	0.1	<0.0	<0.0	<0.0	<0.0	<0.0	0.92
B-49	0.3	0.9	0.07	0.4	0.5	<0.0	0.07	<0.0	0.06	0.1	<0.0	0.04	<0.0	<0.0	<0.0	2.01
B-43	0.6	1.1	0.10	0.6	0.10	0.02	<0.0	<0.0	0.08	0.4	<0.0	0.05	<0.0	<0.0	<0.0	2.80
B-30	0.2	0.2	<0.0	<0.1	<0.0	<0.0	<0.0	<0.0	0.1	0.7	0.03	0.03	<0.0	<0.0	<0.0	1.02
B-19	0.2	0.2	<0.0	<0.1	<0.0	<0.0	<0.0	<0.0	0.1	0.06	0.05	0.03	<0.0	<0.0	<0.0	1.03
B-15	0.1	0.3	<0.0	<0.1	<0.0	<0.0	<0.0	<0.0	0.1	0.6	<0.0	0.04	<0.0	<0.0	<0.0	1.01
B-10	0.3	0.2	0.05	0.3	<0.0	<0.0	<0.0	<0.0	0.06	0.8	<0.0	0.03	<0.0	<0.0	<0.0	1.16
B-6	0.4	0.5	0.02	0.3	0.5	0.04	0.08	0.1	0.09	1.1	0.2	0.08	0.1	0.5	0.02	1.67
B-1*	0.9	1.9	0.18	0.8	0.14	<0.0	0.14	0.01	0.08	0.9	<0.0	0.07	0.1	0.06	0.1	4.34

2. STUDY CONTENT

Petrographic examination of the Saytepe carbonate samples revealed that all but one sample retained their primary sedimentary characteristics (Figure 3). Furthermore, geochemical analysis results also confirmed the preservation of the original characteristics of our samples, supporting the accurate conclusions reached in this study. This is because the degree of diagenetic alteration observed in our samples is very low (average Mn/Sr=0.31). The absence of hydrothermal alteration in our samples, as shown in Figure 4, further supports this view.

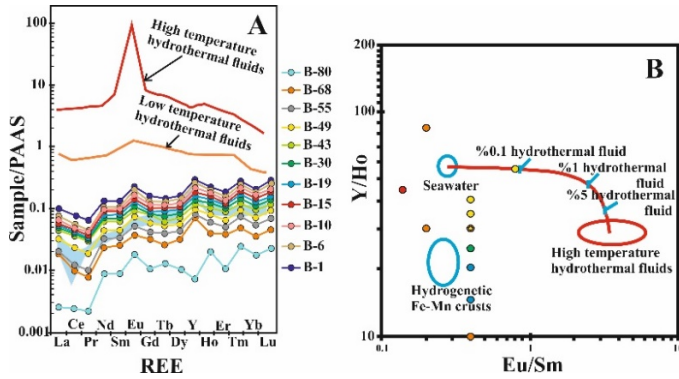


Figure 4. A) REE+Y diagram of Saytepe carbonate samples normalized according to PAAS. B) Diagram of Eu/Sm versus Y/Ho. The diagrams show no hydrothermal alteration

In some of the Saytepe carbonate samples, element values that were measurable at very low or limit values were used in this study by taking limit values into account.

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

Sample	Mo/U	U/Tb	V/Cr	Ni/Co	V/V+Ni	Fe/Al	Cu+Mo/Zn	Ce/Ce*	Carbonate	Detrital
B-80	0.067	7.5	0.584	19.5	0.672	3.962	0.533	0.703	99.02	1
B-68	0.042	12	1.46	23.5	0.809	3.627	0.6	0.705	98.04	1.88
B-55*	0.091	11	1.168	11	0.784	4.288	0.217	1.029	81.23	18.52
B-49	0.333	1.5	0.584	16	0.714	0.353	0.26	0.957	98.08	1.16
B-43	0.167	3	0.584	20.5	0.661	0.556	0.4	1.022	98.58	1.39
B-30	0.091	5.5	0.584	18	0.689	6.604	0.375	0.67	99.35	0.66
B-19	0.2	2.5	0.584	16.5	0.708	5.283	0.333	0.67	99.46	0.54
B-15	0.167	3	0.584	15.5	0.721	5.283	0.467	1.544	99.3	0.67
B-10	0.167	3	0.584	13.5	0.748	9.245	0.275	0.372	99.34	0.7
B-6	0.222	4.5	0.584	13.5	0.748	4.836	0.154	0.986	99.06	0.94
B-1	2.71	8.5	1.752	15.1	0.725	1.41	0.624	1.086	81.22	18.54

Sample	Eu/Eu*	Pr/Pr*	La/La*	(La/Sm) ₀	Baxs	(Dy/Sm) ₀	P/Al	Cd/Mo	(Sm/Yb) ₀	(Sm/Pr) ₀	Al/Ti	Ga/Rb
B-80	1.88	0.399	-0.24	0.29	76	1.18	0.29	3	0.508	3.977	1.77	5
B-68	0.98	0.508	-1.25	0.97	222	1.32	0.22	4	0.914	2.864	3.53	1.67
B-55	1.88	0.399	-0.24	0.29	100	1.19	0.43	2	0.508	3.977	3.53	5
B-49	1.54	0.686	42.74	0.87	523	1.42	0.25	8	0.508	1.136	13.23	0.36
B-43	1.29	0.678	-11.04	0.87	331	0.95	0.32	4	1.016	1.591	16.75	0.26
B-30	1.88	0.399	-0.48	0.58	14	1.19	0.25	3	0.508	3.977	0.88	5
B-19	1.88	0.398	-0.48	0.58	17	1.42	0.24	3	0.508	3.977	0.88	5
B-15	1.88	0.359	-0.24	0.29	20	1.19	0.29	3	0.508	3.977	0.88	5
B-10	1.88	0.997	-11.04	0.87	24	1.42	0.21	2	0.508	1.591	0.88	5
B-6	2.83	0.299	-0.96	1.16	94	2.13	0.37	3.5	0.508	3.977	2.65	2.5
B-1*	0.67	0.859	1.69	0.93	1098	0.68	0.54	0.022	1.185	1.237	19.84	0.12

Sample	Sr/Cu	FeO/MnO	Al ₂ O ₃ /MgO	Mg/Ca	Ca/Mg	Mn/Sr	Fe/Sr	Rb/Sr	Sr/Ca	Sr/Ba	Na/K	P/Ti
B-80	175	6.67	0.028	0.01089	91.83	0.294	1.595	0.00038	0.00067	23.94	0.891	0.716
B-68	210	12.22	0.027	0.02293	43.61	0.217	2.154	0.00084	0.00093	22.31	0.891	0.716
B-55*	74	14.45	0.002	0.44214	2.26	0.433	5.087	0.00056	0.00072	25.53	1.783	0.716
B-49	259	4.44	0.273	0.00847	118.07	0.249	0.899	0.00449	0.000794	31.12	0.297	1.450
B-43	160	8.89	0.311	0.00945	105.83	0.322	2.327	0.00791	0.00062	48.04	0.223	1.450
B-30	219	5.55	0.025	0.00595	167.88	0.252	1.138	0.00032	0.00078	76.87	0.178	0.716
B-19	326	4.44	0.029	0.00215	194.31	0.241	0.873	0.00031	0.00081	64.14	0.446	0.716
B-15	206	4.44	0.027	0.00563	177.71	0.288	1.044	0.00037	0.00067	44.72	0.891	0.716
B-10	368	7.78	0.024	0.00625	159.93	0.21	1.332	0.00027	0.00093	52.54	0.446	0.716
B-6	141	12.22	0.053	0.00858	116.49	0.366	3.634	0.00094	0.00054	23.51	0.891	0.716
B-1	36	53.34	0.027	0.39612	2.52	0.542	23.52	0.02943	0.00057	20.38	0.127	0.358

Sample	C-value	CIX	PIX	MoEF	UEF	Si/Al	Ti/Al	K/Al	Zr/Al	Ba/Al	Y/Ho	Eu/Sm
B-80	0.0013	50	50	0.083	0.083	7.05	0.57	0.78	0.053	0.104	10	0.40
B-68	0.0022	67	75	0.042	0.042	4.85	0.28	0.39	0.023	0.075	85	0.22
B-55*	0.0029	57	60	0.042	0.042	4.4	0.28	0.39	0.028	0.033	15	0.40
B-49	0.0009	71	91	0.011	0.011	1.88	0.07	0.52	0.01	0.012	20	0.40
B-43	0.0017	73	93	0.009	0.009	1.86	0.06	0.49	0.006	0.005	30	0.20
B-30	0.0011	33	0	0.167	0.167	14.09	1.13	1.57	0.098	0.075	35	0.40
B-19	0.0009	33	0	0.167	0.167	8.81	1.13	1.57	0.073	0.094	25	0.40
B-15	0.0009	33	0	0.167	0.167	17.62	1.13	1.57	0.124	0.113	30	0.40
B-10	0.0015	33	0	0.167	0.167	14.09	1.13	1.57	0.066	0.132	40	0.40
B-6	0.0022	60	67	0.055	0.055	5.58	0.38	0.52	0.026	0.057	55	0.80
B-1	0.0099	75	91	0.004	0.004	2.02	0.05	0.42	0.002	0.003	45	0.14

2.1. Paleoredox Conditions

The dominance of CaO over MgO indicates that the primary mineral phase in these carbonates is calcite and that there was no dolomitization in Saytepe limestones during deposition. Furthermore, the very strong negative correlation ($r=-0.99$) observed between CaO and MgO indicates that the fractionation of these elements does not occur simultaneously. This suggests that MgO may be present as small silicate phases within rocks or may have been incorporated into the calcite structure. Ca is mainly of biogenic origin and serves as a diluent for all other major oxides and REE.

Sr concentration and the Ca/Mg ratio are excellent geochemical factors in determining the depth and salinity of limestone depositional environments. Sr concentrations in shallow and deep-sea environments range from 100 to 499 ppm and 500 to 3000 ppm, respectively (e.g., Flugel and Wedepohl, 1967). Additionally, there is a significant relationship between Sr and seawater salinity, with limestone deposition in low-salinity environments leading to Sr depletion. The low Sr concentration (<499; 143-368 ppm; Table 2) in Saytepe carbonate samples indicates that these carbonates were deposited in a shallow marine environment with normal salinity. The salinity of the limestone depositional environment tends to decrease as the Ca/Mg ratio increases (Abedini et al., 2020). The Ca/Mg ratios of Saytepe carbonates are high in most samples, indicating deposition in a relatively low salinity environment (within the normal marine salinity range).

The enrichment values of MoEF, UEF, ZnEF, PbEF, NiEF, CuEF, CdEF, and VEF calculated to determine the paleoredox environment in the carbonate samples of the Saytepe Formation (Table 4) were <1 for all elements, indicating no enrichment. The MoEF versus UEF diagram in Figure 5 shows that all Saytepe carbonate samples fall into an anoxic environment. Additionally, the U/Th ratios >0.5 , Ni/Co ratios >7 , and V/V+Ni ratios >0.46 in Saytepe limestones indicate an anoxic environment (Figure 6). However, the Cu/Cu+Ni ratios <2 and the V/Cr ratios <2 in Saytepe carbonate samples indicate an oxic environment (Figure 6). Furthermore, all samples studied fall into the anoxic zone in the Ce/Ce*-Nd and Ce/Ce*-La_N-Sm_N diagrams (Figure 7).

We can say that the Saytepe carbonates reflect a predominantly anoxic, and to a lesser extent oxic, paleoenvironment.

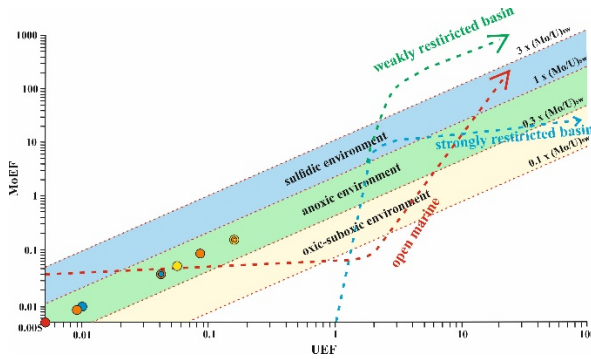


Figure 5. UEF-MoEF diagram for Saytepe samples. All samples indicate anoxic seawater and show that the Saytepe Formation carbonates formed in an open marine basin where anoxic conditions were dominant

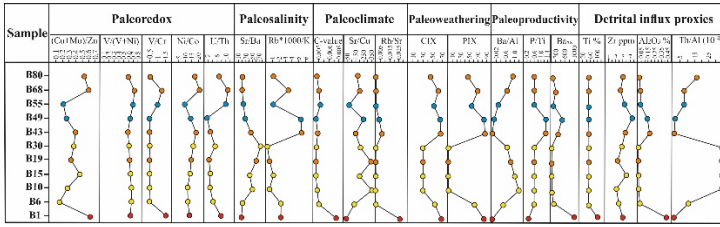


Figure 6. Vertical variations of paleoredox index, paleosalt index, paleoclimate index, paleoweathering index, paleoproductivity index, and detrital input markers for carbonate samples from the Saytepe Formation

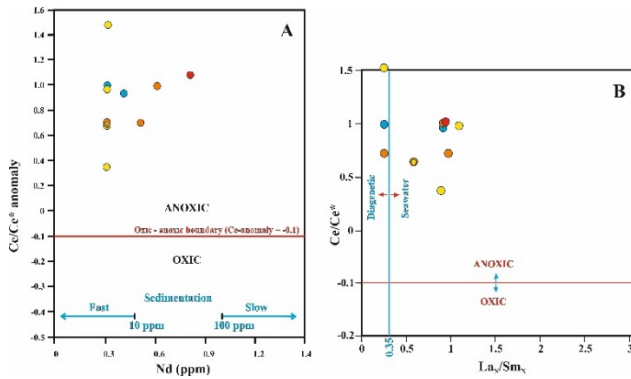


Figure 7. A) Diagram of Ce/Ce* versus Nd. B) Diagram of Ce/Ce* versus LaN-SmN

2.2. Paleosalinity

Sr enrichment in sediments is associated with increased salinity, and high Sr/Ba ratios indicate an increase in seawater depth and salinity (e.g., Gu et al., 2022; Wei and Algeo, 2020).

In the Rb/K versus Sr/Ba diagram (Figure 8a), all our samples fall into the saline (normal seawater) area, indicating a shallow marine (carbonate shelf) environment. Additionally, in the Sr versus Ba diagram (Figure 8b), all of our studied samples fall into the marine area. From this, we can conclude that the

Saytepe carbonates were deposited in a saline, i.e., normally saline marine environment (carbonate shelf).

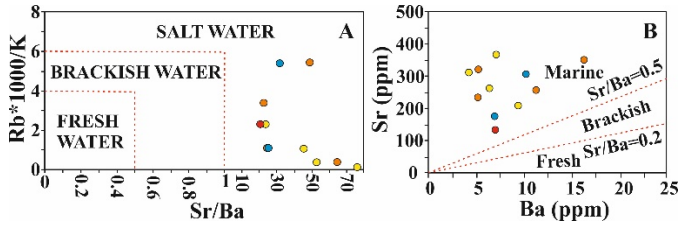


Figure 8. A) Sr/Ba versus Rb*1000/K, B) Sr versus Ba. Both diagrams depict the marine environment

2.3. Paleoclimate

In this study, the ratios of climate-sensitive elements such as Sr/Cu, Sr/Ba, Rb/Sr, and Al/Mg, as well as the C-value parameter, were used to determine the dominant climate during the deposition of the Saytepe Formation carbonates. The Sr/Cu ratios of the Saytepe carbonate samples ranged from 36 to 368, indicating a hot and humid paleoclimate during sedimentation (Table 4). The Sr/Ba ratios of the Saytepe carbonate samples ranged from 20 to 77, indicating a dry and hot paleoclimate during sedimentation (Table 4).

The Rb/Sr values of the Saytepe carbonate samples are <0.5 (0.00027 to 0.029, average 0.0042), indicating sedimentation in an arid climate (Table 4). The Saytepe carbonates examined exhibit very low Al/Mg ratios (0.0056–0.53, average 0.105), and since all our samples are <1, this also indicates an arid climate (Table 4). In addition, the C-values of the Saytepe carbonate samples being <0.4 indicates sedimentation in an arid climate (Table 4). In conclusion, we can say that arid climates were predominantly, and to a lesser extent, humid climates, during the deposition process of Saytepe carbonates.

2.4. Paleoproductivity

Ba/Al values for carbonate samples from the Saytepe Formation range from 0.005 to 0.132 (Table 4), indicating high paleoverproductivity. Additionally, high barium (Baxs) values indicate high productivity in one sample, medium productivity in three samples, and low productivity in seven samples (Table 4; Figure 9a).

P/Ti values of Saytepe Formation carbonate samples vary between 0.36 and 1.45, indicating high paleo-productivity (Table 4; Figure 9a). As seen in Figure 9b, except for one sample in the Cd/Mo-Co*Mn graph, all our other samples fall in the strong upwelling area. Saytepe carbonate samples mostly indicate medium-low productivity and strong upwelling area.

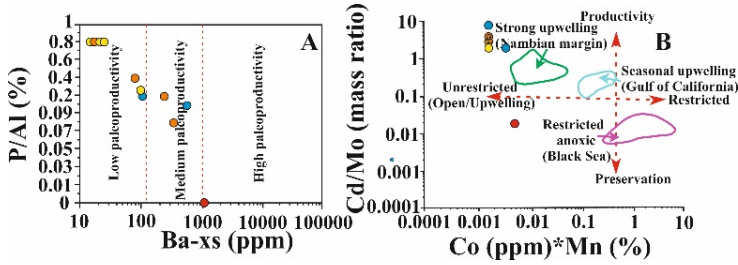


Figure 9. A) P/Al versus Ba-xS. Predominantly low productivity, B) Cd/Mo versus Co*Mn. Predominantly strong upwelling

2.5. Detrital Input and Paleoweathering Indicators

Saytepe carbonate samples show the following ratios: SiO₂/Al₂O₃ (2.1-20; only 6 samples >6), Al₂O₃/Na₂O (1-19; only 3 samples >5), and K₂O/Na₂O (0.5-6; only 3 samples >1) (Table 4). This indicates that sediment reprocessing and/or detrital input occurred at some stages in the Saytepe carbonate samples (Table 4).

The Si/Al, Ti/Al, K/Al, and Zr/Al ratios in the Saytepe Formation carbonates are 1.86 to 17.62, 0.05 to 1.13, 0.39 to 1.57, and 0.002 to 0.124, respectively, indicating low detrital input

(Table 4). Figure 10a shows that our Saytepe carbonate samples exhibit a carbonate tendency, and Figure 10b shows that Si is only taken in from terrestrial input in the SiO₂-Zr diagram.

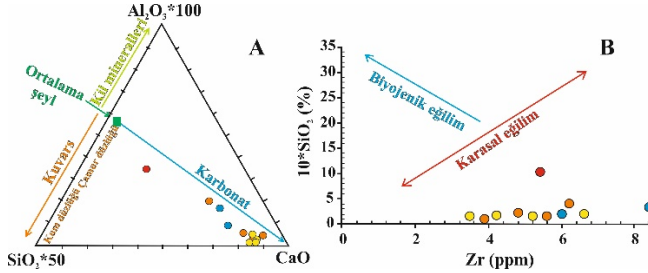


Figure 10. A) In the Al₂O₃-SiO₂-CaO triangular diagram, most of the Saytepe Formation samples show a tendency towards carbonate rocks. B) The SiO₂ versus Zr diagram indicates that the silicon is of terrestrial origin

The Al/Ti ratios of the Saytepe limestone samples range from 0.88 to 19.84 (Table 4), and being lower than the average value of the upper crust (27) indicates that the terrestrial input to the basin during the sedimentation process was via wind transport rather than stream transport. The source of the terrestrial input in the Saytepe samples falls within the arid climate zone, supporting this situation.

In the La versus Th diagram (Figure 11a), the Saytepe limestone samples fall into the mafic source area. In the TiO₂ versus Zr diagram (Figure 11b), all Saytepe formation samples fall into the felsic rock source area. Therefore, the detritus that entered the basin during the deposition of the Saytepe limestones was obtained from a mixed source.

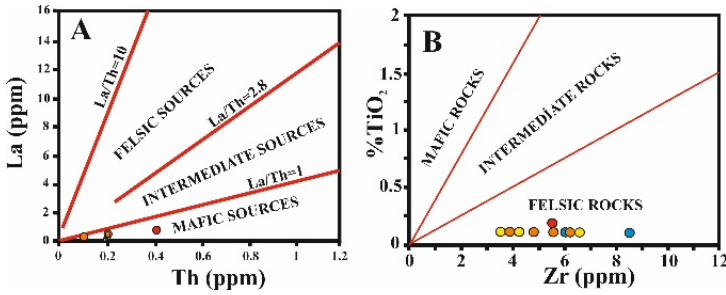


Figure 11. A) Th versus La diagram for Saytepe limestone samples, B) TiO₂ versus Zr diagram

The degree of weathering in the Saytepe carbonate samples was determined by identifying CIX and PIX values (e.g., Garzanti et al., 2019), which are more useful for carbonate rocks in calculating paleo-weathering (Table 4, Figure 6). The CIX values of the Saytepe Formation carbonates ranged from 33 to 75, with four samples <50 showing no weathering, two samples showing initial weathering at 50-60, and five samples showing moderate weathering at 60-80 (Table 4; Figure 6). The PIX values of the Saytepe carbonates ranged from 0 to 93, with four samples <50, one sample 50-60, three samples 60-80, and three samples >80 (Table 4; Figure 6). From this, we can say that the weathering in the Saytepe carbonate samples is mostly at a low level.

2.6. Evolution of the Sedimentation Environment Model

Cd/Mo and Co*Mn have been proposed as effective indicators for distinguishing upwelling and hydrographically restricted environments (Ma et al., 2023). In general, sediments in upwelling systems are represented by Mn and Co reduction, while sediments in restricted basins show high Mn and Co values (Ma et al., 2023). Low Co*Mn (<0.4) or low MnEF*CoEF (<0.5) values are typical for coastal upwelling environments, while high Co*Mn (>0.4) and high CoEF*MnEF (>2) values are typical for

closed environments such as the Black Sea (Ma et al., 2023). The Co*Mn values of Saytepe carbonate samples vary within a narrow range (0.0015 to 0.0046), with an average below 0.4 (Figure 9b). The Co*Mn-Cd/Mo graph (Figure 9b) indicates that the Saytepe carbonate samples formed under strong upwelling and open water conditions.

According to geochemical analysis results, the Neotethys (Late Cretaceous process) Saytepe carbonate layers were deposited in an arid to subhumid climate and a shallow marine (carbonate shelf) oxic to anoxic environment with relatively little detrital input. During the deposition of the Saytepe Formation, there was fluvial and eolian clastic input into the basin at some stages.

In conclusion, we can suggest that the Saytepe limestones formed in a shallow and open marine environment (carbonate shelf environment) (Figure 12a, b).

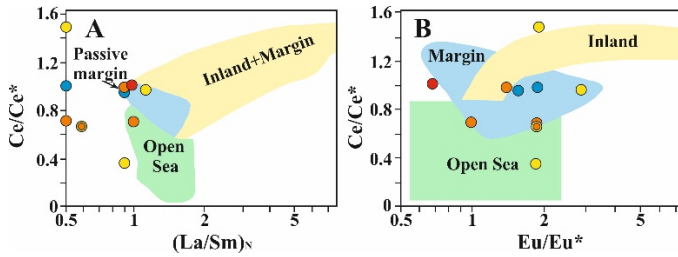


Figure 12. A) Ce/Ce* ile (La/Sm)_N arasındaki ilişkiyi gösteren diyagram. B) Ce/Ce* ile Eu/Eu* arasındaki ilişkiyi gösteren diyagram.

3. CONCLUSIONS

The dominance of CaO over MgO indicates that the primary mineral phase in these carbonates is calcite, and that dolomitization was absent in the Saytepe limestones during deposition. Based on Mn/Sr values, the Saytepe samples show

very weak alteration and retain their primary depositional characteristics. According to CIX and PIX data, the weathering in the Saytepe carbonate samples is mostly at a low level. Furthermore, based on rare earth element values, no hydrothermal activity was observed in the Saytepe carbonates.

Low amounts of terrestrial clastic input occurred during the deposition process of the Saytepe limestones. The source of the detritals observed in the Saytepe samples indicates that they were taken from mixed (felsic-mafic) rocks. The fact that the Al/Ti ratios of the Saytepe limestone samples are lower than the average value of the upper crust suggests that terrestrial input to the basin during the deposition process was via wind transport rather than fluvial transport. In addition, the fact that the source of the terrestrial input in the Saytepe samples is an arid climate region supports this view.

The Ce anomaly values in Saytepe limestone samples range from 0.37 to 1.54, and the fact that they exhibit higher rates than seawater values (0.1-0.4) indicates that the increase in Ce anomaly is due to the presence of clay minerals in the limestones and/or the decomposition of Ce-containing organic matter in seabed sediments.

Saytepe carbonate samples mostly indicate medium-low productivity and a strong upwelling area.

Saytepe samples also indicate deposition in a shallow marine environment in the Sr/Ba versus Sr/Rb graph. The low Sr concentration in Saytepe carbonate samples indicates that these carbonates were deposited in a shallow marine environment with normal salinity and points to diagenetic alteration. Saytepe carbonates exhibit precipitation in anoxic and oxic environments in terms of paleoredox conditions. Again, in the Rb/K versus Sr/Ba diagram, all our samples fall into the saline (normal seawater) area and show a shallow marine (carbonate shelf) environment. In addition, all of our studied samples fall into the marine area in the Sr versus Ba diagram. From this, we can state that Saytepe carbonates

were deposited in a marine environment with normal salinity (carbonate shelf).

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RARE EARTH ELEMENT GEOCHEMISTRY OF EARLY-MIDDLE CAMBRIAN ÇALTEPE FORMATION CARBONATES IN CANKURTARAN NEIGHBOURHOOD (AKŞEHİR, TÜRKİYE)

Ali Müjdat ÖZKAN¹

1. INTRODUCTION

Carbonate minerals formed through inorganic chemical or biochemical processes in marine environments can record and preserve the geochemical characteristics of paleo-seawater from the time of their precipitation to the present day. It is known that valuable information regarding depositional environments can be obtained by interpreting the REE contents, PAAS-normalized REE patterns, and Eu and Ce anomaly values of chemically precipitated sediments of marine origin. The distribution of REEs in seawater is primarily controlled by the input of terrigenous material associated with continental weathering, the influx of hydrothermal fluids along mid-ocean ridges and tectonic lines, scavenging processes that vary in intensity with depth, seawater salinity, and the oxygenation level of the environment (Elderfield, 1988; Greaves et al., 1999). Due to their similar atomic structures and ionic radii, all elements within the REE+Y group exhibit similar geochemical properties and generally coexist in nature; they behave conservatively and do not migrate easily. Consequently, REE+Y signatures in carbonates are widely used to track the geochemical characteristics of ambient fluids (such as

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seawater and pore water) and environmental conditions prevailing during primary carbonate precipitation (Nothdurft et al., 2004; Li et al., 2019; Liu et al., 2019; Zhao et al., 2021).

The study area encompasses the vicinity of Cankurtaran Neighborhood (Akşehir, Konya)-located in the southeastern part of the Sultandağları Massif, which lies along the northern margin of the central section of the Menderes-Taurus block, within the Taurides Main Tectonic Unit (Figure 1).

Paleozoic-aged carbonates and detrital sedimentary rocks, which have undergone low-grade metamorphism during the Alpine Orogeny, crop out in the region (Figure 2). These are tectonically overlain by the Mesozoic Hoyran nappes, which consist of allochthonous ophiolitic rocks and the limestone olistoliths contained within them. These units are unconformably overlain by Miocene-Pliocene alluvial fan and lacustrine deposits.



Figure 1. Location map of the study area (from Google Maps)

Except for Ce and Eu, rare earth elements generally exhibit trivalent behavior; however, Ce and Eu can possess different oxidation states depending on environmental conditions. Although Y and Ho are similar in terms of valence and ionic radius, Ho has a higher capacity to form complex ions than Y. Consequently, Ho is removed from seawater and precipitates more rapidly than Y (Nozaki et al., 1997). As a result, the Y/Ho ratio of the Ho-depleted seawater can reach values significantly higher ($Y/Ho > 45$) than that of terrigenous material, which is approximately 27 (Bau, 1996).

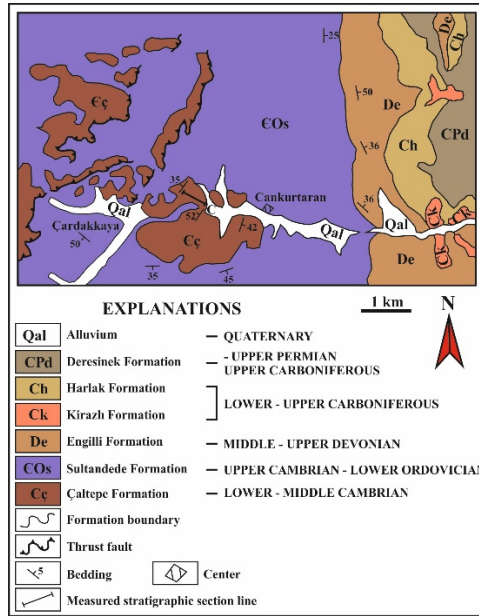


Figure 2. Geological map of the study area (from Özkan and Küpeli, 2017)

Thin sections were prepared from samples collected at appropriate intervals along a measured stratigraphic section line selected in the western part of the Cankurtaran Neighborhood; these were examined under a polarizing microscope to determine their microfacies characteristics (Figure 3). Major oxide, trace element, and rare earth element (REE) analyses were performed

on 24 samples taken from the Cankurtaran section (Figure 3; Tables 1-3) to elucidate the geochemical characteristics (particularly REE+Y) of the Çaltepe Formation carbonates. In this context, studies were conducted to determine the depositional environment conditions (oxic vs. anoxic) of the Çaltepe carbonates; to assess whether there was terrestrial clastic input or hydrothermal influx into the basin; to evaluate the preservation of original carbonate phase characteristics; to identify the source rock types (felsic, mafic, or mixed) in the event of terrestrial input; and to ascertain the extent to which the carbonates were affected by diagenetic processes and whether they underwent metamorphism.

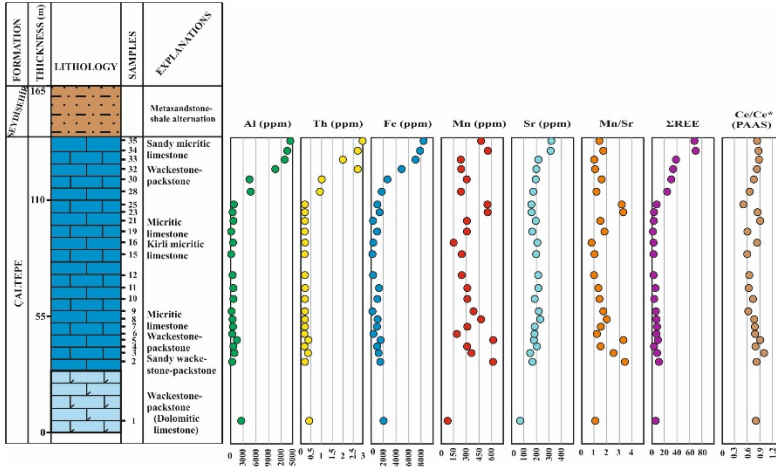


Figure 3. Cankurtaran measured the stratigraphic section, mineralogical composition, and geochemical composition of Çaltepe carbonates.

Table 1. Major oxide (%), and minor element (ppm) concentrations of carbonates in the Çaltepe Formation (*dolomitic limestone)

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	Si	Al	Ti	Fe	Mn	Sr	Th	Mn/Sr
MDL	0.01	0.01	0.04	0.01	0.01	1	0.5	0.1	0.1	0.05	0.5	0.2	
C-35	12.1	2.74	1.2	0.14	0.06	56531	14498	839	8393	465	324	3	1.43
C-34	11.39	2.57	1.13	0.12	0.07	53214	13598	719	7904	542	321	2.7	1.69
C-33	9.74	2.45	1.03	0.13	0.03	45505	12964	779	7204	232	218	2	1.06
C-32	10.97	2.03	0.68	0.13	0.03	51252	10741	779	4756	232	197	2.7	1.18
C-30	5.54	0.85	0.33	0.04	0.04	25883	4497	240	2308	310	194	1	1.6
C-28	8	0.93	0.27	0.05	0.03	37376	4921	300	1888	232	178	0.9	1.3
C-25	0.5	0.16	0.15	<0.01	0.07	2336	847	60	1049	542	167	0.2	3.24
C-23	0.19	0.09	0.2	<0.01	0.07	887	476	60	1399	542	164	0.2	3.3
C-21	0.37	0.13	0.08	<0.01	0.04	1728	688	60	559	310	198	0.2	1.56
C-19	0.09	0.04	0.15	<0.01	0.04	420	211	60	1049	310	168	0.2	1.84
C-16	0.34	0.1	0.08	<0.01	0.02	1588	529	60	559	155	211	0.2	0.73
C-15	0.1	0.04	0.05	<0.01	0.03	467	212	60	350	232	202	0.2	1.15
C-12	0.39	0.09	0.08	<0.01	0.03	1822	476	60	559	232	221	0.2	1.05
C-11	0.4	0.15	0.19	<0.01	0.04	1869	794	60	1329	310	220	0.2	1.41
C-10	0.42	0.15	0.14	<0.01	0.04	1962	794	60	979	310	194	0.2	1.6
C-9	0.17	0.07	0.08	<0.01	0.05	794	370	60	559	387	222	0.2	1.74
C-8	0.34	0.11	0.17	<0.01	0.06	1588	582	60	1189	465	229	0.2	2.03
C-7	1.43	0.14	0.15	<0.01	0.04	6681	741	60	1049	310	188	0.2	1.65
C-6	0.37	0.06	0.1	<0.01	0.03	1728	317	60	699	232	188	0.2	1.23
C-5	2.24	0.28	0.26	0.02	0.08	10465	1481	120	1818	619	183	0.3	3.38
C-4	3.06	0.15	0.15	0.01	0.04	14296	794	60	1049	310	203	0.2	1.53
C-3	1.12	0.19	0.17	<0.01	0.05	5233	1005	60	1189	387	149	0.3	2.6
C-2	5.06	0.1	0.22	<0.01	0.08	23640	529	60	1539	619	180	0.2	3.44
C-1*	4.81	0.49	0.29	0.02	0.01	22472	2593	120	2028	77	70	0.4	1.1

Table 2. Rare earth element (ppm) concentrations of Çaltepe Formation carbonates (*dolomitic limestone)

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	TRE
MDL	0.1	0.1	0.0	0.3	0.05	0.0	0.0	0.01	0.05	0.1	0.02	0.03	0.01	0.05	0.01	
C-35	15.1	24.7	3.3	12.4	2.72	0.6	2.5	0.43	2.67	17.6	0.54	1.55	0.23	1.41	0.21	68.84
C-34	22.5	22.5	3.0	13.7	2.58	0.5	2.3	0.36	2.05	6.13	0.4	1.06	0.15	0.86	0.13	71.6
C-33	8.6	15.1	1.9	7.2	1.41	0.3	1.2	0.21	1.22	8.2	0.22	0.65	0.1	0.57	0.09	39.53
C-32	9	14.2	1.8	7.2	1.08	0.3	1.1	0.18	1	6.6	0.24	0.64	0.11	0.54	0.09	37.58
C-30	7.2	11.3	1.6	7	1.35	0.3	1.2	0.19	1.14	7.3	0.2	0.5	0.06	0.44	0.04	32.74
C-28	6.3	7.6	1.1	4.8	0.98	0.2	0.9	0.14	0.81	5.7	0.16	0.43	0.07	0.37	0.05	24.03
C-25	2.8	1.9	0.2	0.7	0.13	0.0	0.1	0.02	0.1	0.9	0.03	0.08	0.01	0.06	<0.0	6.25
C-23	0.9	1.3	0.1	0.6	0.09	0.0	0.0	0.01	0.07	0.7	<0.0	0.06	1	<0.0	<0.0	4.23
C-21	1.1	1.7	0.5	0.7	0.08	0.0	0.1	<0.0	0.1	0.6	<0.0	0.04	<0.0	<0.0	<0.0	4.15
C-19	1	0.9	0.1	0.4	0.05	0.0	0.0	<0.0	<0.0	0.3	<0.0	<0.0	<0.0	<0.0	<0.0	2.75
C-16	1.1	1.4	0.1	0.4	<0.0	0.0	0.0	<0.0	<0.0	0.5	<0.0	<0.0	<0.0	<0.0	<0.0	3.37
C-15	1.6	1.4	0.1	0.4	0.08	0.0	0.0	<0.0	0.06	0.4	2	3	1	5	1	3.93
C-12	1.2	1.2	0.1	0.6	0.06	0.0	0.0	<0.0	0.05	0.4	2	3	<0.0	<0.0	<0.0	3.5
C-11	2	2.1	0.2	0.8	0.12	0.0	0.1	0.02	0.09	0.6	0.02	0.05	<0.0	<0.0	<0.0	5.72
C-10	1.4	1.6	0.1	0.5	0.08	0.0	0.0	0.01	0.06	0.6	<0.0	<0.0	<0.0	<0.0	<0.0	4.07
C-9	2.3	2.2	0.2	0.8	0.07	0.1	0.0	<0.0	0.09	0.3	0.02	0.03	<0.0	<0.0	<0.0	5.99
C-8	2.4	2.5	0.2	0.9	0.1	0.1	0.1	0.01	0.07	0.6	<0.0	0.03	<0.0	<0.0	<0.0	6.57
C-7	2.2	3	0.3	1.3	0.24	0.1	0.4	0.03	0.17	1	0.02	0.05	1	5	1	7.77
C-6	1.9	2.5	0.2	0.7	0.1	0.0	0.1	0.02	0.12	0.5	<0.0	<0.0	<0.0	<0.0	<0.0	5.94
C-5	2.2	3.9	0.4	1.6	0.26	0.1	0.2	0.04	0.21	1.3	0.04	0.14	0.02	0.11	0.02	9.36
C-4	1.2	1.6	0.1	0.6	0.07	0.0	0.0	0.01	0.09	0.3	<0.0	<0.0	<0.0	<0.0	<0.0	4.02
C-3	1.9	3.3	0.3	1.1	0.22	0.0	0.2	0.03	0.16	0.9	0.03	0.09	0.01	0.06	1	8.14
C-2	3.3	4.5	0.4	1.8	0.32	0.1	0.3	0.05	0.27	1.2	0.04	0.08	1	0.06	<0.0	11.39
C-1*	1.7	2.4	0.2	0.9	0.16	0.0	0.2	0.03	0.16	1	0.03	0.11	0.02	0.08	<0.0	6.13

Table 3. Some anomaly values and element ratios of carbonate samples from the Çaltepe Formation (*dolomitic limestone)

Sam ple	Y/ Ho	Ce/ Ce*	Pr/ Pr*	Eu/ Eu*	(Pr/Y b) _N	(Nd/ Yb) _N	(Dy/S m) _N	(La/S m) _N	(La/Y b) _N	La/ La*	Gd/ Gd*	(Sm/ Pr) _N	(Sm/ Yb) _N
C-35	32	0.80	1.10	1.09	0.76	0.76	1.16	0.81	0.79	1.04	1.01	1.29	0.98
C-34	34	0.85	1.04	1.04	1.14	1.26	0.94	0.68	1.04	1.15	1.10	1.34	1.52
C-33	37	0.86	1.03	1.15	1.08	1.15	1.03	0.89	1.11	1.21	0.98	1.17	1.26
C-32	27	0.80	1.09	1.28	1.11	1.11	1.10	1.21	1.23	1.10	1.09	0.91	1.02
C-30	36	0.75	1.09	1.25	1.22	1.32	1.00	0.77	1.21	1.19	1.13	1.28	1.56
C-28	36	0.64	1.14	1.15	1.03	1.08	0.98	0.93	1.26	1.36	1.07	1.31	1.34
C-25	30	0.50	1.02	2.44	1.06	0.97	0.91	3.13	3.45	2.75	1.20	1.03	1.10
C-23	35	0.83	0.93	3.66	0.89	1.00	0.92	1.45	1.33	1.94	1.37	1.02	0.91
C-21	30	0.93	0.81	3.51	0.96	1.16	1.48	2.00	1.62	2.98	1.75	0.85	0.81
C-19	15	0.60	0.98	2.98	0.64	0.67	1.19	2.91	1.48	2.52	1.47	0.79	0.51
C-16	25	0.81	1.00	4.30	0.83	0.67	1.19	3.20	1.62	1.40	1.10	0.61	0.51
C-15	20	0.60	1.16	3.40	0.96	0.67	0.89	2.91	2.36	1.53	0.96	0.85	0.81
C-12	20	0.65	0.90	2.56	0.83	1.00	0.99	2.91	1.77	3.58	1.57	0.73	0.61
C-11	30	0.66	1.09	3.02	1.53	1.33	0.89	2.42	2.95	1.52	1.14	0.79	1.22
C-10	30	0.75	0.97	3.15	0.96	0.83	0.89	2.54	2.07	1.71	1.12	0.85	0.81
C-9	15	0.65	0.97	7.40	1.40	1.33	1.52	4.77	3.40	2.19	1.17	0.51	0.71
C-8	30	0.72	0.86	6.29	1.40	1.50	0.83	3.49	3.54	2.90	1.61	0.72	1.02
C-7	50	0.78	1.01	2.16	2.17	2.16	0.84	1.33	3.25	1.48	1.28	1.12	2.44
C-6	25	0.80	1.09	2.69	1.60	1.16	1.42	2.76	2.81	1.14	1.38	0.64	1.02
C-5	32	0.93	0.99	1.89	1.22	1.21	0.96	1.23	1.48	1.19	1.24	0.98	1.20
C-4	15	0.78	1.08	2.97	1.15	1.00	1.52	2.49	1.77	1.22	1.50	0.62	0.71
C-3	30	0.96	0.98	1.93	1.70	1.53	0.86	1.25	2.34	1.13	1.20	1.09	1.86
C-2	30	0.82	0.95	2.69	2.45	2.50	1.00	1.50	4.06	1.72	1.06	1.11	2.71
C-1*	33	0.80	1.08	1.58	0.76	0.94	1.19	1.54	1.57	1.15	1.20	0.94	1.02

2. STUDY CONTENT

Petrographic examination of the Çaltepe carbonate samples reveals that primary depositional features have been preserved in all of them (Figure 3). Furthermore, geochemical analysis indicates that most samples have retained their original characteristics, thereby supporting the validity of the results obtained in this study; the observed degrees of diagenetic alteration are very low (average Mn/Sr = 1.78). Mn/Sr ratios exceed the value of 3 only slightly in four samples (ranging from 3.24 to 3.44; Table 1). While most samples show no signs of hydrothermal alteration (Figure 4), a small number do exhibit such alteration. Consequently, this suggests an influx of fresh water-carrying detrital material-and, to a lesser extent, submarine hydrothermal solutions into the depositional environment of the Çaltepe Formation limestones.

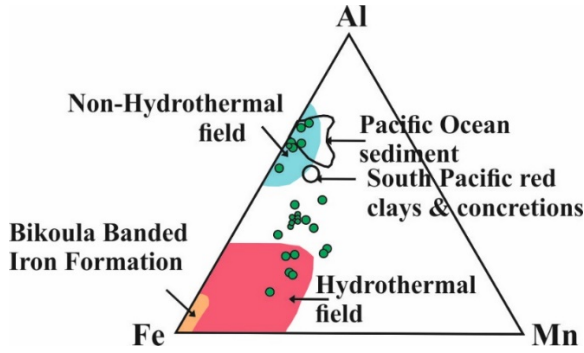


Figure 4. Distribution of Çaltepe limestone samples on Al-Fe-Mn ternary diagrams

The PAAS-normalized REE+Y patterns are presented in Figure 5, and enrichment was observed in most of our samples. The greatest enrichment occurred in the MREE+Y values.

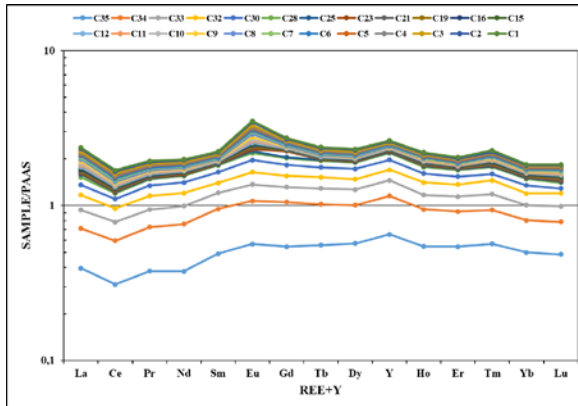


Figure 5. REE+Y diagram of Çaltepe carbonate samples normalized according to PAAS

Based on average REE+Y values, the Çaltepe carbonate samples are characterized by PAAS-normalized REE+Y patterns that are mutually very similar, depleted in LREE and HREE but relatively enriched in MREE, and exhibit distinct negative Ce, positive Eu, and weak positive Y anomalies (Figure 5). Although the PAAS-normalized REE+Y patterns of the studied samples show some deviations from seawater patterns, it has been

determined that characteristic features typical of seawater, such as the negative Ce anomaly, low LREE content, and positive La, Gd, and Y anomalies, are preserved in many of the samples.

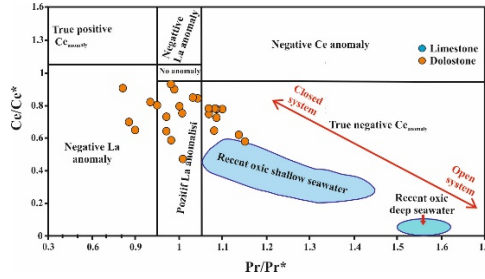
The very low elemental values-or those measurable only below detection limits-observed in some of the Çaltepe carbonate samples indicate that these elements are adsorbed onto clay minerals (Kuchenbecker et al., 2016). In this study, elemental analysis values falling below the detection limit have been treated as the detection limit values themselves.

2.1. Paleoredox Conditions

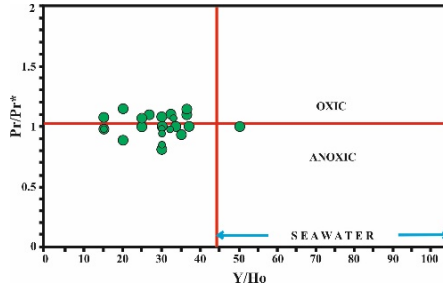
Specific trace element contents and/or ratios in both young and ancient sedimentary rocks (detrital and/or carbonate) are widely used as indicators of redox conditions. Since the enrichment of redox-sensitive elements reflects the depositional environment of organic-carbon-rich ancient sedimentary rocks, it is also utilized to elucidate the paleoceanographic conditions that facilitated their formation (Akinyemi et al., 2013). In this study, Fe_T/Al , Y/Ho versus Pr/Pr^* , and Pr/Pr^* versus Ce/Ce^* anomaly values were employed to determine the redox conditions of the depositional environment of the Çaltepe carbonates (predominantly limestone) (Table 3; Figures 6, 7). Based on Fe_T/Al ratios, two samples indicate an anoxic paleoenvironment, while 22 samples point to an oxic one. Among the rare earth elements, Ce anomaly values can sensitively reflect the redox conditions of a sedimentary environment (Yan et al., 2021). A Ce/Ce^* value greater than 1 (or a positive anomaly) indicates a reducing environment, whereas a value below 0.95 (or a negative anomaly) signifies an oxidizing environment. Although one sample of the Çaltepe carbonates has a value of 0.96 (>0.95) and 23 samples are below 0.95, the Ce/Ce^* vs. Pr/Pr^* diagram (Figure 6) shows that 5 samples fall into the positive Ce anomaly field, indicating a reducing environment, while 9 samples fall into the

true negative C_e anomaly field, signifying an oxic environment. Similarly, in the Y/Ho vs. Pr/Pr^* diagram (Figure 7), some of the studied samples indicate anoxic environmental conditions, while others point to oxic conditions.

In light of all this data, we can state that oxic and anoxic conditions developed during the deposition of the Çaltepe carbonates.



Şekil 6. Ce/Ce^* versus Pr/Pr^* diagram of Çaltepe limestone samples



Şekil 7. Pr/Pr^* versus Y/Ho diagram of Çaltepe limestone samples

Sr concentration and the Ca/Mg ratio serve as excellent geochemical indicators for determining the depositional depth and salinity of limestones. Sr concentrations in shallow and deep marine environments range from 100 to 499 ppm and 500 to 3000 ppm, respectively (e.g., Flügel and Wedepohl, 1967). Furthermore, there is a significant relationship between Sr and seawater salinity; limestone deposition in low-salinity

environments leads to strontium depletion. The low Sr concentrations observed in the Çaltepe carbonate samples (<499; 70-324 ppm; Table 1) indicate that these carbonates were deposited in a shallow marine environment with normal salinity. The salinity of the limestone depositional environment tends to decrease as the Ca/Mg ratio increases (Abedini et al., 2020). The Ca/Mg ratios of the Çaltepe carbonates are high in most samples, indicating deposition under relatively low salinity conditions (within the normal marine salinity range).

Since a positive La anomaly (Figure 5) causes a spurious negative Ce anomaly, Bau and Dulski (1996) developed a simple diagram to distinguish true Ce anomalies (Figure 6). This diagram allows for the identification of samples that appear to exhibit a negative Ce anomaly but do not actually possess one, as well as those that display a positive rather than a negative Ce anomaly, and those that show no anomaly at all. The Ce anomaly values of the Çaltepe carbonate samples range from 0.50 to 0.96 (mean 0.76) (Table 3; Figure 6). Some of our samples exhibit a true negative Ce anomaly, others show a positive Ce anomaly, and some display no Ce anomaly (Figure 6). Consequently, the Ce anomaly values of the studied carbonate samples indicate oxic-anoxic environmental conditions.

2.2. Paleosalinity

Paleosalinity is a key indicator for determining paleo-sedimentary environments. Ba and Sr are two tracer elements sensitive to paleosalinity (e.g., Gu et al., 2022). Sr enrichment in sediments is associated with increased salinity, and high Sr/Ba ratios indicate an increase in seawater depth and salinity (e.g., Gu et al., 2022). Furthermore, the Sr/Ba ratio can be used to distinguish between marine and terrestrial environments. All Çaltepe carbonate samples fall within the saline water field, indicating a marine environment (Özkan and Küpeli, 2017).

Based on this, we can infer that the Çaltepe limestones were deposited in a normal-salinity marine environment (carbonate shelf).

2.3. Paleoclimate

As highlighted by Worash (2002), paleoclimate can be recorded through the distribution, composition, and relative concentrations of certain trace elements (e.g., Fe, Mn, Cr, Ni, V, Co, Ca, Mg, Sr, Ba, K, Na, Cu, and Rb) in sedimentary rocks. The elements Sr and Cu are highly sensitive to climate change; Sr/Cu ratios are <5 for hot and arid climates, whereas they are >5 for hot and humid climates (Xie et al., 2018).

Ratios of climate-sensitive elements such as Sr/Cu, Sr/Ba, and Rb/Sr were used to determine the prevailing climate during the deposition of the Çaltepe Formation carbonates. The Sr/Cu ratios of the Çaltepe carbonate samples range from 25 to 727 (average 230), indicating a hot and humid paleoclimate during sedimentation. Sr/Ba values >1 and <1 indicate arid and humid climate conditions, respectively (e.g., Dai et al., 2020; Eric et al., 2023). The Sr/Ba ratios of the Çaltepe carbonate samples range from 0.6 to 31 (average 13), indicating an arid and hot paleoclimate during sedimentation (with only one sample suggesting a humid climate). Rb/Sr values >0.5 and <0.5 indicate humid and arid climate conditions, respectively (Eric et al., 2023). Since the Rb/Sr values of the Çaltepe carbonate samples are <0.5 (ranging from 0.0015 to 0.11, with an average of 0.023), they point to an arid and hot climate. We can suggest that an arid climate was dominant during the deposition of the Çaltepe carbonates, with a humid climate prevailing only to a very limited extent.

2.4. Detrital Input Indicators

Key major oxide ratios such as $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$, and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ serve as excellent proxies for interpreting

sediment recycling and detrital input (e.g., Subramanyam et al., 2021). High levels of sediment recycling and detrital input within the sedimentary depositional system are characterized by an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio >6 ; similarly, the $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ ratio exceeds 5, and the $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio exceeds 1. The Çaltepe carbonate samples exhibit $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 2.11-50 (with only 8 samples >6), $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ ratios of 2.63-19 (with 19 samples >5), and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios of 0.43-29 (with 19 samples >1). This indicates that sediment recycling and/or detrital input occurred over multiple stages in the Çaltepe carbonate samples.

The strong to very strong correlations between SiO_2 and Al_2O_3 , Fe_2O_3 , Na_2O , K_2O , TiO_2 , and TREE in the Çaltepe carbonates ($r=0.93$, $r=0.90$, $r=0.75$, $r=0.91$, $r=0.93$, and $r=0.91$, respectively) indicate that these elements are derived from aluminosilicates and clay minerals. Furthermore, $\text{Zr}+\text{Rb}/\text{Sr}$ ratios are used to distinguish between the siliciclastic and carbonate contents of the rocks, with higher values suggesting lower carbonate content and higher siliciclastic content (e.g., Sajid et al., 2020). The $(\text{Zr}+\text{Rb})/\text{Sr}$ values of the Çaltepe carbonate samples range from 0.0049 to 0.2477 (mean 0.0594), indicating very low siliciclastic input into the basin.

It has been suggested that Rb/Sr ratios reflect the relative abundance of the siliciclastic component and the carbonate fraction (e.g., Kuchenbecker et al., 2016). The Rb/Sr values of the Çaltepe Formation carbonate samples range from 0.0015 to 0.11 (mean 0.023). This indicates that some Sr loss occurred as a result of diagenetic alteration, as half of our samples exhibited values higher than the 0.0008 Rb/Sr value expected for carbonate rocks.

The $(\text{Nd}/\text{Yb})_N$ ratio, a significant LREE/HREE ratio, serves as a good indicator of contamination (e.g., Zhang & Nozaki, 1996). The Çaltepe carbonate samples exhibit $(\text{Nd}/\text{Yb})_N$ ratios ranging from 0.67 to 2.50 (mean 1.18); these values are far

lower than those of shale (PAAS: 11.4) but exceed the ratios of ~ 0.205 to 0.497 observed in normal ocean waters at a depth of 50 m. LREE depletion characteristics are responsible for these high ratios in the Çaltepe samples (Figures 5 & 8).

Interestingly, both MREE enrichment and depletion have been observed. It is known that MREE enrichment can occur as a result of diagenetic alteration and fluid interaction (e.g., Singh & Patra, 2025). Normal, unaltered seawater is typically depleted in middle rare earth elements (MREE) relative to heavy rare earth elements (HREE). However, during diagenesis, pore fluids interacting with Fe-Mn oxides or organic matter can become significantly enriched in MREE. As these fluids migrate through the limestone, they precipitate minerals (such as secondary calcite or dolomite) that incorporate this MREE-enriched signature (Singh & Patra, 2025). Conversely, if parts of the limestone retain their pristine marine signature or have interacted with oxidized, dilute meteoric waters, which are devoid of MREE, these specific zones will exhibit MREE depletion (Singh & Patra, 2025).

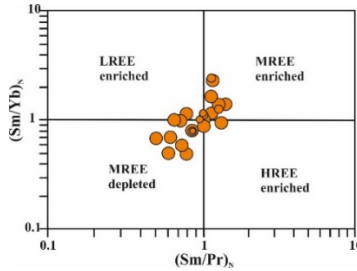


Figure 8. $(\text{Sm}/\text{Yb})_N$ versus $(\text{Sm}/\text{Pr})_N$ diagram

Al/Ti ratios are used to determine whether terrestrial input originates from fluvial or aeolian sources. The Al/Ti ratios of the Çaltepe limestone samples range from 3.5 to 21.6 (average 12.1); the fact that these values are lower than the average upper crustal value (27) indicates that terrestrial input into the basin during the depositional process occurred primarily through wind transport rather than fluvial transport. The source of the terrestrial input in

the Çaltepe samples corresponds to an arid climate zone, further supporting this interpretation.

In the Th vs. La diagram (Figure 9a), the Çaltepe limestone samples plot within the intermediate and felsic source area. The TiO_2/Zr ratio is another indicator of source rocks (McLennan et al., 1993); TiO_2/Zr ratios exceed 200 for mafic rocks and are less than 55 for felsic rocks. Since the TiO_2/Zr ratios of the Çaltepe limestone samples are $<<1$ (0.029–0.143), this indicates that the terrigenous clastics were derived from a felsic source. In the Zr vs. TiO_2 diagram (Figure 9b), all samples from the Çaltepe Formation plot within the felsic source field. Therefore, the detritus supplied to the basin during the deposition of the Çaltepe limestones was derived from mixed (intermediate and felsic) sources.

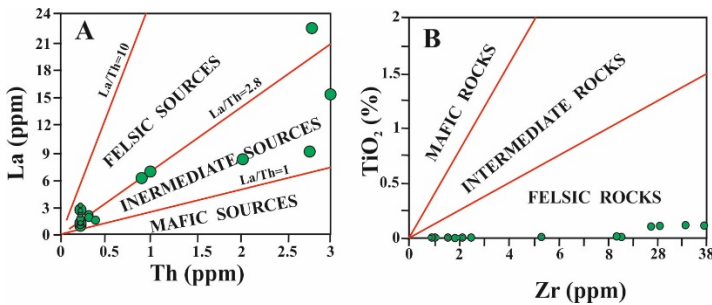


Figure 9. A) Th versus La diagram for Çaltepe limestone samples, B) TiO_2 versus Zr diagram

2.5. Evolution Of The Sedimentation Environment Model

Many researchers (Li et al., 2019; Zhang et al., 2020; Hou et al., 2022) have emphasized that the climate during deposition can influence the lacustrine/marine environment (i.e., depth, salinity, stratification, and aquatic biomass) and that the evolution of the depositional environment controls the input, accumulation, and preservation of organic matter. Based on geochemical analysis results, the Paleo-Tethys (Proto-Tethys: a vast, shallow

epicontinental marine platform situated along the northern margin of the Gondwana supercontinent) Çaltepe carbonate strata (Early-Middle Cambrian) were deposited in a shallow marine, oxic-to-anoxic environment characterized by an arid-to-semi-humid climate and relatively low detrital input (Figure 10).

Ultimately, when all the obtained geochemical data are evaluated together, it can be concluded that the Çaltepe carbonates were deposited under carbonate shelf conditions in a sedimentation basin where three phases, (1) open marine water, (2) shallow marine water influenced by freshwater influx rich in terrigenous clastic materials, and (3) relatively deep marine water influenced by hydrothermal fluid influx, mixed in varying proportions.

It is suggested that the influx of freshwaters rich in terrigenous clastic material may have resulted from the rapid melting of glaciers, correlatives of the Early Cambrian Baykonurian glaciation (distinct traces of which are found in Kazakhstan), located in the region of present-day Turkey (then part of North Gondwana) due to climatic warming. This climatic shift appears to have driven a rapid increase in biodiversity and productivity, facilitating the entry of small-shelled organisms (particularly trilobites) into the ecosystem (Göncüoğlu et al., 2007).

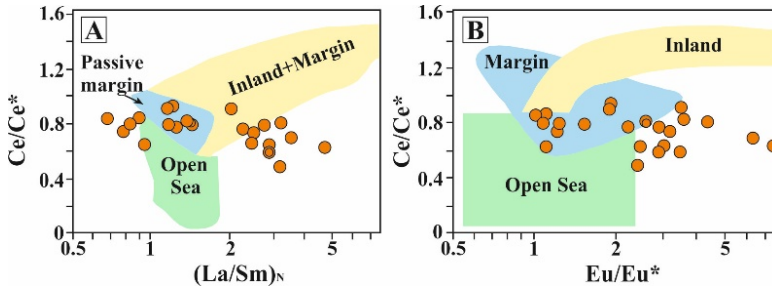


Figure 10. A) Diagram showing the relationship between Ce/Ce^* and $(La/Sm)_N$. This diagram illustrates the formation of the Çaltepe samples in passive margin, continental margin, and open-ocean environments. B) Diagram showing the relationship between Ce/Ce^* and Eu/Eu^* . In this diagram, the Çaltepe samples predominantly exhibit formation in a continental margin setting and, to a lesser extent, in an open-ocean environment

3. CONCLUSIONS

The predominance of CaO over MgO indicates that calcite was the primary mineral phase in these carbonates and that no dolomitization occurred in the Çaltepe limestones (within the studied succession) during precipitation. Based on Mn/Sr ratios (ranging from 0.73 to 3.44, with most samples <3), we can infer that the Çaltepe samples underwent very slight alteration and have preserved their primary depositional characteristics.

During the deposition of Çaltepe limestones, a low amount of terrestrial clasts was input. The source of the detritics observed in the Çaltepe samples indicates that they are taken from mixed (felsic-intermediate) rocks. The Al/Ti ratios of Çaltepe limestone samples indicate that the terrestrial input (sand to clay size) to the basin during the sedimentation process was through wind transport rather than streamflow.

The Ce anomaly values in the Çaltepe limestone samples range from 0.50 to 0.96 (mean 0.76); the fact that these values are higher than those of seawater (0.1-0.4) indicates that the increase in

the Ce anomaly stems from the presence of clay minerals within the limestones and/or the degradation of organic matter containing Ce in seafloor sediments. Furthermore, while some of the Çaltepe limestone samples exhibit a true negative Ce anomaly, others display a positive Ce anomaly. Additionally, the positive Eu anomaly observed in the Çaltepe carbonates suggests an origin linked to hydrothermal fluids rather than terrestrial input. Interestingly, both enrichment and depletion of MREEs have been observed in the Çaltepe carbonates.

In terms of paleoredox conditions, the Çaltepe carbonates exhibit depositional characteristics ranging from anoxic to oxic environments. This view is supported by the fact that the element Ce displays both true negative and positive anomalies in the Çaltepe carbonates (showing a negative anomaly under oxic conditions and a positive anomaly under anoxic conditions). From this, we can infer that the Çaltepe carbonates were deposited in a saline environment, specifically, a normal-salinity marine environment (a carbonate shelf).

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A NEOTECTONIC EVOLUTION OF THE AREA BETWEEN ACIGÖL AND GÖRE (CENTRAL ANATOLIA, TURKEY)

Ramazan DEMİRCİOĞLU¹

1. INTRODUCTION

According to the research conducted by Okay and Tüysüz (1999), the study area is situated within the Kırşehir Massif (see Figure 1a). This area is located in Central Anatolia, specifically within the province of Nevşehir, and encompasses the region between Acıgöl and Göre (Figure 1b).

The study area and its surroundings are situated within a region characterised by intense recent volcanism, known as the Cappadocia Volcanic Province (KVK). This area comprises the Cappadocia volcanic province, which is approximately 250–300 km long and extends in a NE–SW direction (Dirik, 2009).

As tectonic, volcanic and magmatic activity is very intense in this region, a large number of studies have been carried out. Some of these include Sassano (1964), Beekman (1966), Pasquare (1968), Innocenti et al., Batum (1975), Ercan et al. (1990), Ercan et al. (1991), Aydar et al. (1994), Toprak (1998), Aydar and Gourgaud (1998), Aydın (2009), Demircioğlu (2014), Kazancı and Suludere (2020), Gençoğlu et al., (2022), Başokur et al., (2022) Atakay et al., (2023), Demircioğlu and Oktar, (2024), Bozkurt, (2024). In recent years, pollution of surface and groundwater has significantly heightened the importance of water

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quality. To the north of the study area, in the Kızılırmak graben, a study was conducted by Demircioğlu et al. (2023).

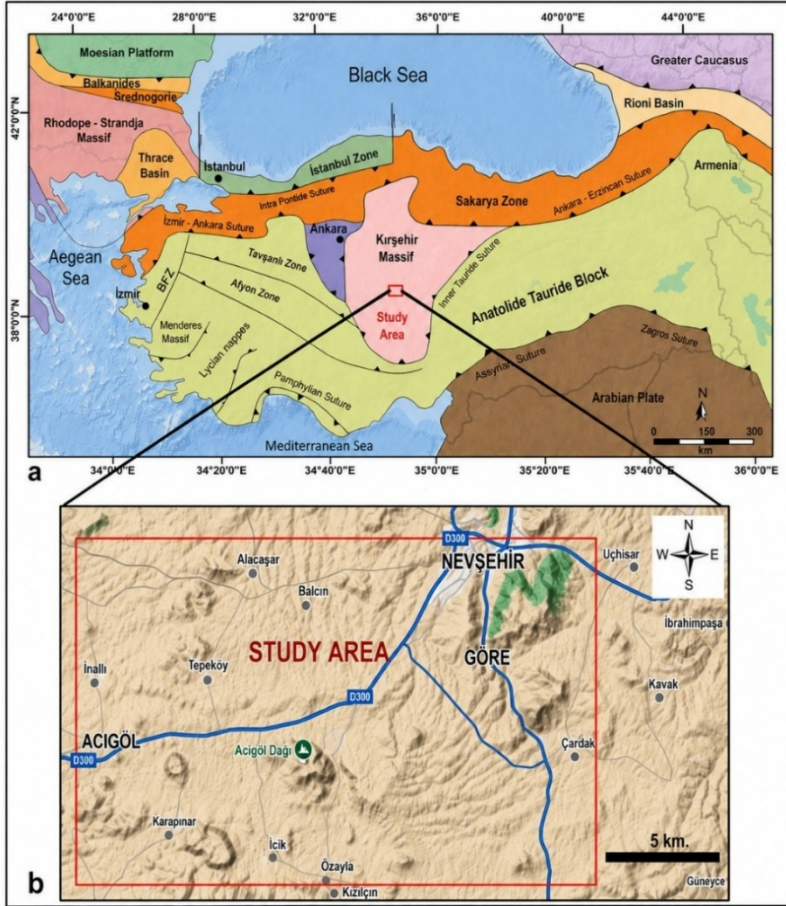


Figure 1. a- Map of tectonic units in Turkey (Modified from Okay and Tüysüz, 1999).b- The study area and its surroundings.

The study area, particularly the graben regions, contains significant water resources. Globally, a large number of studies have been carried out on water and water quality in graben-basin areas. Some of these studies include: (Schuster and Grismer, (2004), Zaidi et al., (2016), Linhoff et al., (2016), Khound and Bhattacharyya, (2018), Hamlat and Guidoum, (2018), Mesele and Mechal, (2020), Nguyen et al., (2020), Fierro et al., (2021),

Ogunribido, (2022), Fentahun et al., (2023), Tesema et al., (2023), Shuaibu et al., (2024). Research on this topic continues intensively to this day. In this study, however, the focus was specifically on the horst-graben structures formed during the neotectonic period and the general geological characteristics of that period.

2. GEOLOGICAL SETTING

2.1. Stratigraphy

Although not exposed in the study area, the Paleozoic–Mesozoic units that form the region’s bedrock consist of metamorphic rocks belonging to the Kırşehir Massif. The oldest units in the study area are those known as the Central Anatolian Ophiolites (Figure 2).

These units are cut through by the late Cretaceous Central Anatolian granitoids. These units form the bedrock in the study area. Overlying these units, in an unconformable relationship, are Late Palaeocene–Eocene sedimentary units (Figure 2).

Overlying these sedimentary units, and also unconformably, are units of volcanic-sedimentary and volcanic origin dating from the Late Miocene to the Quaternary. Over all these units, modern units consisting of slope debris and alluvium are deposited unconformably. Volcanic activity continued into the Quaternary period within the study area and its surroundings. In their study, Innocenti et al. (1975) reported, based on radiometric dating of volcanic rocks in the region, ages of 10.1 ± 1.6 and 5.5 ± 0.2 million years for the lavas, 8.0 ± 1.6 and 7.8 ± 1.6 million years for the tuffs, and 8.6 ± 1.7 and 8.2 ± 1.2 million years for the ignimbrites and stated that volcanic activity began in the Late Miocene. In his 2011 study, Doğan (2011), determined the age of the Gülşehir

basalts, located just to the north of the study area, to be $1,989.4 \pm 38.9$ (ka) thousand years using radiometric dating.

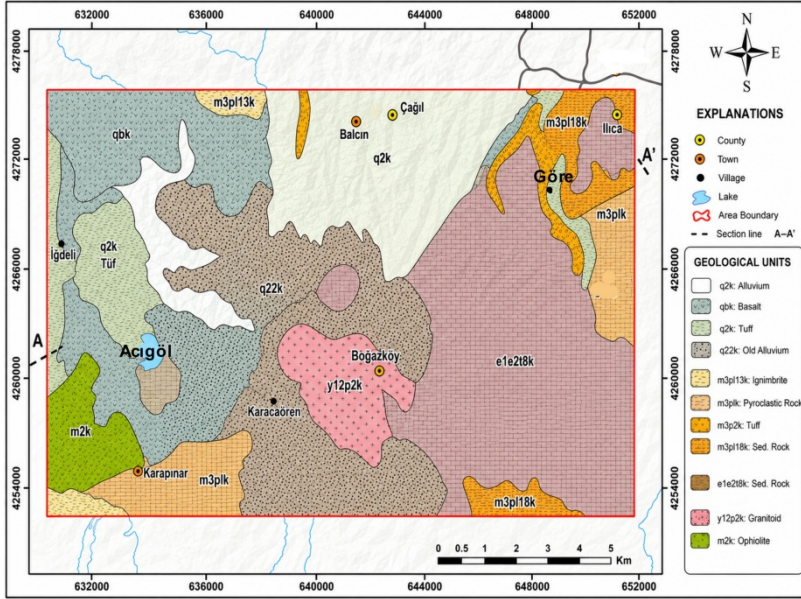


Figure 2. Geological map of Acıgöl-Göre and the surrounding area (Modified from MTA, 2025).

2.2. Structural geology

According to the study by Göncüoğlu et al. (1991), the study area is situated within the region known as the Central Anatolian Crystalline Complex. According to the study by Okay and Tüysüz (1999), this area is referred to as the Kırşehir Massif. This study also states that the study area lies within the Kırşehir Massif. Within the study area (between Acıgöl and Göre), the metamorphic rocks belonging to the Kırşehir Massif are overlain by Late Palaeocene–Eocene-aged sedimentary units and Late Miocene–Quaternary-aged volcano-sedimentary units.

The oldest rocks in the region are metamorphic rocks belonging to the Kırşehir Massif, dating from the Palaeozoic–Mesozoic and having undergone medium-to-high-grade metamorphism. These rocks have undergone multi-stage

deformation and folding under the influence of the Kimmeridgian and Alpine orogenies (Seymen, 1982; Demircioğlu, 2014).

3. MATERIALS AND METHODS

In the study area, prior to conducting this research, previous studies were examined in detail, followed by site reconnaissance and fieldwork. During the fieldwork, particular attention was paid to the examination of rocks and structures dating from the neotectonic period. A relief map of the region was produced. A cross-section illustrating the horst-graben structure of the study area was also prepared.

4. RESULTS

4.1. Neotectonic period in study area

In the study area and its surroundings, a compressional tectonic regime persisted until the Late Miocene. Central Anatolia, which includes the study area, has been under the influence of an extensional tectonic regime since the Late Miocene–Pliocene (Koçyiğit, 2003; Demircioğlu, 2014). Under the influence of the north-east–south-west-trending extensional tectonic regime, horst–graben structures developed in the region and within the study area (Figure 3). Faults formed during this period, particularly normal faults, led to intense volcanism. There are numerous sites in the region where volcanic outcrops of varying sizes have been observed.

The volcanism in the study area and its surroundings is closely linked to tectonic lines and faults. Eruptions of volcanic material have been observed along these faults (Doğan, 2011; Demircioğlu, 2014). In his study (1978), Öngür proposed that there is a large caldera in the vicinity of Acıgöl, that stepped faults are present around the caldera, and that tuffs and ignimbrites

erupted in several phases were caused by these faults, leading to the formation of this caldera.

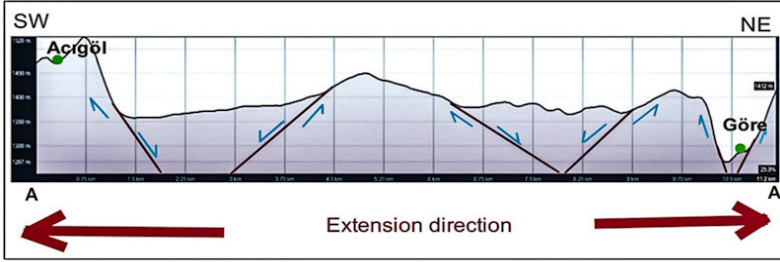


Figure 3. Schematic cross-section of the horst-graben structure between Acıgöl and Göre.

The study area, situated between Acıgöl and Göre, exhibits a horst-graben structure formed during the neotectonic period as a result of an NE–SW-trending extensional tectonic regime. The morphology of the region has been shaped by intense tectonism and the associated effects of volcanism and magmatism (Figure 4a).



Figure 4. Morphological view of the study area and its surroundings.

The higher elevations within the study area consist of volcanic rocks, as well as rocks belonging to the Kırşehir Massif and the Central Anatolian granitoids (Figure 4b).

The region generally has a gentle topography due to the prevalence of fragile volcanic rocks (Figure 5).

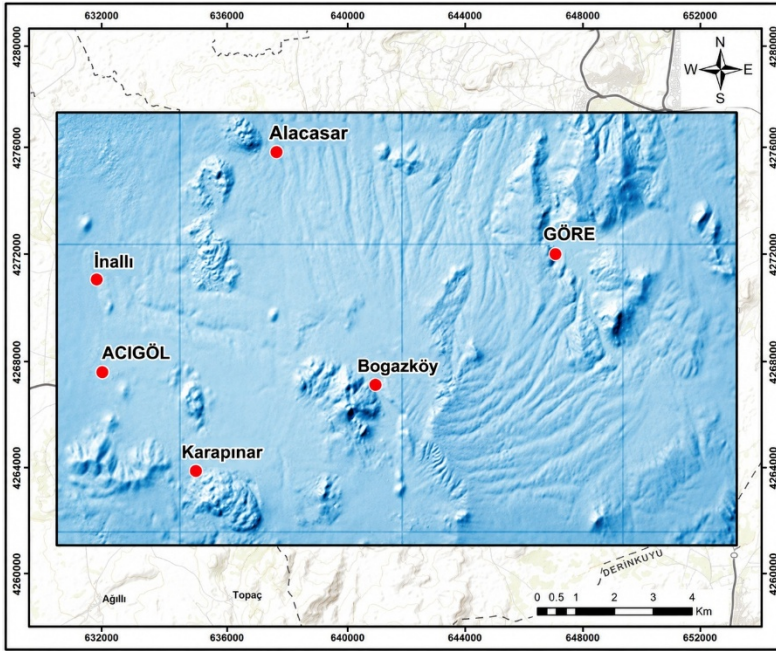


Figure 5. The morphology of Acıgöl-Göre and the surrounding area.

5. CONCLUSION

The study area and its surroundings are situated within the region known as the Cappadocian Volcanic Province. During the neotectonic period—that is, the post-Late Miocene–Pliocene period—this area was subject to an extensional tectonic regime. During this period, intense volcanic activity shaped the morphology of the area. Normal faults, which typically form under an extensional tectonic regime, have also made a significant

contribution to the formation of the morphology. Under the influence of this regime, horst-graben structures have generally formed. The faulting that occurred during this period created the volcanic vent areas. This regime also led to the formation of volcanic rocks of numerous types and varieties. Horst-graben structures have developed in the area around Acıgöl-Göre.

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**YER BİLİMLERİ VE MÜHENDİSLİĞİ ALANINDA
GÜNCEL KONULAR VE
AKADEMİK DEĞERLENDİRMELER**

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yayınları

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