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# 11

Editor

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# Major Oxide And Trace Element Characteristics Of The Bozdağ Formation Dolomites (Konya Northwest, Türkiye)

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## Introduction

The aim of this study is to examine the dolostones (Middle Devonian-Lower Carboniferous) belonging to the Bozdağ Formation, located around the Söğütözü-Ladik district in the northwest of Konya (Figure 1), according to their major and trace element properties.

The study area is located in the Kütahya-Bolkardağı belt, in the Konya region (Figure 1). The Bozdağ Formation, which forms the basis of the study area, is defined as consisting of massive bedded limestone, dolomitic limestone, dolostone, and calcitic dolostone (Özkan, 2016). The Bozdağ Formation dolostone types are defined as (1) dolomicrite, (2) euhedral dolomite disseminated in the micritic matrix, (3) crack and void fill dolomite, and (4) stylolytic dolomite (Özkan, 2016).

The Sr content (20-123 ppm) of the Bozdağ Formation dolostones is consistent with the Sr values of the burial dolostones. The Na content of Bozdağ Formation dolostones (122-371 ppm) is also consistent with the Na content of burial dolostones. The Fe and Mn contents of Bozdağ Formation dolostones (0-4616 and 0-232 ppm, respectively) support the Fe and Mn contents of the burial dolostones. Major oxide and trace element properties of Bozdağ Formation dolostones indicate diagenetic alteration and insignificant terrigenous input.

The Bozdağ Formation dolostones must have been formed late diagenetically at elevated temperatures in a medium-deep burial environment from partially evaporative, altered sea water with some meteoric water effect.

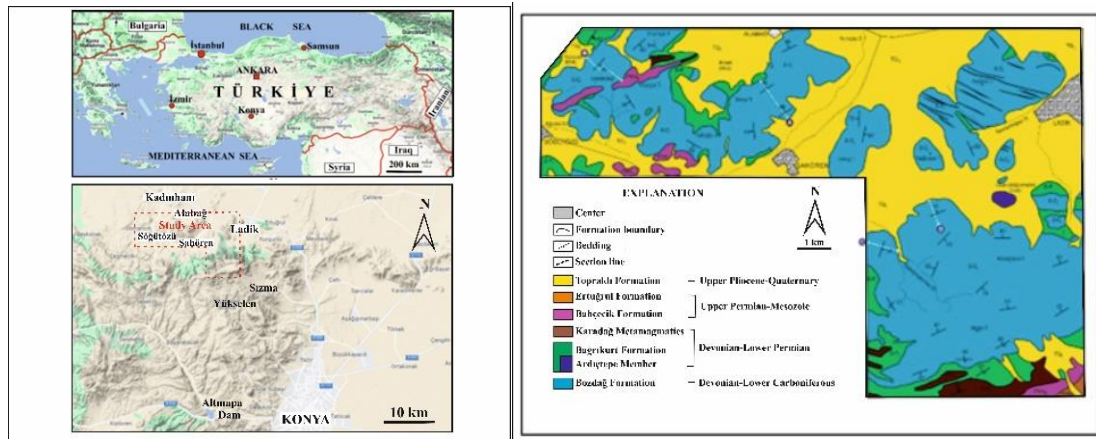


Figure 1. Location (GoogleMaps) and geological map of the study area (modified from Özkan 2016)

Four measured stratigraphic sections were taken from the Bozdağ Formation by Özkan (2016). Stromatoporoid bioherms are also encountered in the Bozdağ Formation dolostones, which contain abundant fossils (mostly *Amphipora*).

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## Major Oxide and Trace Element Properties of the Bozdağ Formation Dolostones

Analysis results of 16 dolostone samples are given in Tables 1 and 2. Based on this analysis data, major oxide and trace element values and geochemical interpretation of the Bozdağ Formation dolostones were made.

*Table 1. Major oxide contents of dolostones in the Bozdağ Formation*

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	LOI
A185	0.25	0.04	0.25	20.99	29.64	0.04	0.02	<0.01	<0.01	0.02	48.6
A115	0.54	0.26	0.30	21.32	30.17	0.03	0.08	<0.01	<0.01	0.02	46.7
A50	0.35	0.08	0.19	21.10	30.56	0.03	0.02	<0.01	<0.01	0.03	46.6
A1	0.17	<0.01	0.31	20.83	29.93	0.04	<0.01	<0.01	<0.01	0.02	48.2
B291	0.63	0.32	0.17	21.12	30.65	0.02	0.11	0.02	<0.01	<0.01	46.1
B234	0.86	0.47	0.05	20.89	30.04	0.02	0.16	0.02	<0.01	<0.01	46.4
B210	0.32	0.13	0.23	20.59	30.23	0.03	0.04	<0.01	0.01	0.01	47.0
B77	0.30	0.13	0.66	21.48	30.53	0.02	0.04	<0.01	<0.01	0.01	46.6
B6	0.17	0.05	<0.04	20.36	31.91	0.03	0.02	<0.01	0.01	<0.01	47.0
C153	0.52	0.26	0.16	20.94	30.70	0.02	0.09	0.01	<0.01	<0.01	46.6
C78	0.34	0.15	0.13	20.86	30.59	0.05	0.05	<0.01	<0.01	<0.01	46.9
C22	0.36	0.13	0.47	21.12	30.10	0.02	0.05	<0.01	0.02	0.03	47.3
D17	0.14	0.04	0.14	21.48	30.65	0.03	0.02	<0.01	<0.01	<0.01	47.2
D11	0.16	0.07	0.10	21.35	30.53	0.03	0.02	<0.01	<0.01	<0.01	47.2
D8	0.23	0.10	0.19	21.09	30.82	0.03	0.03	<0.01	<0.01	<0.01	47.0
D4	0.30	0.15	0.20	21.38	30.77	0.02	0.05	<0.01	<0.01	<0.01	46.7

*Table 2. Trace element contents of dolostones in the Bozdağ Formation*

Sample	Sr	Ba	Rb	Fe	Mn	Al	Na
A185	27.9	<1	0.3	1748	155	212	297
A115	28.1	2	1.7	2098	155	1376	222
A50	106.1	4	0.2	1329	232	423	222
A1	24.8	1	<0.1	2168	155	0	297
B291	55.8	5	2.1	1189	0	1693	148
B234	66.5	2	2.6	350	0	2487	148
B210	81.8	1	0.6	1609	77	688	222
B77	20.1	2	0.6	4616	77	688	148
B6	82.8	5	0.1	0	0	264	122
C153	73.3	3	1.9	1119	0	1376	148
C78	67.7	4	0.9	909	0	794	371
C22	30.1	1	0.6	3287	232	688	148
D17	54.7	2	0.1	979	0	212	297
D11	83.2	2	0.2	699	0	370	297
D8	66.4	2	0.5	1329	0	529	297
D4	122.5	3	0.9	1399	0	794	148

In the mole %MgCO<sub>3</sub>-mol%CaCO<sub>3</sub> graph, it is observed that there is a strong positive relationship between the MgCO<sub>3</sub> content and the CaCO<sub>3</sub> content (Figure 2). A positive correlation is observed between SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the %SiO<sub>2</sub>-%Al<sub>2</sub>O<sub>3</sub> graph (Figure 3).

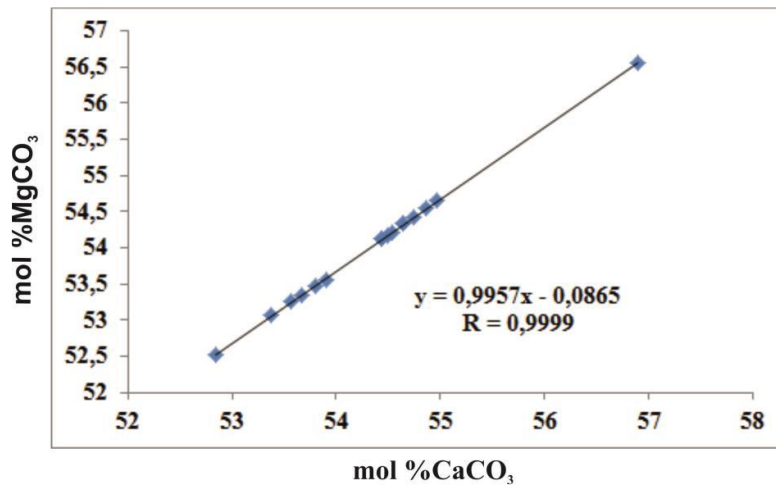


Figure 2. mol %MgCO<sub>3</sub>-mol %CaCO<sub>3</sub> graph (from Özkan, 2016)

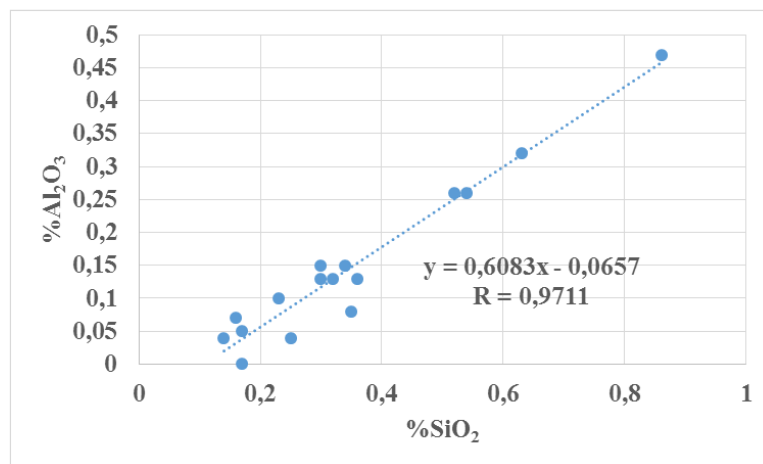


Figure 3. % SiO<sub>2</sub>-% Al<sub>2</sub>O<sub>3</sub> graph (from Özkan, 2016)

In the %K<sub>2</sub>O-Rb graph, a positive correlation is observed between Rb content and %K<sub>2</sub>O (Figure 4). In the Fe-Mn graph, a positive relationship is observed between Mn and Fe content in dolomites, that is, as the Fe content increases, so does the Mn content (Figure 5).

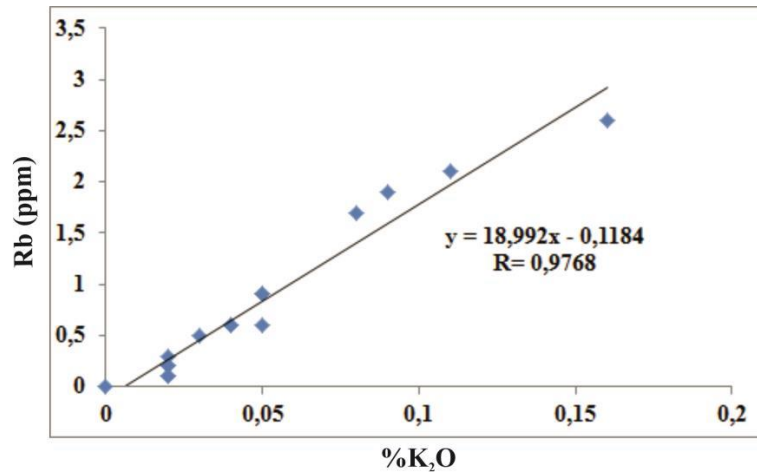


Figure 4. %K<sub>2</sub>O-Rb graph (from Özkan, 2016)

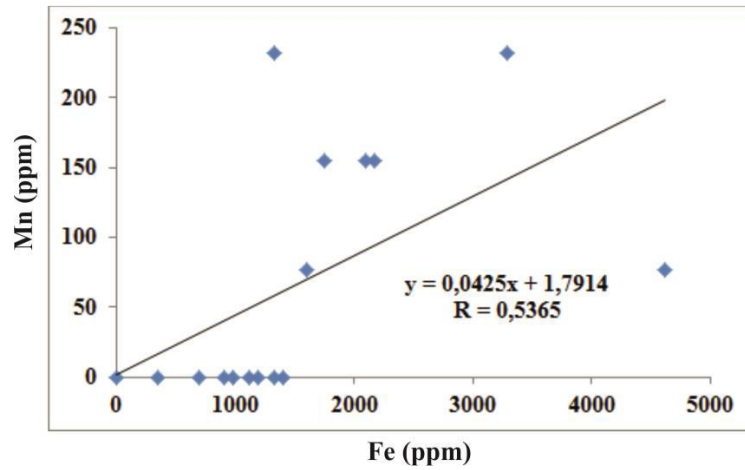


Figure 5. %Fe-Mn graph (from Özkan, 2016)

In the Fe-Al graph, a negative relationship is observed between the Al content and the Fe content in the dolostones (Figure 6). A positive correlation is observed between the Sr content and the CaCO<sub>3</sub> content in the dolostones in the Sr-CaCO<sub>3</sub> graph (Figure 7). In the Sr-MgCO<sub>3</sub> graph, a positive correlation is observed between Sr content and MgCO<sub>3</sub> content in dolostones (Figure 8). In the Sr-Mn graph, a negative correlation is observed between Sr content and Mn content in dolostones (Figure 9). In the Sr-Fe graph, a negative correlation is observed between the Sr content and the Fe content in the dolostones (Figure 10). In the Fe-MgCO<sub>3</sub> graph, a negative correlation is observed between the Fe content and MgCO<sub>3</sub> content in the dolostones (Figure 11). In the Fe-CaCO<sub>3</sub> graph, a negative correlation is observed between the Fe content and the CaCO<sub>3</sub> content in the dolostones (Figure 12).

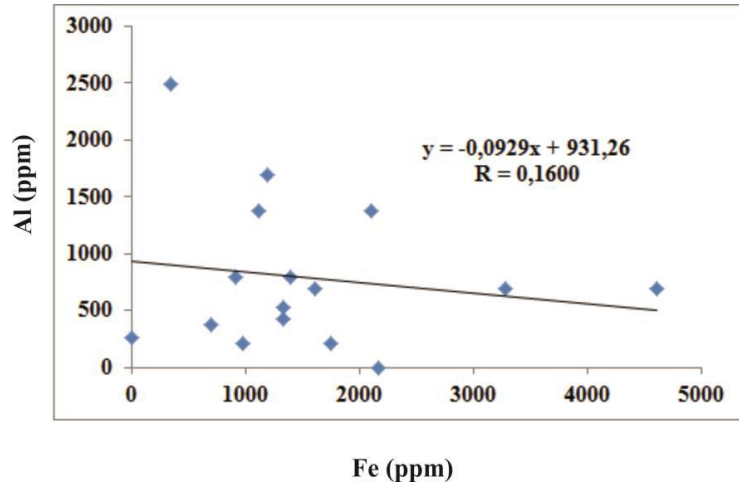


Figure 6. %Fe-Al graph (from Özkan, 2016)

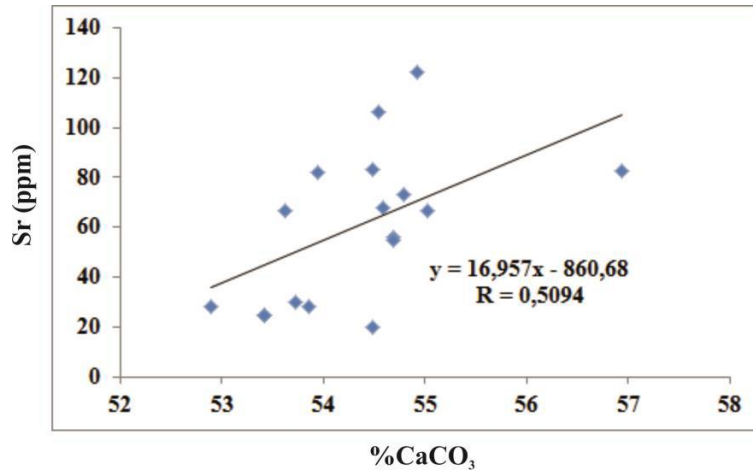


Figure 7. %CaCO<sub>3</sub>-Sr (ppm) graph (from Özkan, 2016)

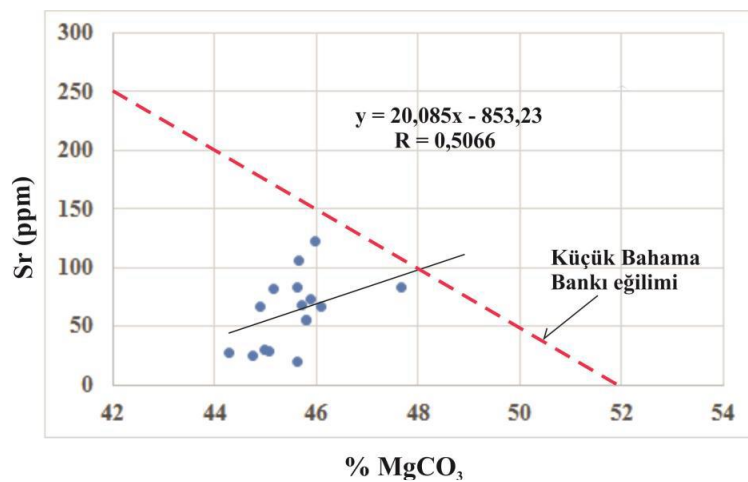


Figure 8. %MgCO<sub>3</sub>-Sr (ppm) graph. Sr/Ca seawater: 0.0195, Sr/Ca the Bozdağ Formation dolostones: 0.0001-0.0006 (from Özkan, 2016)

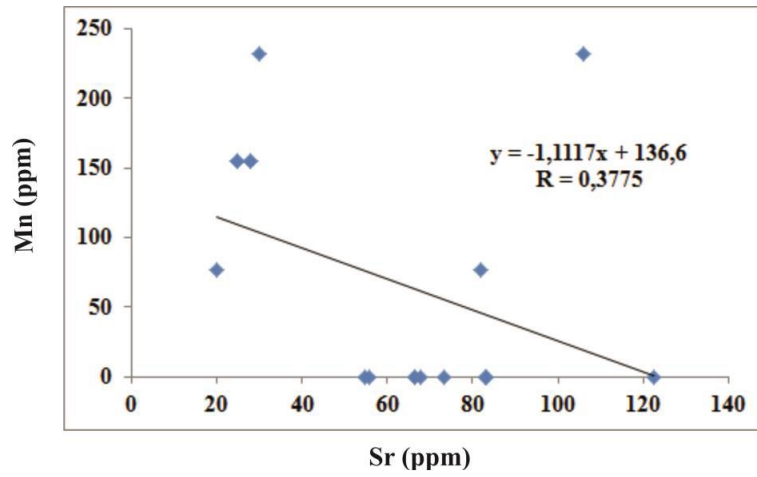


Figure 9. Sr (ppm)-Mn (ppm) graph (from Özkan, 2016)

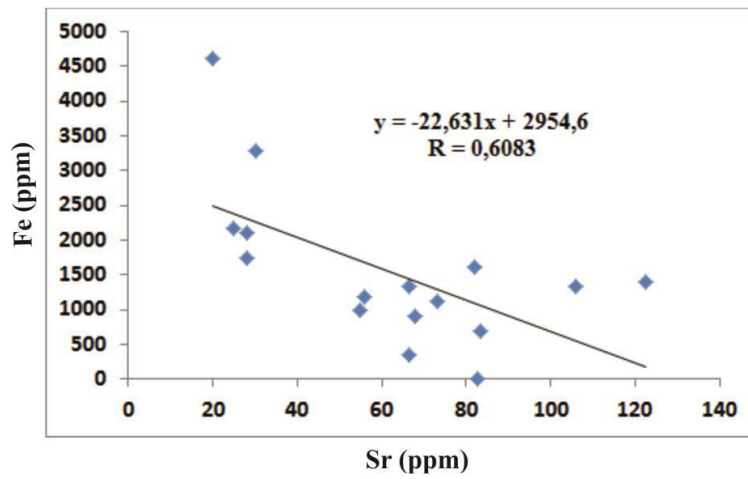


Figure 10. Sr (ppm)-Fe (ppm) graph (from Özkan, 2016)

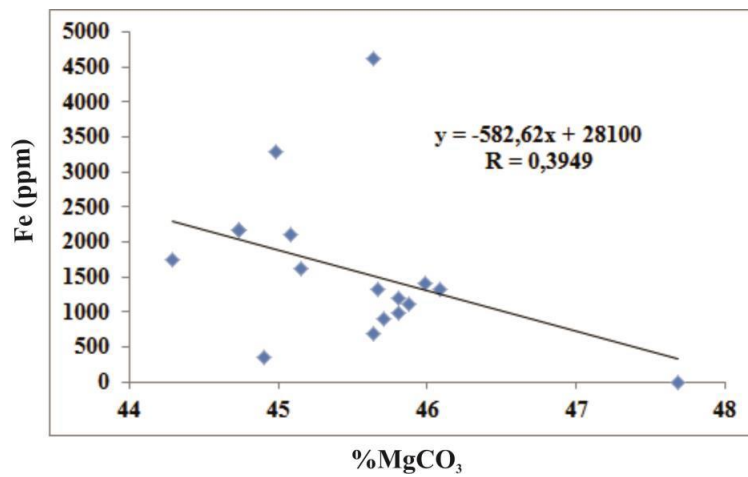


Figure 11. %MgCO<sub>3</sub>-Fe (ppm) graph (from Özkan, 2016)



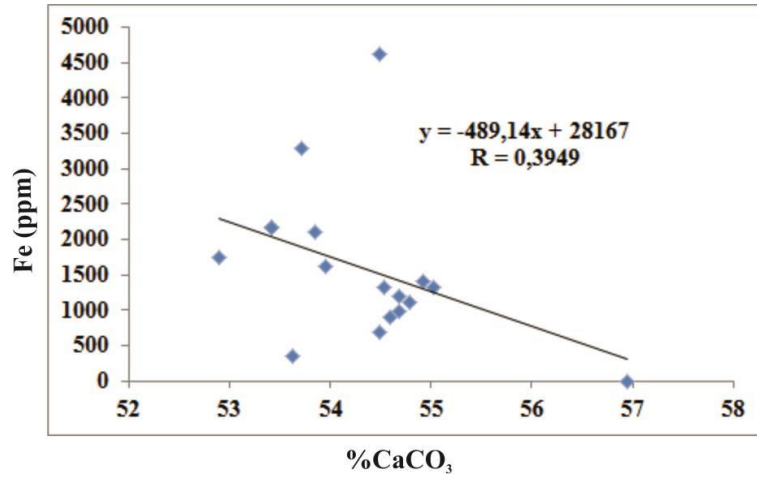


Figure 12. %CaCO<sub>3</sub>-Fe (ppm) graph (from Özkan, 2016)

### Geochemical Comments

The positive correlation between mol% CaCO<sub>3</sub> and mol% MgCO<sub>3</sub> observed in the Bozdağ Formation dolostones (Figure 2) indicates dolomitization developed from evaporative waters. During dolomitization, as the Ca ions in the dolomite minerals move away from the environment, the ratio of Mg ions increases. Thus, the composition of the dolomite formed approximates that of the ideal dolomite (stoichiometric dolomite). However, the dolomites in our samples are in Ca-rich non-stoichiometric dolomite composition (Figure 2). Due to the semi-stable nature of the dolomites, they are expected to become more stoichiometric during progressive recrystallization (Gao and Land 1991; Malone et al. 1994, 1996; Kırmacı and Akdağ 2005). However, some researchers have suggested that Ca-rich dolomites may remain stable for long periods of time (Lumsden and Chimahusky 1980; Reinhold 1998; Kırmacı and Akdağ 2005). Ca-rich non-stoichiometric dolomite is generally expressed as a function of the Mg/Ca ratio of the dolomitized solution and the liquid/rock ratio during dolomitization. As these ratios decrease, non-stoichiometric dolomite rich in Ca is formed. The presence of calcian dolomites indicates that it is composed of a solution with a low Mg/Ca ratio. Non-stoichiometric calcian dolomite can easily form in a partially closed system under rock control (Sperber et al. 1984; Török 2000; Kırmacı and Akdağ 2005).

The Mg/Ca ratio in the Bozdağ Formation dolomites is 0.6, which refers to the non-stoichiometric calcium-rich dolomites attributed to the basinal salty formation waters, which shows that the formation waters are enriched in calcium and depleted in magnesium with increasing temperature during burial.

Concentrations of trace elements in dolostones; can be determined by the concentrations of these elements in the pore fluids, the degree of openness of the diagenetic system, and the effective distribution coefficient of trace elements between dolomite and water (Suzuki et al. 2006).

Although Fe<sup>2+</sup> and Mn<sup>2+</sup> are in lower concentrations than Na<sup>+</sup> and K<sup>+</sup> in meteoric waters, if Fe and Mn increase while Na decreases in samples, this is probably related to the continuous reduction of abundant organic matter (Mahboubi et al., 2002). In addition, reducing forms of Fe<sup>2+</sup> and Mn<sup>2+</sup> are found in carbonate minerals; therefore, an increase in Fe and Mn concentrations indicates that carbonates precipitate under reducing conditions (Land, 1986; Mahboubi et al., 2002; Adabi, 2009). The reducing conditions increase with increasing burial depth (Adabi, 2009).

Barnaby and Read (1992) emphasized that the positive correlation between Fe and Mn is a commonly observed feature in burial dolomites. The positive correlation between Fe and Mn observed in Bozdağ formation dolomites (Figure 5) indicates burial dolomitization.

Primary oxic marine carbonates have been estimated to have <100 ppm Fe and <10 ppm Mn (Veizer 1983; Satterley et al. 1994), where levels of these elements reflect the degree of diagenetic enrichment. Fe (0-4616 ppm, average 1551.7 ppm) and Mn (0-232 ppm, average 67.7 ppm) contents in the Bozdağ Formation dolostone samples also indicate diagenetic enrichment.

It is difficult to determine whether Mg, Fe, and Mn are obtained from previous carbonates (Srinivasan et al., 1994). Rich Fe concentrations may be the result of primary formation from Fe-rich fluids (Srinivasan et al., 1994). Iron oxide incrustations are likely to form on detrital grains during atmospheric exposure (Srinivasan and Walker, 1993; Srinivasan et al., 1994), so they can be preserved as local sources of Fe under reducing diagenesis conditions. Alternatively, recrystallization of early fine-grained dolomites (poorly ordered and very low stoichiometric) during burial in the presence of compaction from basinal fluids (Mazzullo, 1992) may contribute to increasing Fe<sup>2+</sup> concentrations (Srinivasan et al., 1994).

The infiltration of near-surface oxidized liquids into dolomites may explain dolomite dissolution and subsequent oxy/hydroxide precipitation (Nader et al., 2007). Near-surface waters, such as meteoric water, are generally oxidized and promote rapid precipitation of insoluble Fe-oxy/hydroxide and Mn-oxy/hydroxide (Lohmann, 1988; Nader et al., 2007). It is believed that the oxidation-reduction system results in the evacuation of Mn and Fe within the matrix dissolution porosity and subsequently controls their proper incorporation into and/or subsequent cement phases (Brand and Veizer 1980; Lohmann, 1988; Nader et al., 2007).

Moss and Tucker (1995) stated that the low Sr (average 127 ppm) concentrations of the Cretaceous-aged shallow burial dolomites of southeast France may be due to the replacement of low strontium stabilized marine carbonates or the subsequent crystallization of dolomites. Therefore, we can say that the low Sr concentration (25-122 ppm, average 62 ppm) in the Bozdağ Formation dolostones developed as a result of burial recrystallization.

Rao (1996) stated that the Na content in current dolomites varies between 100-2500 ppm; with low values of mixed zone dolomites, and high values of hypersaline dolomites. The Na content in old dolomites ranges between 114-982 ppm (Baum et al. 1985). Veizer (1983) stated that Na concentrations in old dolomites are expected to be above 600 ppm for hypersaline dolomites. A marine source without significant evaporation effects shows values much lower than 600 ppm (110-380 ppm; average 226 ppm). Marine burial dolomites contain about 300-500 ppm Na (Holail et al. 1988). The Na content of Bozdağ formation dolomites (148-371 ppm, average 227 ppm) also indicates that there is no significant evaporation effect and that they are formed from seawater changed at high temperatures in the burial environment.

The Fe/Al ratio in marine sediments depends on the geochemistry of the source rock and the absolute values of Fe and Al affected by the total amount of terrigenous material associated with the biogenic fraction (Lamy et al., 2000). The negative correlation, albeit weak, between Fe and Al in the Bozdağ Formation dolostones indicates that the dolomitization developed in a reducing environment. Therefore, this situation also indicates that terrigenous material input is low in the Bozdağ Formation dolomites.

A strong positive correlation is observed between SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the Bozdağ Formation dolomites. This shows a variable mixture of marine carbonates and clay minerals. Therefore, it indicates clay input to the basin during the deposition of the Bozdağ carbonates.

The strong positive correlation observed between Rb and K<sub>2</sub>O in the Bozdağ Formation dolostones indicates that the clays in the carbonates are of marine origin (Rao, 1989). Therefore, this feature supports that the Bozdağ Formation is of marine origin.

The low Sr content and low Sr/Ca ratio of the Bozdağ Formation dolostones suggest altered sea water rather than meteoric water or evaporative concentrated brine. The low Sr content in the Bozdağ Formation dolomites and the positive correlation between Sr and CaCO<sub>3</sub> and MgCO<sub>3</sub> indicate recrystallization.

The negative correlation observed between Sr and Fe and Mn in the Bozdağ Formation dolostones, low Sr content, and high Fe and Mn content indicates a diagenetic alteration in the reducing burial environment. The negative correlation between Fe and Mn and CaCO<sub>3</sub> and MgCO<sub>3</sub> in the Bozdağ Formation dolomites also indicates the diagenetic alteration in the reducing burial environment.

Most diagenetic brines are meteoric and marine mixed waters modified by burial processes, and they are usually unsaturated with calcite but supersaturated with dolomite (Lapponi, 2007). The dolomite-calcite balance changes towards higher Ca/Mg ratios at higher temperatures (Lapponi, 2007). The temperature increase during burial in sedimentary basins will increase the saturation level of dolomite relative to calcite in solution with constant Ca/Mg ratios (Lapponi, 2007).

Mattes and Mountjoy (1980), Zenger (1983), and Mountjoy and Amthor (1994) have shown widespread replacement of limestones with an estimated depth of at least 1000 m. The most recommended fluid sources for burial dolomitization are magnesium-rich residual evaporitic brines, altered seawater, and shale compaction waters. Fluids can be transmitted to the dolomitization environment via porous aquifers or along faults by a series of transport mechanisms brought to the dolomitization environment by sediment compaction, thermal convection, and topographically or tectonically.

Trace element (especially Na and Sr) contents of carbonate rocks are important in determining the salinity of the original fluids that formed the carbonates (Wanas, 2002). This is a view based on the fact that both hypersaline and marine carbonates are enriched in Na and Sr relative to their freshwater origin (Kinsman, 1969; Land and Hoops, 1973; Land, 1980; Morrow, 1988) (Wanas 2002). It is also known that the Na and Sr contents of carbonate rocks are also reduced by meteoric waters during their diagenesis (Land et al., 1975; El-Hinnawi and Loukina, 1993; Wanas, 2002).

Wanas (2002) stated that the Na content of 1030-5120 ppm (mean=3008 ppm) is very similar to that of hypersaline or evaporitic dolostones (Land and Hoops, 1973; Mitchell et al., 1987); He stated that the Na content of 520-890 ppm (mean=656 ppm) corresponds to the concentrations of marine and marine-meteoric water mix dolomites (Land et al. 1975; Holail 1989).

Wanas (2002) found that the Sr content of 387-610 ppm (mean=508 ppm) was close to the Sr content of marine-hypersaline dolomites (Land and Hoops 1973; Land 1980); He stated that 64-140 ppm (average=108 ppm) Sr content reached the content of old marine and marine-meteoric water mix dolomites (Land 1980; Brand and Veizer 1980; Mitchell et al. 1987).

Low Sr concentrations (<300 ppm) confirm an origin from seawater (Budd, 1997; Suzuki et al., 2006). Veizer (1977) stated that the approximate average of the Sr content of pre-Quaternary limestones was around 320 ppm (Rao, 1989). The Sr ratios in the Bozdağ Formation dolostone samples are 20 ppm-122 ppm (mean=62 ppm), which is far below the rate stated by Veizer (1977). Therefore, he states that this loss is the result of meteoric diagenesis and/or recrystallization (diagenetic alteration during burial).

Milliman (1974) stated that aragonite in current marine carbonate deposits contains about 2500 ppm Na and calcite contains about 250 ppm Na. During diagenesis, Na is gradually lost due to the increasing influence of meteoric waters (Rao, 1989). Therefore, the high (148-371 ppm; mean=227 ppm) Na ratios observed in the Bozdağ formation dolomite samples indicate that the original rock is aragonite rather than calcite, as 6 out of 16 samples are higher than the current value despite diagenetic alteration.

Milliman (1974) and Rao (1989) stated that <20 ppm Mn is present in recent aragonitic marine sediments. Oxidation conditions greatly inhibit the association of Mn in CaCO<sub>3</sub>, whereas under reducing conditions calcite may have several percentages of Mn (Shanmugam and Benedict, 1983; Rao, 1989). The Bozdağ Formation dolostone samples (7 out of 16 samples) have Mn content of 77-232 ppm (average = 155 ppm for seven samples; mean = 68 ppm for sixteen samples) and originally defined aragonite mineralogy, oxidation conditions during shallow marine deposition (in most samples). Mn was not observed) and was interpreted as reflecting enrichment under reduced conditions during burial.

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