Gemological features of diaspore in sodra—Milas (mugla) region

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Diaspore, is related to bauxite in terms of its formation mechanism. Diaspore is one of the gemstone quality stones used in jewelry and jewelry making. It is possible to come across gemstones in various regions of the world. In our country, there are gemstone deposits in all regions. In these deposits, diaspore crystals are considered very valuable. Within the scope of this study, it was aimed to determine the gemological features of the diaspore formations in Sodra (Milas-Mugla) and its surroundings, as well as to determine other minerals and their formation conditions. Main oxide, trace, and rare earth element analyses were performed on seven collected samples. The classification was made using the Al_2O_3-SiO_2-Fe_2O_3 triangular variation and it was determined that bauxite samples were in the "ferric bauxite" and "bauxite" areas. SEM imaging and EDS analyzes were performed on the samples and according to this result, it was determined that the samples mainly contained O, Al, and Si. The data obtained as a result of Raman Spectroscopy were matched with the device's own data library and it was determined that the samples taken from the Sodra region were diaspore. In addition, according to the results of the FTIR analysis performed on the faceted sample taken from the Sodra region, it was seen that the samples were compatible with the reference standards and it was scientifically proven to be a diaspore crystal with gemstone quality. During the field studies carried out in the study area, diaspore crystals were encountered in the Milas-Sodra region, together with chloritoid and muscovite, within the metabauxite formations and in the altered zones close to the metabauxite limestone contact. Rock were classified as "muscovitequartzschist," "quartzschist" with grano-lepidoblastic texture, "micaquartzschist" with lepidoblastic texture, "phyllite" with lepidoblastic texture, and "chlorite-epidote fels" with nematoblastic texture as a result of petrographic analyzes performed on the country rock samples. It is predicted that these gemstone-quality diaspore crystals can be evaluated economically.

KEYWORDS

gemology, metabauxite, Raman spectroscopy, Sodra, diaspore (AlOOH)

1 Introduction

Diaspore is a bauxite mineral, with the chemical formula [Al(OH)O], it has the feature of being a single mineral, and about 40% of its crystals have a transparent-translucent structure. Diaspore, which has the ability to change color like Alexandrite, is a rare stone due to this feature. While the diaspore is green-yellow in white light, it turns pink-red in daylight. Since it is not too hard, it can break while cutting. Diaspore, which has a hardness level of 6.5–7 according to the Mohs Hardness Scale, is used in jewelry and jewelry making. This is the main reason why the Turkish diasporic stone is so popular and in demand. Since diaspore is a bauxite mineral, its formation mechanism is related to bauxite formation.

Bauxite rock contains different minerals in varying amounts, and it has more than 45% Al_2O_3 in its composition. In addition to aluminum hydroxide minerals, this rock also contains iron oxide, hydroxide minerals, clay minerals, secondary amounts of silica, titanium, and other minerals. Iron compounds in bauxites are amorphous iron hydroxide, goethite, hematite, lepidocrosite, magnetite, maghemite, pyrite, marcasite, siderite, and leukoxene. The main clay minerals are kaolinite, halloysite, chlorite and illite. Silica is found in the form of quartz and chalcedony. Apart from these, bauxite may contain up to 4% rutile and anatase (Temur, 2001).

In order to avoid confusion/difficulties in the classification of bauxite deposits, various researchers have proposed a general classification model based on previous studies. Accordingly, bauxite deposits can be genetically divided into three main groups: lateritic, sedimentary (tikhvin), and karstic species (Bogatyrev et al., 2009). Lateritic-type bauxites are residual deposits derived from underlying aluminosilicate rocks whose preserved texture and composition can be directly associated with the underlying source rocks. Sedimentary (tikhvin) type bauxites are clastic bauxite deposits that cover the eroded surface of aluminosilicate rocks, and karstic type deposits overlie the karstified surfaces of carbonate rocks (Bárdossy and Aleva, 1990). Karstic type bauxites are subdivided into autochthonous, para-autochthonous, allochthonous, and para-alloctonous subtypes (Bárdossy, 1982). In Turkey, there are mostly karstic type and less laterite type bauxite deposits among the main three deposit types (Robertson and Ustaömer, 2009).

There are important and current studies on bauxite in the world and our country (Karadag et al., 2003; Hanilci, 2013; Yalcin and Ilhan, 2013; Nyamsari and Yalcin, 2017; Sidibe and Yalcin, 2019; Nyamsaria et al., 2020; Ozer and Yalcin, 2020; Ozturk et al., 2021; Kinaci and Ozturk, 2022). Karadag et al. (2003), determined that the study area did not differ much from other deposits in the Seydişehir region, and they distinguished five types of ores in the deposit: massive, oolitic, pisolithic, clayey, ferrous, and brecciated. They stated that the prevalence of oolitic-type ore in the deposit indicates the presence of a warm, shallow and turbulent environment during the ore formation. Hanilci (2013) stated that bauxitization processes started with the formation of lateritic soil rich in kaolinite after the Upper Triassic and pre-Aalenian. In particular, it was stated that Rb, K, Ba, Ce, Si, Y, Sr, P, Ca, Mg, and U elements were lost by weathering/abrasion during bauxitization, while Fe, V, Pb, Ni, and Cr elements were gained in the bauxite area (Hanilci, 2013). Yalcin and Ilhan (2013) found the average modulus of bauxites to be 18.04 according to the Al_2O_3/SiO_2 ratio, and it was determined that Küçükkoraş bauxite was the best quality bauxite. Geochemical data showed that the limestone was formed as a result of the transformation of limestone into bauxite first and then into terra rossa. Nyamsari and Yalcin (2017), origin rock research showed that the source of bauxite is mafic, basaltic andesite igneous rocks with medium pH (basic-acidic characteristic). Sidibe and Yalcin (2019) determined that the mineralogy of both bauxite types (sedimentary and lateritic) of the Balaya plateau is almost the same. Nyamsari et al. (2020) stated that the rocks in the Haléo-Danielle Plateau bauxite deposit were subjected to intense weathering, which led to the formation of industrial bauxite deposits. Examination of the

bedrocks revealed that bauxite was formed due to weathering of magnesium-iron andesite-basalts under conditions with near-neutral redox potential. Ozturk et al. (2021) stated that bauxites in the Payas region occur in two types, cover and pocket, are chemically and texturally homogeneous, and have a thrust structure with ophiolitic melange formations. They stated that bauxite is mainly composed of diaspore, hematite, rutile, anatase, rare kaolinite, boehmite, and pyrite minerals, and prismatic and stave-shaped euhedral rutile in bauxites, and bauxites are formed *in situ* from Ti-rich basaltic pyroclastics.

Diaspore is an extremely rare, gemstone-quality form of aluminum oxide hydroxide, one of the three main mineral components of bauxite, an important aluminum ore widely used for many industrial purposes. It has the unique feature of changing color under different lighting conditions. The color-changing diaspore is easily distinguishable from other similar gemstones by the unique presence of pleochroism and its excellent color-changing ability. Choo and Kim (2003) determined that tourmaline found in the Milyang clay deposit, diaspore nodules from the Milyang clay deposit in southeast Korea form as clusters or diffused crystals in the clay matrix, and diaspore nodules occur next to or near fracture zones that develop in the clay bed. Hatipoglu et al. (2010) revealed that the diaspore [AlO(OH)] is polycrystalline in their study in the Ilbirdagı diasporic metaboxite (diasporite) deposit in Milas (Mugla) region of Turkey. The reason why the diaspore crystals in this deposit are more unique than those in other deposits is that the diaspore is optically uniform and pure. Hatipoglu (2011) detected diaspore, gibbsite, corundum, specular hematite, ilmenite, chloritoid, goethite, ferroalluaudite and Fe-Mg-rich muscovite in his microscopic studies in the diaspore mineralizations in the Upper Cretaceous Early Paleogene aged marble succession in the Menderes Massif. It was also concluded that the composition of the primary fine-grained mineralization in the unaltered (original) bauxite ore is sufficient to be considered a source for much later mineralization in the fracture zones.

The increase in diaspore prices in recent years (96-carat diaspore jewelry designed in London is valued at 1.5 million dollars) has increased the attention and importance of this mineral. Within the scope of this study, it was aimed to determine the diaspore and other accompanying minerals in the metabauxite ores found in Sodra and its surroundings (Supplementary Figure S1), and to determine their formation conditions and gemological properties. It is thought that diaspore is very rare in the world and it will make significant contributions to the semi-precious stone industry as a result of bringing the minerals discovered for the first time in the Milas—Sodra region with this study to the literature.

2 Materials and methods

Detailed geological and structural investigations were made at the contact of core and cover units, which are important in terms of diaspore mineralization in field studies; samples from the Sodra (Milas) region were collected in numbers and qualities that could represent the region, and a total of 16 samples were sent for analysis. In the laboratory studies, the preparation of the samples and petrographic analyzes were performed in the Geological Engineering Department of Konya Technical

University (Turkey), and the chemical analyzes and gemological analyzes were performed in domestic (BİTAM) and foreign accredited laboratories (ACME).

Petrographic thin sections were prepared from the samples. Petrographic studies in mineral determinations were completed by using a scanning electron microscope (SEM-EDS) for local element determination and imaging purposes. Qualitative element analysis was performed with the Hitachi-SU 1510 device at 10 and 100 μ zooms with point and mapping methods. SEM-EDS imaging procedures were performed in the Necmettin Erbakan University BİTAM laboratory (Turkey).

Whole rock (main oxide, trace element, and rare earth element) and mineral chemistry analyzes samples were chemically analyzed to make geochemical and geostatistical evaluations on the rock and mineral samples taken from the study area. The samples collected from the field for geochemical investigations were reduced to less than 0.5 cm by hammering or through jaw crushers. Then, rock samples weighing 20–50 g were ground in automatic mortars or agate mortars so that the grain size was below 70 μ. Analyzes were made at Bureau Veritas (Canada) ACME Laboratory.

Since diaspore samples are few and economically important, non-destructive analysis methods are preferred in gemology. For this purpose, scans with FTIR (Fourier Transform Infrared Spectroscopy/Fourier transform infrared spectroscopy) device equipped with MAGILABS GemmoFtir™ spectrometer low noise DLATGS- detector obtained at a resolution of 4 cm-1 for a measurement time of 20 s. With these methods, peaks were formed by detecting the characteristic fingerprint of each sample and these peaks were used for chemical identification.

Measurements were made with Renishaw in *via* Reflex Raman, which is used for another non-destructive identification purpose. A silicon wafer was used to calibrate the device before measurement. Raman Spectrometer analysis was performed in Necmettin Erbakan University BİTAM laboratories to verify the FTIR analysis.

3 Research results and findings

3.1 Regional geology

Studies conducted in the last two decades have largely revealed the relationship between the Menderes Massif and the Lycian nappes in the area between Bafa Lake and Mugla, and the stratigraphy of these units (Konak et al., 1987). In the north of Kale-Tavas regions, the extent to which the Menderes Massif extends to the east and its relationship with the Lycian nappes is little known. The region between Bafa Lake and Mugla, where the geology of the Menderes Massif is best known, should be taken as a standard region. The main points defining the Menderes Massif in this region are given below (Okay, 1985).

From bottom to top, the Menderes Massif sequence consists of Precambrian gneisses, Lower Paleozoic mica schists, Permo-Carboniferous metaquartzite, black phyllite, and black recrystallized limestones, Mesozoic age, bauxite-level, thick-bedded, recrystallized, neritic limestones and recrystallized limestones up to the Lower Eocene flysch. Lycian nappes, which were emplaced in the Middle Eocene with a tectonic contact, overlie the Eocene flysch, the youngest unit of the massif. In the Menderes

Massif, regional metamorphism of Eocene aged Barrovian type, gradually decreasing from bottom to top, is observed. This regional metamorphism (Sengor et al., 1984b), which developed due to the emplacement of the Lycian nappes on the Menderes Massif, also affected the lower parts of the Lycian nappes. In terms of metamorphism, there is no discontinuity between the Menderes Massif and the nappes overlying it. Apart from the Eocene metamorphism in the Menderes Massif, traces of old metamorphism of the Pan-African age were found in Precambrian gneisses. The Menderes Massif constitutes the lowest tectonic unit between Lake Bafa and Mugla and is in a relatively autochthonous position. The massif has a simple south-dipping structure, which developed due to regional uplift and erosion during the Oligocene. Large-scale thrusts and isoclinal folds are not observed in the massif (Satir and Friedrichsen, 1986).

Metabauxite formations were observed as a karstic fill at the border of white-colored recrystallized limestone and dark-colored recrystallized limestone (recrystallized dolomitic limestone). Diaspore formations, on the other hand, were observed in the carbonate-altered zone at the contact of metabauxite and recrystallized dolomitic limestones and in the cracks of metabauxites, generally together with mica (muscovite)-chloritoid formations (Supplementary Figure S2).

3.2 Geochemistry

A triangular variation of Al_2O_3-SiO_2-Fe_2O_3 (Meshram and Randive, 2011; Gu et al., 2013; Zamanian et al., 2016) was used. With the bauxite samples taken according to the classification, Milas-Yatagan Area (ORT_1), Seydisehir-Akseki Area (ORT_2), Isparta-Sarkikaraagac area (ORT_3), Kokaksu area (ORT_4), Bolkardagi area (ORT_5) and Payas-Islahiye area (ORT_6) in Turkey was evaluated together with the bauxite formations (Hanilci, 2019) and it was determined that the bauxite formations in the study area had "ferric bauxite" and "bauxite" characteristics (Supplementary Figure S3). In addition, it is seen that the bauxite formations have undergone a high degree of chemical change/alteration according to the Chemical Index of Alteration (CIA) degree of alteration.

The Si ratios in the metabauxite and diaspore samples taken to represent the general study area vary between 0.88% - 15.52% and 0.18%–0.32%, respectively. The arithmetic value of the population (Samples) is 4.25% (metabauxite) and 0.25% (diaspore). These values obtained are the Al value is between 16.27% and 28.80% (metabauxite) and 38.80%–40.15% (diaspore) and their average values are 24.59% and 39.31%, respectively. The Al value in the earth's crust is 8.13% (Krauskopf, 1979). The average values obtained are approximately 3 and 5 times higher, respectively, than the value in the earth's crust. The Fe average was 13.90% (metabauxite) and 0.56% (diaspore). The lowest values among the samples taken were 9.76% (metabauxite) and 0.59% (diaspore); the highest values are 16.79% and 0.64% (diaspore). These values are approximately 2.5 (metabauxite) times higher than the average Fe in the earth's crust, which has a value of 5% (Krauskopf, 1979) (Supplementary Tables S1–S3).

Diaspore samples collected from the study area were normalized according to chondrite (Taylor and McLennan, 1981; Boynton,

1984) (Supplementary Table S4). Their normalization graph was prepared according to LREE (light rare earth elements), MREE (medium rare earth elements) and HREE (heavy rare earth elements) (Supplementary Figure S4). According to this chart; a clear agreement is seen in the normalization graph of S-1, S-2, S-3, and S-4 diaspore samples according to chondrite.

In order to determine the color changes of the diaspore samples in the study area, the main and trace elements that can cause color changes were made logarithmically according to the chondrites (Pearce et al., 1984) and the analysis values were compared (Supplementary Figure S5).

It is seen that the lightly rare earth element enrichment (LREE) in the samples is higher than the medium (MREE) and heavy rare earth element (HREE) enrichment. This may be due to material coming from the upper continental crust to the source magma. In addition, a negative Eu anomaly is observed. The presence of negative Eu anomaly indicates that plagioclase differentiation (Kalkan and Ozpinar, 2018) plays an important role in the development of these rocks.

3.3 SEM-EDS studies

According to the results of the point and mapping method made for the determination of the elements that can be found in the crystal lattice structure of three diaspore samples collected from the region, oxygen was determined as 55% and aluminum as 42%. As a result of SEM imaging and EDS analyses, it was determined that the samples mainly contain O, Al, and Si, and the presence of K, Na, Fe, Ca, and Mg in addition to these elements in close-ups (Supplementary Figures S6–S9).

3.4 Raman spectroscopy studies

Due to its non-destructive nature and fast measurement times, low material and sample preparation requirements, Raman spectroscopy is routinely used for gemstone identification, examination of inclusions, and possible value enhancement (Bersani and Lottici, 2010). As a result of the shooting, in the light of the match values taken from the microscope's own database, it was determined that the sample was diaspore, and Brucite $[Mg(OH)_2)]$ was found at 79 cm^{-1} (Supplementary Figure S10).

Raman spectra of the diaspore crystal are shown in Supplementary Figure S10. Raman bands showing diaspore in the spectra of the samples were observed at peaks at 867, 675, 627, and 571 cm^{-1}.

3.5 Studies for the determination of gemological characteristics

In mineralogical research, FTIR spectroscopy is widely used to characterize molecular water and hydroxyl groups in various minerals such as silicates, clays, aluminum oxides, and iron oxides. In gemology, FTIR spectra can also be applied to determine the molecular and/or structural vibration of–OH. This

vibration is the result of reflections of OH-containing mineral inclusions such as boehmite, diaspore, goethite, and mica (Phlayrahan et al., 2018).

FTIR analysis was performed on the faceted sample taken from the study area to determine the origin, and according to the results of this analysis, the strong peaks in the range of (600–640) cm^{-1}, (680–720) cm^{-1}, 1,000 cm^{-1}, $^{-}$1,040 cm^{-1}, 1,140 cm^{-1}, weak peaks in the $^{-}$1,200 range (in red) were found to be consistent with reference to the standard wavelength (colored black) (Supplementary Figure S10).

It has been scientifically proven that the facetted samples collected from the region (Supplementary Figure S11) are gemstone-quality diaspore crystals with various color variations.

The sample was cut with a standard diamond cut, with 45°, 90°, and 43° angles on the cone part, and then on the stone part with 47°, 42°, 27°, and 0° angles, 57 facets on the stone and cone part, and 16 facets on the belt part, a total of 73 facet surfaces were processed (Supplementary Figure S12).

It is a cutting technique applied to faceted gemstones for the highest shine and best appearance and is usually applied for transparent, precious gemstones. The reflection or brilliance depends on the optical, physical, and facets of the gemstone. The facet-cutting technique can turn a gemstone containing inclusions into a valuable piece, or it can turn a high-end gemstone into a rather worthless piece.

4 Discussion

The Sodra bauxite deposit is located very close to the Milas settlement and 23 km from the port of Güllük. Etibank (1975) extracted about 4,000 tons of ore from this deposit. The ore zone is located within the Menderes Massif marble. The bauxite zone is E-W to N80° W and slopes 40° Northeast. It is also 150 m long and about 5.5 m thick. Etibank (1975) estimated the ore reserves to be 0.23 Mt with an average content of 56% Al_2O_3, 5% SiO_2, and 2.8% TiO_2 (Hanilci, 2019).

Inert element compositions (Cr, Zr, Ga, V, Ni, Nb, *etc.*) and various diagrams were used to elucidate the possible source of bauxite and diaspore formations in the region (Supplementary Figure S13).

According to the Cr-Ni distributions of the samples collected from the study area, bauxite occurrences are in the karst-bauxite region, and diaspore occurrences are in the high-iron bauxite and nepheline syenite bauxite regions.

V/(V+Ni) and Ni/Co diagrams of bauxite and diaspores were drawn to reveal oxic, semi-oxic, anoxic, and redox conditions in the study area (Supplementary Figure S14A). Ni/Co ratios of <5 in rocks reflect oxygenated conditions, >5 reflects suboxic and anoxide conditions (without oxygen) in the formation of clays in the basin, and V/(V+Ni) ratios (0.4–0.60) reflect dioxide conditions (Rimmer, 2004; Akinyemi et al., 2012). In light of these data, bauxite formations in the region are concentrated mainly in the semi-oxic region, and diaspores are concentrated in the anoxic region according to their V/(V+Ni) ratios.

The pH value in the environment during bauxite formation is expressed as the dominant control parameter for the mobility of REEs and it is stated that REEs cause separation/decomposition in acidic

conditions and accumulation in alkaline conditions. Among the trace elements, REEs are generally accepted as the most suitable geochemical tools for evaluating the source of sedimentary rocks in general and a bauxite deposit in particular (Calagari and Abedini, 2007; Mameli et al., 2007; Mongelli et al., 2016; Sinisi, 2018). REEs are thought to be relatively inert elements during decomposition processes. In conclusion, the enrichment of REEs in bauxite indicates that alkaline conditions were dominant during its evolution (Abedini and Calagari, 2014). Measuring changes in the La/Y ratio is a useful geochemical tool to determine changes in pH during bauxitization (Salamab Ellahi et al., 2016). La/Y <1 values indicate the prevalence of acidic conditions and La/Y >1 values indicate alkaline conditions/basic conditions. It was determined that the La/Y ratio of bauxite samples collected from the study area had values above 1. In diaspore samples, on the other hand, the La/Y ratio was found below 1. According to these data, we can state that diaspore formations in the Sodra region occur under acidic conditions.

However, Cerium (Ce) is degradable relative to other rare earth elements because its geochemical behavior during weathering can be strongly influenced by changes in the redox state. As a result, the altered/decomposed material may be enriched or depleted in cerium and show positive or negative Ce anomalies accordingly. Although the stable valence is trivalent for most REEs, Ce has been shown to be redox-sensitive under weathering and oxidized to the tetravalent state (Ma et al., 2007). It has been shown that positive Ce anomalies in lateritic profiles and bauxites are mineralogically related to cerianite (CeO_2) precipitation due to Ce^{3+} to Ce^{4+} redox change (Mongelli et al., 2016). In addition, Ce^{4+} is prone to hydrolysis. It is stated that it is separated from other REEs by precipitating after adsorption by Fe and Mn oxides, and this effect leads to a Ce deficit. It is stated that the traces of goethite and hematite in the examinations indicate that the region is oxic and therefore Ce is probably in the tetravalent state and therefore precipitated as CeO_2 (Yusoff et al., 2013). It is stated that such a process causes the formation of a positive Ce anomaly (Sinisi, 2018). In addition, studies generally accept 0.78 (Ce) as a reference value to indicate a redox environment, and Ce > 0.78 is expressed as a positive anomaly and Ce < 0.78 as a negative anomaly (Ji et al., 2000; Zhang et al., 2020). Negative Ce values indicate that the ore formation process is likely under suboxic water body/deoxidized conditions. According to the Ce_{anom}–Nd diagram, Ce/Ce* (Ce_{anom}-NASC). If > −0.1, the water in the environment where the mineralizations occur or are stored in the sedimentary storage environment is insufficient in terms of oxygen, Ce_{anom} <-0.1 indicates that the sedimentary water in the environment is rich in oxygen (Ozyurt et al., 2020). Ce/Ce* of bauxite mineralization values in the study area (NASC) were obtained as 0.86 on average, and 0.90 of diaspore formations. With these data, it was determined that these formations occur in an oxygen-poor environment (anoxic) and bauxite formation processes occur slowly, while diaspore formation processes occur rapidly (Supplementary Figure S14B).

In order to determine the origin of bauxite and diaspore formations in the study area, the relations between Eu anomaly (Eu/Eu*) and Sm/Nd and TiO_2/Al_2O_3 ratios were also used. Similar to Eu anomalies, the Sm/Nd ratio is also used as an index of chemical differentiation during intense tropical weather conditions (Viers and Wasserburg, 2004) (Supplementary Figure S15).

Eu anomaly is an index of chemical differentiation and represents the proportion of crust exposed in the source area(s) (Condie et al., 2001; Sinisi, 2018) during bauxidization (Mameli et al., 2007; Mondillo

et al., 2011). In addition, Eu anomaly values can be of great help in understanding the physicochemical conditions of various geochemical systems, such as the sedimentation environment of limestones. Positive Eu anomalies (normalized to PAAS) are generally observed in limestones affected by hydrothermal processes (Siby et al., 2008; Madhavaraju and Lee, 2009). Negative Eu/Eu* anomalies are a geochemical feature of post-Archean cratonic deposits and are generally associated with mafic source rocks (Sinisi, 2018). In addition, intense diagenesis, and differences in the amount of feldspar and wind input are other factors that can have a positive effect (Madhavaraju and Lee, 2009). Also, based on the SHAB (Hard/Soft of Acids and Bases) theory proposed by Dai (1987), some reduced species such as CO, CH_4, $S_2O_3^{2-}$, S_2- and HS- increase in the aqueous system under low oxygen fugacity. In such an environment, Eu^{2+} prevails widely and remains in solution as a stable Eu^{2+}- complex and is therefore suitable for inclusion in Eu precipitates (positive anomaly). In contrast, under higher oxygen fugacity, Eu^{3+} dominates in the aqueous system and requires hard bases such as OH^-, SO_4^{2-} and CO_3^{2-} (especially OH^-) to precipitate, as a result, negative Eu anomaly can be considered. In addition, Abedini et al. (2019) suggested that the strong negative Eu anomaly may be associated with higher O_2 and lower pH of the solutions. Post-Archean Australian Shale (PAAS) =0.61 in the evaluation of Eu anomaly (Eu/Eu*); Post/Archean upper continental crust (UCC)=0.66 is accepted as the post-Archean upper continental crust (Sinisi, 2018). The Eu/Eu* values (PASS) of the bauxite mineralizations in the study area were found to be 1.05 on average, and 1.33 (SO) in the diaspore formations. The bauxite formations in the study area are concentrated in the region between cratonic sandstones-PAAS-bedrock limestone and we can consider these formations as the dominant clastic material product, probably derived from a distant source, carried by wind/water (?).

It has been stated that the bauxites in the region have undergone metamorphism under the conditions of approximately 10–25 km depth, 5–10 kb pressure and 500°C–620 °C temperature conditions due to burial due to tectonic movements. In addition, as a result of metamorphism, gibbsite and boehmite formations were transformed into diaspore and corundum, while ferrous compounds transform into magnetite, and clays were thought to transform into minerals such as muscovite and chloritoid (Temur et al., 2003).

In recent years, stones of dubious origin have been encountered quite frequently in the precious stone market, and it is becoming more and more difficult to distinguish synthetic and/or fake gemstones produced with developing technologies from the originals. Raman spectroscopy becomes an ideal method in terms of the fact that gemstone identification is non-destructive and gives fast results. The disappearance of the human factor in Raman shots seems to prevent possible concerns (Jenkins and Larsen, 2004). With the Raman spectrometry method used in this study, diaspore peak values were determined to be 867, 675, 627, and 571 cm^{-1} depending on the wavelengths. With increasing pressure, the Raman peaks move towards the high wave number direction, the intensity of the Raman peaks increases, and the vibrational mode of the diaspore changes linearly (Huang et al., 2020). Juan-Farfan et al. (2011) obtained 22 Raman peaks in the range of 150–1,300 cm^{-1} by theoretical calculation. However, only 13 Raman peaks were observed in the same wavenumber range in the experiments because the other peaks were determined to be too weak to be observed in the experiments (Ruan et al., 2001; Juan-Farfán et al.,

2011). Raman spectrometer values of diaspores in the Sodra region are in agreement with literature values. This shows that diaspora has an ornamental quality.

5 Results

The properties and distributions of major and trace elements were investigated to reveal bauxite formation processes. It was thought that the clayey/clastic metamorphic-igneous rocks with high Al content in the study area were the source of bauxite formation and the enrichment was repeated more than once. In addition, it has been determined that bauxite formations are related to a bedrock with intermediate magmatic or clayey composition, while diaspore formations provide data close to ultrabasic-basic properties.

It has been observed that the bauxites in the region have undergone metamorphism at a depth of approximately 10–25 km, a pressure of 5–10 kb, and a temperature of $500°C–620°C$ due to burial due to tectonic movements. With this metamorphism, it was thought that while gibbsite and boehmite were transformed into diaspore and chorus, ferrous compounds turned into magnetite, and clays into minerals such as muscovite and chloritoid. As a result of SEM imaging and EDS analyses, it was observed that the samples in the study area mainly contained O, Al, and Si, and the presence of K, Na, Fe, Ca, and Mg in addition to these elements were detected in close-ups. Chemical and EDS analysis results support each other, and no different results were found during sample scanning. It was observed that the diaspores collected from the Sodra field had gemstone qualities in terms of physical and chemical properties. When the crystals suitable for shaping collected in these samples were subjected to facet processing and cut at appropriate angles, they were well polished and attained a glassy shine. As a result of the Raman shots, it was determined that the sample was diaspore in the light of the match values obtained from the microscope's own database, and Brucite $[Mg(OH)_2)]$ was determined to be at 79 cm^{-1}. Raman spectra of the diaspore crystal are shown in Supplementary Figure S10. Raman bands showing diaspore in the ranges of the samples were observed at peaks at 867, 675, 627, and 571 cm^{-1}. Although the presence of diaspore crystals within the borders of Mugla province in the Southwest Anatolia region has been determined by previous studies, the discovery of diaspore crystals was revealed for the first time in the Sodra region, where this study was conducted. It is predicted that these gemstone-quality diaspore crystals can be evaluated economically.

Data availability statement

The datasets presented in this study can be found in online repositories. The names of the repository/repositories and accession number(s) can be found in the article/ Supplementary Material.

Author contributions

The manuscript was prepared from EH PhD's thesis. Supervisor AO determined the area where the study was conducted, and after determining the sample locations together, EH made the samples. Samples were sent for analysis with the approval of supervisor AO. EH evaluated the results of chemical analysis, and the manuscript was prepared with the recommendations and approval of supervisor AO. AO made a great contribution in the preparation of this publication. All authors have read and approved this article.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2023.1145674/full#supplementary-material

SUPPLEMENTARY FIGURE S1
Location map of the study area ((**A**): Turkey map, (**B**): Map of the study area, (**C**): Geological map of the study area) (modified from MTA, 2002).

SUPPLEMENTARY FIGURE S2
Diaspore formations in the study area (**A**) Diaspore crystal (**B**) Diaspore containing vein (**C**) formation containing diaspore crystals in recrystallized limestone.

SUPPLEMENTARY FIGURE S3
SiO_2- Fe_2O_3- Al_2O_3 diagram (Meshram and Randive, 2011; Gu et al., 2013; Zamanian et al., 2016) and Chemical Change Index (CIA) with alteration (Nesbitt and Young 1982; Shao et al., 2012) degree (Ozturk et al., 2021).

SUPPLEMENTARY FIGURE S4
Normalized logarithmic (y-axis) distribution plot of diaspore samples in the study region according to chondrite.

SUPPLEMENTARY FIGURE S5
Logarithmic (y-axis) distribution graphs of some elemental major and trace elements of diaspore formations.

SUPPLEMENTARY FIGURE S6
10μ magnification SEM-EDS dot and mapping images of the S-1 diaspore sample in the Sodra region.

SUPPLEMENTARY FIGURE S7
SEM-EDS dot and mapping images with 10 μ magnification of the S-2 diaspore sample in the Sodra region.

SUPPLEMENTARY FIGURE S8
SEM-EDS dot and mapping images with 10 μ magnification of the diaspore sample S-3 in the Sodra region.

SUPPLEMENTARY FIGURE S9
10 μ magnification SEM-EDS dot and mapping images of the S-4 diaspore sample in the Sodra region.

SUPPLEMENTARY FIGURE S10
Mineral contents determined by Raman spectroscopy (S-1, S-2, S-3 and S-4) in diaspore samples from the Sodra region. FTIR plots of diaspore samples taken in the Sodra region (blue lines are FTIR standards, red lines are diaspore samples).

SUPPLEMENTARY FIGURE S11
The image of the diaspore samples collected from the field **(A)** Round-Brilliant Cut (GIA, 2016). **(B,C)** The image of the sample cut from the samples under yellow light and white light.

SUPPLEMENTARY FIGURE S12
Schematic representation of the technique used on diaspore samples collected from the field (Gemmology Project, 2022).

SUPPLEMENTARY FIGURE S13
Cr-Ni diagram showing the distribution of Bauxite-Diaspore formations in the study area (Sinisi, 2018).

SUPPLEMENTARY FIGURE S14
(A): V/(V + Ni) (Hatch and Leventhal, 1992). and Ni/Co; (Jones and Manning, 1994) diagram (Rimmer, 2004; Aydogan, 2021). **(B)**: Diagram showing oxic, semi-oxic, anoxic, and redox conditions (Wright et al., 1987; Hatch and Leventhal, 1992; Jones and Manning, 1994; Aydogan, 2021).

SUPPLEMENTARY FIGURE S15
Diagram of Sm/Nd and Eu/Eu* **(A)** TiO_2/Al_2O_3 and Eu/Eu* **(B)** outlining the comparison between mean standard lithologies (Viers and Wasserburg, 2004).

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