International Journal of Engineering Inventions
e-ISSN: 2278-7461, p-ISSN: 2319-6491
Volume 14, Issue 8 [August 2025] PP: 72-84

Isotope (δ^{13}C, δ^{18}O, δ^{87}Sr/^{86}Sr) Chemostratigraphy of Çaltepe Formation Carbonates (Lower-Middle Cambrian) (Akşehir, Konya, Türkiye)

Ali Müjdat ÖZKAN
Geological Engineering Dept., Faculty of Engineering and Natural Sciences, Konya Technical University, Konya, TÜRKİYE
Corresponding Author: amozkan@ktun.edu.tr. ORCID Code: (0000-0001-6686-327X)

ABSTRACT: *The study area covers an area around the Sultandağları Massif Cankurtaran-Akşehir (Konya) district, located on the northern edge of the central part of the Menderes-Toros block within the Taurus Main Tectonic Unit. The purpose of this study is to reveal the chemostratigraphy of Çaltepe carbonates using carbon ($\delta^{13}C$), oxygen ($\delta^{18}O$), and strontium ($\delta^{87}Sr/^{86}Sr$) isotope values. The base of the Çaltepe Formation limestones is not seen in the study area. However, in the study conducted in the Afyon-Sandıklı area, it was stated that the Çaltepe carbonates overlie the Lower Cambrian Hüdai Formation (consisting of sandstone and siltstone alternation) with a conformable contact. The Mn/Sr ratios of Çaltepe carbonate samples range from 0.73 to 3.44. This indicates that our samples, except for one, are all <3, indicating that they have undergone insignificant diagenetic change and can be used to give accurate results in chemostratigraphy studies. Fe/Sr ratios of the studied samples range from 2.52 to 29. Two samples are low (<5), and eight samples are high, indicating some changes. This view is also consistent with Fe >1000 ppm (except for two samples). In addition, the very weak positive correlation between Fe and Mn also indicates very low diagenetic Fe and Mn enrichment and very low alteration. Four chemozones (C1, C2, C3, C4) were distinguished based on the isotope ($\delta^{13}C$, $\delta^{18}O$, $\delta^{87}Sr/^{86}Sr$) properties of the Çaltepe carbonates. Since the Rb/Sr ratios of the studied samples are <0.5, it indicates sedimentation in arid and hot climates. We predict that the Çaltepe limestones in our study area are a stack that developed in the Toyonian-Kulyumbean time interval. Because the Çaltepe limestones in the study area are tectonically limited by the Seydişehir Formation at their lower limit and are in the position of a discontinuous stack.*

Keywords: *Akşehir, Cankurtaran, Carbonate, Chemostratigraphy, Isotope.*

Date of Submission: 07-08-2025 Date of acceptance: 18-08-2025

I. INTRODUCTION

Türkiye, represented by Thrace in the European continent and Anatolia in the Asian continent, is located in the central part of the Alpine Orogenic Belt between the Balkans and Western Asia (Göncüoğlu et al., 2012). It consisted of the closure of at least three oceanic stands of Neotethys between the continents of Laurasia to the north and Gondwana to the south. During the closure of Neotethys by the counterclockwise rotation of Africa during the Late Mesozoic-Early Tertiary period, oceanic and continental units merged to form a complex mosaic and formed what is now Türkiye (Göncüoğlu et al., 2012; Figure 1).

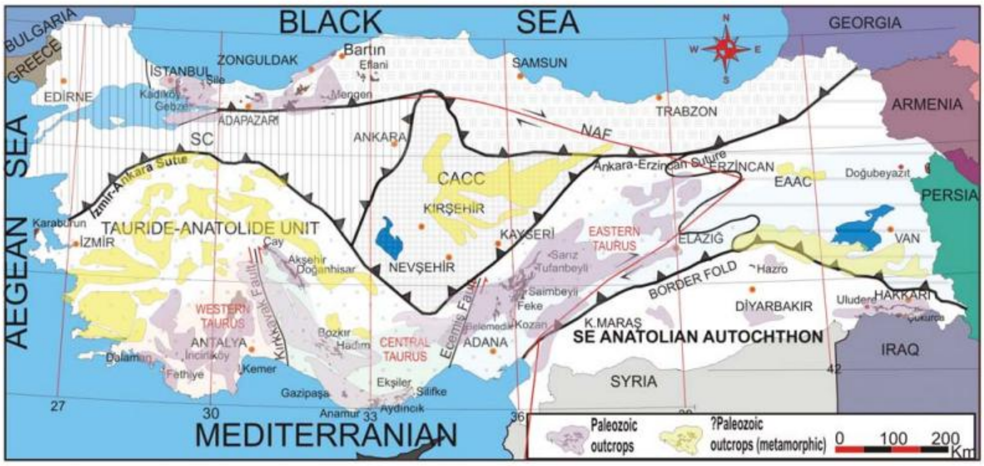

Fig. 1 Dispersion of Paleozoic rocks in the Alpine tectonostratigraphic units of Turkey (from Göncüoğlu et al, 2012)

From north to south these alpine units are: Istranca Terrane with a complex pre-alpine history including the Variscan arc; İstanbul-Zonguldak Mixed Terrane including the Cadomian basement and the Variscan passive margin; Triassic-Cretaceous Intra-Pontide Suture Belt including the remnants of the northernmost Neotethys; Sakarya Mixed Terrane including the Variscan and Cimmerian compounds; İzmir-Ankara-Erzincan Suture Belt including the remnants of the middle branch of Neotethys; Tauride-Anatolide Terrane with a well-developed Paleozoic platform sequence underlying the Cadomian/Pan-African basement and the Mesozoic platform cover; The Amanos-Elazığ-Van-Zagros Suture Belt, the remnants of the southern branch of the Neotethys and the Southeastern Anatolian Autochthonous with well-developed Paleozoic-Mesozoic platform sequences in the northern extension of the Arabian Continent (Göncüoğlu et al, 2012). The presence of at least three pre-alpine orogenic events in the alpine terrains of Türkiye is the Cimmerian, Variscan, and Cadomian/Pan-African events of the continental and oceanic microplates (Göncüoğlu et al., 2012).

The study area covers an area around the Sultandağları Massif Cankurtaran-Akşehir (Konya) district, located on the northern edge of the central part of the Menderes-Toros block within the Taurus Main Tectonic Unit (Figure 2). The purpose of this study is to reveal the chemostratigraphy of Çaltepe carbonates using carbon ($\delta^{13}C$), oxygen ($\delta^{18}O$), and strontium ($\delta^{87}Sr/^{86}Sr$) isotope values. The base of the Çaltepe Formation limestones is not seen in the study area (Figure 3). However, in the study conducted in the Afyon-Sandıklı area, it was stated that the Çaltepe carbonates overlie the Lower Cambrian Hüdai Formation (consisting of sandstone and siltstone alternation) with a conformable contact (Ghienne et al., 2010).

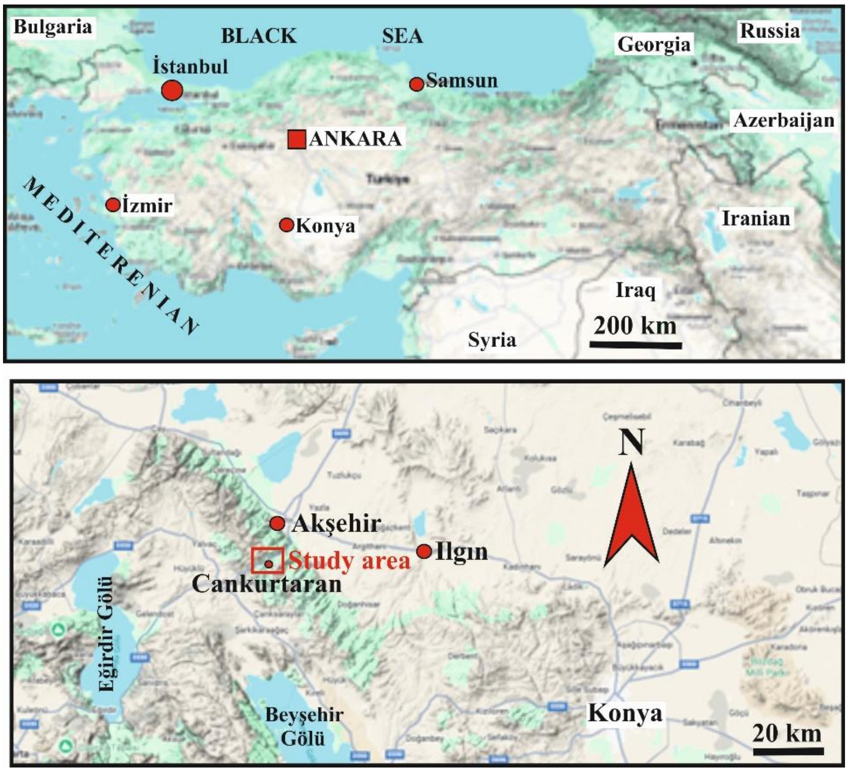

Fig. 2 Location map in the study area (modified from Google Maps)

As noted by Delpomdor and Préat (2013), a very important issue in any study of clastic/carbonate chemostratigraphy is whether the original depositional features are preserved. The Çaltepe carbonates in this study show little change (Mn/Sr ratios range from 0.73 to 3.44; average 1.62) and are suitable for accurate chemostratigraphic studies. Sediments are reliable records of changes in physical, chemical, and biological conditions before, during, and after their deposition, and the changes can be identified through mineralogical and geochemical compositions (Hayashi et al., 1997). Chemostratigraphy is a subject that enables the stratigraphy of the sequences to be revealed based on the elemental and isotopic changes of the geochemical analysis values obtained from sedimentary rocks, and its applicability to sediments of any lithology found in any place and deposited in any environment is an important characteristic of chemostratigraphy. In chemostratigraphy studies, a systematic order can be classified as zones, subzones, sections, subsections, units, and subunits.

Geochemical assessment of post-sedimentation alteration of carbonate rocks is largely based on the relative abundances of Mn, Fe, Rb, and Sr (Brand and Veizer, 1980). Element ratios such as Mn/Sr, Fe/Sr, Ca/Sr, and Rb/Sr are widely used as geochemical criteria to identify the least decomposed carbon, oxygen, and Rb-Sr systems. The strontium isotopic record provides possible constraints on the importance of various factors affecting global weathering, weathering rates and the types of rocks eroded; for example, the relative importance of orogenic events (Edmond, 1992) and glacial activity (Hodell et al., 1989), and putative changes in mid-ocean ridge hydrothermal production (Madhavaraju et al., 2015).

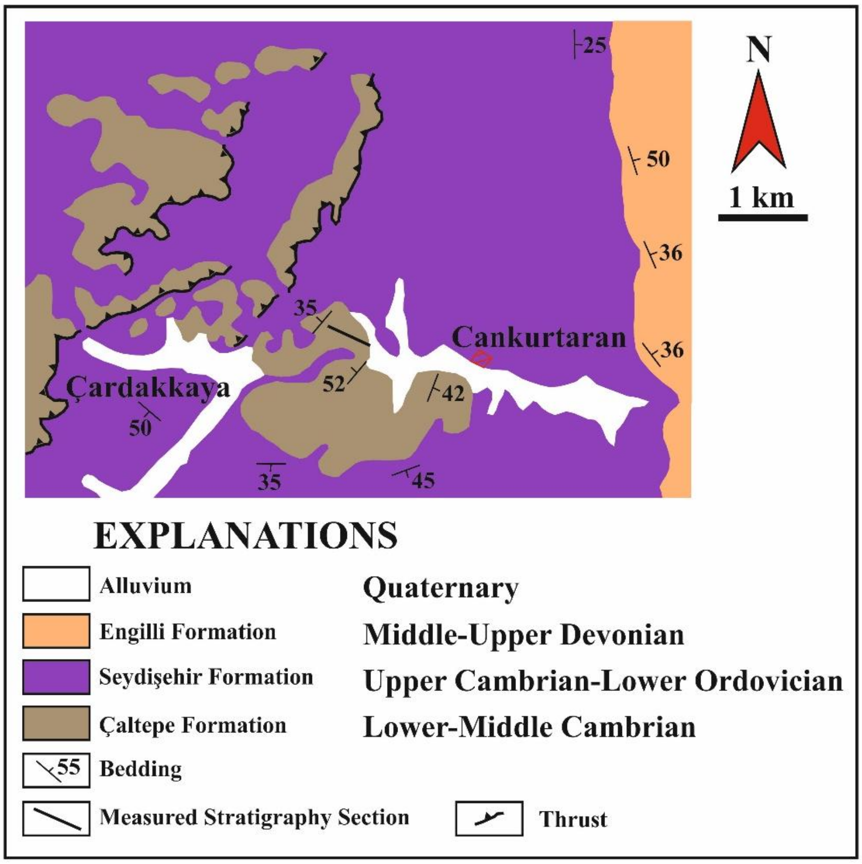

Fig. 3 Geological map in the study area (modified from Özkan & Küpeli, 2017)

The $^{87}Sr/^{86}Sr$ ratio of the modern oceans (0.7092) is a combination of detrital input, mainly from continental erosion (0.7120) and hydrothermal alteration of the oceanic crust (0.7035; Edmond, 1992) (Madhavaraju et al., 2015).

II. MATERIALS AND METHODS

The material of the study consists of Çaltepe Formation limestone and dolomitic limestone. Ten samples (9 limestone and one dolomitic limestone) were collected along a measured stratigraphic section line (Figure 4) from the Early-Middle Cambrian Çaltepe carbonates, washed thoroughly with deionized water to remove surface contaminants, and broken into small pieces to remove visually eroded fragments and altered materials. The dried sample pieces are then ground into powder (<200 mesh) using a vibrating disk mill for geochemical analysis. Approximately 0.12 g of each sample is dissolved in 30% acetic acid using a 10 mL pre-cleaned centrifuge tube at room temperature to prevent dissolution of non-carbonate phases (Hu et al., 2022). The samples are then centrifuged to separate the supernatant from insoluble residues.

Prepared carbonate samples, $\delta^{13}C$ and $\delta^{18}O$ isotope analyses (10 samples) were performed at the UC Davis Stable Isotope Facility Laboratory at California University, USA. $\delta^{87}Sr/^{86}Sr$ isotope analyses (3 samples) were performed at the GEOMAR Helmholtz Centre for Ocean Research Kiel, Germany. The results of these analyses were evaluated and interpreted in various diagrams in accordance purpose of the study.

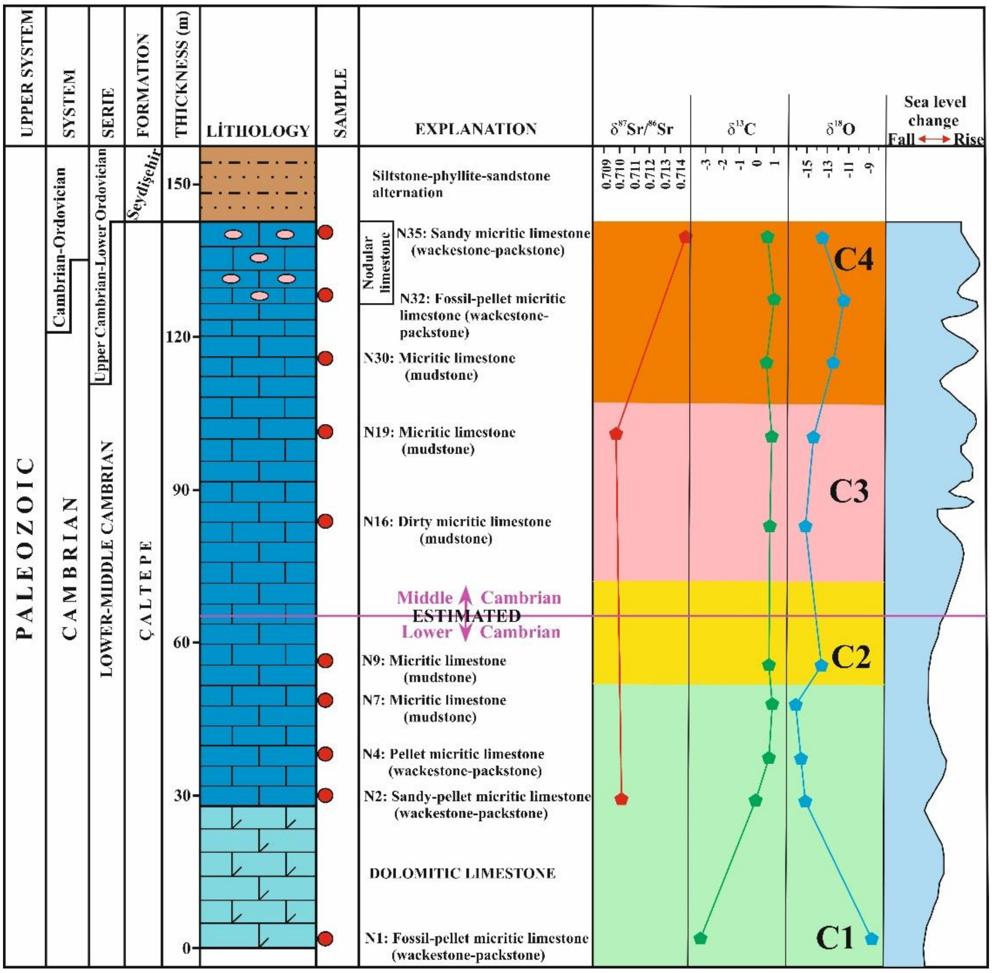

Fig. 4 Measured stratigraphic section of the Çaltepe Formation. (Early to Middle Cambrian sea-level change graph taken from Ogg et al., 2016)

III. RESULTS AND DISCUSSION

In the study area, Çaltepe Formation carbonates form the foundation. While the Seydişehir Formation comes in some areas with conformable contact over Çaltepe carbonates, in some areas, since Çaltepe Formation is located over Seydişehir Formation with tectonic contact, its base is observed as a discontinuous stack (Figure 3).

Çaltepe Formation starts with beige-grey colored, thick-bedded dolomitic limestone in the study area, continues with beige-grey colored, medium-thick bedded limestones towards the top, and ends with pink, thin-medium bedded nodular limestones at the top. The Çaltepe Formation limestones consist of the following microfacies from bottom to top: fossiliferous-pellet micritic dolomitic limestone/wackestone-packstone, sandy-pellet micritic limestone/wackestone-packstone, pelleted micritic limestone/wackestone-packstone, micritic limestone/mudstone, dirty micritic limestone/mudstone, micritic limestone/mudstone, nodular limestone: fossiliferous-pellet micritic limestone/wackestone-packstone and sandy micritic limestone/wackestone-packstone (Figure 4). The microfacies characteristics of the Çaltepe Formation limestones developed in the Early-Middle Cambrian period indicate that they were deposited in a shallow and open marine (carbonate shelf) environment.

The geochemical ($\delta^{13}C$, $\delta^{18}O$, $\delta^{87}Sr/^{86}Sr$ isotope, and some elements) analysis results of Çaltepe carbonates are given in Table 1.

Mn/Sr, Fe/Sr, Rb/Sr, Mg/Ca, Ca/Sr, Fe, and Sr values were used in the evaluation of atmospheric alteration and diagenetic alteration degrees of the Çaltepe Formation carbonate samples (Table 1). The Mn/Sr ratios of Çaltepe carbonate samples range from 0.73 to 3.44 (avg., 1.62) (Table 1). The Fe/Sr ratios of the studied samples range from 2.52 to 29 (avg., 12.15) (Table 1). It is low in two samples (<5) and high in eight samples. The Rb/Sr ratios of the studied samples range from 0.0024 to 0.0814 (avg., 0.0264) (Table 1). The Mg/Ca ratios of the studied samples range from 0.0044 to 0.1841 (avg., 0.0245) (Table 1). The Ca/Sr ratios of the studied samples range from 995 to 4329 (avg., 2058) (Table 1). The Fe values of the studied samples range from 559 to 8393 (avg., 2329) (Table 1). The Sr values of the studied samples range from 70 to 324 (avg., 196) (Table 1). The Mn values of the studied samples range from 77 to 619 (avg., 317) (Table 1).

The $\delta^{13}C$ values of the studied samples range from -3.3 to +1.0 (Table 1). The $\delta^{18}O$ values of the studied samples range from -16.15 to -8.85 (Table 1). The $\delta^{87}Sr/^{86}Sr$ values of the studied samples range from 0.709775 to 0.714308 (Table 1).

Table 1. $\delta^{13}C$, $\delta^{18}O$, $\delta^{87}Sr/^{86}Sr$ isotope values, some element ratios, and element values (ppm) of the Çaltepe Formation carbonates

Sample	$\delta^{13}C$	$\delta^{18}O$	$\delta^{87}Sr/^{86}Sr$	Mn/Sr	Fe/Sr	Rb/Sr	Mg/Ca	Ca/Sr	Fe	Sr	Mn
N35	0.69	-13.53	0.714308	1.43	25.9	0.0651	0.0114	995	8393	324	465
N32	1.00	-11.49		1.18	24.0	0.0543	0.0078	1714	4756	197	232
N30	0.66	-12.46		1.60	11.9	0.0371	0.0075	1856	2308	194	310
N19	0.97	-14.35	0.709775	1.84	6.24	0.0024	0.0044	2387	1049	168	310
N16	0.88	-15.13		0.73	2.65	0.0028	0.0054	1899	559	211	155
N9	0.70	-13.71		1.74	2.52	0.0036	0.0060	1797	559	222	387
N7	0,96	-16.15		1.65	5.58	0.0069	0.0076	1612	1049	188	310
N4	0,71	-15.73		1.53	5.17	0.0064	0.0061	1905	1049	203	310
N2	-0.02	-15.17	0.710510	3.44	8.55	0.0044	0.0051	2089	1539	180	619
N1	-3.30	-8.85		1.10	29.0	0.0814	0.1841	4329	2028	70	77

The binary diagrams of $\delta^{13}C$, $\delta^{18}O$, $\delta^{87}Sr/^{86}Sr$, Mn/Sr, Fe/Sr, Ca/Sr, Mg/Ca, Rb/Sr, and Sr of the Çaltepe Formation carbonate samples are given in Table 2. In Table 2, strong to very strong positive/negative correlations are observed among some parameters, while other parameters show moderate to weak to very weak positive/negative correlations.

Table 2. Correlation of some isotopes and elements of Çaltepe carbonate samples. Green color: strong-very strong positive correlation, red color: strong-very strong negative correlation

	$\delta^{13}C$	$\delta^{18}O$	$\delta^{87}Sr/^{86}Sr$	Mn/Sr	Fe/Sr	Ca/Sr	Mg/Ca	Rb/Sr	Sr
$\delta^{13}C$	1								
$\delta^{18}O$	-0.71	1							
$\delta^{87}Sr/^{86}Sr$	0.09	0.78	1						
Mn/Sr	0.07	-0.34	-0.54	1					
Fe/Sr	-0.55	0.80	0.99	-0.25	1				
Ca/Sr	-0.90	0.64	-0.99	-0.10	0.32	1			
Mg/Ca	-0.97	0.76	0.99	-0.26	0.60	0.89	1		
Rb/Sr	-0.59	0.85	0.99	-0.37	0.97	0.35	0.66	1	
Sr	0.70	-0.45	0.99	-0.01	-0.09	-0,90	-0.70	-0.11	1

Four chemozones (C1, C2, C3, C4) were distinguished based on the isotope ($\delta^{13}C$, $\delta^{18}O$, $\delta^{87}Sr/^{86}Sr$) properties of the Çaltepe carbonates (Figure 4). In Chemozone C1, the $\delta^{13}C$ isotope value shows a continuous increase, while, conversely, the $\delta^{18}O$ isotope value shows a continuous decrease (Figure 4). No increase or decrease is observed in the $\delta^{87}Sr/^{86}Sr$ isotope value (Figure 4). In Chemozone C1, the Sr value first increases and then decreases, the Fe value continuously decreases, and the Mn value first increases and then decreases (Table 1).

In Chemozone C2, the $\delta^{13}C$ isotope value shows a slight decrease, the $\delta^{18}O$ isotope value shows a significant increase, and the $\delta^{87}Sr/^{86}Sr$ isotope value shows a slight decrease (Figure 4). In this zone, Sr increases, Fe decreases, and Mn increases (Table 1).

In Chemozone C3, the $\delta^{13}C$ isotope value is initially stable and then slightly decreases, the $\delta^{18}O$ isotope value first decreases and then increases, and the $\delta^{87}Sr/^{86}Sr$ isotope value increases (Figure 4). In this zone, the Sr value first increases and then decreases, the Fe value increases, and the Mn value first decreases and then increases (Table 1).

In Chemozone C4, the δ^{13}C isotope value decreases-increases-decreases, the δ^{18}O isotope value first increases and then decreases, and the δ^{87}Sr/^{86}Sr isotope value increases (Figure 4). In this zone, the Sr value continuously increases, the Fe value continuously increases, and the Mn value continuously increases (Table 1).

IV. DISCUSSION

Post-depositional diagenetic processes generally result in Mn and Fe enrichment and Sr depletion in carbonates with high ^{87}Sr/^{86}Sr ratios (Halverson et al., 2007; Hu et al., 2022) because Mn and Fe have larger partition coefficients and can be preferentially incorporated into carbonate from diagenetic fluids (Kaurova et al., 2010; Hu et al., 2022). Therefore, diagenetically altered carbonates can theoretically be expected to have lower [Sr] than the primary phase and hence higher [Mn] and [Fe] with higher Mn/Sr and Fe/Sr ratios (Halverson et al., 2007; Hu et al., 2022). Therefore, a comprehensive study of [Mn], [Sr], and [Fe] as well as ^{87}Sr/^{86}Sr is useful to evaluate the intensity of post-depositional change in the original ^{87}Sr/^{86}Sr of carbonates (Kaurova et al., 2010; Hu et al., 2022). Previous studies have used [Sr], [Mn], [Fe], Mn/Sr, and Fe/Sr values as geochemical criteria to identify the least altered carbonates (Hu et al., 2022). For instance, Burke et al. (1982) plotted the Phanerozoic ^{87}Sr/^{86}Sr curve using bulk carbonates with [Sr] >200 ppm, and Denison et al. (1994) utilized values of [Sr] >900 ppm, [Mn] <300 ppm, and Mn/Sr <0.5 for Late Paleozoic shelf carbonates. Edwards et al. (2015) analyzed the paired ^{87}Sr/^{86}Sr of well-preserved conodont apatite and bulk carbonates from the Ordovician and indicated that the original seawater ^{87}Sr/^{86}Sr could be faithfully recorded in bulk carbonate with [Sr] >300 ppm, and Wang et al. (2018) emphasized that samples with [Mn] <300 ppm, [Fe] <1000 ppm, and Mn/Sr <1 could preserve Permian seawater ^{87}Sr/^{86}Sr signals. When Fe/Sr ratios are included, Kuznetsov et al. (2003) suggested that carbonates are likely to preserve the primary Sr isotopic composition if Mn/Sr <0.2 and Fe/Sr <5. Collectively, [Sr] >300 ppm, [Mn] <300 ppm, [Fe] <1000 ppm, Mn/Sr <0.2, and Fe/Sr <1.6 can be interpreted as more serious and more stringent geochemical criteria for Sr isotope preservation in Ordovician carbonate rocks (Hu et al., 2022).

Kaufman and Knoll (1995) stated that limestones and dolostones with Mn/Sr ratios <10 generally preserve the primary δ^{13}C isotope signatures of seawater during deposition. The Mn/Sr ratios of Çaltepe carbonate samples range from 0.73 to 3.44 (avg., 1.62) (Table 1). This indicates that our samples, except for one, are all <3, indicating that they have undergone insignificant diagenetic change and can be used to give accurate results in chemostratigraphy studies.

Fe/Sr ratios of the studied samples range from 2.52 to 29 (avg., 12.15) (Table 1). Two samples are low (<5), and eight samples are high, indicating some changes. This view is also consistent with Fe >1000 ppm (except for two samples) (Table 1). In addition, the very weak positive correlation between Fe and Mn (r = 0.21; Table 2) also indicates very low diagenetic Fe and Mn enrichment and very low alteration.

The Mg/Ca value of >0.4 indicates diagenetic alteration (Halverson et al., 2007). Since Mg/Ca values in our Çaltepe carbonate samples are <0.4, they indicate insignificant diagenetic alteration. Furthermore, calcite components with Sr/Mn ratios between 2 and 5 and dolomites with Sr/Mn <10 have high ^{87}Sr/^{86}Sr values, which contradict the general trend and indicate diagenetic change of ^{87}Sr/^{86}Sr values (Montanez et al., 1996). Sr/Mn values of the Çaltepe carbonates vary between 0.29 and 1.36 (avg., 0.71), indicating insignificant diagenetic alteration in ^{87}Sr/^{86}Sr isotope values. Again, the low Sr values of Çaltepe carbonate samples indicate diagenetic alteration.

Limestones and dolostones are considered unaltered if Rb/Sr <0.01 (Bartley et al., 2001). The Rb/Sr values of the Çaltepe carbonates are >0.01 in four samples and <0.01 in six. This suggests that most samples have undergone minor alteration and are suitable for chemostratigraphic studies. Additionally, Rb/Sr ratios >0.5 indicate humid climate conditions, while <0.5 represents arid climate conditions (Zou et al., 2021). The Rb/Sr values of the Çaltepe carbonate samples are <0.5 (0.0024 to 0.0814, mean 0.0264; Table 1), indicating deposition in an arid climate.

Global-scale carbon isotope deviations may be related to marine biological evolution events or, consequently, to changes in the marine depositional environment (Zhu et al., 2006; Ding et al., 2020). In this context, positive δ^{13}Ccarb deviations are commonly explained as the result of increased marine primary productivity and/or the burial of large amounts of organic matter, while negative δ^{13}Ccarb deviations may be related to biocrisis or extensive oxidation of buried organic matter (Zhu et al., 2006). Additionally, carbon isotope offsets are also driven by long-term sea level fluctuations, seafloor uplift, or methane emissions (Chen et al., 2022), as positive δ^{13}Ccarb offsets always correspond to sea level rises (Stephens and Sumner, 2003), and negative δ^{13}Ccarb offsets generally correspond to sea level falls that trigger hydrate disequilibrium (Zuo et al., 2023).

When there is net storage of organic matter on a global scale, the δ^{13}C value of dissolved inorganic carbon in the ocean increases. When there is net oxidation of organic matter on a global scale, the δ^{13}C value of dissolved inorganic carbon in the ocean decreases (Maslin and Swann, 2005).

The δ^{13}Ccarb values observed in the Çaltepe carbonate samples are eight positive and two negative (Table 1). Therefore, sea level changes occurred during the deposition of the Çaltepe carbonates. This is consistent with the Early-Late Cambrian sea-level change curve given by Ogg et al. (2016) in Figure 4. The -3.30 δ^{13}C isotope value observed in the dolomitic limestone sample in the C1 chemozone suggests that organic matter is enriched at this level (Table 1; Figure 4). The -0.02 negative δ^{13}C isotope value in the C1 chemozone indicates that the organic matter in the limestone at this level is very low (Table 1; Figure 4). Similarly, the two positive δ^{13}C isotope values in the C1 chemozone (0.71 and 0.96) indicate that the organic matter is not enriched at this level either (Table 1; Figure 4).

The slightly decreasing positive δ^{13}C isotope value in the C2 chemozone (0.70) demonstrates that the organic matter is not enriched at this level either (Table 1; Figure 4). The two positive δ^{13}C isotope values (0.88 and 0.97) in the C3 chemozone, which exhibit a slight and continuous increase, indicate that the organic matter is not enriched at this level, is not oxidized, and the water level continues to rise (Table 1; Figure 4). The three positive δ^{13}C isotope values (0.66, 1.0, and 0.97) in the C4 chemozone exhibiting a decrease-increase-decrease indicate that the organic matter is not enriched at this level, is not oxidized, and the water level continues to rise (Table 1; Figure 4).

Diagenesis can result in slightly decreased δ^{13}C values, significantly decreased δ^{18}O values, and possibly elevated $^{87}Sr/^{86}Sr$ values (Derry et al., 1994). The δ^{13}C signature is more conservative than the δ^{18}O signature in its response to subsequent diagenesis, so δ^{18}O values can be an effective proxy for defining diagenesis (Kaufman et al., 1991; Veizer et al., 1999). It is generally believed that δ^{18}O values lower than around -10‰ indicate that the samples have undergone strong diagenetic alteration, and that oxygen and carbon isotope values are no longer reliable (Derry et al., 1994). However, since Phanerozoic seawater has an initial δ^{18}O value of -8‰ and Cambrian seawater has δ^{18}O values ranging from -10‰ to -7‰ (Veizer et al., 1999¸Montañez et al., 2000), it can be concluded that carbonate rocks may still retain a primary environmental signal even with δ^{18}O values lower than -10‰. The δ^{18}O isotope values of the Çaltepe carbonate samples range from -16.15 to -8.85, indicating low diagenetic alteration and are suitable for use in chemostratigraphic studies (Table 1).

The different responses of δ^{13}C and δ^{18}O signatures to diagenesis allow these relationships to be used to distinguish carbonate samples that have undergone diagenetic changes (Burdett et al., 1990; Frank et al., 1997). If there is no positive correlation between δ^{13}C and δ^{18}O values in marine carbonate samples, it can be concluded that they have retained their original carbon and oxygen isotopic signatures (Derry et al., 1994; Veizer et al., 1999). The strong negative correlation (r = -0.71) observed between δ^{13}C and δ^{18}O in Figure 5 indicates that the δ^{13}C isotope values of the Çaltepe samples are not altered, but the δ^{18}O isotope values are relatively affected by alteration. Furthermore, the strong positive correlation observed between δ^{18}O and $^{87}Sr/^{86}Sr$ isotope values (r = 0.78) also indicates that the Çaltepe carbonates were affected by diagenetic alteration (Figure 6).

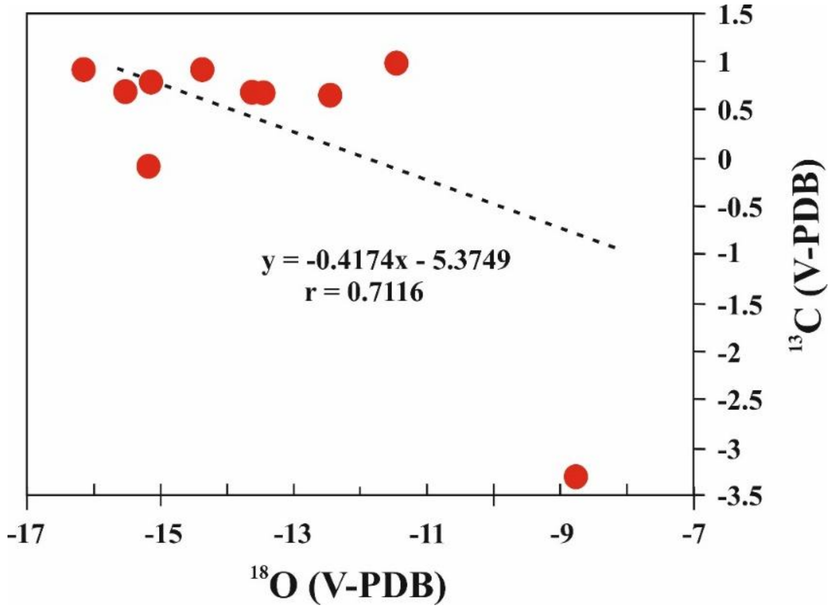

Fig. 5 Diagram of $\delta^{18}O$ versus $\delta^{13}C$

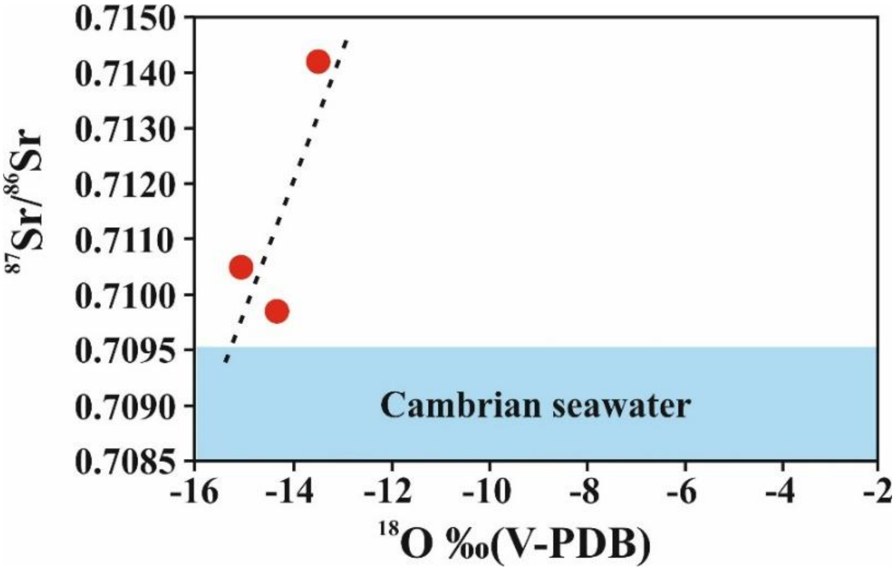

Fig. 6 Diagram of $\delta^{18}O$ versus $^{87}Sr/^{86}Sr$ (r = 0.78)

The $\delta^{18}O$ isotope values of the Çaltepe carbonate samples in the C1 chemozone first show a significant (-8.85), then a slight (-15.17, -15.73, and -16.15) continuous decrease (Table 1; Figure 4). The $\delta^{18}O$ isotope values of Çaltepe carbonate samples in the C2 chemozone first display a significant increase (from -16.15 to -13.71) and then a significant decrease (from -13.71 to -15.13; Table 1; Figure 4). The $\delta^{18}O$ isotope values of the Çaltepe carbonate samples in the C3 chemozone demonstrate a significant decrease first and then a significant increase (from -15.13 to -14.35; Table 1; Figure 4). The $\delta^{18}O$ isotope values of Çaltepe carbonate samples in the C4 chemozone first increase (from -12.46 to -11.49) and then decrease (from -11.49 to -13.53; Table 1; Figure 4).

Diagenesis can generally result in elevated $^{87}Sr/^{86}Sr$ values (Derry et al., 1994). The very strong positif correlation between $^{87}Sr/^{86}Sr$ and ^{18}O (r = 0.78), Fe/Sr (r = 0.99), Mg/Ca (r = 0.99), Rb/Sr (r = 0.99), and Sr (r = 0.99) indicate the exposure of a very strong positive diagenetic alteration (enrichment and/or impoverishment) (Table 2). While $^{87}Sr/^{86}Sr$ and Ca/Sr (r = -0.99), a very strong negative correlation is observed, no relationship is observed between ^{13}C (r = 0.09) (Table 2; Figure 7). A moderate negative correlation is observed between $^{87}Sr/^{86}Sr$ and Mn/Sr (r = -0.54; Table 2). Additionally, a very strong positive correlation as well as some diagenetic alteration is seen in the $^{87}Sr/^{86}Sr$ versus Sr diagram (Figure 8). The $^{87}Sr/^{86}Sr$ value is low in chemozone C1, decreasing slightly until chemozone C3 and showing a very pronounced increase in chemozone C4 (Table 1; Figure 4). In addition, the $^{87}Sr/^{86}Sr$ values are higher (0.7097 to 0.7143) than the Cambrian seawater values (0.7085 to 0.7095), indicating some diagenetic enrichment (Table 1; Figures 4, 6-8).

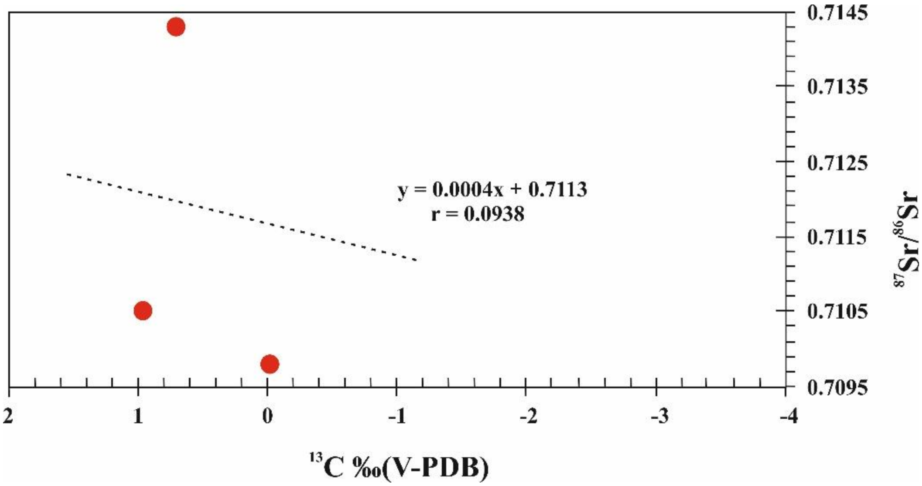

Fig. 7 Diagram of $\delta^{13}C$ versus $^{87}Sr/^{86}Sr$

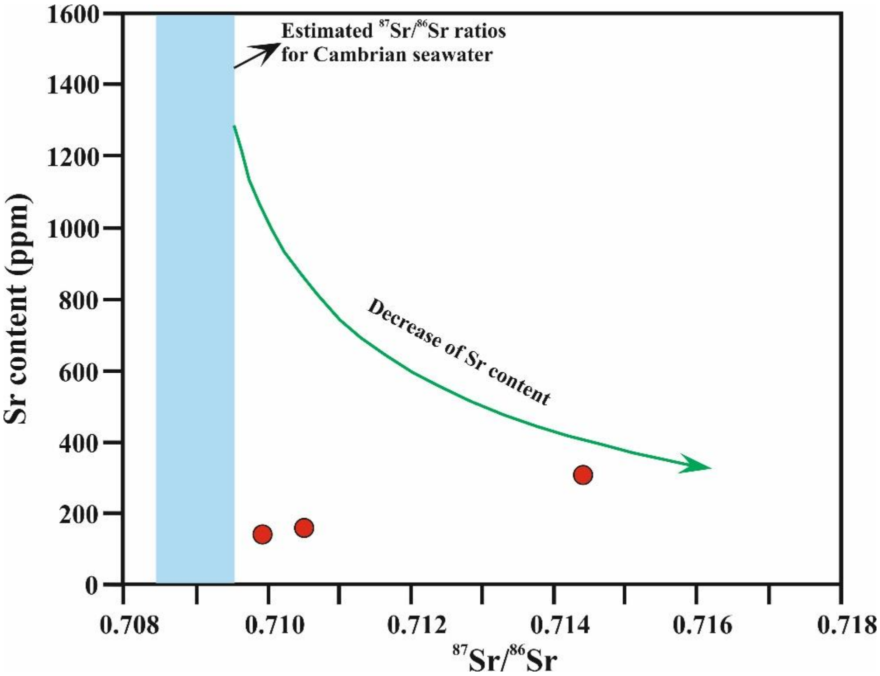

Fig. 8 Diagram of Sr versus $^{87}Sr/^{86}Sr$

The strontium isotopic composition of seawater is determined by the balance between radioactive Sr delivered to the oceans primarily by continental erosion (global mean river $^{87}Sr/^{86}Sr$ 0.7119; Palmer and Edmond, 1989; Qing et al., 1998) and relatively nonradioactive Sr released by mid-ocean ridge hydrothermal systems (approximately $^{87}Sr/^{86}Sr$ 0.7035; Palmer and Elderfield, 1985; Qing et al., 1998). An increase in the rate of continental erosion would theoretically increase the $^{87}Sr/^{86}Sr$ ratio of seawater, while an increase in hydrothermal activity would have the opposite effect (Qing et al., 1998). Continuous changes in the strontium isotopic values of seawater over geological time are mainly caused by the increase and decrease of Sr mass and/or isotope fluxes from these two sources. The observed linear correlations between $^{87}Sr/^{86}Sr$ and 1/Sr and Sr/Ca in the Çaltepe carbonate samples (r = -0.99 and r = 0.99, respectively; Figure 9) indicate that $^{87}Sr/^{86}Sr$ is related to salinity and that there is a mixing of freshwater and marine saltwater brought to the sea by rivers (e.g., Höpker et al., 2022).

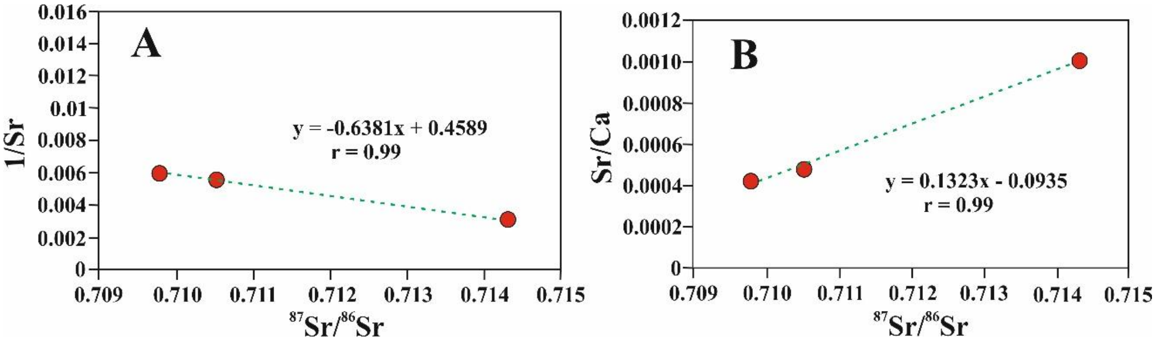

Fig. 9 Diagram of $^{87}Sr/^{86}Sr$ versus 1/Sr (A) and Sr/Ca (B)

We predict that the Çaltepe carbonates are a sequence developed in the Toyonian-Kulyumbean time interval. Çaltepe carbonates in the study area have a tectonic boundary (thrust) with the Seydişehir Formation at their lower limit and are in the position of a discontinuous underlying sequence (Figure 10).

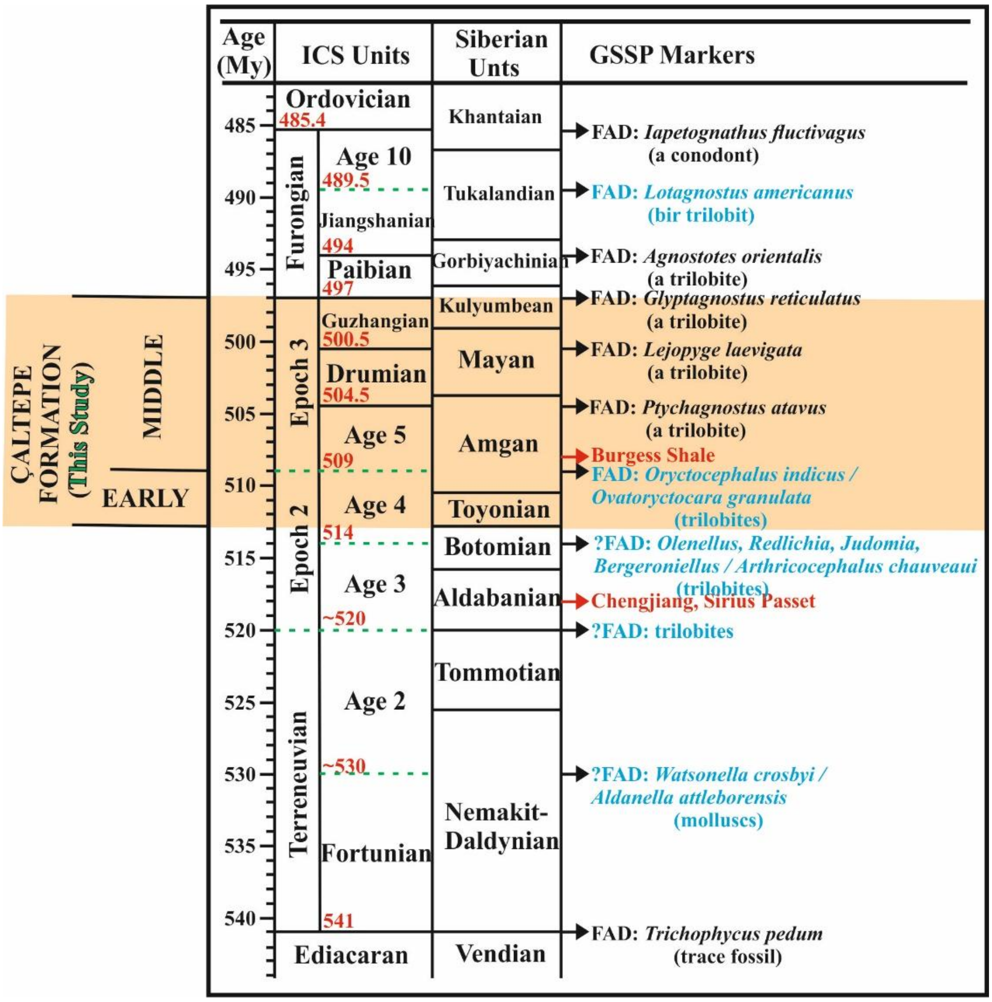

Fig. 10 Estimated deposition process of the discontinuous Çaltepe carbonates in the study area (modified from Ogg et al., 2016)

V. CONCLUSION

Chemostratigraphic features of the Çaltepe Formation carbonates (Lower-Middle Cambrian) in the Konya-Akşehir district of Türkiye were determined based on isotope geochemistry. The main results are given below:

1. The Mn/Sr ratios of Çaltepe carbonate samples range from 0.73 to 3.44 (avg., 1.62) (Table 1). This indicates that our samples, except for one, are all <3, indicating that they have undergone insignificant diagenetic change and can be used to give accurate results in chemostratigraphy studies.
2. The Rb/Sr values of the Çaltepe carbonates are >0.01 in four samples and <0.01 in six. This suggests that most samples have undergone minor alteration and are suitable for chemostratigraphic studies. The Rb/Sr values of the Çaltepe carbonate samples are <0.5 (0.0024 to 0.0814, mean 0.0264; Table 1), indicating deposition in an arid climate.
3. Fe/Sr ratios of the studied samples range from 2.52 to 29 (avg., 12.15) (Table 1). Two samples are low (<5), and eight samples are high, indicating some changes. This view is also consistent with Fe >1000 ppm (except for two samples).
4. The δ^{13}Ccarb values observed in the Çaltepe carbonate samples are eight positive and two negative (Table 1). Therefore, sea level changes occurred during the deposition of the Çaltepe carbonates. This is consistent with the Early-Late Cambrian sea-level change curve given by Ogg et al. (2016).
5. Four chemozones were identified from the Çaltepe carbonates based on δ^{13}C, δ^{18}O, and ^{87}Sr/^{86}Sr isotope values.
6. The observed linear correlations between ^{87}Sr/^{86}Sr and 1/Sr and Sr/Ca in the Çaltepe carbonate samples indicate that ^{87}Sr/^{86}Sr is related to salinity and that there is a mixing of freshwater and marine saltwater brought to the sea by rivers.
7. The δ^{18}O isotope values of the Çaltepe carbonate samples range from -16.15 to -8.85, indicating low diagenetic alteration and are suitable for use in chemostratigraphic studies.

8. The strong positive correlation observed between δ^{18}O and ^{87}Sr/^{86}Sr isotope values (r = 0.78) also indicates that the Çaltepe carbonates were affected by diagenetic alteration.
9. The strong negative correlation observed between δ^{13}C and δ^{18}O (r = -0.71) indicates that the δ^{13}C isotope values of the Çaltepe samples remained unchanged, but the δ^{18}O isotope values were relatively affected by the alteration.
10. I predict that the Çaltepe carbonates are a sequence developed in the Toyonian-Kulyumbean time interval. Because Çaltepe carbonates in the study area have a tectonic boundary (thrust) with the Seydişehir Formation at their lower limit and are in the position of a discontinuous underlying sequence.

ACKNOWLEDGEMENTS

This study was supported by Selçuk University Scientific Research Projects Coordination Office with project number 14401127. The researcher would like to thank the Selcuk University BAP Coordination Office. The researcher would also like to thank Prof. Dr. Şuayip Küpeli for his help during the field and office work.

REFRENCES

[1]. Bartley JK, Semikhatov MA, Kaufman AJ, et al. 2001. Global Events across the Mesoproterozoic-Neoproterozoic boundary: C and Sr isotopic evidence from Siberia. Precambrian Res., 111(1-4), 165-202.

[2]. Brand U, Veizer J 1980. Chemical diagenesis of a multicomponent carbonate system-1: Trace elements. Journal of Sedimentary Petrology, 50, 1219-1236.

[3]. Burdett JW, Grotzinger JP, Arthur MA 1990. Did major changes in the stable-isotope composition of Proterozoic seawater occur? Geology, 18: 227-230.

[4]. Burke WH, Denison RE, Hetherington EA, Koepnick RB, Nelson HF, Otto JB 1982. Variation of seawater ^{87}Sr/^{86}Sr throughout Phanerozoic time. Geology, 10(10), 516–519.

[5]. Chen X, Zhou Y, Shields GA 2022. Progress towards an improved Precambrian seawater ^{87}Sr/^{86}Sr curve. Earth-Science Reviews, 224, 103869.

[6]. Delpomdor F, Préat A 2013. Early and late Neoproterozoic C, O, and Sr isotope chemostratigraphy in the carbonates of West Congo and Mbuji-Mayi supergroups: A preserved marine signature? Palaeogeography, Palaeoclimatology, Palaeoecology, 389, 35-47.

[7]. Denison RE, Koepnick RB, Fletcher A, Howell MW, Callaway WS 1994. Criteria for the retention of original seawater ^{87}Sr/^{86}Sr in ancient shelf limestones. Chemical Geology, 112(1-2), 131–143.

[8]. Ding W, Hou D, Jiang L, Jiang Y, Wu P 2020. High abundance of carotanes in the brackish-saline lacustrine sediments: A possible cyanobacteria source? International Journal of Coal Geology, 219, 103373.

[9]. Derry LA, Brasier MD, Corfield RM, Rozanov AY, Zhuravlev AY 1994. Sr and C isotopes in Lower Cambrian carbonates from the Siberian craton: a paleoenvironmental record during the 'Cambrian explosion'. Earth and Planetary Science Letters, 128, 671-681.

[10]. Edmond J 1992. Himalayan tectonics, weathering processes, and strontium isotope record in marine limestones. Science, Washington, 258, 1594-1597.

[11]. Edwards CT, Saltzman MR, Leslie SA, Bergström SM, Sedlacek ARC, Howard A, Bauer JA, Sweet WC, Young SA 2015. Strontium isotope (^{87}Sr/^{86}Sr) stratigraphy of Ordovician bulk carbonate: Implications for preservation of primary seawater values. Geological Society of America Bulletin, 127(9-10), 1275–1289.

[12]. Frank TD, Lyons TW, Lohmann KC 1997. "Isotopic Evidence for the Paleoenvironmental Evolution of the Mesoproterozoic Helena Formation, Belt Supergroup, Montana," Geochim. Cosmochim. Acta 61(23), 5023– 5041.

[13]. Ghienne JF, Monod O, Kozlu H, Dean WT 2010. Cambrian–Ordovician depositional sequences in the Middle East: A perspective from Turkey. Earth Sci Rev., 101, 101-146.

[14]. Göncüoğlu MC, Elicki O, Kozlu H, Gürsu S 2012. Cambrian. Paleozoic of northern Gondwana and its petroleum potential: a field workshop. Turkish Association of Petroleum Geologists, Special Publication, 7, 22-41.

[15]. Halverson GP, Dudás FÖ, Maloof AC, Bowring SA 2007. Evolution of the ^{87}Sr/^{86}Sr composition of Neoproterozoic seawater. Palaeogeography, Palaeoclimatology, Palaeoecology, 256(3–4), 103–129.

[16]. Hayashi K, Fujisawa H, Holland H, Ohmoto H 1997. Geochemistry of ∼1.9 Ga sedimentary rocks from northeastern Labrador, Canada. Geochimica et Cosmochimica Acta, 61(19), 4115-4137.

[17]. Hodell DA, Mead GA, Mueller PA 1989. Variation in the strontium isotopic composition of seawater (8 Ma to present): Implications for chemical weathering rates and dissolved fluxes to the oceans. Chemical Geology: Isotope Geoscience Section, 80, 291-307.

[18]. Höpker SN, Wu HC, Lucassen F, Sadio O, Brochier T, Nuworkpor IY, Kasemann SA, r Merschel P, Westphal H 2022. Sr Isotope Ratios (^{87}Sr/^{86}Sr) in Water and Fish Otoliths as Estuarine Salinity Tracers: Case Studies from Three NW African Rivers. Estuaries and Coasts, 45, 1780–1802.

[19]. Hu D, Li D, Zhou L, Sun L, Xu Y 2022. Diagenetic effects on strontium isotope (^{87}Sr/^{86}Sr) and elemental (Sr, Mn, and Fe) signatures of Late Ordovician carbonates. JUSTC, 53(5): 0503.

[20]. Kaufman AJ, Hayes JM, Knoll AH, Germs GJB 1991. Isotopic compositions of carbonates and organic carbon from upper Proterozoic successions in Namibia: stratigraphic variation and the effects of diagenesis and metamorphism. Precambrian Res., 49, 301-327.

[21]. Kaufman AJ, Knoll AH 1995. "Neoproterozoic Variations in the C-Isotopic Composition of Seawater: Stratigraphic and Biogeochemical Implications," Precambrian Res. 73(1-4), 27–49.

[22]. Kaurova OK, Ovchinnikova GV, Gorokhov IM 2010. U-Th-Pb systematics of Precambrian carbonate rocks: Dating of the formation and transformation of carbonate sediments. Stratigraphy and Geological Correlation, 18(3), 252–268.

[23]. Kuznetsov AB, Semikhatov MA, Gorokhov IM, Mel'nikov NN, Konstantinova GV, Kutyavin EP 2003. Sr isotopic composition in carbonates of the Karatau Group, southern Urals, and standard curve of ^{87}Sr/^{86}Sr variations in the Late Riphean ocean. Stratigraphy and Geological Correlation, 11(5), 415–449.

[24]. Madhavaraju J, Scott RW, Sooriamuthu R 2015. Facies, biostratigraphy, diagenesis, and depositional environments of Lower Cretaceous strata, Sierra San José section, Sonora (Mexico). Carnets de Géologie [Notebooks on Geology], 15, 103-122.

[25]. Maslin MA, Swann GEA 2005. Isotopes in marine sediments. In: Leng MJ (ed.), Isotopes in Paleoenvironmental Research. Springer, Dordrecht, Netherlands, pp. 227-290.

[26]. Montañez IP, Banner JL, Osleger DA, Borg LE, Bosserman PJ 1996. Integrated Sr isotope variations and sea-level history of Middle to Upper Cambrian platform-carbonates: implications for the evolution of Cambrian seawater 87Sr/86Sr. Geology, 24(10), 917–920.

[27]. Montañez IP, Osleger DA, Banner JL, Mack LE, Musgrove M 2000. Evolution of the Sr and C isotope composition of Cambrian oceans. GSA Today 10, 1e7.

[28]. Ogg JG, Ogg GM, Gradstein FM 2016. A Concise Geologic Time Scale. Elsevier, Cambridge, USA., p. 42.

[29]. Özkan, A. M. ve Küpeli, Ş., 2017. Sultandağları masifinde (Konya-Isparta) Kambro-Ordovisiyen yaşlı Çaltepe ve Seydişehir formasyonlarının C, O, Sr izotop ve REE+Y jeokimyasının incelenmesi. Selçuk Üniversitesi, Bilimsel Araştırma Projeleri, Proje No: 14401127, 192 s.

[30]. Palmer MR, Elderfield H 1985. Sr isotopic composition of seawater over the past 75 Myr. Nature, 314, 526-528.

[31]. Palmer MR, Edmond JM 1989. The strontium isotope budget of the modern ocean. Earth and Planetary Science Letters, 92(1), 11-26.

[32]. Qing H, Barnes CR, Buhl D, Veizer J 1998. The strontium isotopic composition of Ordovician and Silurian brachiopods and conodonts: Relationships to geological events and implications for coeval seawater. Geochimica et Cosmochimica Acta, 62(10), 1721-1733.

[33]. Stephens NP, Sumner DY 2003. Late Devonian carbon isotope stratigraphy and sea level fluctuations, Canning Basin, Western Australia. Palaeogeography, Palaeoclimatology, Palaeoecology, 191(2), 203-219.

[34]. Veizer J, Ala D, Azmy K, Bruckschen P, Buhl D, Bruhn F, Carden GAF, Diener A, Ebneth S, Godderis Y, Jasper T, Korte C, Pawellek F, Podlaha OG, Strauss H 1999. $^{87}Sr/^{86}Sr$, $\delta^{13}C$ and $\delta^{18}O$ evolution of Phanerozoic seawater. Chemical Geology, 161, 59-88.

[35]. Wang WQ, Garbelli, C, Zheng QF, Chen J, Liu XC, Wang W, Shen SZ 2018. Permian $^{87}Sr/^{86}Sr$ chemostratigraphy from carbonate sequences in South China. Palaeogeography, Palaeoclimatology, Palaeoecology, 500, 84–94.

[36]. Zhu M, Babcock LE, Peng SC 2006. Advances in Cambrian stratigraphy and paleontology: Integrating correlation techniques, paleobiology, taphonomy and paleoenvironmental reconstruction. Palaeoworld, 15, 217–222.

[37]. Zou H, Li QL, Bagas l, Wang XC, Chen AQ, Li XH 2021. A Neoproterozoic low-$\delta^{18}O$ magmatic ring around South China: implications for configuration and breakup of Rodinia supercontinent. Earth Planet. Sci. Lett., 575, 117-196.

[38]. Zuo J, Zhu X, Chen Y, Zhai W 2023. Carbon Isotopes from Shallow Marine System in North China: Implications for Stratigraphical Correlation and Sea-Level Changes in Cambrian. Journal of Earth Science, 34(6), 1777-1792.