

Geochemical Features of Rare Earth Elements in the Dolomites of the Bozdağ Formation (Early Silurian–Middle Devonian) from Söğütözü-Ladik (Konya/Turkey) Area

Ali Müjdat Özkan

Department of Geological Engineering, Faculty of Engineering, Selcuk University, Konya, Turkey

ABSTRACT:

The objective of this study is to determine the properties of dolomites (Early Silurian-Middle Devonian) in terms of geochemistry of rare earth element, which belong to the Bozdağ Formation existing at the surroundings of Söğütözü-Ladik at the northwest of Konya City in Turkey. The Bozdağ Formation formed the basis in the study area, is made up Early Silurian-Middle Devonian reefal complex. The Bozdağ Formation dolomite samples are displayed rare earth elements depletion such as precursor limestones. The rare earth element content of the Bozdağ Formation dolomites no related to the carbonate phase, detrital alumina-silicate (eg. feldspar and clay minerals such as kaolin) and iron containing minerals (eg. pyrite and possibly ankerite or siderite) was checked by phase. The NASC-normalized rare earth element values of the Bozdağ Formation limestone and dolomite samples show very similar rare earth element patterns characterized by positive Eu and slightly negative Ce anomalies and a clear depletion in all rare earth element species. Our samples display lower Ce/Ce* ratio and lower Pr/Pr* ratio than modern shallow seawater. This indicates that dolomitization took place from altered seawater in moderate to deep burial environment during the late diagenesis. The Bozdağ dolomites have Y/Ho values changing clearly from 5 to 50 (average 25.31). This indicates that Y/Ho values of the Bozdağ carbonates represent enters terrestrial rather than marine. Dolomite samples of the Bozdağ Formation display a negative correlation between Eu/Eu* and Ce/Ce*, therefore they indicate the terrestrial effect rather than diagenetic effect for rare earth elements. As a result, the reefal complex carbonate diagenetic history of the Bozdağ Formation includes to dolomitization from partially evaporative and some amount meteoric water doped modified seawater, medium-deep burial diagenesis, elevated temperature diagenesis, and late diagenesis.

Anahtar Kelimeler: Bozdağ, Dolomite, Söğütözü, Ladik, Rare earth element

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I. INTRODUCTION

Rare earth elements (including the lanthanides and Y) have analogical chemical properties and low solubility, and they are not easy to transfer and take inter-element fractionation during geological processes such as weathering, disintegration, transportation, deposition and early diagenesis related to the formation of marine sediments (Chen et al., 2003). Therefore, REEs can be used as powerful tracers of geochemical processes to discover sources and origins of marine sediments together with climate change influencing chemical weathering of terrigenous materials (Chen et al., 2003).

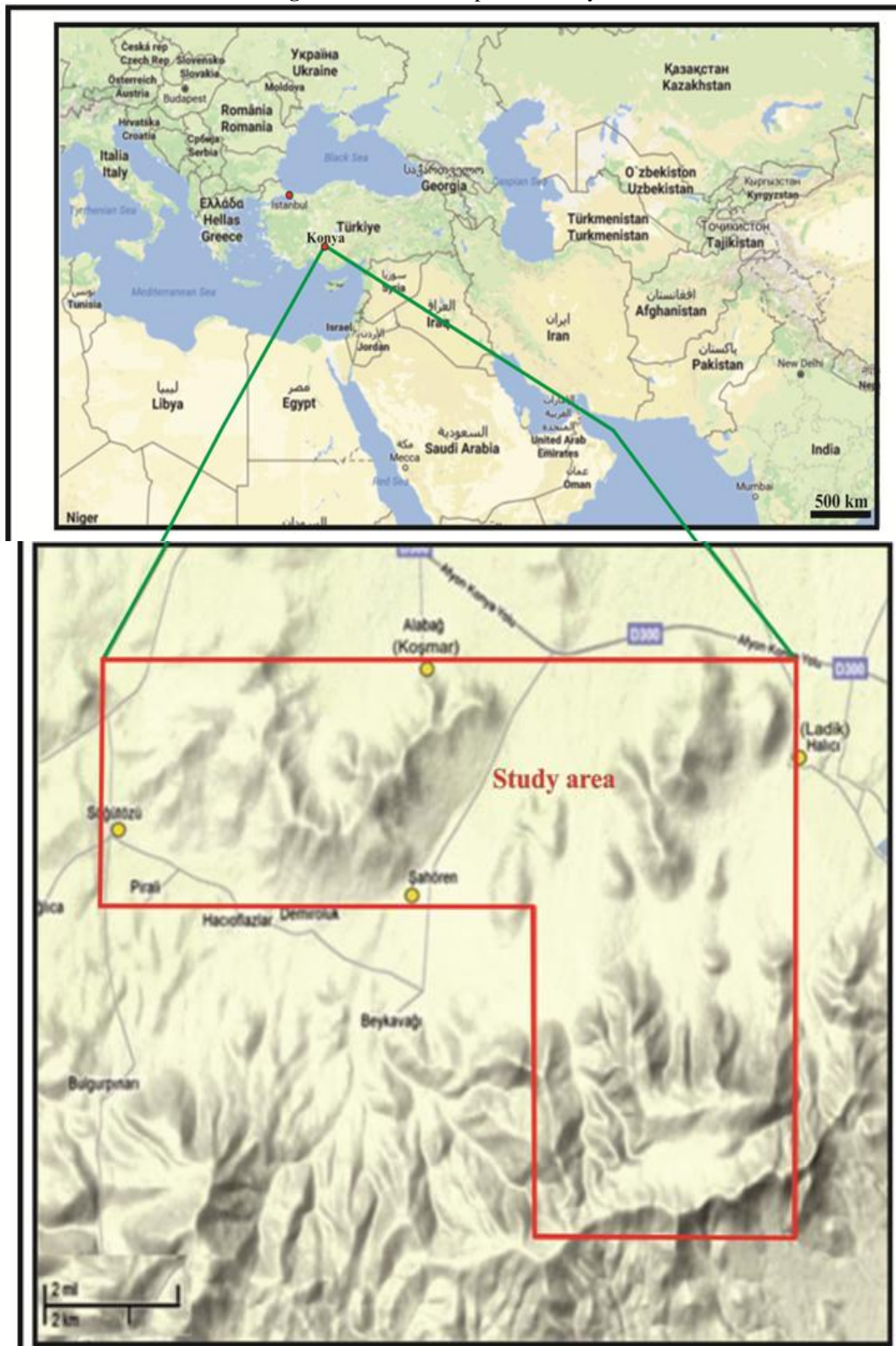
Rare earth elements (REE) concentrations were highly related by many geologists for their matchless features (Henderson, 1984; Song et al., 2014). Although the REE concentrations in carbonate rocks are low (Goldberg, 1963; Tlig and M'Rabet, 1985; Song et al., 2014), they are helpful to detect the marine versus non-marine sources of REE (Frimmel, 2009; Zhao, 2009; Song et al., 2014). REE is considered as a determiner to specify the depositional environmental system (e.g. prevalent marine anoxia, oceanic redox conditions, proximity to source area, lithology and diagenesis, and paleogeography and depositional models), for the dispersion of REE is susceptible to water depth, salinity, oxygen level, and input sources (Northdurft, 2004; Song et al., 2014).

The previous study indicated that marine chemical sediments (e.g. carbonates) are characterized by a uniform light REE depletion, a negative Ce anomaly, a slight positive La anomaly and remarked positive Y anomaly in NASC/PASS-normalized diagrams, which are conform to the seawater REE patterns (Northdurft, 2004; Song et al., 2014), however, the acidic hydrothermal fluids demonstrate very different REE+Y patterns (e.g. positive Eu anomaly and MREE enriched) (Bau, 1999; Song et al., 2014).

Söğütözü-Ladik area is located on the Anatolia (southwest Turkey), with enormous Early Silurian-Middle Devonian sedimentary which constituted chiefly by carbonates (Fig. 1). Since 1960's, many related researches on stratigraphy and petrology, have been accomplished (Doğan, 1975; Özcan et al., 1988, 1990; Eren, 1993, 1996). But, no systematic study has yet been executed on REE geochemistry of the Bozdağ

Formation limestone and dolomite in Söğütözü-Ladik area. In this essay, I present new REE data and its variations in mostly dolomite, and limestone. My aim is to trace the depositional environment, and to commentate the source of REE and anomalies (e.g. Ce, Eu, and Y).

Figure 1. Location map of the study area.



II. GEOLOGICAL SETTING

Göncüoğlu (2012) remarked that Turkey with Thrace in the European continent and Anatolia on the Asiatic one is located in the central part of the Alpine Orogenic Belt between the Balkans and the western Asia. The study area is located in the Konya Closed Basin, in the Central Anatolian region of Turkey in Paleotethys at Late Silurian to Middle Devonian. The stratigraphy of the study area and its surroundings was studied in detail by Eren (1996) (Fig. 2, 3). Eren (1996) pointed out to include different tectonostratigraphic unities of the Bozdağlar Massive in the study area units; the Upper Permian-Cretaceous metamorphic Gökçeyurt group which comprises originally shallow marine rocks is the autochthonous (?parautochthonous) unit of the massif, they are overthrust, in turn, by allochthonous Mesozoic Çayırbağı ophiolite and by Silurian-Mesozoic Ladik Metamorphites. The Ladik Metamorphites contain Sızma and Ardıçlı Groups. Eren (1996) said that the Sızma Group, in ascending order, is made up of Silurian-Lower Carboniferous reef complex (Bozdağ Formation: but Göncüoğlu, 2012, had given Late Silurian-Middle Devonian), Devonian-Lower Permian pre-flysch, flysch, wild flysch (Bağrıkkurt Formation: but Göncüoğlu, 2012, had given Late Devonian-Visean) and intruding Devonian-Lower Permian metamagmatic rocks (Karadağ Metamagmatites: but Göncüoğlu, 2012, had given Late Devonian-Visean). The Ardıçlı Group consists of originally Upper Permian (?)–Triassic continental (Bahçecik Formation: but Göncüoğlu, 2012, had given Late Permian-Early Triassic) and Upper Permian (?)–Mesozoic mixed-shore (Ertuğrul Formation: but Göncüoğlu, 2012, had given Late Permian-Early Triassic) rocks (Eren, 1996). It rests on the Sızma Group unconformably. The stratigraphic development of the Sızma Group indicates that the passive continental margin existed during Devonian, turned into continental margin arc in the Late Carboniferous (Eren, 1996). Compressional deformations probably lasted before the Late Permian time and then molas-like rocks of the Ardıçlı Group deposited. The massif also bears traces of the Neo-Tethian evolution (Eren, 1996). It has undergone metamorphism and gained its napped and imbricated structure during the Alpine Orogeny. Later, at Late Miocene-Early Pliocene (Dilekçi Group), and at Late Pliocene-Quaternary (Topraklı Formation) time the neo-autochthonous rocks were developed on the massif rocks (Eren, 1996).

The Bozdağ Formation (Late Silurian-Middle Devonian) of the oldest units in the study area is occurred black to white colored dolomite, limestone, crystallized limestone and dolomitic limestone. The Bozdağ Formation dolomites contain *Amphipora* sp. in some levels. In addition, Eren (1996) expressed to be contained such as fossils *Thamnopora reticulata*, *Amphipora ramosa*, *Thamnopora cervicornis*, *Syringopora* sp. and *Canina* sp.

The Bozdağ Formation formed the basis in the study area, is made up Early Silurian-Middle Devonian reefal complex. The Bozdağ Formation has been described as consisting of massive-stratified limestone, dolomitic limestone, dolomite and calcitic dolomites (Özkan, 2016). The Bozdağ Formation dolomite types: type I) dolomiticrite, type II) the planar-e textured dolomites are scattered in a micritic matrix, type III) fracture and void filling dolomite, and type IV) stylolitic dolomite (Özkan, 2016).

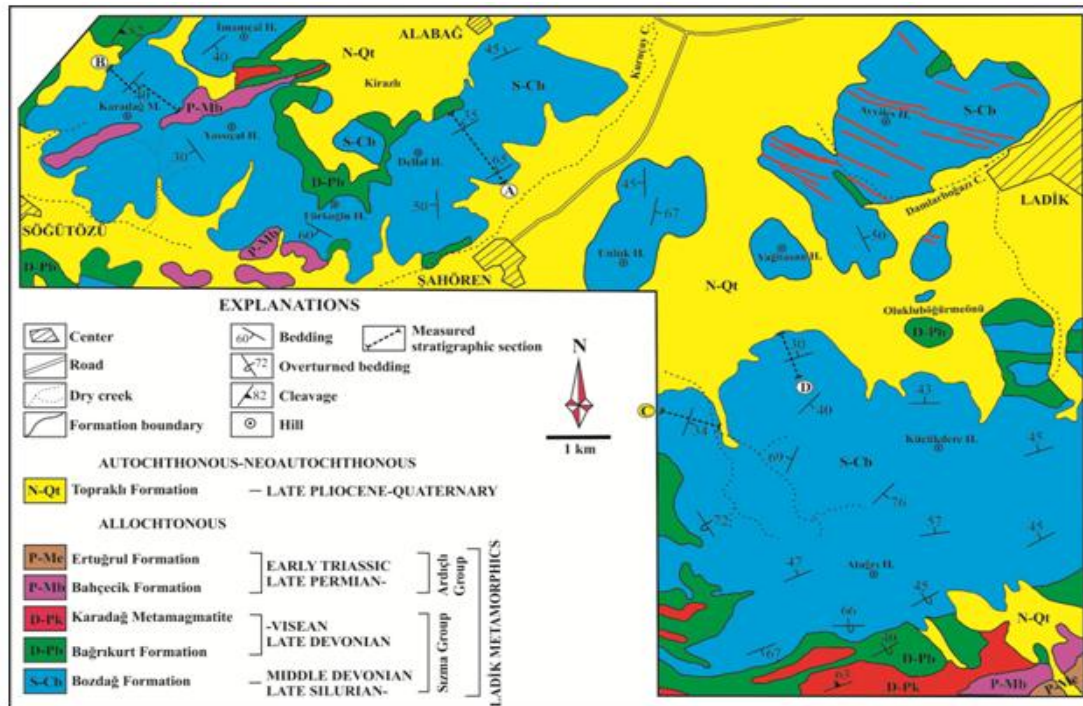


Figure 2. Geological map of the study area (modified from Eren, 1996).

UNIT	LITHOLOGY	EXPLANATIONS	AGE
Neotautochthonous		Topraklı Formation: conglomerate, sandstone, mudstone	-Quaternary Late Pliocene
		Unconformity	
Allochthonous		Ertuğrul Formation: metacarbonate phyllite, metasandstone	Early Triassic Late Permian-
		Bahçecik Formation: metaconglomerate, metasandstone, phyllite	
		Unconformity	
Allochthonous		Karadağ metamagmatites: metadacite, metarhyolite, metatrachytes, metaandesite, metadiorite, metabasite, metatuff	Late Devonian-Visean
		Bağrıkurt Formation: schist, phyllite, metasandstone, metaconglomerate, metaquartzite, metachert, crystalline limestone, marble	
		Olistoliths: marble-crystalline limestone blocks	
		Metachert, graphite-phyllite, phyllite Crystalline limestone, dolomite	
		Bozdağ Formation: marble, dolomite, crystalline limestone, dolomitic limestone	Middle Devonian Late Silurian-

Figure 3. Stratigraphic section of study area (unscaled; modified from Eren, 1996).

III. METHODS

The features of stratigraphic and tectonic of the study area and its surroundings was studied in detail by Eren (1996). However, sedimentological property of the Bozdağ Formation carbonates in the study area were not investigated in detail. In this study, sedimentary geochemical characteristics of the Bozdağ Formation carbonates (Early Silurian-Middle Devonian) were investigated in detail. Sample collection for geochemical analysis formed part of a sedimentological analysis of the Bozdağ Formation carbonates in the southern Anatolia, Turkey. A total of 69 samples were collected from 4 measured stratigraphic sections (MSS: A: Dellal, MSS: B: Karadağ, MSS: C: Unluk, MSS: D: Yağbasan), and the correlation of the MSS have made (Fig. 4).

The samples were crushed using an agate pestle and mortar to less than 200 meshes. To annihilate potential contamination of non-carbonate materials such as siliciclastics, oxide and sulfide, 1 M acetic acid was used to selectively dissolve the carbonate. Twenty one samples were sent to the ACME analytic laboratory for chemical analysis (major, trace and rare earth element) and were read with Inductively Coupled Plasma Emission and Mass Spectrometry (ICP-ES-MS) devices.

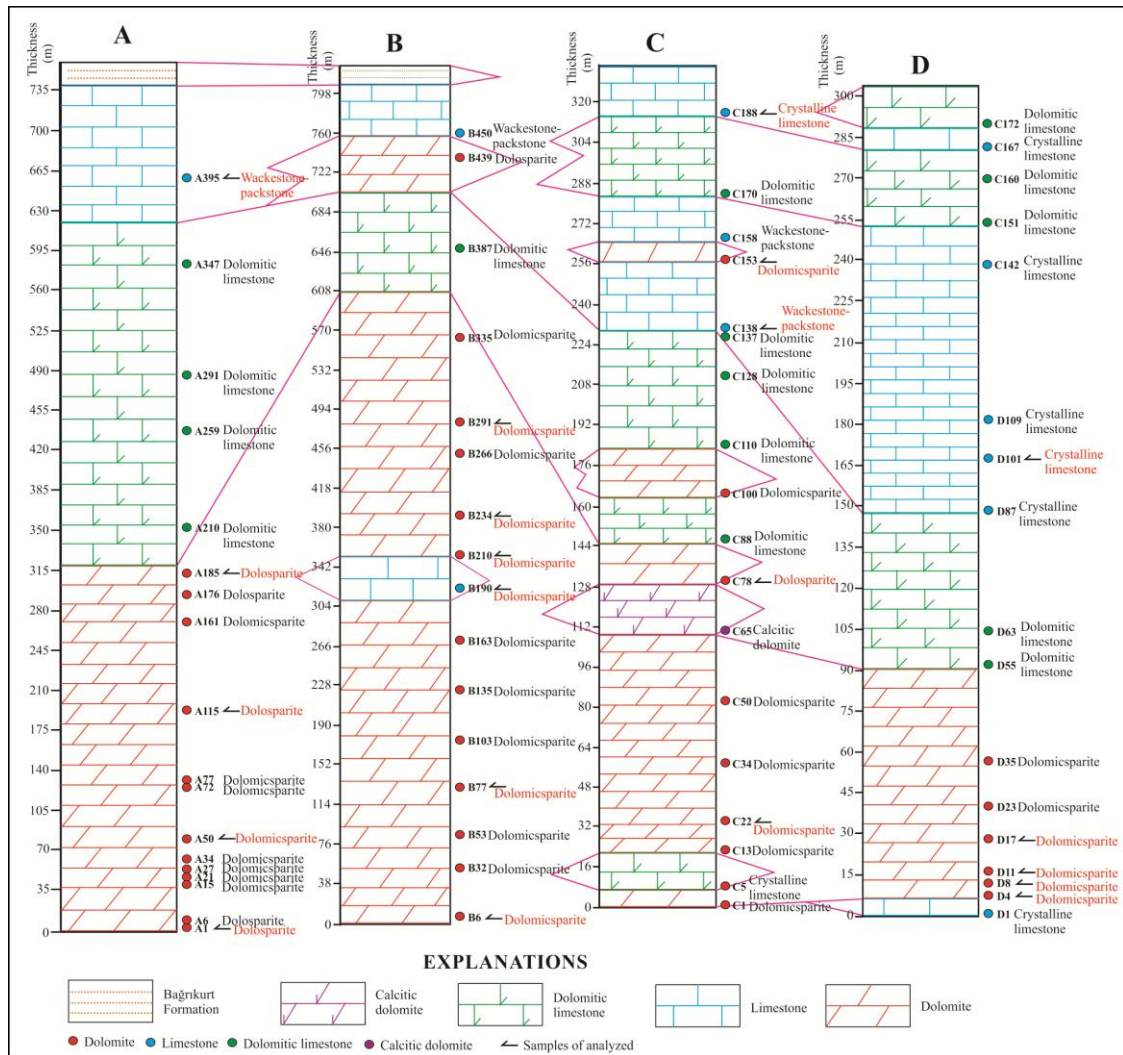


Figure 4. Correlation of measured stratigraphic sections of The Bozdağ Formation. A: Dellal measured stratigraphic section, B: Karadağ measured stratigraphic section, C: Unluk measured stratigraphic section, D: Yağbasan measured stratigraphic section.

IV. GEOCHEMISTRY

The contents of the total REE+Y of the studied limestone (5 samples) and dolomite (16 samples) sample groups are listed in Table 1. The contents of the some REE+Y and major, trace elements of the studied limestone (5 samples) and dolomite (16 samples) sample groups are listed in Table 2. The North American Shale Composition [NASC]-normalized REE+Y values of both the limestone and dolomite sample groups show very similar REE patterns characterized by slight negative Ce, mostly positive Eu, positive and negative Y anomalies, and a clear depletion in all REE species (Table 1, Fig. 5, 6). The total REE content of the Bozdağ dolomites display a strong positive correlation with Si, Al, Fe, K, Ti, Zr, and negative correlation with Mg and Ca (Fig. 7).

Table 1. NASC-normalized rare earth element concentrations of dolomites and limestones in the Bozdağ Formation dolomites. It should be noted limit values are taken as the values at the values below limits in the graphic drawings.

Sample	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm ppm	Yb ppm	Lu ppm	Y ppm	ΣREE ppm
A-1	0.4	0.4	0.07	0.5	0.07	0.02	0.06	<0.01	0.06	<0.02	0.04	<0.01	0.05	<0.01	0.8	1,65
A-50	0.4	0.8	0.11	<0.3	0.08	0.04	0.07	<0.01	0.16	<0.02	0.04	<0.01	<0.05	<0.01	0.6	1,70
A-115	1.8	2.3	0.26	0.7	0.19	0.03	0.12	0.01	0.11	<0.02	0.04	<0.01	0.07	<0.01	0.8	5,63
A-185	0.4	0.4	0.06	<0.3	0.05	<0.02	<0.05	<0.01	<0.05	<0.02	0.04	<0.01	0.05	<0.01	0.4	1,00
A-395*	0.1	<0.1	<0.02	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01	<0.1	0,1
B-6	0.3	0.4	0.03	0.5	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01	0.2	1,23
B-77	0.8	1.4	0.17	0.5	0.09	0.03	0.13	0.01	0.16	<0.02	<0.03	<0.01	0.05	0.01	0.7	3,35
B-190*	1.3	2.4	0.24	1.1	0.13	0.03	0.19	0.02	0.05	0.02	0.05	<0.01	0.07	<0.01	1.1	5,6
B-210	0.7	1.6	0.13	0.5	0.12	<0.02	0.08	<0.01	0.07	<0.02	<0.03	<0.01	<0.05	<0.01	0.7	3,2
B-234	2.1	4.1	0.50	1.7	0.37	0.06	0.25	0.04	0.31	0.06	0.13	0.01	0.09	0.01	1.2	9,73
B-291	1.0	2.1	0.24	0.5	0.14	0.02	0.10	0.02	0.18	<0.02	0.08	<0.01	0.09	<0.01	0.5	4,47
C-22	1.3	2.8	0.32	1.5	0.23	0.04	0.26	0.03	0.17	0.02	0.10	<0.01	0.11	<0.01	1.0	6,88
C-78	0.5	1.0	0.09	<0.3	0.07	<0.02	0.09	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01	0.5	1,75
C-138*	0.4	0.8	0.05	0.4	0.08	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01	0.6	1,73
C-153	0.6	1.2	0.15	0.9	0.09	<0.02	0.09	<0.01	0.08	<0.02	0.05	<0.01	<0.05	<0.01	0.4	3,16
C-188*	2.4	3.1	0.32	0.9	0.18	0.06	0.14	0.01	<0.05	<0.02	0.04	<0.01	<0.05	<0.01	0.9	6,34
D-4	0.3	0.5	0.06	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01	0.5	0,86
D-8	0.3	0.4	0.04	<0.3	0.06	<0.02	<0.05	<0.01	<0.05	<0.02	0.03	<0.01	<0.05	<0.01	0.2	0,83
D-11	0.2	0.3	<0.02	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01	0.1	0,5
D-17	0.2	0.3	<0.02	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01	0.3	0,5
D-101*	0.3	0.5	0.04	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01	0.3	0,84

*Limestone

Table 2. Some of NASC-normalized rare earth element and major, trace elements concentrations of dolomites and limestones in the Bozdağ Formation dolomites. It should be noted limit values are taken as the values at the values below limits in the graphic drawings.

*Limestone

Sample	Y/Ho	Er/Nd	La/Ho	(La/Lu) _N	(La/Yb) _N	(La/Nd) _N	Ti/Eu	(Eu/Eu*) _N	(Ce/Ce*) _N	(Pr/Pr*) _N	(Nd/Yb) _N	Na ₂ O/Al ₂ O ₃	K ₂ O/AI ₂ O ₃
A-1	40	0.08	20	0.59	0.80	0.70	0.30	1.44	-0.39	0.73	1.14	0	0
A-50	30	0.13	20	0.59	0.80	1,17	0.15	2.51	-0.01	1.21	0.68	0.37	0.25
A-115	40	0.06	90	2.64	2.57	2,26	0.40	0.93	-0.13	1.09	1.14	0.11	0.31
A-185	20	0.13	20	0.59	0.80	1,17	0.30	1.88	-0.31	0.89	0.68	1.00	0.50
A-395*	5	0.1	5	0.15	0.20	0.29	0.30	1.88	-0.59	0.41	0.68	0	0
B-6	10	0.06	15	0.44	0.60	0,53	0.30	1.88	-0.32	0.31	1.14	0.60	0.40
B-77	35	0.06	40	1.17	1.60	1,41	0.20	1.30	-0.04	1.09	1.14	0.15	0.31
B-190*	55	0.04	65	1.91	1.86	1.04	0.20	0.90	-0.06	0.80	1.78	0	0.38
B-210	35	0.06	35	1.03	1.40	1,23	0.30	0.96	0.06	0.78	1.14	0.23	0.31
B-234	20	0.08	35	3.08	2.33	1,09	0.20	0.93	-0.03	1.02	2.15	0.04	0.34
B-291	25	0.16	50	1.47	1.11	1,76	0.60	0.80	0.06	1.22	0.63	0.06	0.34
C-22	50	0.07	65	1.91	1.18	0,76	0.15	0.77	-0.04	0.84	1.5	0.15	0.38
C-78	25	0.1	25	0.73	1.00	1,47	0.30	1.18	0.02	0.88	0.68	0.33	0.33
C-138*	30	0.07	20	0.59	0.80	0,88	0.30	1.49	-0.05	0.48	0.91	0	0.5
C-153	20	0.05	30	0.88	1.20	0,59	0.30	1.05	-0.12	0.75	2.04	0.08	0.35
C-188*	45	0.04	120	3.52	4.80	2,35	0.10	1.77	-0.13	1.02	2.04	0	0.2
D-4	25	0.1	15	0.44	0.60	0,88	0.30	1.88	-0.13	0.82	0.68	0.13	0.33
D-8	10	0.1	15	0.44	0.60	0,88	0.30	1.71	-0.23	0.60	0.68	0.3	0.30
D-11	5	0.1	10	0.29	0.40	0,59	0.30	1.88	-0.25	0.33	0.68	0.43	0.29
D-17	15	0.1	10	0.29	0.40	0,59	0.30	1.88	-0.25	0.33	0.68	0.75	0.50
D-101*	15	0.1	15	0.44	0.60	0,88	0.30	1.88	-0.13	0.55	0.68	0	0.5

Table 2. Continued.

Sample	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	MgO %	CaO %	K ₂ O %	TiO ₂ %	Fe Wt%	Zr (ppm)	Th (ppm)	U (ppm)	Sr (ppm)
A-1	0.17	<0.01	0.31	20.83	29.93	<0.01	<0.01	0.22	0.4	<0.2	0.4	24.8
A-50	0.35	0.08	0.19	21.10	30.56	0.02	<0.01	0.13	0.5	<0.2	0.1	106.1
A-115	0.54	0.26	0.30	21.32	30.17	0.08	0.02	0.21	2.4	0.3	0.5	28.1
A-185	0.25	0.04	0.25	20.99	29.64	0.02	<0.01	0.17	1.1	<0.2	0.3	27.9
A-395*	0.08	<0.01	<0.04	0.53	56.27	<0.01	<0.01	0.03	0.7	<0.2	0.5	307.4
B-6	0.17	0.05	<0.04	20.36	31.91	0.02	<0.01	0.03	0.6	<0.2	1.5	82.8
B-77	0.30	0.13	0.66	21.48	30.53	0.04	<0.01	0.46	1.4	<0.2	1.7	20.1
B-190*	0.58	0.21	0.13	0.40	55.24	0.08	0.01	0.09	1.8	0.4	0.7	159.4
B-210	0.32	0.13	0.23	20.59	30.23	0.04	<0.01	0.16	1.4	<0.2	1.4	81.8
B-234	0.86	0.47	0.05	20.89	30.04	0.16	0.02	0.04	4.3	0.9	2.0	66.5
B-291	0.63	0.32	0.17	21.12	30.65	0.11	0.02	0.12	2.8	0.5	2.8	55.8
C-22	0.36	0.13	0.47	21.12	30.10	0.05	<0.01	0.33	1.6	<0.2	0.5	30.1
C-78	0.34	0.15	0.13	20.86	30.59	0.05	<0.01	0.09	2.0	<0.2	1.7	67.7
C-138*	0.19	0.04	<0.04	0.64	56.09	0.02	<0.01	0.03	0.6	<0.2	1.7	211.1
C-153	0.52	0.26	0.16	20.94	30.70	0.09	0.01	0.11	1.8	0.3	2.8	73.3
C-188*	0.17	0.05	0.10	0.41	55.31	0.01	<0.01	0.07	0.9	<0.2	5.2	173.3
D-4	0.30	0.15	0.20	21.38	30.77	0.05	<0.01	0.13	0.8	<0.2	0.2	122.5
D-8	0.23	0.10	0.19	21.09	30.82	0.03	<0.01	0.13	0.8	<0.2	0.4	66.4
D-11	0.16	0.07	0.10	21.35	30.53	0.02	<0.01	0.07	0.7	<0.2	1.0	83.2
D-17	0.14	0.04	0.14	21.48	30.65	0.02	<0.01	0.10	0.3	<0.2	0.4	54.7
D-101*	0.13	0.02	0.23	0.44	55.66	0.01	<0.01	0.16	0.2	<0.2	<0.1	5.9

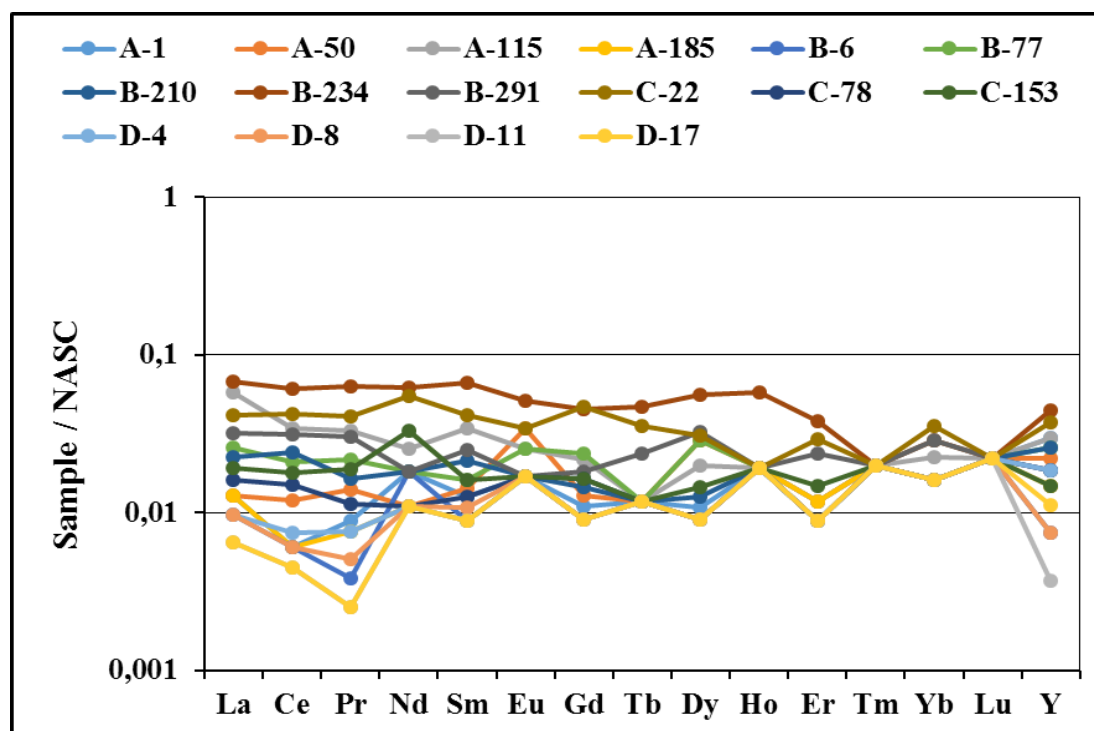


Figure 5. The North American Shale Composite (NASC)-normalized REE+Y distribution patterns of the Bozdağ Formation dolomites (NASC data after Haskin et al., 1968). (While drawing the diagram, the lower limit values are taken as the limit values).

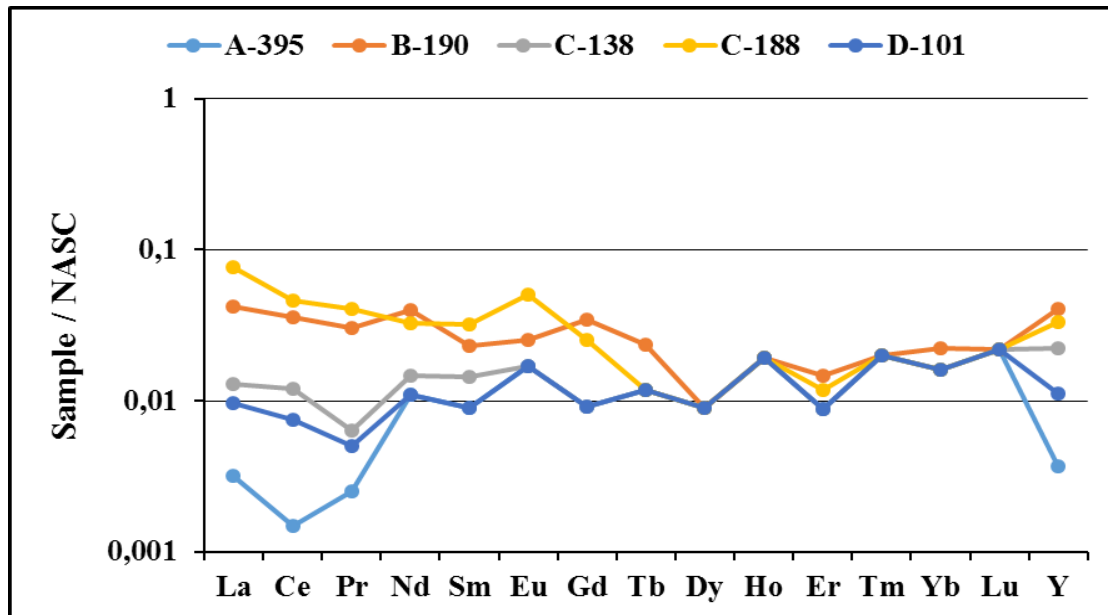


Figure 6. The North American Shale Composite (NASC)-normalized REE+Y distribution patterns of the Bozdağ Formation limestones (NASC data after Haskin et al., 1968). (While drawing the diagram, the lower limit values are taken as the limit values).

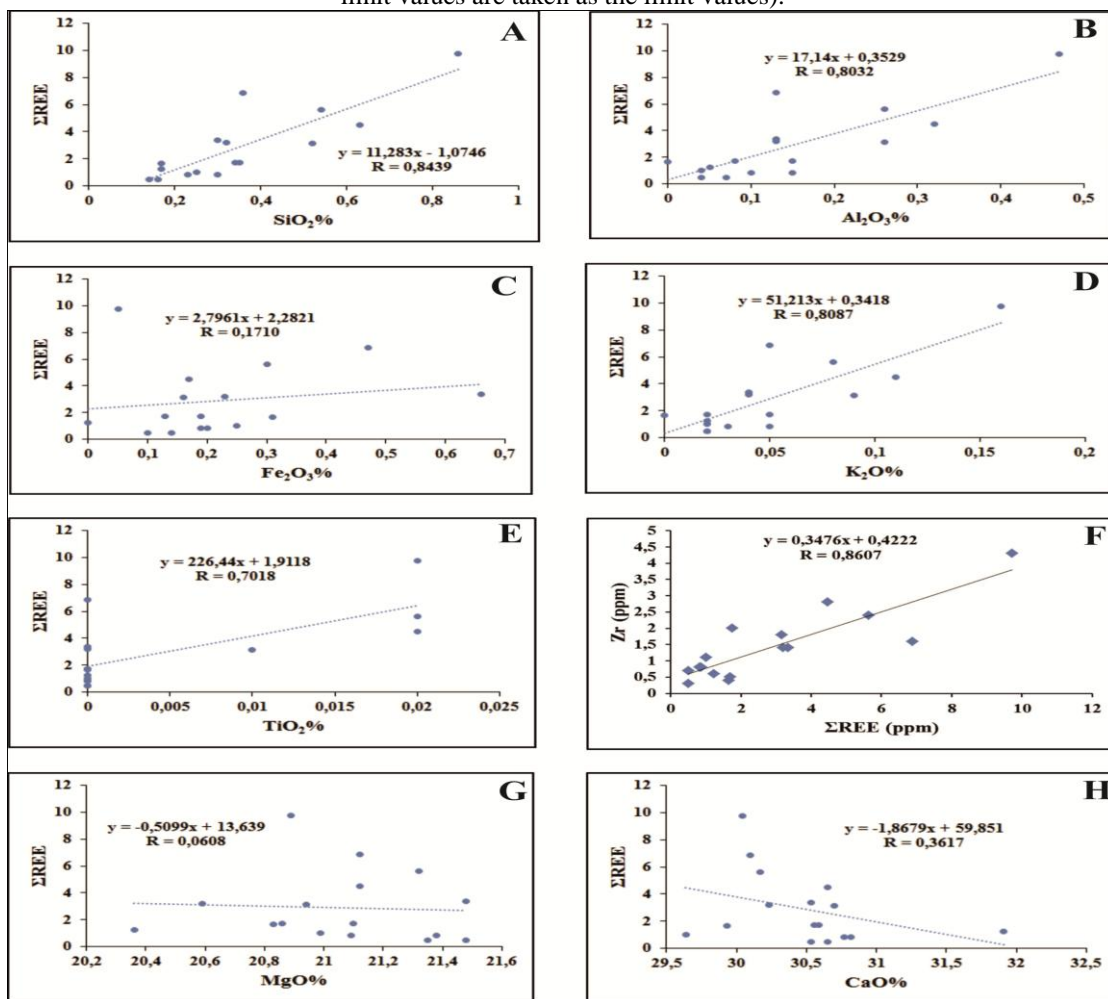


Figure 7. Plot of Si, Al, Fe, K, Ti, Zr, MgO and CaO versus total rare earth element (REE) concentration for the Bozdağ dolomites.

The Bozdağ dolomites display that La/Ho versus Y/Ho strong positive correlation, (La/Yb)_N versus Ti/Eu no correlation, Fe (wt%) versus Eu/Eu* weakly negative correlation, Er (ppm) versus Nd (ppm) strong positive correlation, Eu/Eu* versus Ce/Ce* medium negative correlation, total REE versus Ce/Ce* medium negative correlation, Zr (ppm) versus Eu/Eu* and Ce/Ce* strong and medium correlation, respectively (Fig. 8).

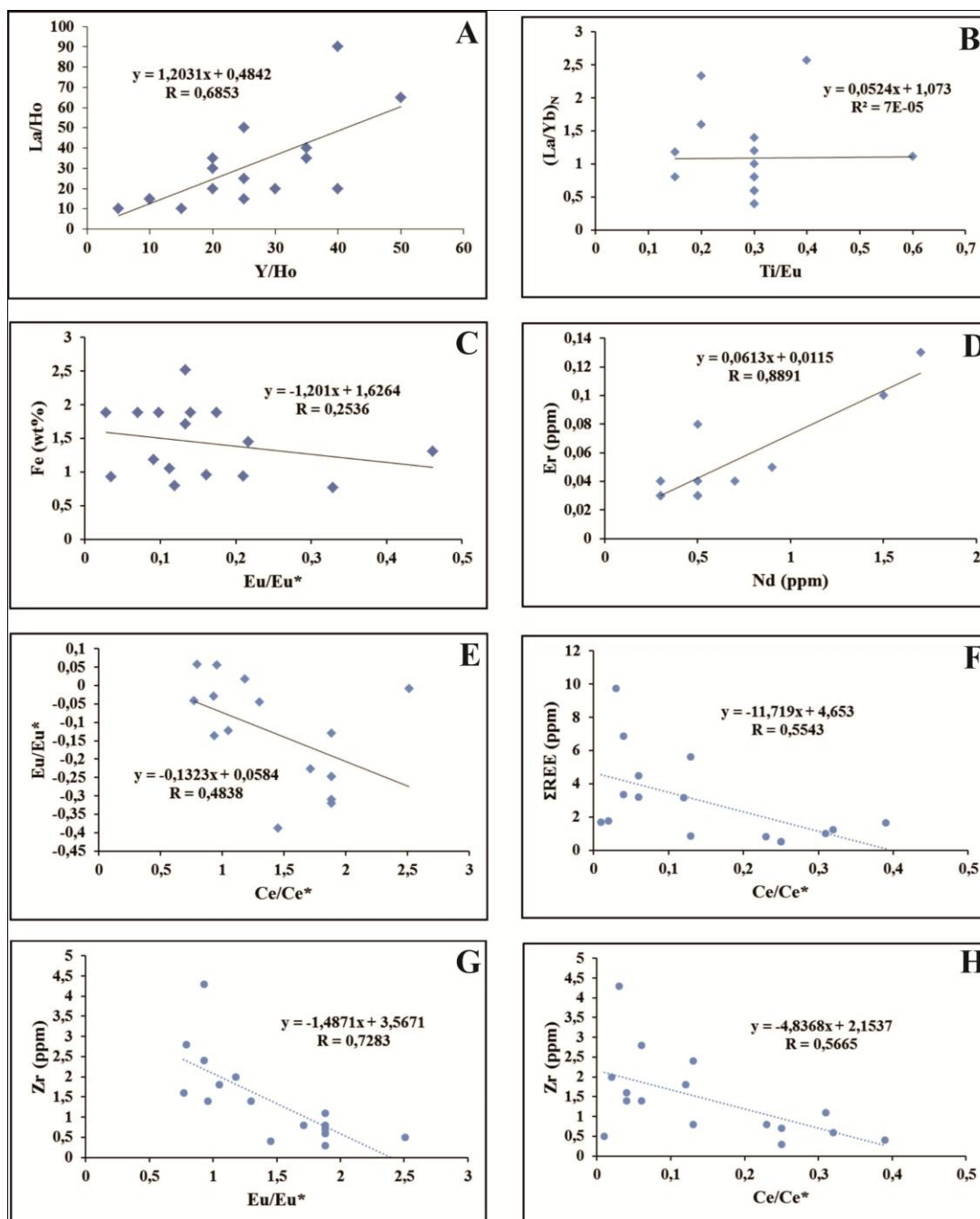


Figure 8. Plot of Y/Ho versus La/Ho, (La/Yb)_N versus Ti/Eu, Fe (wt%) versus Eu/Eu*, Er (ppm) versus Nd (ppm), Eu/Eu* versus Ce/Ce*, ΣREE (ppm) versus Ce/Ce*, Zr (ppm) versus Eu/Eu* and Zr (ppm) versus Ce/Ce* in the Bozdağ Formation dolomites.

V. DISCUSSION

Factors that potentially effect the TREE+Y in carbonates contain (1) mineralogy (calcite or aragonite) (Webb et al., 2009), (2) diagenesis (Miura et al., 2004; Azmy et al., 2011), and/or (3) variation in the TREE+Y of the seawater from which the carbonates occurred (Bertram and Elderfield, 1993; Azmy et al., 2011). Webb et al. (2009) proposed that the TREE+Y of carbonates boosts as aragonite changes to calcite because the

distribution coefficient of REE+Y between calcite and the parent solution is higher than that between aragonite and its parent solutions (Terakado and Masuda, 1988; Zhao and Jones, 2012).

Seawater REE patterns have hardly altered throughout the Phanerozoic (Shields and Webb, 2004; Li et al., 2015). The signatures of REE+Y patterns and Σ REE+Y barely altered during the dolomitization process (Zhao and Jones, 2013; Wang et al., 2014; Li et al., 2015). REE patterns of dolomite can subserve as a deputy to study the nature of dolomitization fluids and environmental conditions during carbonate precipitation (Zhao and Jones, 2013; Li et al., 2015).

Some investigators have stressed (e.g. Banner et al., 1988; Dorobek and Filby, 1988; Qing and Mountjoy, 1994; Shmulovich et al., 2002; Cetiner et al., 2005; Kučera et al., 2009) the total concentrations of REE+Y in dolomites may be affected by other factors such as the first concentration of REE+Y in hydrothermal fluids, pH, pressure, compound of fluids and their temperature.

Li et al. (2015) emphasized that the Geshan dolomite has depleted of $\delta^{18}\text{O}$ values and low Sr but high Fe, Mn concentration and Ce/Ce* ratios, proposing that dolomitization formed in an anoxic subsurface environment with increasing temperature during compaction at shallow to intermediated burial. The Bozdağ Formation dolomites have depleted of $\delta^{18}\text{O}$ values and low Sr but high Fe, Mn concentration (Özkan, 2016), suggesting that dolomitization formed in an anoxic subsurface environment with increasing temperature during at intermediate to deep burial.

Further, Shields and Webb (2004) and Li et al. (2015) have stated that the shale-normalized REE pattern of modern shallow seawater is personified by manifest negative Ce anomalies, relative enrichment of the heavy REE, positive La anomalies, and high Y/Ho ratios. The shale normalized REE pattern of Bozdağ Formation dolomites are characterized by low REE contents and nearly a flat REE pattern (Fig. 5). A weakly negative Ce anomalies and REE depletion were monitored (Fig. 5).

Azomani et al. (2013) emphasized that the suite of rare earth elements is a beneficial tool for the recognition of the origin of fluids, the state of equilibrium in rock-water interactions and modifies in fluid composition, which is fundamental in understanding fluid-rock systems. Again, Azomani et al. (2013) stressed that REEs have relatively short residence time (several hundred years; Alibo and Nozaki, 1999) and are lithophile elements that invariably consist together naturally because all are trivalent (except for Ce^{4+} and Eu^{2+} in certain environments) and have similar ionic radii with chemical characteristics that modify systematically along the series, which results in the preferential absorption of LREE relative to MREE and HREE in seawater (Sholkovitz and Shen, 1995).

5.1. Cerium anomaly

Ce anomaly, especially negative anomaly, is widely supposed as a characteristic of seawater by many researchers (e.g., Sholkovitz and Shen, 1995; Webb and Kamber, 2000; Kamber and Webb, 2001; Felitsyn and Morad, 2002; Picard et al., 2002; Kemp and Trueman, 2003; Bolhar et al., 2004; Lécuyer et al., 2004; Nothdurft et al., 2004; Wyndham et al., 2004; Zhang et al., 2008; Webb et al., 2009; Azmy et al., 2011; Wang et al., 2014). This is on account the concentration of Ce in seawater is interested to the oxidized level. Oxidized Ce^{4+} is comparatively not dissolvable in seawater, and in this way easily absorbed onto particles (De Baar et al., 1991; Moller et al., 1994; Alibo and Nozaki, 1999; Frimmel, 2009; Wang et al., 2014). As a result, the shallow seawater is characterized by negative Ce anomalies, at all events of being normalized to PAAS or other standards (Wang et al., 2014).

Dolomite samples of the Bozdağ Formation exhibit a positive Ce anomaly (Fig. 9) and they refer to the development associated with the anoxic sediments during burial conditions. Because many researchers (e.g., Wright et al., 1987; Wilde et al., 1996; Mazumdar et al., 1999; Guo et al., 2007; Chen et al., 2012) point out that most of the black shales, Cambrian chert-phosphorite assemblages, fossil apatite debated during past years have a positive cerium anomaly related with anoxic sediments during warmer climate and transgressive conditions.

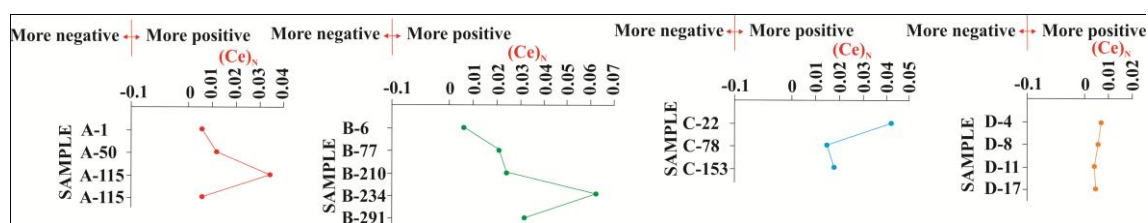


Figure 9. Cerium anomaly of the Bozdağ Formation. All samples exhibit a positive Ce anomaly and they refer to the development associated with the anoxic sediments during warmer climate and transgressive conditions.

The Ce anomaly values of the Bozdağ Formation dolomites vary from 0.06 to 0.004 and display a rise in sea level (transgression) (Fig. 9). In this way, that can deduce that the shallow to open sea-water (in shelf) formed the Bozdağ Formation carbonates, which is in coherent with the appearance of abundant *Amphipora*.

Zhao and Jones (2012) had said that cerium is redox-sensitive and Ce/Ce* is a beneficial deputy to attainment redox condition under which dolomite subsided. The Ce/Ce* ratios of carbonates from the Bozdağ Formation, however, are not harmonious with the modern surface seawater (Table 2; Fig. 10A,B). Our samples display lower Ce/Ce* ratio and lower Pr/Pr* ratio than modern shallow seawater (Fig. 10A,B). This indicates that dolomitization took place from altered seawater in moderate to deep burial environment during the late diagenesis.

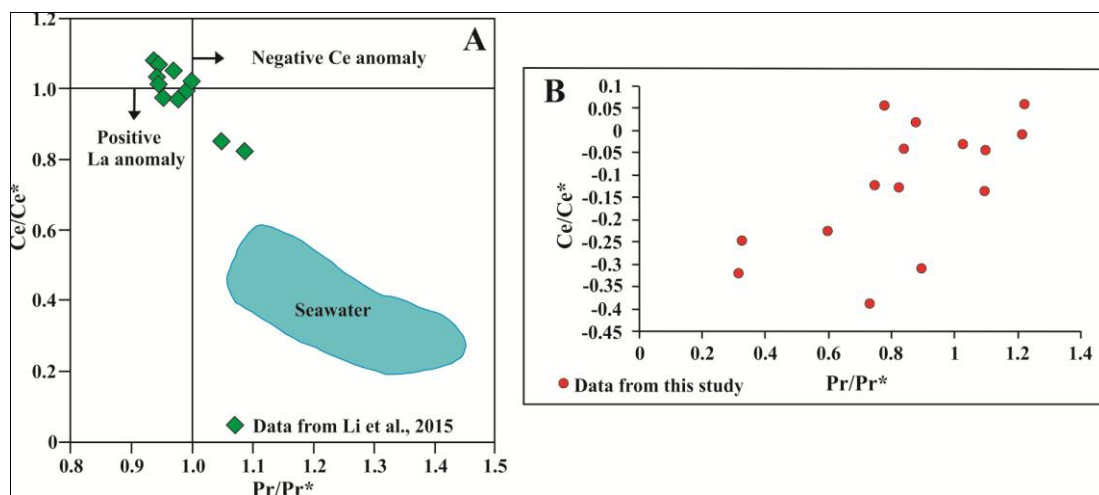


Figure 10. Cross plot showing relationship between Ce/Ce* and Pr/Pr* using the method of Bau et al., 1997. Shaded area shows the range of modern seawater (after Nothdurft et al., 2004).

The Ce/Ce* values indicate negative correlation with U and CaO, showing that the variations in Ce anomalies are not related to the paleo-redox conditions of the depositional environment (Abedini and Calagari, 2015). The Ce/Ce* values indicate positive correlation with U ($r = -0.08$; Fig. 11) and negative correlation with CaO ($r = -0.08$; Fig. 11), showing that the variations in Ce anomalies of the Bozdağ formation dolomite are related to the paleo-redox conditions of the depositional environment.

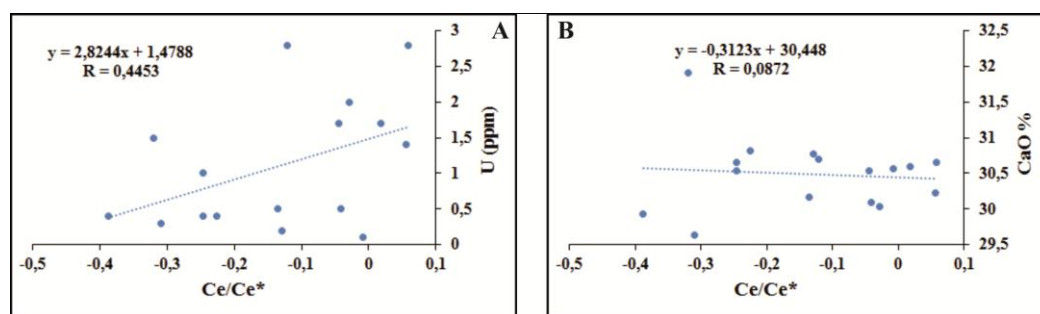


Figure 11. Bivariate plots for pairs of Ce/Ce* – U (A), Ce/Ce* – CaO (B) in the dolomite at the Bozdağ Formation.

5.2. Europium anomalies

Frimmel (2009) has stated that $\text{Eu}^{3+} / \text{Eu}^{2+}$ redox potential is highly addicted on temperature, thence high temperature hydrothermal or basinal diagenetic fluid results in Eu anomalies. Therefore, it will be able to say that positive Eu anomalies are associated with pyrite-bearing carbonates and acidic, reducing hydrothermal fluids, while negative Eu anomalies form in Fe-oxide rich carbonates (Frimmel, 2009). In some of the Bozdağ dolomites, the presence significant positive Eu anomalies (Figure 5) express terrigenous contamination rather than hydrothermal effect, inasmuch as hydrothermal fluids have high temperature (>200-250 °C; Bau and Dulski, 1996; Azomani et al., 2013), but the formation temperatures of the Bozdağ dolomites range from 55 to 110 °C (Özkan, 2016). Also, positive correlation between Al and Si (Özkan, 2016) that was observed in this study supports this approach.

Numerous studies propose that REE are mobile during black shale diagenesis (Lev et al., 2008; Haeri-Ardakani, 2012). Hannigan and Basu (1998) stated during early diagenesis and breakdown of sediment organic

matter, LREE associated with clay mineral surfaces have the potential to migrate from the sediments into pore waters. High organic matter contents demonstrate highly reducing conditions, which is consistent with the production of a negative Eu anomaly in some of the Bozdağ Formation samples (Fig. 5).

Bolhar and Van Kranendonk (2007) and Zhang et al. (2014) stated that LREE enrichment in dolomite has been ascribed to dolomitization by hydrothermal fluids, however in many cases when LREE is present there is also a strong positive Eu anomaly due to the temperature of the hydrothermal fluids. The Bozdağ Formation dolomite samples no LREE enrichment, so that has not been ascribed to dolomitization by hydrothermal fluids. Also, Low Ba values in the Bozdağ dolomites (Özkan, 2016) forestall hydrothermal diagenetic fluid interaction. Furthermore, hydrothermal fluids usually display high TREE values, but the Bozdağ Formation samples show very low values.

Derry and Jacobsen (1990) stated that Eu anomaly values can supply major help in comprehending the physicochemical conditions of various geochemical systems such as the depositional environment of limestones (Abedini and Calagari, 2015). The result of computations for Eu anomalies in the Bozdağ Formation dolomites indicates positive anomalies ranging from 0.77 to 2.51, with a mean of 1.44. The Bozdağ Formation dolomites display positive correlations between $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and Eu/Eu^* ($r = 0.60$; Figure 12A) but no correlation between $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ and Eu/Eu^* ($r = 0.04$; Figure 12B). Thereby, it would appear that additionally diagenetic processes, the existence of plagioclase in the investigated limestone also acted a significant role in the nascence of positive Eu anomalies.

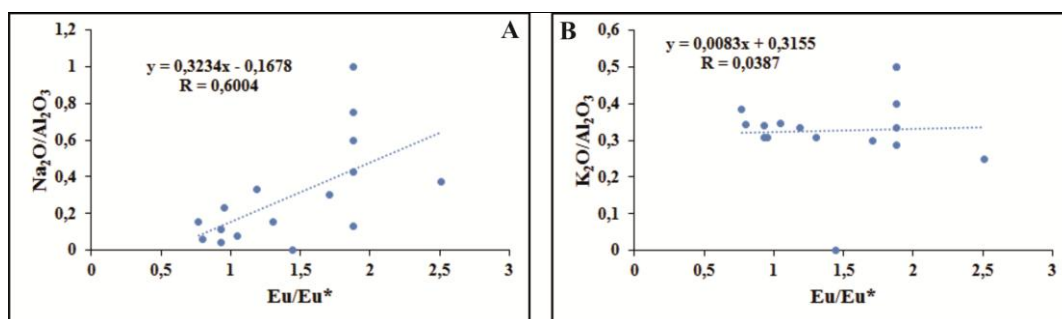


Figure 12. Bivariate plots for pairs of Eu/Eu^* – $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (A) and Eu/Eu^* – $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ (B) in the Bozdağ Formation dolomites.

5.3. Ratios of Y/Ho and Er/Nd, and some of trace element anomalies

Bau (1996) and Nozaki et al. (1997) stressed although Y and Ho have analogue geochemical conduct, Ho can be abolished from seawater twice as fast as Y. In addition, they said that this phenomenon is interrelated to the difference in degree of surface complex stabilities, which spearheads to a remarkable superchondritic marine ratio of Y/Ho (Abedini and Calagari, 2015). Terrigenous materials and volcanic ashes possess stationary chondritic values of Y/Ho (approximately 28). The Y/Ho values of seawater are greater than those of volcanic ashes, ranging from 44 to 74 (Bau, 1996; Nozaki et al., 1997; Abedini and Calagari, 2015). The Bozdağ dolomites have Y/Ho values changing clearly from 5 to 50 (average 25.31). Therefore, Y/Ho values of the Bozdağ carbonates represent enters terrestrial rather than marine.

De Baar et al. (1988) stressed that the value of Er/Nd in normal seawater is ~ 0.27 (Abedini and Calagari, 2015). The Er/Nd value in limestones can efficiently unclose the seawater signature held by the marine carbonates (Abedini and Calagari, 2015). German and Elderfield (1990) and Bellanca et al. (1997) said that both detrital materials and diagenetic processes can give rise to preferential concentration of Nd relative to Er and also can diminish the Er/Nd values to < 0.1 (Abedini and Calagari, 2015). The Er/Nd values in our dolomites show a range of 0.05–0.16, which in turn displays the active role of detrital materials and diagenetic processes in the dispersion of Er and Nd in the Bozdağ carbonates. Additionally, Song et al. (2014) pointed out the controlling role of diagenetic processes in the distribution of REEs in limestones can be specified by a superb positive correlation between Eu/Eu^* and Ce/Ce^* (Abedini and Calagari, 2015). However, our dolomite samples display a negative correlation between Eu/Eu^* and Ce/Ce^* , therefore they indicate the terrestrial effect rather than diagenetic effect.

Abedini and Calagari (2015) have expressed the concentration of Al_2O_3 in limestones is closely related to clay content. In addition Veizer (1983) said that the average values of siliciclastic-contaminated limestones are 0.42 wt.%. All of samples (except one sample) of the Bozdağ dolomites display strong positive correlation with the ΣREE content ($r = 0.80$; Fig. 7), however, analytical values of Al_2O_3 show < 0.42 wt.%, so it will be able to say that it is a negligible amount of siliciclastic-contamination in the Bozdağ carbonates. Generally, REEs with detrital origin have positive correlations with elements such as Si, Ti, Al, K, Sc, Cr, Co, Rb, Y, V, Ni, and Nb, and negative correlation with CaO (Madhavaraju et al., 2010; Nagarajan et al., 2011; Nagendra et

al., 2011; Abedini and Calagari, 2015). Consideration of correlation coefficients between elements in the Bozdağ dolomites displays that the REEs have a positive correlations with SiO_2 ($r = 0.84$), Al_2O_3 ($r = 0.80$), K_2O ($r = 0.81$), TiO_2 ($r = 0.70$), and negative correlation with CaO ($r = -0.36$). Also, the samples of Bozdağ dolomites display positive correlation between $(\text{Nd}/\text{Yb})_N$ and Al_2O_3 ($r = 0.57$). These relations plainly supply exact reasons to attribute a terrigenous origin to REEs in the Bozdağ carbonates.

Haeri-Ardakani (2012) has stated that the typical features of REE shale-normalized model of marine carbonates are: 1) relative depletion of LREE over HREE ($(\text{La}/\text{Yb})_{SN} < 1$); 2) negative Ce and positive La anomalies (Webb and Kamber, 2000); 3) a slight Gd anomaly; and $(\text{La}/\text{Nd})_{SN}$ between 0.8 to 2 (Shields and Stille, 2001). The typical characteristics of REE shale-normalized pattern of the Bozdağ dolomites do not display the typical seawater pattern, because half of the samples have $(\text{La}/\text{Yb})_{SN} > 1$ and, $(\text{La}/\text{Nd})_{SN} > 2$ (only one sample) and $(\text{La}/\text{Nd})_{SN} < 0.8$ (6 of the samples; in 16 samples), so while some of the Bozdağ dolomites express marine feature, some of them show modified marine waters.

The value of Er/Nd ratio is about 0.27 in normal seawater (De Baar et al., 1988; Song, et al., 2014). The high Er/Nd ratio of limestone effectively uncloses the seawater indication retained by the marine carbonate. The detrital material or diagenesis can decrease the Er/Nd value to lower than 0.1, for the preferential concentration of Nd relative to Er (Bellanca, et al., 1997). The Er/Nd ratios of the Bozdağ dolomites are changing from 0.05 to 0.13 (Table 1), with a good positive correlation between Nd and Er ($r = 0.89$; Fig. 8D), demonstrating that the efficacy of detrital materials in original limestone are reliable.

Bau et al. (1996) has stated that the deficiency of correlation between TREE+Y and Fe and Mn contents of the Cayman carbonates, however, demonstrate that there is no contamination due to the presence of Fe- hydroxides and Mn-hydroxides (Zhao and Jones, 2012). From here, the shortage of correlation between TREE+Y and Fe and Mn contents of the Bozdağ carbonates (Fig. 7C, 13A), however, point out that there is no contamination due to the presence of Fe- and Mn-hydroxides.

Song et al. (2014) pointed out that trace elements (such as Zr and Th) could deduce terrigenous material, what are concentrated in different detrital minerals. Good positive correlations between TREE and Zr, and between TREE and Th of samples were hoped for terrestrial clastic contaminating. The Bozdağ Formation dolomites show that a good positive correlation observed between Zr and Th ($r = 0.87$; Fig. 13C), and a positive correlation observed between Zr and TREE ($r = 0.86$; Fig. 7F), and a positive correlation also observed between Th and TREE ($r = 0.76$; Fig. 13B), and a negative correlation also observed between Sr and TREE ($r = 0.30$; Fig. 13D). In this way, the appearance that REE in the Bozdağ carbonates having been variously influenced by detrital materials could be dependable. In addition to, the weak positive correlation between Mn and TREE+Y ($r = 0.5$, Fig. 13A) point out that diagenetic stabilization affected the REE+Y concentrations.

The temperature of dolomitization liquid calculated from the calcite-dolomite pair of the Bozdağ Formation ranges between 55 to 110 °C, with the average being 82 °C (Özkan, 2016). These values reveal (increase in temperature depending on geothermic gradient [1 km ~30 °C]) intermediate to deep burial (1 to 3 km).

As a result, the reefal complex carbonate diagenetic history of the Bozdağ Formation includes to dolomitization from partially evaporative and some amount meteoric water doped modified seawater, medium-deep burial diagenesis, elevated temperature diagenesis, and late diagenesis (Özkan, 2016).

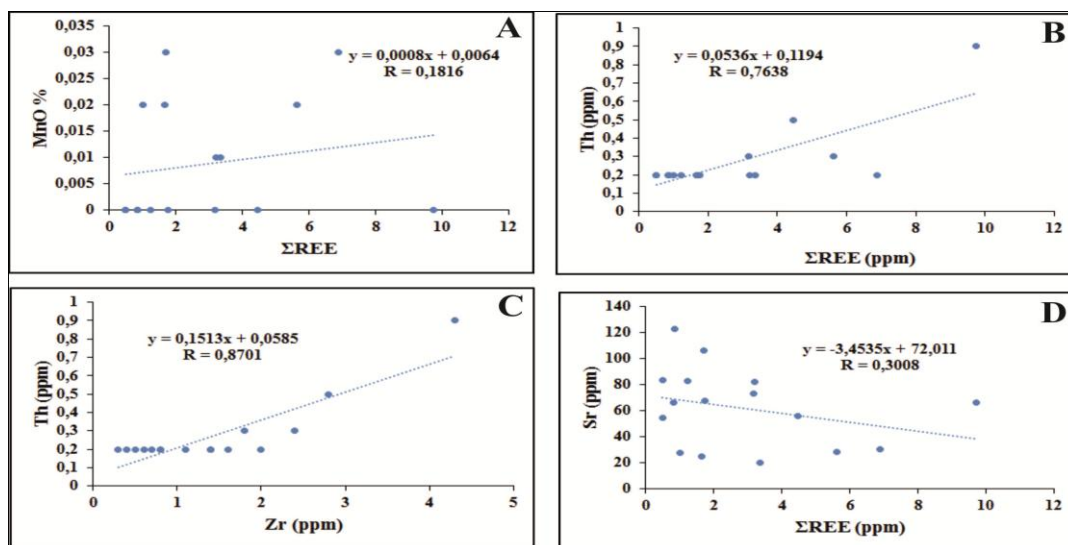


Figure 13. Plot of MnO, Th and Sr versus total rare earth element (TREE), and Zr versus Th concentration for the Bozdağ dolomites.

VI. DYNAMICS OF THE TETHYAN REALM IN SILURIAN TO DEVONIAN TIMES

Stampfli and Borel (2002) had expressed that Gondwana-directed subduction beget to the opening of the PaleoTethys (Fig. 14) associated with the separation of the strip-like Hun superterrane along the northern margin of Gondwana. Diachronous subsidence patterns of Tethyan margins since the early Paleozoic ensure limitations for PaleoTethys opening during the Late Ordovician and the Silurian and the splitting of the Hun terranes in two parts, the European and Asiatic (Stampfli and Borel, 2002). Again, Stampfli and Borel (2002) stated that the Asiatic was influenced by terranes amalgamation in Ordovician/Silurian times (Serindia terranes containing parts of North China and Tarim). The Variscan orogeny in Europe was not a continent-continent collision but a major development of peri-Gondwanan terranes, which happened chiefly in Devonian times (Fig. 14).

Göncüoğlu (2012) specified that on the continental microplates, such as the Tauride-Anatolide Unit, platform-type carbonates were deposited. The Paleozoic Turkish terranes in in the S (Tauride- Anatolide and SE Anatolia) although originated from N Gondwana, went through entirely different evolutionary ways (Göncüoğlu, 2012). Furthermore, Göncüoğlu (2012) pointed out that the Bozdağ Formation took place from lower to upward nodular limestone with conodont, dolomite, nautiloid bearing limestone with conodonts, and Amphipora bearing limestone. In the our study area, the Bozdağ Formation occur Amphipora bearing dolomite, calcitic dolomite, dolomitic limestone and limestone as a reef complex in shelve environment.

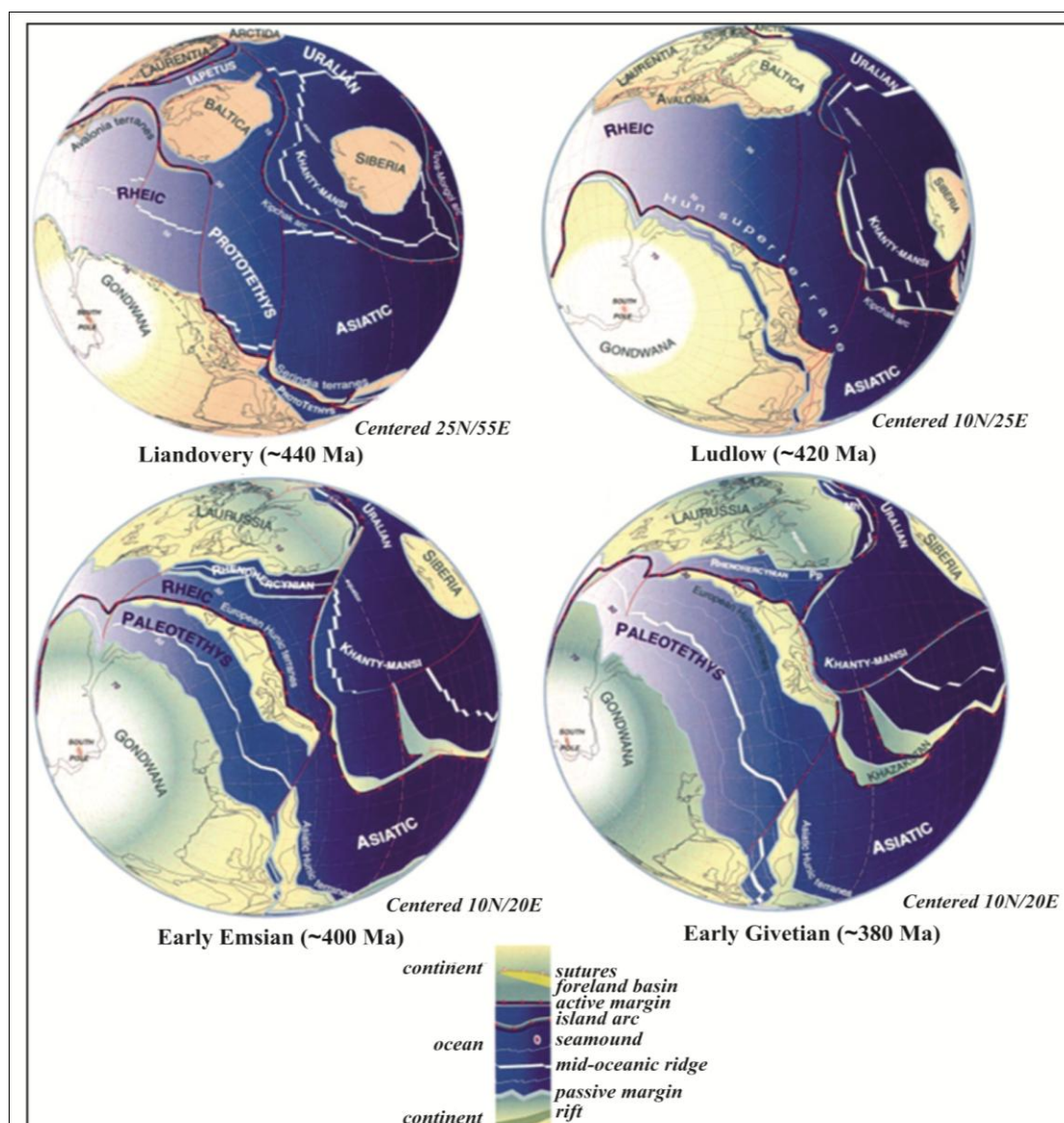


Figure 14. Drift history of Gondwana-derived basement areas between Silurian to Middle Devonian. A complete legend for chosen key reconstructions (440 Ma, 420 Ma, 400 Ma and 380 Ma) are existent in the EPSI (from Stampfli and Borel, 2002).

VII. CONCLUSIONS

The NASC-normalized rare earth element values of the Bozdağ Formation limestone and dolomite samples show very similar rare earth element patterns characterized by positive Eu and slightly negative Ce anomalies and a clear depletion in all rare earth element species.

The distribution of rare earth elements in both the dolomite and limestone in the Bozdağ Formation is not related to carbonate phases; their distribution in the dolomite and limestone are essentially controlled by a detrital alumino-silicate phase (e.g. feldspar and clay mineral like kaolinite) and iron-bearing minerals such as pyrite and probable ankerite or siderite.

Dolomite samples of the Bozdağ Formation exhibit a positive Ce anomaly and they refer to the development associated with the anoxic sediments at during burial conditions.

Our samples display lower Ce/Ce* ratio and lower Pr/Pr* ratio than modern shallow seawater. This indicates that dolomitization took place from altered seawater in medium to deep burial environment during the late diagenesis.

In some of the Bozdağ dolomites, the presence significant positive Eu anomalies express terrigenous contamination rather than hydrothermal effect, inasmuch as hydrothermal fluids have high temperature (>200-250 °C), but the formation temperatures of the Bozdağ dolomites range from 55 to 110 °C (Özkan, 2016). Also, positive correlation between Al and Si (Özkan, 2016) that was observed in this study supports this approach.

High organic matter contents of the Bozdağ Formation dolomites demonstrate highly reducing conditions, which is consistent with the production of a negative Eu anomaly in some of our samples.

The Bozdağ Formation dolomites display positive correlations between Na₂O/Al₂O₃ and Eu/Eu* (r = 0.60) but no correlation between K₂O/Al₂O₃ and Eu/Eu* (r = 0.03). Thereby, it would appear that additionally diagenetic processes, the existence of plagioclase in the investigated limestone also acted a significant role in the nascence of positive Eu anomalies.

The Bozdağ dolomites have Y/Ho values changing clearly from 5 to 50 (average 25.31). This indicates that Y/Ho values of the Bozdağ carbonates represent enters terrestrial rather than marine.

Dolomite samples of the Bozdağ Formation display a negative correlation between Eu/Eu* and Ce/Ce*, therefore they indicate the terrestrial effect rather than diagenetic effect for rare earth elements.

Er/Nd ratios of the Bozdağ dolomites are changing from 0.05 to 0.13, with a good positive correlation between Nd and Er (r=0.89), demonstrating that the efficacy of detrital materials in original limestone are reliable.

The Bozdağ Formation dolomites show that a good positive correlation between Zr and Th (r=0.87), and a positive correlation between Zr and REE (r=0.86), and a positive correlation also between Th and REE (r=0.76). In this way, the appearance that REE in the Bozdağ carbonates having been variously influenced by detrital materials could be dependable.

The reefal complex carbonate diagenetic history of the Bozdağ Formation includes to dolomitization from partially evaporative and some amount meteoric water doped modified seawater, medium-deep burial diagenesis, elevated temperature diagenesis, and late diagenesis.

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