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Geology, geochemistry and isotope compositions of carbonate-hosted barite deposit in Koçaşlı (Gülnar-Mersin, Türkiye)

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Abstract

Due to the closure of the Neotethys ocean's branches, Precambrian-Mesozoic aged rocks are seen together along the Taurus Orogenic Belt. Significant barite deposits associated with carbonate rocks observed here. The Central Taurus Mountains' Devonian carbonates have evidence of the mineralization of Koçaşlı (Gülnar, Mersin) barite. The ore is oriented N10°W, with a slope and dip toward 60°SW. The ore zone is 7 meters thick and 15 meters long on average. Koçaşlı barite deposit is hosted in Paleozoic aged limestones in the Central Taurus Mountains. In accordance with the results of the geochemical analysis, the BaO concentration of the ore samples ranges from 63.76% to 68.56%. Regarding geochemical characteristics, it is similar to sedimentary type deposits and has a low SrO content. The REE-poor ore zone has no significant trace element anomalies. Stable oxygen, sulfur, and $^{87}Sr/^{86}Sr$ isotopes were each used in sequence for the initial investigations of the barite in this region. In comparison to the isotope ratio of modern sea water, the ^{34}S values of the Koçaşlı barite samples are quite high, indicating that they are enriched in the heavy isotope ^{34}S. The amount of ^{18}O isotope detected in barites is close to the amount of sulfates found in Devonian seawater. The barite samples utilized in this study have greater $^{87}Sr/^{86}Sr$ ratios than the isotopic composition of modern seawater. These 87Rb isotope levels for the barite sample indicate a significant input from the continental crust. Depending on the conclusions of the isotope analysis, sedimentary processes play an essential role in this region's mineralization.

1. Introduction

Barite ($BaSO_4$), an intensive mineral, is an important industrial raw material. Barite lacks magnetic properties despite its ability to withstand high pressure and heat without losing its chemical properties. Because of these properties, it is an essential mineral in heavy concrete implementations. Barite is still thought to be involved in the formation of Pb, Zn, Cu, and Au deposits in low, medium, and high sulfidation classes [1-2], despite being mostly found in marine environments [3-4].

The Taurus Orogenic Belt is located within the Anatolid-Torid Block, one of the three important tectonic units in Turkey [5-7], and on the Tethys Metallogenic Belt extending from Europe to Asia [8]. The Taurus Mountains within this belt, which hosts important mineral deposits, are also known to have important mineral deposits in carbonate rocks [9]. This belt, which is divided into 3 Western, Central, and Eastern Taurus Mountains (Figure 1a), consists of unities where tectonic slices are together [10]. There are many barite mineralizations associated with carbonate rocks within these units.

The Central Taurus Mountains (Koçaşlı-Gülnar, Mersin) region contains (Figure 1b) tectonic slices that are part of the Geyikdağı Unit [10]. Upper Devonian-aged limestones have been enriched with barite in the Ovacık and Araca Tectonic Slices [11]. The concentrations of BaO range from 64.76 to 67.09%, with SO_3 being the only significant oxide. Barites with an average SrO composition of 0.39% are comparable to sedimentary deposits [12]. This paper highlights the isotope geochemistry data of the local barite deposit in Koçaşlı (Mersin, Türkiye).

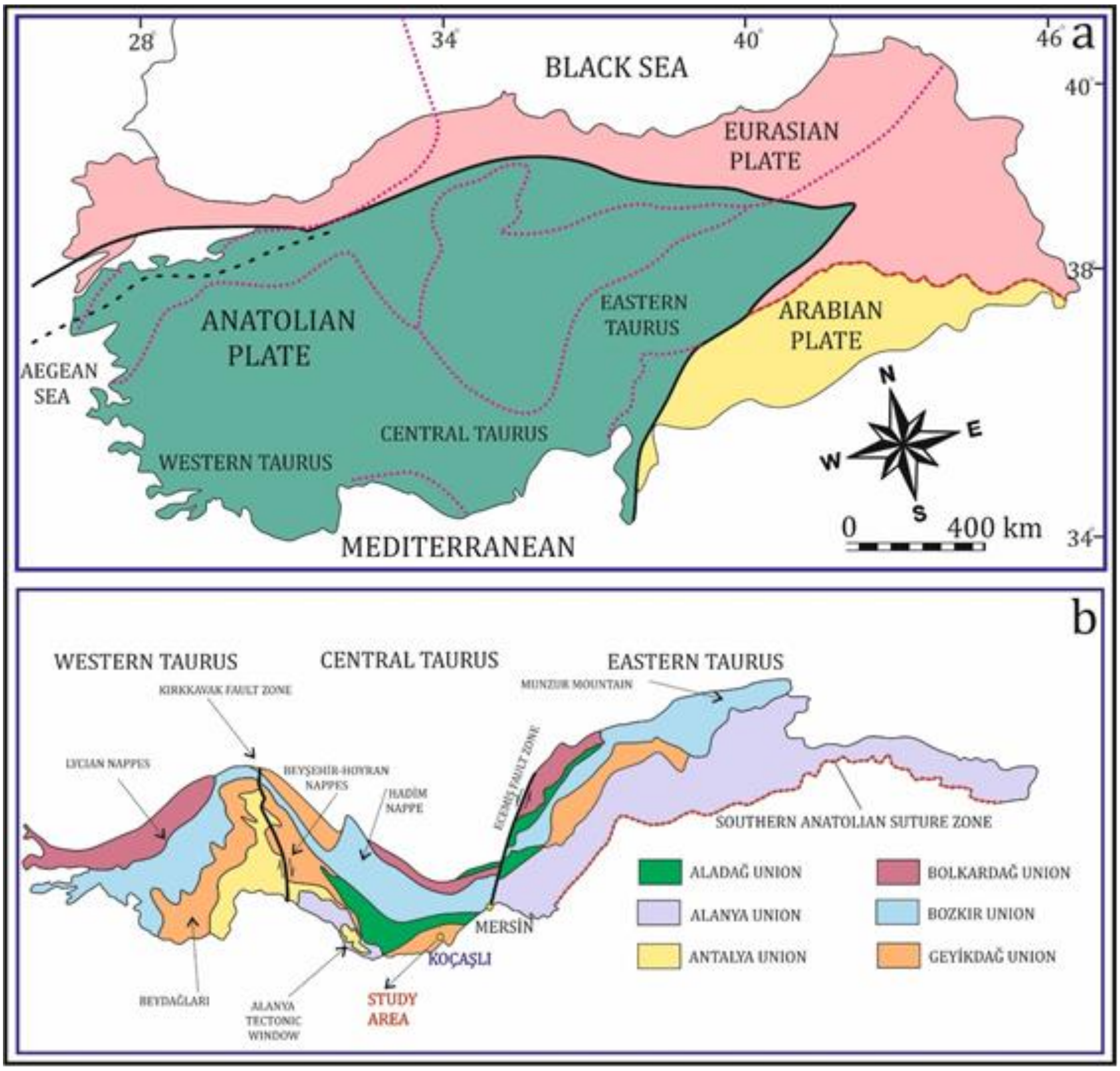

Figure 1. Tectonic location map of the study area (Modified from [13])

The Geyikdağı Union consists of shelf-type carbonate and clastic rocks of Cambrian-Tertiary age [14-16]. Paleozoic-aged sedimentary rocks form the basis of the Geyikdağı Union, which consists of two tectonic slices in the Koçaşlı region [11]. Silurian-aged sedimentary rocks consist of sandstones, gravel stones, mudstones, and limestones. The Devonian age consists of sandstone, mudstone, and limestone successions. The Paleozoic-aged basement is overlain by Mesozoic-aged sedimentary rocks with angular unconformity.

Barite deposits have been identified on a Devonian-aged limestone outcropping southeast of Koçaşlı district (Figure 2). The ore is oriented N10°W, with either a slope and dip oriented 60°SW. The ore zone is 15 meters long and 7 meters thick on average. The upper levels of this ore zone are rich in iron (Figure 3) [12].

2. Material and Method

Samples were taken from the field in order to clarify the barite mineralization. In order to determine the geochemical properties of the mineralization, powdered barite and ferrous zone samples were sent to ACME (Vancouver-CANADA) laboratory. The samples were analyzed by ICP-AES/ICP-MS method and the main oxide, trace element and Rare Earth Element concentrations of the samples were determined (Table 1).

Stable oxygen, sulphur, and $^{87}Sr/^{86}Sr$ isotope analyses were completed (Table 2) to demonstrate the formation of barite deposits. Barite isotope analyses of ^{18}O and ^{34}S were performed at Washington State University in the United States, whereas $^{87}Sr/^{86}Sr$ isotope analyses of the same specimens were performed at the Middle East Technical University's Central Laboratory R&D Training and Measurement Center (Ankara).

Figure 2. General view of ore zones

Figure 3. General view of iron-rich zone

3. Geochemistry

The results of geochemical analysis show that the BaO value in ore samples ranges from 63.76% to 68.56%. The same samples' SrO values range from 0.36 to 0.52%. Although other main oxide values in the ore samples are fairly low, SO_3 concentrations range from 28.40 to 29.80%. Fe_2O_3 values are quite high in samples from the iron-rich zone, and no significant results were found for the other oxides.

The trace element contents of the samples examined within the scope of the study is generally very low and below the measurement limits for many elements. According to these data, no significant concentration could be obtained.

Finally, when we look at the Rare Earth Element (∑REE) amounts of the analyzed samples, very poor concentration values were obtained. These values are between 5.74-9.03 ppm and iron-rich samples are even poorer.

Table 1. Major oxide, trace and rare earth element concentrations of the samples

SAMPLE	KO-1	KO-2	KO-3	KO-4	KO-5	KO-6	KO-7	KO-8
SiO_2	3,79	0,24	0,13	0,01	0,56	0,52	0,67	1,66
Al_2O_3	0,48	0,05	0,29	0.01	0,25	0,13	0,04	0,11
Fe_2O_3	91,70	0,12	0,22	0,06	0,22	0,13	75,60	64,30
CaO	0,58	0,86	0,76	0,28	0,66	0,46	5,68	20,71
MgO	0,01	0,47	0,66	0,05	0,18	0,11	0,01	0,01
Na_2O	0,01	0.01	0,45	0.01	0,44	0,52	0,01	0,01
K_2O	0,05	0.01	0,03	0.01	0,03	0,03	0,04	0,03
MnO	0,08	0,01	ND	0.01	ND	ND	0,07	0,06
P_2O_5	0,04	0.01	0,01	0.01	0.02	0.03	0,04	0,04
BaO	0,01	**63,74**	**65,20**	**65,09**	**66,20**	**68,50**	ND	ND
SO_3	0,77	29,80	29,60	29,30	29,60	28,40	0,65	0,62
SrO	ND	0,37	0,36	0,45	0,43	0,52	ND	ND
LOI	2,46	1,34	2,13	0,33	1,29	0,65	16,26	12,20
TOTAL	**99,98**	**97,00**	**99,85**	**95,57**	**99,87**	**99,97**	**99,07**	**99,75**
				TRACE ELEMENT (PPM)				
Hf	1,2	1,1	1,1	1	0,9	0,8	1,1	1,2
Nb	0,2	0,2	0,1	0.1	0,1	0,2	0,1	0,1
Rb	0,1	0,4	0,1	0.1	0,1	0,2	0,2	0,1
Ta	2,2	2,6	2,3	3	2,6	2,4	2,8	2,6
Zr	ND	0,9	ND	0,1	0,1	0,1	0,2	0,1
Cu	2,2	3,3	1,3	17,2	3,4	5,2	5,3	6,2
Pb	1,2	5,5	2,3	14	2,4	3,2	1,2	1,4
Cr	ND	6,8	ND	6,8	ND	ND	ND	ND
Y	1,2	1,4	1,1	1	0,9	1,1	1,2	0,8
				REE (PPM)				
La	1,20	3,60	2,50	3,90	3,40	2,20	1,20	0,90
Ce	1,00	1,10	0,20	0,30	0,30	1,20	0,70	1,10
Pr	0,06	0,17	0,03	0,07	0,04	0,12	0,11	0,09
Nd	0,10	0,30	0,20	0.3	0,10	0,20	0,10	0,10
Sm	0,47	0,57	0,56	0,68	0,65	0,48	0,62	0,55
Eu	0,10	0,10	0,20	0,10	0,20	0,10	0,10	0,20
Gd	2,34	2,53	2,56	2,76	2,73	2,12	2,43	2,32
Tb	0,02	0,06	0,03	0,05	0,04	0,03	0,02	0,02
Dy	0,32	0,42	0,34	0,49	0,45	0,32	0,43	0,40
Ho	0,01	0.02	0,01	0.02	0,02	0,01	0,03	0,02
Er	0,01	0,04	0,02	0.03	0,03	0,02	0,01	0,02
Tm	0,02	0,02	0,01	0,02	0,02	0,03	0,01	0,01
Yb	0,08	0,12	0,11	0,09	0,07	0,12	0,11	0,09
Lu	0,01	0.01	0,02	0.01	0.01	0,02	0.01	0,02
∑ REE	**5,74**	**9,03**	**6,79**	**8,46**	**8,05**	**6,97**	**5,87**	**5,84**

Many researchers have suggested that the amount of SrO in barite deposits formed by hydrothermal solutions is usually 1.5% larger [17]. On the other hand, Puchelt [17] and Striebel [18] stated that this ratio is generally 1% smaller in sedimentary or exhalative sedimentary mineralizations formed by colder solutions. The SrO contents of the ore samples in the study area vary between 0.36% and 0.52%, indicating that sedimentary processes were effective in the mineralization. Additionally, Scherp [19] and Puchelt [17] both noted that barites generated in marine environments contain relatively little Sr, despite the fact that the Ba/Sr ratio is large in aqueous sedimentary contexts. In this regard, it can be noticed that Koçaşlı barites are of sedimentary type formation when compared to various types of deposits (Figure 4).

Table 2. Oxygen, Sulphur, and $^{87}Sr/^{86}Sr$ isotope contents of barites

SAMPLE	MINERAL	$\delta^{18}O_{SMOW}$	$\delta^{34}S_{VCDT}$	$^{87}Sr/^{86}Sr$
KO-4	Barite	14.61	32.07	0.710618
KO-2	Barite	14.95	31.90	0.710623
AVERAGE		**14.78**	**31.99**	**0.710621**

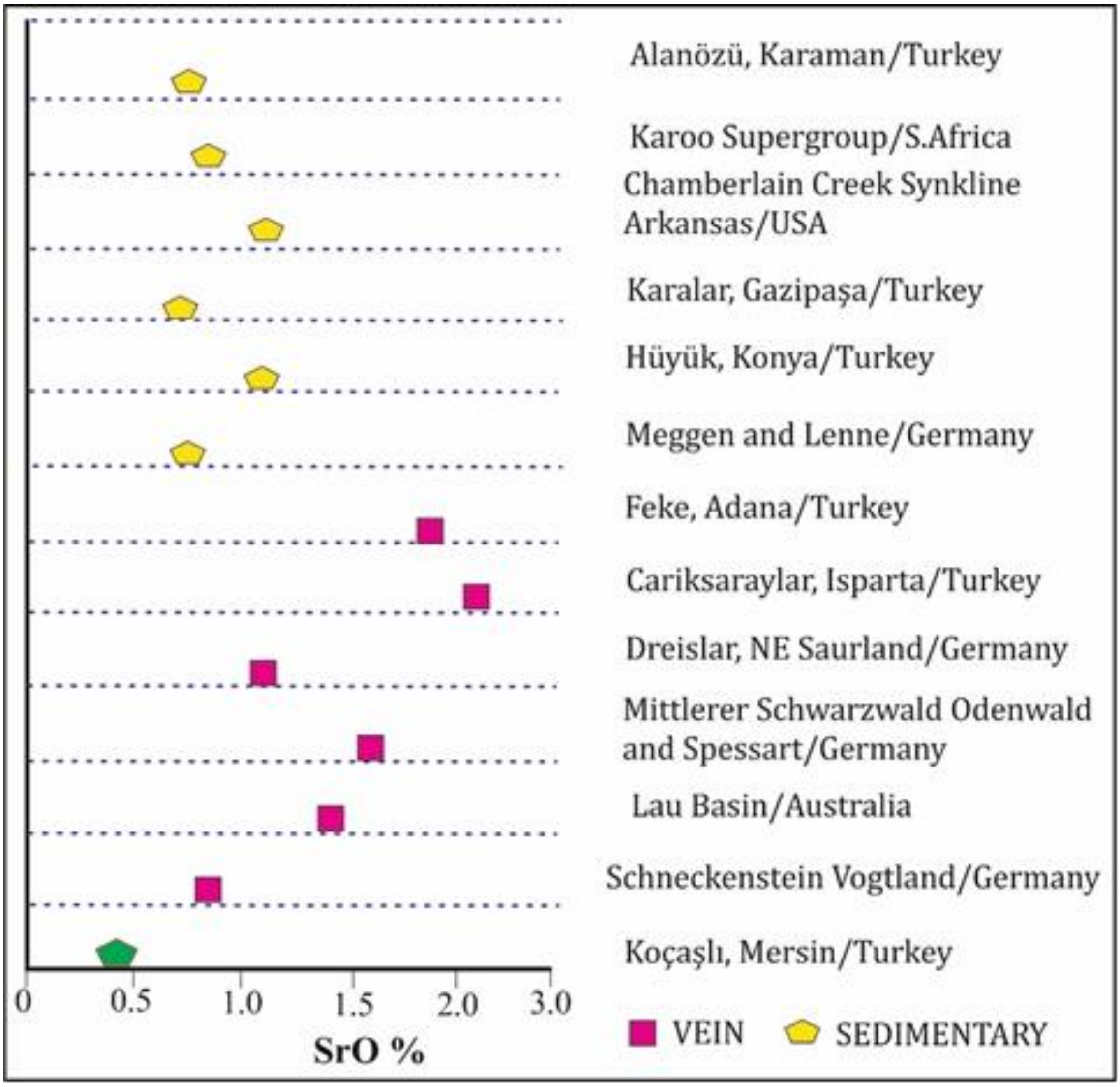

Figure 4. Percentage of strontium oxide content of different types of barite deposits (modified from [20])

The isotope compositions of sulfur, oxygen, and strontium in 2 barites (almost pure) from the ore zone were detected. Table 2 shows the results of the isotope analysis.

The composition of the sulfur isotope ($\delta^{34}S$) in barite is very similar to the sulfate $(SO4)_2^-$ anion that it precipitates [21]. Therefore, the composition of the $\delta^{34}S$ isotope in barite ($BaSO_4$) characterizes its forming liquids. The average $\delta^{34}S$ values of Koçaşlı barites were determined as 32.07 and 31.90 ‰, respectively. These values are quite high compared to the SO_4^{2-} ($\delta^{34}S$=21‰) isotope composition in today's seawater, indicating that it is enriched in ^{34}S.

In this respect, it may be suggested that diagenetic processes and microorganisms have a major impact on the formation of regional barites. The amount of $\delta\ ^{18}O$ isotope observed in barites exhibits similarities with the sulfates observed in saltwater from the Devonian period.

The $\delta^{34}S$ and $\delta^{18}O$ compositions of marine sulfate have evolved significantly from the Precambrian to the present. The results of this inquiry are shown in Figure 5 in terms of these values.

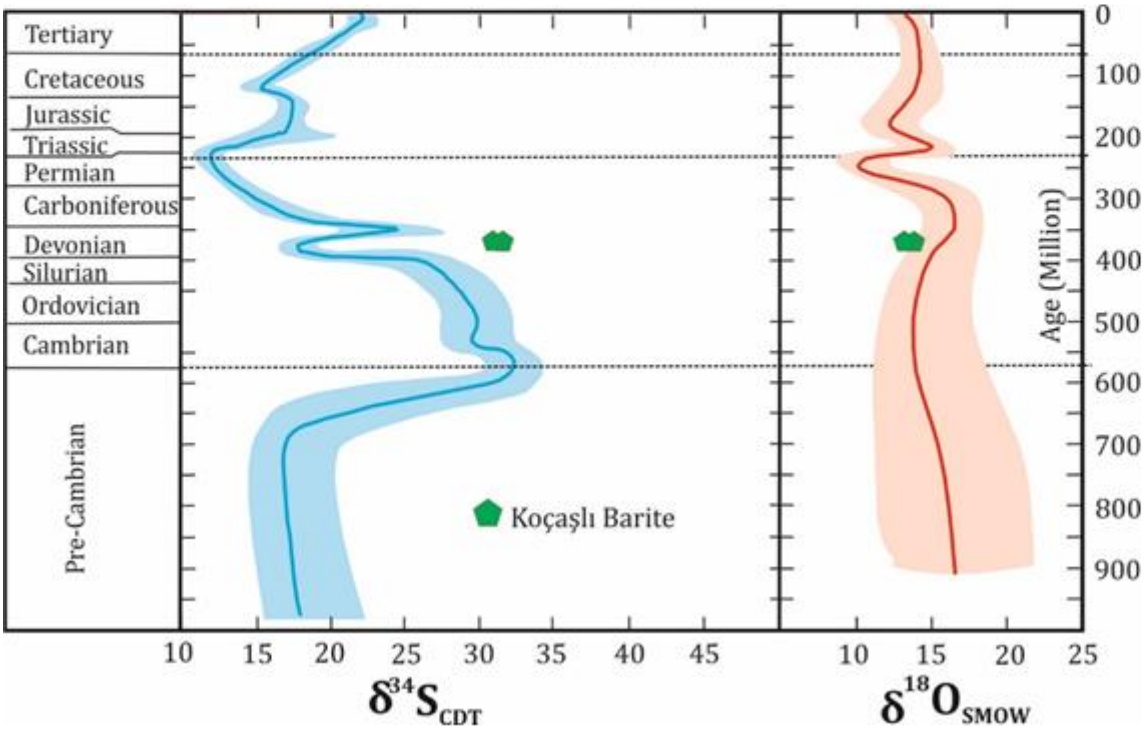

Figure 5. The $\delta^{34}S$ and $\delta^{18}O$ isotopic composition of marine sulphate and Koçaşlı barites examined in the study in different geological periods from the Precambrian to the present [22]

Sulfur and oxygen isotope results of Koçaşlı barites are compared with mineralization occurring in different regions of the world and given in Figure 6. The isotopic composition of the samples is very similar to cold seep barites.

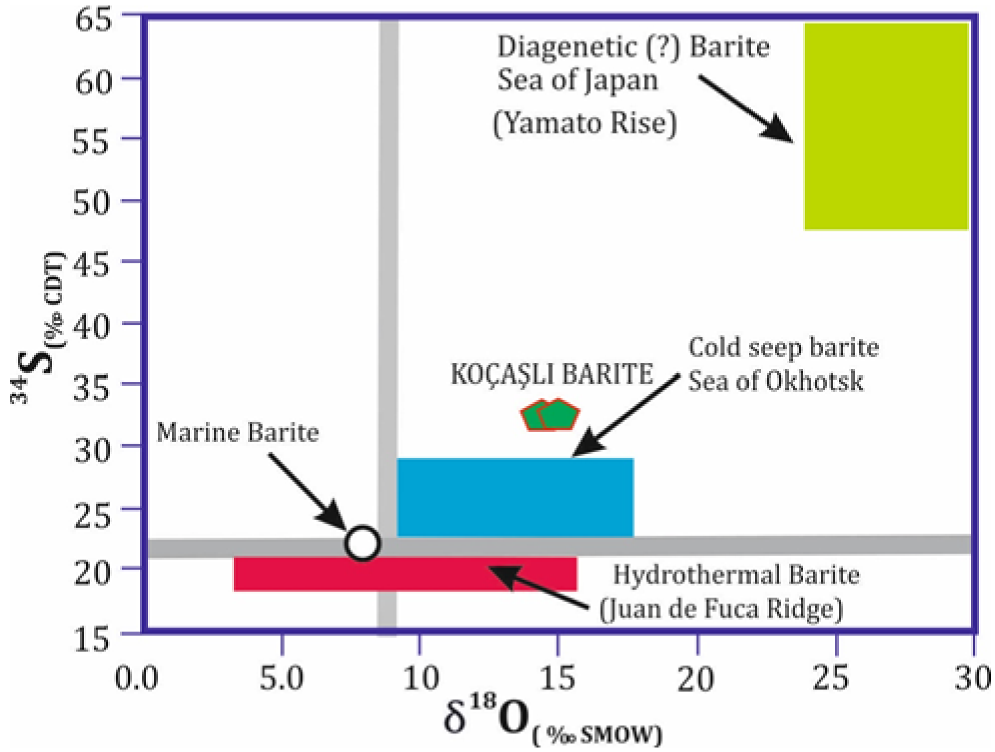

Figure 6. Position in the diagram created using oxygen and sulfur isotope data for Koçaşlı barite. Modified from [23]

The crystal structure of barite mineral contains up to 3% Sr and the $^{87}Sr/^{86}Sr$ isotope content reflects the characteristics of the formation environment of barite [23-25]. Furthermore, $^{87}Sr/^{86}Sr$ isotope ratios are used for the correlation of many barite deposits [24]. The $^{87}Sr/^{86}Sr$ ratios of the barite samples examined within the scope of the study are considerably higher than the isotope composition of modern seawater. Figure 7 shows the isotope ratios of barite deposits of different ages in the world and the ratios in this study together. This diagram shows that Koçaşlı barites exhibit a unique isotopic character.

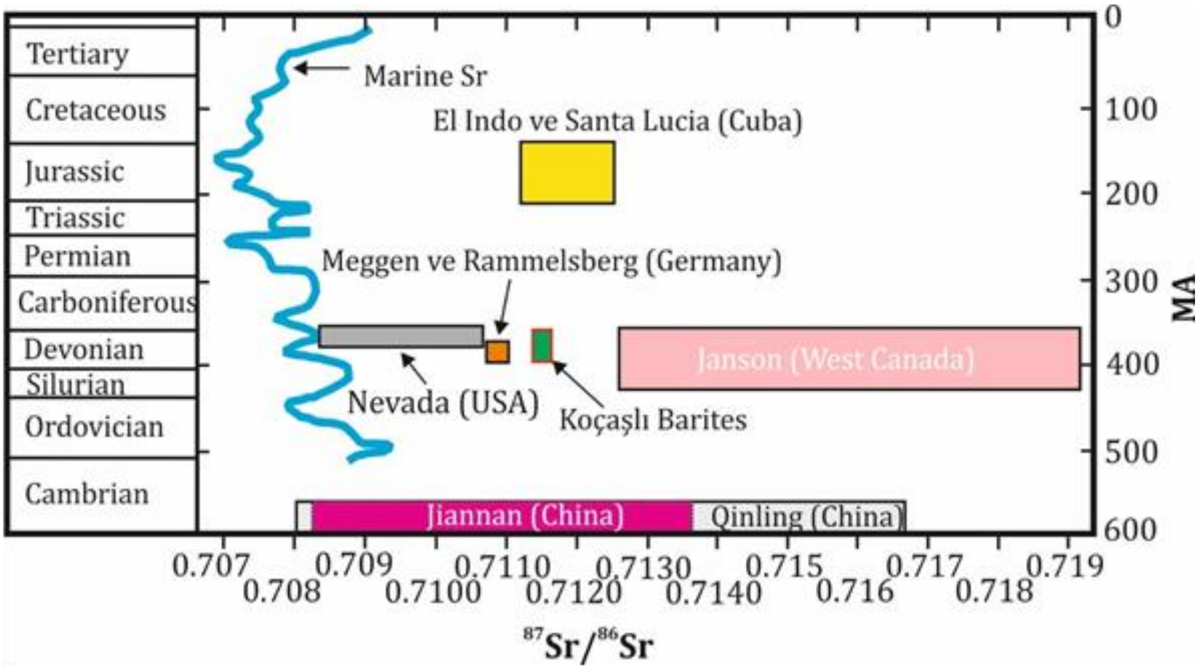

Figure 7. Comparison of strontium isotope values of Koçaşlı barites with barites from different time periods in the world [26]

The Koçaşlı barite has higher $^{87}Sr/^{86}Sr$ ratios than the isotopic composition of modern seawater. These barite sample isotope values indicate a rich source of ^{87}Rb, implying a significant contribution from the continental crust. Figure 8 compares the isotope values of barite samples to values from hydrothermal, diagenetic, and terrigenous (terrigen) sources. The graphic shows that Koçaşlı barites have characteristics in common with diagenetic and cold seep barites. Additionally, it is evident that the mineralization is overly influenced by the terrigenous material.

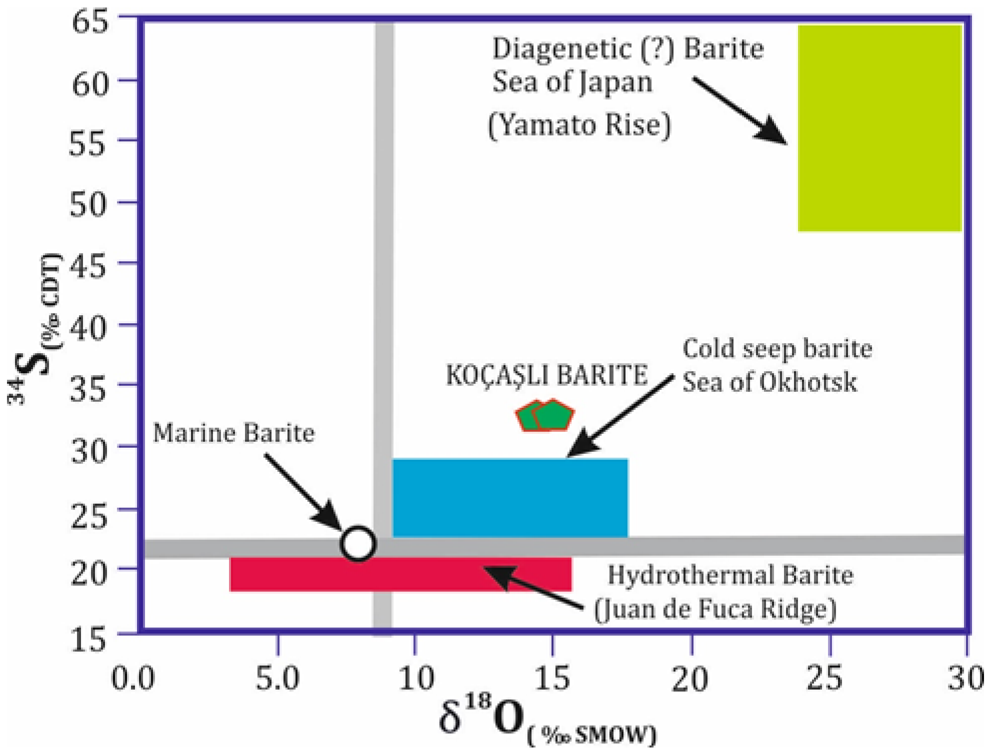

Figure 8. $^{87}Sr/^{86}Sr$ and $\delta^{34}S$ isotopic composition of barites formed in different processes [4]

4. Discussion

Barite mineralization is observed in carbonate rocks along the Taurus Orogenic Belt. In some regions, barite is observed in pure form, while in other regions, galenite, sphalerite and fluorite are formed together with barite. In general, there is a lot of information in the literature about barite mineralization observed in Paleozoic successions. However, apart from the Taurus Orogenic belt, there are also barite mineralizations associated with carbonate rocks on the Arabian Plate [27-29]. In Turkey, the potential for barite formation in carbonate sequences within both tectonic units is quite high.

5. Conclusion

Koçaşlı barite deposit is hosted in Paleozoic aged limestones in the Central Taurus Mountains. It has low SrO content in terms of geochemical characteristics and is similar to sedimentary type deposits. There are no significant trace element anomalies in the REE-poor ore zone.

The isotope data indicate that the majority of the Koçaşlı barite deposit was formed by sedimentary processes. It has been discovered that the highly sulfur-rich oxygen isotopes of barites represent the ocean sulfates from the Devonian period.

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Author contributions

Volkan Karasu: Geology, Geochemistry. **Cihan Yalçın**: Data curation, Methodology, Writing-Original draft preparation, Reviewing, and Editing, Software. **Yusuf Uras:** Geochemistry, Investigation

Conflicts of interest

The authors declare no conflicts of interest.

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