Geochemistry of the Igdekoy-Doganlar Na-Ca borate deposit, Emet Province (western Anatolia, Turkey)

İsmail KOÇAK[1, *]

[1] Department of Engineering Science, Bandırma Onyedi Eylül University, Bandırma-Balıkesir, 10200, Turkey

Borates at the Igdekoy-Doganlar locality were deposited in a Miocene lacustrine environment during periods of Paleogene to Early Quaternary volcanic activity. The mineral paragenesis consists of probertite – $NaCaB_5O_7(OH)_4 \cdot 3H_2O$, ulexite – $NaCa[B_5O_6(OH)_6] \cdot 5H_2O$, hydroboracite – $CaMg[B_3O_4(OH)_3]_2 \cdot 3H_2O$, colemanite – $Ca[B_3O_4(OH)_3] \cdot H_2O$, halite, anhydrite, glauberite, smectite and illite. The major element, Ca, is higher in the Igdekoy-Doganlar deposits compared to the averages for andesite and the Earth's crust. Within the trace elements, notable enrichment is identified in Li, Se, As, Sb, Sr and Cs. Lithium and Se occur in sufficient concentrations to be considered as economically valuable by-products. B and Sr anomalies can be used as an important marker in the exploration for boron deposits. The Y/Ho ratio of the Igdekoy-Doganlar borates is close to chondritic values. The negative Ce anomaly in borates from the Igdekoy-Doganlar deposit suggests that deposition occurred under oxidative conditions. The Eu and Ce anomalies reflect a hydrothermal contribution of REE. Geochemical and geological data suggest that the Igdekoy-Doganlar borate deposits were formed in high-pH playa lakes that were discharged from volcanic and terrestrial environments under evaporative conditions due to the effect of arid-semi arid climate.

Key words: REE, trace element, borate, mineralogy, ulexite, probertite.

INTRODUCTION

Nearly 72% of borate reserves in the world are located in the west part of Turkey. In addition to well-known deposits, there is a new deposit near Igdekoy-Doganlar villages in the Emet region (Fig. 1). The deposit is located 3 km north of the town of Hisarcık. In previous studies, the formation of borate deposits in the Emet region was discussed in terms of general geology and mineralogical findings (Gawlik, 1956; Ozpeker, 1969; Inan, 1975; Yalcin, 1984; Yalcin et al., 1985; Gundogdu and Yalcin, 1985; Yalcin and Gundogdu, 1987; Floyd et al., 1998; Helvacı and Orti, 1998, 2004; Colak et al., 2003; Gemici et al., 2004; Sayin, 2007; Ozkul, 2008; Garcia-Veigas et al., 2010, 2011; Unlu et al., 2011; Helvacı, 2015a, b; Ozkul et al., 2015, 2017; Cooper et al., 2016; Orti et al., 2016). In these studies, it was suggested that the borate deposits were deposited in Miocene lacustrine environments in association with volcanic activity spanning from Paleogene to Quaternary times. Compositions of major, trace and rare earth element (REE) of borates were also investigated (Ilhan, 2006; Kocak and Koc, 2009, 2012, 2016, 2018; Koc et al., 2017; Kocak, 2017).

Geochemical data showed the following element enrichments: Ca, As, Li, Sb, Cs, Se and Sr in the Kestelek deposit (Koc et al., 2017); Ca, Se, Sr, As, Li, Mo and Sb in the Bigadiç deposit (Kocak and Koc, 2012); Ca, Na, Mg, Sr, Li, Se, As and Cs in the Kırka deposit (Kocak and Koc, 2016); Ca, Sr, Li, Se, As, Cs, Sb and Pb in the Emet (Hisarcık and Espey) deposit (Kocak and Koc, 2018); and Sb, Li, Se, Cs, As and Sr in the Şeyhler (Emet) deposit (Kocak, 2017). There has been no study of the relationship between element contents and the formation environment of borates in the Igdekoy-Doganlar deposit. In this study, the abundances of major, trace and rare earth elements and their geochemical features were used to define the deposition conditions of the borate minerals. The results are compared with other deposits. Although present day technology and economics are not sufficient to acquire by-products of the ore elements, this may be the possible in the future.

This study provides new geochemical data from the Igdekoy-Doganlar Na-Ca borate deposit. The data were used to reconstruct the depositional conditions that control formation of the Na-Ca and Ca rich borates.

GEOLOGIC SETTING

The Anatolian Plate is located in the collision zone between the Eurasia and the Afro-Arabian plates. The western Anatolian borate deposits were formed in parallel with the Aegean volcanic arc formed by the African plate sinking along the Hellenic trench, which was developed in subduction environments (Helvacı, 2015a). The geology of the borate deposit and the surrounding Emet Basin within the region was compiled from Ozkul (2008). In the Emet basin, pre-Miocene rocks (Helvacı and Firman, 1977; Yalcin, 1984) consist of schist (Sarıcasu Formation), marble (Arıkaya Formation), Budağan limestone and
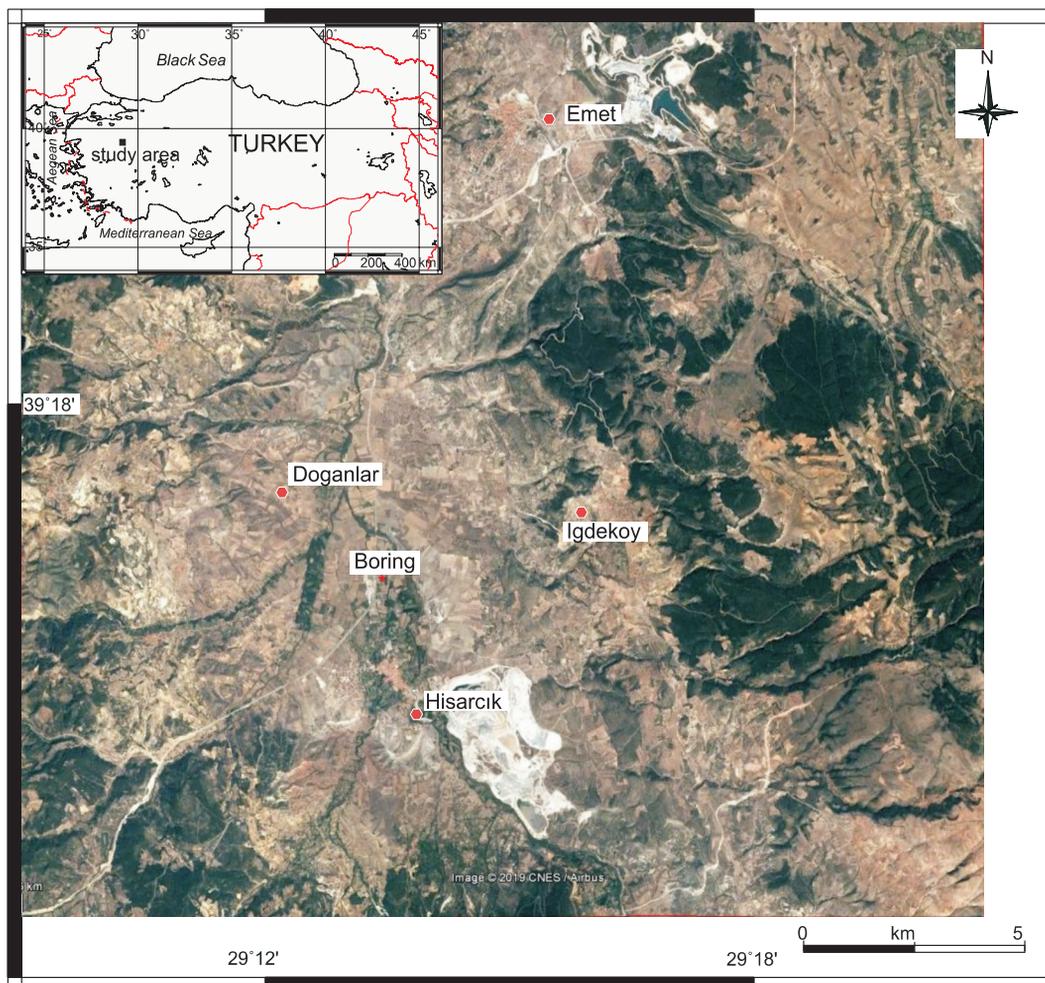
Fig. 1. Location map for study area in western Anatolia

Eğrigöz granitoid (Akdeniz and Konak, 1979). These units are overlain by Neogene conglomerate-sandstone (Taşbaşı Formation), Koprucek felsic basement volcanics, basal sediments [limestone (Karbasan Formation), Yeniceköy limestones, conglomerate, sandstone (Beykoy Formation), Ergunler limestones, Igdekoy Formation], cover sediments [Emet cover limestones, sandstone (Merkezsihlar Formation)] and Derekoy mafic upper volcanics, respectively. The Neogene units are covered by Quaternary travertine, old river terraces and alluvium (Fig. 2).

The Igdekoy Formation that hosts the borate levels is dominated by green, moderately consolidated siltstone and claystone and lesser amounts of thin limestone-marl and tuff interlayers. The formation is exposed in a narrow area east of Igdekoy and Hamamköy, NW of Hisarcık and around the Merkezsihlar and the Killik sites. The thickness of the formation is between 30 and 450 m (Akdeniz and Konak, 1979; Yalcin, 1984; Yalcin et al., 1985; Dundar et al., 1986; Ozkul, 2008). The marl, claystone and thin-bedded limestone levels of the Igdekoy Formation conformably overlie the Ergunler limestones. Towards the top, the sequence changes to greenish claystone and siltstone interbedded with small amounts of tuff layers which include the borate layers. The colemanite nodules are radial and may attain a radius of 5–60 cm. The clay mineralogy in this layer is illite and montmorillonite (Helvacı and Firman, 1977; Gundogdu and Yalcin, 1985; Yalcin and Gundogdu, 1985, 1987; Dundar et al., 1986). Clays mostly surround the colemanite nodules as a film. In some levels arsenic-rich claystone contains orpiment and realgar crystals up 5–10 cm across, together with native sulphur. In the upper section of the sequence, marl layers dominate. The marls show a colour difference from dirty white at the base to grey to the top. They have an eathy appearance and include peat and colemanite nodules. The marl and clay layers are rich in organic-material (as evidence by the presence of peat; Ozkul, 2008).

MATERIALS AND METHODS

In this study, mineralogical and geochemical analyses were carried out on 17 borate samples collected from borehole BME 2003/1 which was drilled in 2003 by Etimine Emet Bor Exploitation Management. The locations of the collected samples are shown in the borehole log (Fig. 3) drawn from the raw data.

For mineralogical studies, an optical, *Confocal Raman* spectrometer and X-ray diffractometry (XRD) methods were used. XRD determinations were conducted at the Turkish Pe-
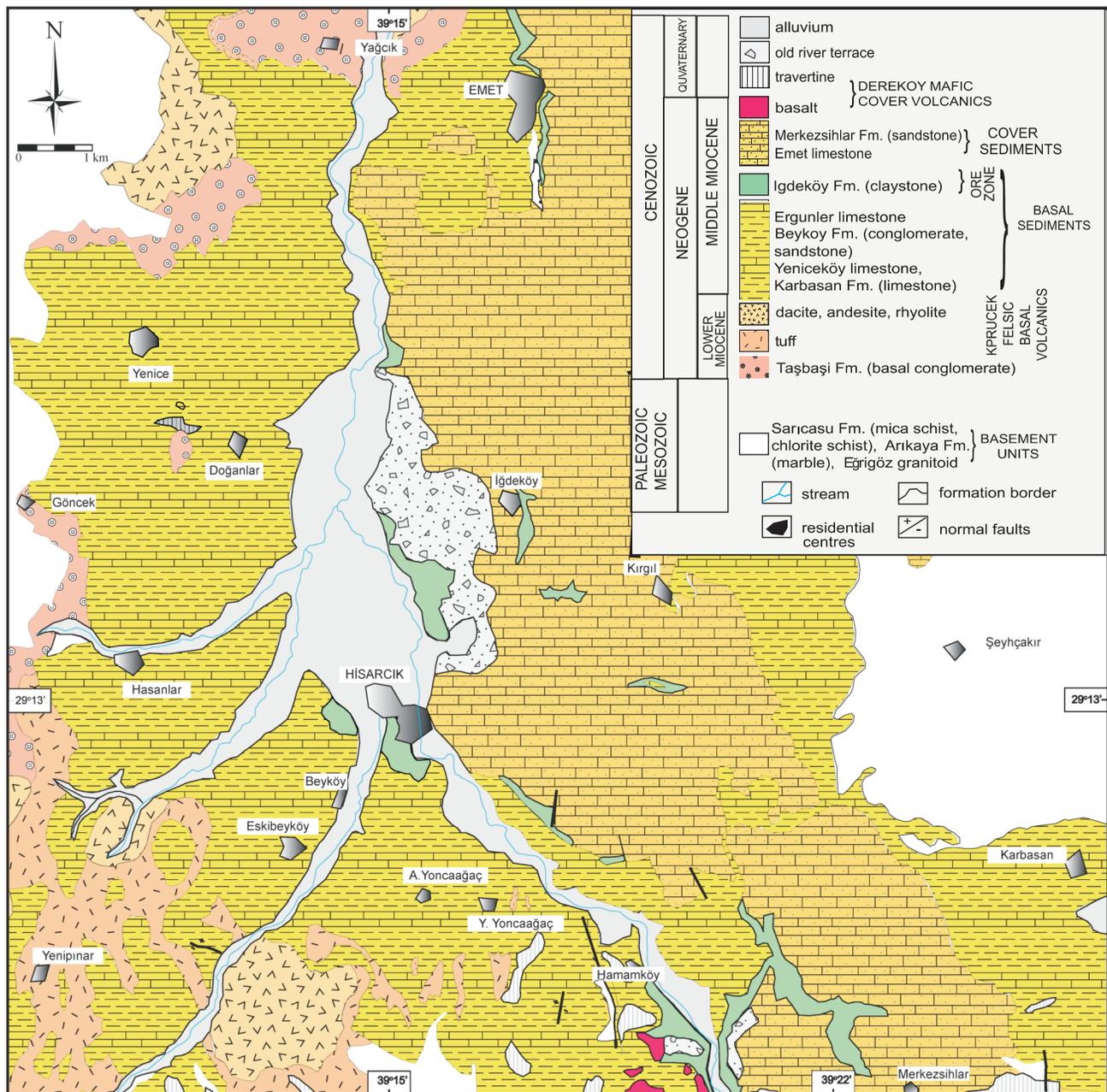
Fig. 2. Geology map of study area and surroundings (simplified after Ozkul, 2008)

troleum Corporation (TPAO) laboratories with a *Rigaku D brand Max 2200 Ultima/Pc* device with a Cu-tube under conditions of 40 kV, 20 mA, 1.54059 A° (CuKα1) wave length and 2°/min scanning speed. The *Raman* measurements were carried out with an *Olympus BX41* model *Confocal Raman* spectrometer at the Geology Department in Ankara University. A *Horiba Jobin Yvon* system equipped with a 633 nm laser set was used for the *Raman* measurements. An electrical cooled charging coupling device (CCD) detector was used to obtain spectra, and the laser spot was set on borate surfaces with 10x or 50x long-focused objectives, enabling a working distance of 65 and 13 mm, with a lateral resolution of 5 and 2 μm respectively. The polarization of the incident laser beam was chosen analogous with the preferential domain orientation of samples (y) and

spectra were obtained in a strict backscattering geometry. The phonon mode intensity values for borate were obtained using the *Labspec 4.02* (*Horiba Jobin Yvon*) kit, based on Gaussian-Lorentzian mixed functions after subtracting a baseline and applying the initial mode approximations according to the borate and mineral *Raman* analyses by Kadioglu et al. (2009) and Gullu and Kadioglu (2017).

Before chemical analysis, samples were cleaned with pressurized air and then distilled washed to remove impurities. The geochemical analyses were conducted as the *LF202* package at Bureau Veritas Mineral Laboratory (*LF202* package). REE analysis was performed using *Inductively Coupled Plasma-Mass Spectrometry* (ICP-MS) and major and trace elements were determined by *Inductively Coupled Plasma-*
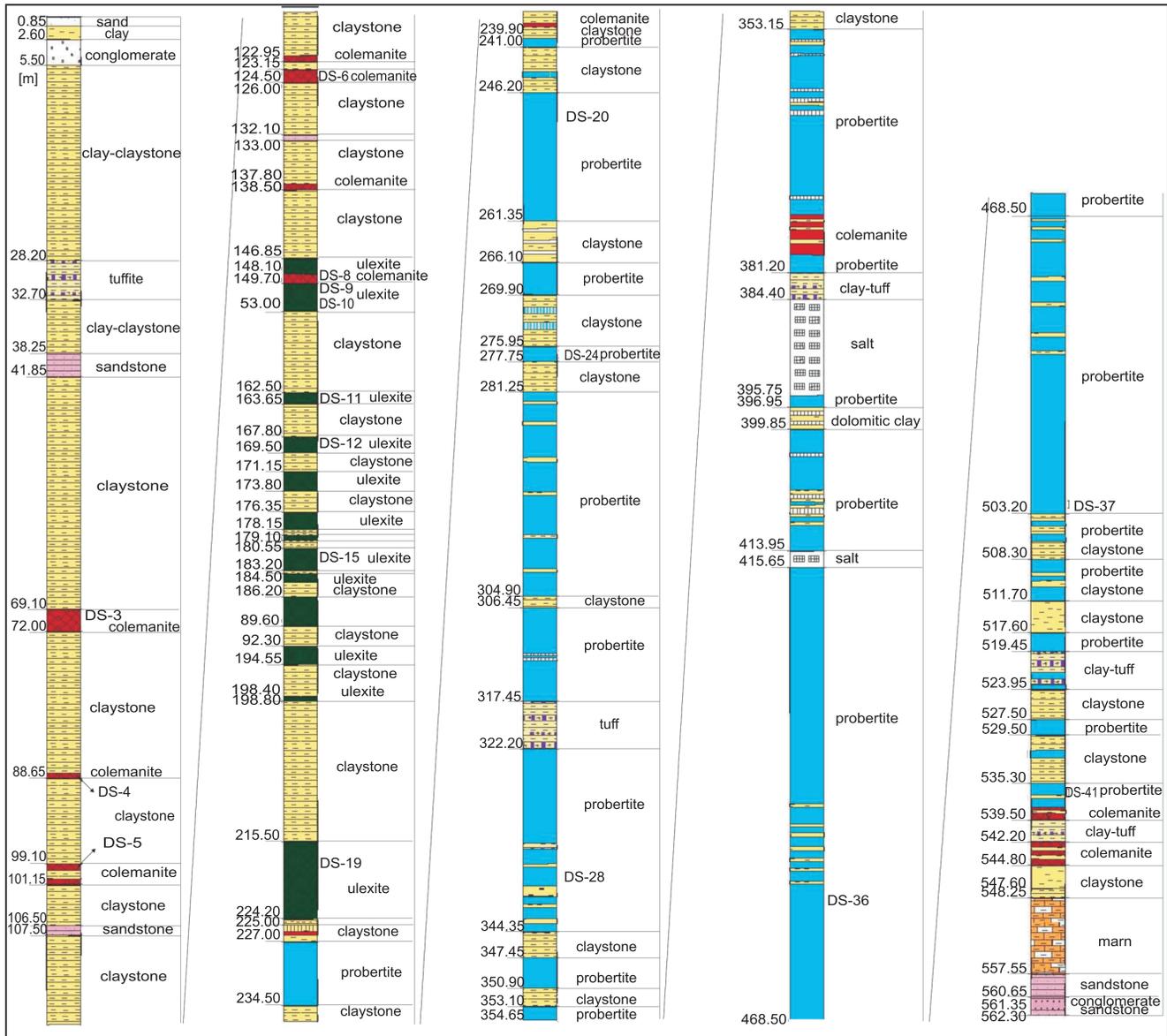
Fig. 3. Log of BME 2003/1 drilling and borate sample depths

-Emission Spectroscopy (ICP-ES) method. B_2O_3 analysis was completed with Thermo Scientific ARL Perorm'x wave dispersive X-ray Fluorescence (WD-XRF) spectrometer at the Science and Technology Application and Research Center of Bozok University.

RESULTS AND DISCUSSION

MINERALOGY

From the optical, confocal Raman spectroscopy and X-ray diffractometry (XRD) studies, colemanite, ulexite, hydroboracite and probertite were identified, together with halite, anhydrite, glauberite, smectite and illite.

MICROSCOPY INVESTIGATIONS

Microscopy studies revealed the presence of colemanite, hydroboracite, ulexite and probertite. Ulexites show radial growth formed as separate crystals (Fig. 4A). In thin-section ulexite is radial, yellowish-white under plane polarized light. It shows second order interference colour under cross polars (Fig. 4B). Probertite is recognized as small crystals (Fig. 5A) and is characterized by a dirty white-grey colour under plane polarized light and bluish green, grey, blue, orange and purplish blue under cross polars (Fig. 5B).

CONFOCAL RAMAN SPECTROMETER ANALYSES

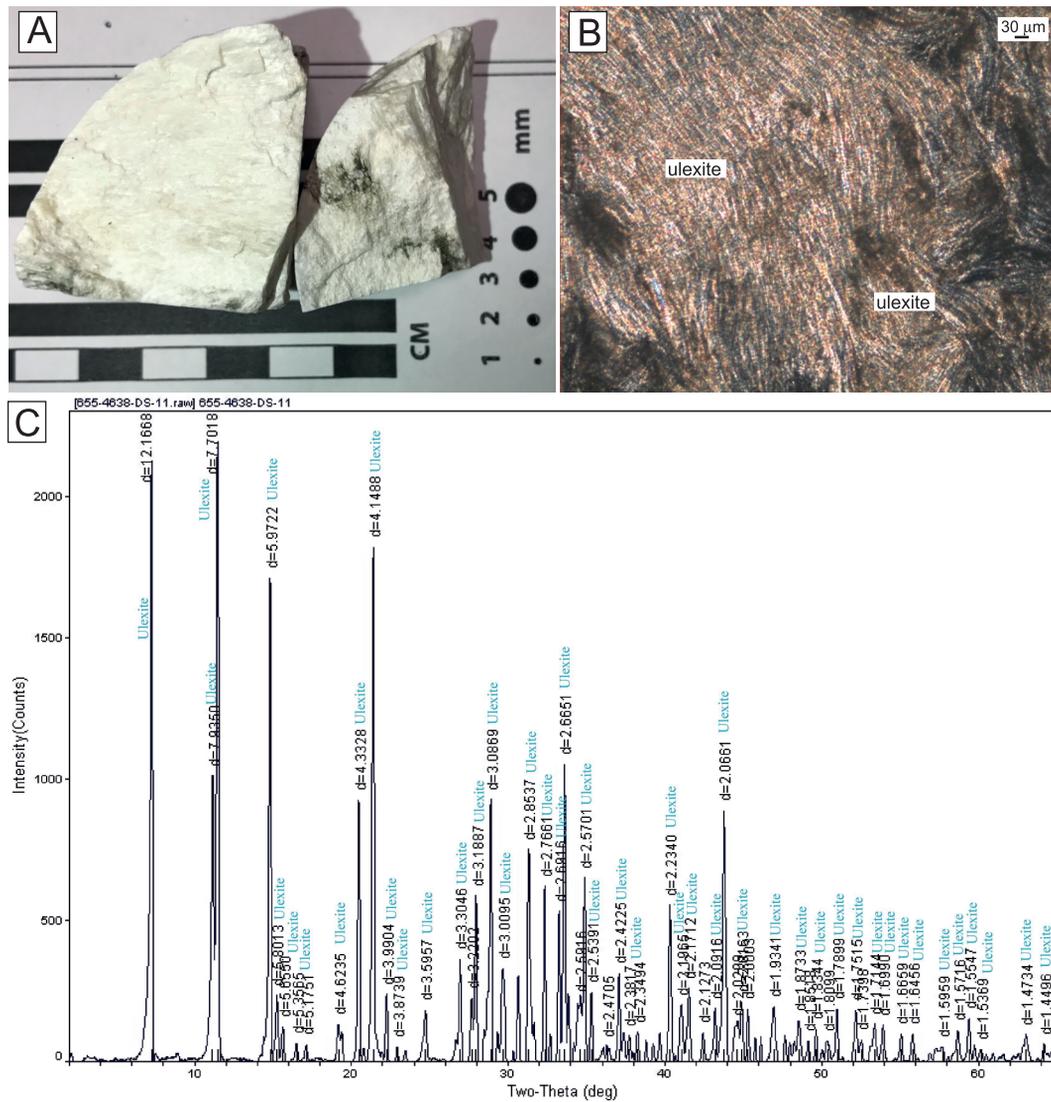The Confocal Raman spectroscopy method allows determination of the mineralogy of a sample based on the results of

Fig. 4A – radial ulexite, B – ulexite under crossed polars, C – XRD patterns for ulexite

point analysis. Minerals identified under thin-section were also verified from *Raman* spectra. In Figure 5C, the blue line in confocal *Raman* spectroscopy is the reference line for probertite and the red line is the peak value for sample. The presence of colemanite, hydroboracite, and ulexite minerals was identified by the confocal *Raman* spectroscopy.

X-RAY DIFFRACTOMETRY (XRD) ANALYSES

The XRD was used to define clay types and minerals which could not be recognized by microscopy and confocal *Raman* spectroscopy studies. XRD study of the Igdekoy-Doganlar borates revealed the presence of colemanite, ulexite (Fig. 4C), hydroboracite and probertite minerals. Halite and anhydrite accompany the borate minerals. Smectite and illite are the major clay types.

GEOCHEMISTRY OF THE IGDEKOY-DOGANLAR DEPOSIT

MAJOR ELEMENTS

The major element concentrations with the average values, and average concentrations in the Earth's crust – ECA (values after Krauskopf, 1979), andesites – AA (values after Schroll, 1975) and fresh waters – FWA (values after Sahinci, 1991; Abollino et al., 2004) are shown in Appendix 1*. The ranges of major element oxides of the borate samples are: 0.06–5.06 wt.% for SiO_2, <0.04–0.88 wt.% for Fe_2O_{3tot}, 0.03–3.53 wt.% for MgO, 12.95–27.49 wt.% for CaO, 0.02–19.70 wt.% for Na_2O, and 28.46–46.26 wt.% for B_2O_3. Based on these values, the average concentrations of major element oxides are calculated: 2.38 wt.% for SiO_2, 0.22 wt.% for Fe_2O_{3tot}, 1.22 wt.% for MgO,

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* Supplementary data associated with this article can be found, in the online version, at doi: 10.7306/gq.1555
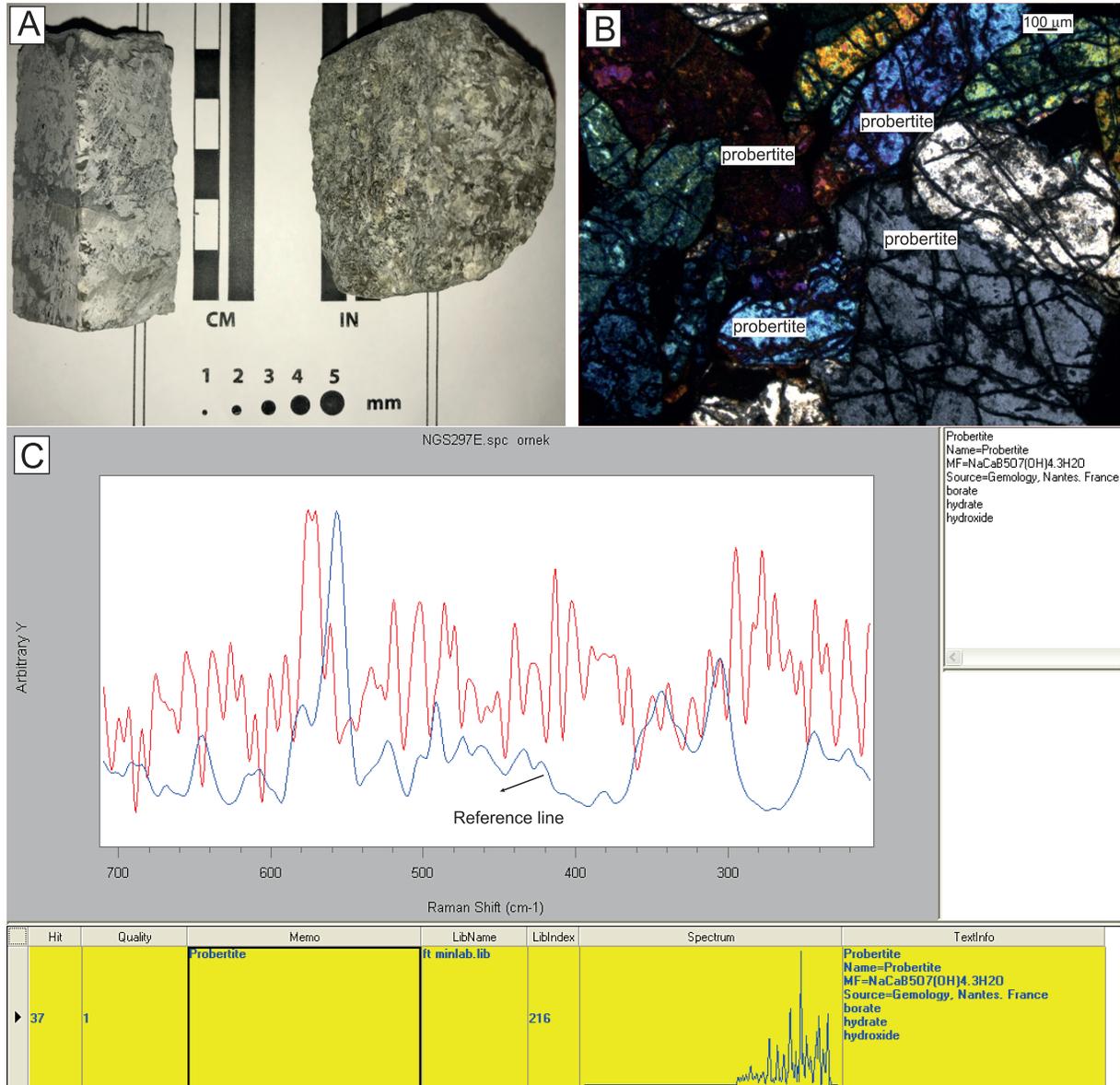
Fig. 5A – granular crystalline probertite, B – probertite under crossed polars, C – *Raman* spectrum for probertite

19.39 wt.% for CaO, 5.82 wt.% for Na_2O, and 41.05 wt.% for B_2O_3 (Appendix 1). The averages values of CaO, Na_2O and B_2O_3 concentrations in Igdekoy-Doganlar borates are increased 3.38, 1.80 and 41047-fold with respect to ECA and 2.98, 1.44 and 27364-fold with respect to AA. All other major element oxides show proportional depletions compared to both ECA and AA (Table 1).

TRACE ELEMENT

The concentrations and average concentration of trace elements in the Igdekoy-Doganlar borates and their average concentrations in the ECA, AA and FWA are shown in Appendix 2. All trace elements in Igdekoy-Doganlar borates are enriched with respect to FWA (Appendix 2). According to the results of analysis, Ni, Co, Cu, Pb, Mo, S, As, Se, Sb, Te, Ag, Rb, Ba, Sr, Cs, Li, Nb, Zr, Y, Th, and U were determined in borate samples.

Regarding ECA and AA, content of Se, As, Sr, Sb, Cs and Li in the Igdekoy-Doganlar borates are found to be higher than other elements. The concentrations of these elements-vary in the range: 0.3–21.4 ppm for Se, 6.6–8250 ppm for As, 459–13154 ppm for Sr, <0.02–3.57 ppm for Sb, 2.2–101 ppm for Cs, and 3.7–296 ppm for Li. According to these results, the average value of Se, As, Sr, Sb, Cs and Li is calculated as 12.9, 1523, 3607, 0.7, 44.8, and 91.3 ppm, respectively. With respect to ECA and AA, respectively, the concentrations are increased by: As (845–801 fold), Se (258–258 fold), Cs (14.92–19.46 fold), Sr (9.62–4.51 fold), Sb (3.63–3.63 fold), and Li (4.56–4.56 fold) elements are variably increased (Appendix 2). S content is increased 14.39–21.58 fold.

Previous studies in western Anatolia revealed similar results. Reported element enrichments are As, Sb, Se, Mo, Li and Sr (Kocak and Koc, 2012); for the Bigadiç deposit; Li, Se, Mo, Sr, Sb, Cs and As (Koc et al., 2017); for the Kestelek deposit; Cs, Se, Sr, As and Li (Kocak and Koc, 2016); for the Kırka de-

Enrichment and depletion coefficients for Igdekoy-Doganlar borate samples

	Coefficient of enrichment by Earth crust	Coefficient of enrichment by andesite	Coefficient of depletion by Earth crust	Coefficient of depletion by andesite
B_2O_3	46904	31269	–	–
SiO_2	–	–	25.39	23.41
Al_2O_3	–	–	50.59	55.28
Fe_2O_{3tot}	–	–	34.67	37.56
MgO	–	–	3.13	2.96
CaO	3.38	2.98	–	–
Na_2O	1.80	1.44	–	–
K_2O	–	–	8.70	9.53
TiO_2	–	–	32.43	51.89
P_2O_3	–	–	12.60	18.33
Se	257.88	257.88	–	–
Li	4.56	4.56	–	–
As	845.88	801.36	–	–
Cs	14.92	19.46	–	–
Sr	9.62	4.51	–	–
Sb	3.63	3.63	–	–
S	14.39	21.58	–	–

posit; Sb, Se, Li, Pb, As, Sr and Cs (Kocak and Koc, 2018) for the Espey-Hisarcık (Emet); and As, Cs, Li, Se, Sb and Sr (Kocak, 2017) for Ţeyhler (Emet) borate deposit. These data show that Se, Sr, Li and As enrichments are common for Kırka, Bigadiç, Emet (Espey-Hisarcık), Kestelek, Şeyhler (Emet) and the studied Igdekoy-Doganlar deposits.

Gundogdu and Yalcin (1985) have examined the relationship between the distribution of borate formation and trace elements and they mention that the use of Sr in borate exploration is more important than Li and Ba. Furthermore, geochemical studies of Emet soils by Ozkul et al. (2017) revealed Na, K, Sr, As, Sb, Cs, Li and Be anomalies. As indicated by this study, B, Sr, Sb, Cs, Li, Se and As that especially enhanced in the borate deposit can be utilized as indicator elements for exploration of borate deposits.

As known in many ore deposits, other elements may be extracted as by-products in addition to the main ore (e.g., Se in Cu deposits). Flotation concentrates of most copper ores contain 100–400 ppm Se which is an important source for Se production (Habashi, 1997). The same is also valid for Li. Li is produced from salt deposits, lakes and sea. Li concentrations are 320 ppm in Salar de Uyuni (Bolivia), 52 ppm in Great Salt Lake (Utah), 65 ppm in Searles Lake (California), 160 ppm in Clayton Valley (Nevada) and 10 ppm in Dead Sea (Israel–Jordan) (Munk et al., 2016). In addition, there are studies about obtaining Li from seawater in which Li concentration is 0.17 ppm (Habashi, 1997). Therefore, when evaluating boron deposits extraction of Se (0.34–21.4 ppm) and Li (3.7–295 ppm) elements could also be considered.

According to Webb and Kamber (2000) low concentrations of Th, Sc, and Hf and absence of a strong correlation between Y/Ho and Zr (0.3 for this study) shows a low terrestrial contribution. In the present study, concentrations Sc and Hf are below detection limit and Th has a low concentration.

Li and Cs are concentrated mainly in the water of rhyolitic or andesitic environments or of sedimentary areas of comparable rock compositions (Ellis, 1979). Li can be associated with hydrothermal phases of volcanic activity. Absorption of lithium

ions by clay minerals caused high concentrations in sedimentary formations. Hydrothermal alterations and leaching mobilize lithium. Cs is found especially in Li-bearing micas and K-bearing minerals (Burkut, 1977). Cs, one of the largest alkali cations, is larger than that of major elements, but it can replace K. During the course of magmatic crystallization, Cs is in volatile phase and since it is more volatile than Rb and K, Cs is mostly found in K-rich volcanic rocks (Koc et al., 2017). The main source of Se, a chalcophile element, is volcanic activity. Se is generally found in hydrothermal formations especially epithermal Sb, Ag, Au and Hg, sulphur deposits and volcanic rocks (Elkin and Margrave, 1968; Halilova, 2004). In addition, Se is enriched in low temperature thermal bicarbonate waters in volcanic areas (Malisa, 2001). Volcanic input and hydrothermal solutions are the main cause of As enrichment (Goldschmidt, 1954). Arsenic enters the sedimentary cycle by alteration of magmatic rocks, volcanic gasses, and hot waters (Krauskopf, 1979). It is known that strontium is found in acidic rocks and volcanics rather than basic rocks and enriched in supergenic environments and hydrothermal systems (Kocak and Koc, 2012). Sb is a chalcophile element and associated with low temperature hydrothermal fluids, together with Au, Ag, As, Sb, Pb, Zn, Cd, Hg, Tl, Ga (Hannington et al., 1991; Lorand et al., 2018) It is known that Sb is closely related to volcanic activity (Petrascheck and Pohl, 1982). Following the solidification of magmas, Sr can be enriched in volatile-rich solutions (e.g., Cl, F, and B) and post-magmatic formations (Burkut, 1977). Additionally, many studies show that Sr is carried into borate deposits via boron-rich hydrothermal solutions (Ataman and Baysal, 1978; Yalcin, 1984; Gundogdu and Yalcin, 1985).

RARE EARTH ELEMENTS

REE concentrations were used to define some of physicochemical conditions of the Igdekoy-Doganlar deposit. For this purpose, results of REE analysis (Appendix 3) were normalized relative to Post Archean Australian Shale (PAAS) averages

(Taylor and Mclennan, 1985), and spider diagrams were created (Fig. 6).

ΣREE data of Igdekoy-Doganlar samples are very low ranging from 1.4 to 23.7 ppm (Appendix 3) which is attributed to low REE accumulation under high pH (>7.5) conditions (Michard and Albarede, 1986). Also the REE content of mineralizing fluids depends on the pH, water/rock ratio, temperature, redox potential, and the distance between the magmatic source and the deposition site (Palinkas et al., 2013).

There are Eu and Ce anomalies in the studied samples (Fig. 6 and Appendix 3). These anomalies were calculated from the equations of Eu/Eu* = [Eu /(Sm×Gd)]0.5 (Yang et al., 2014), Ce/Ce* = [Ce/(0.5La+0.5Pr)]$_N$ (Bau, 1991; Webb and Kamber, 2000) and Ce$_{anom}$= log [3Ce / (2La+Nd)] $_N$ (Wright et al., 1987).

In the Igdekoy-Doganlar area, the average Ce/Ce* is 1.07 (0.73–1.78) and average Eu/Eu* value is 1.96 (0.87–3.77).

If Ce$_{anom}$>–0.1 Ce is enriched, whereas Ce$_{anom}$<–0.1 is indicative of negative Ce anomaly (Wright et al., 1987). As shown in Figure 6 and Appendix 3, negative Ce anomaly is present in 6 of the Igdekoy-Doganlar borate samples and positive Ce anomaly in 5 borate samples. In addition, positive Eu anomaly was found in 13 samples and negative Eu anomaly in 4 samples, respectively.

Ce and Eu anomalies are related with changes in redox conditions (Loveland, 1989; Wood, 1990; Bau, 1991). A negative Ce anomaly, demonstrates high oxygen fugacity in the environment. Early-stage fluids are represented by positive Eu and Ce anomalies and high ΣREE, whereas hydrothermal fluids of later stages are represented by negative Eu and Ce anomalies and low REE (Jiang et al., 2004). For the Igdekoy--Doganlar borates, Ce$_{anom}$<–0.1 (Appendix 3) indicates a high oxygen fugacity (f$_{O2}$) of the environment and positive Eu anomaly is representative of a hydrothermal source (Constanto-poulos, 1988; Canet et al., 2005). Hence, it appears that low REE content, late-stage, hydrothermal fluids entered the depositional environment. Both negative and positive Ce anomalies may indicate that the environment underwent redox processes due to the effect of oxygenated and H$_2$S-bearing hydrothermal solutions. These anomalies show that the lake water in the depositional environment had a contribution from hy-

drothermal fluids. Kato (1999) and Habaak (2004) found LREE enrichment (LREE/HREE is ~8), enrichment in La and low total REE content in the iron deposit and suggested that mineralization formed under shallow oxidized conditions from meteoric and hydrothermal fluids. A slightly negative Ce anomaly is interpreted to indicate the influence of volcanic material (Fleet et al., 1976; Sasmaz et al., 2014).

As shown in Figure 6 and Appendix 3, there are positive Eu anomalies in the Igdekoy-Doganlar area in 13 samples and negative Eu anomalies in 4 samples. It is difficult to make an evaluation based on this anomaly because negative Eu anomalies are recognized in various environments. Considering the relationship of boron with a lacustrine environment and volcanic activity (by hydrothermal fluids) in the Igdekoy-Doganlar deposit, REE distribution in hydrothermal fluids and natural should also be taken into consideration. Mclennan (1989) separated the terrestrial waters into low and high-pH types. Waters with a negative Eu anomaly are defined as high-pH hydrothermal waters in the terrestrial environment (Mclennan, 1989). Within the Igdekoy-Doganlar depositional environment a negative Eu anomaly may record discharge from high-pH hydrothermal waters. Alternatively, a negative Eu anomaly is also suggested as an indicator of reducing environments (Henderson, 1984; Constantopoulos, 1988). Hydrothermal fluids (Sverjensky, 1984; Bau, 1991) and leaching processes cause a reduction of Eu^{3+} to Eu^{2+} and accordingly, a negative Eu anomaly. A negative Eu anomaly may also be generated by low-temperature hydrothermal waters (Hekinian et al., 1993). A positive Eu anomaly is regarded as an indicator of a magmatic source (Nance and Taylor, 1977; Bhatia, 1985; Sant'anna et al., 2006). It also shows the presence of CO$_2$ (Graf, 1977; Gale et al., 1997) that can be related to CO$_2$ produced by volcanic exhalations. Hence, the negative Eu anomaly in the Igdekoy-Doganlar region becomes a problematic in interpreting the borate occurrences as forming within oxygenated lake waters. In such an oxygenated environment, Eu^{2+} is easily oxidized to Eu^{3+} and is incorporated in borate formation because its ionic radius is similar to that of Na and Ca which results in positive Eu anomaly (Constantopoulos, 1988; Canet et al., 2005). So, there must be another explanation for the negative Eu anomaly in the
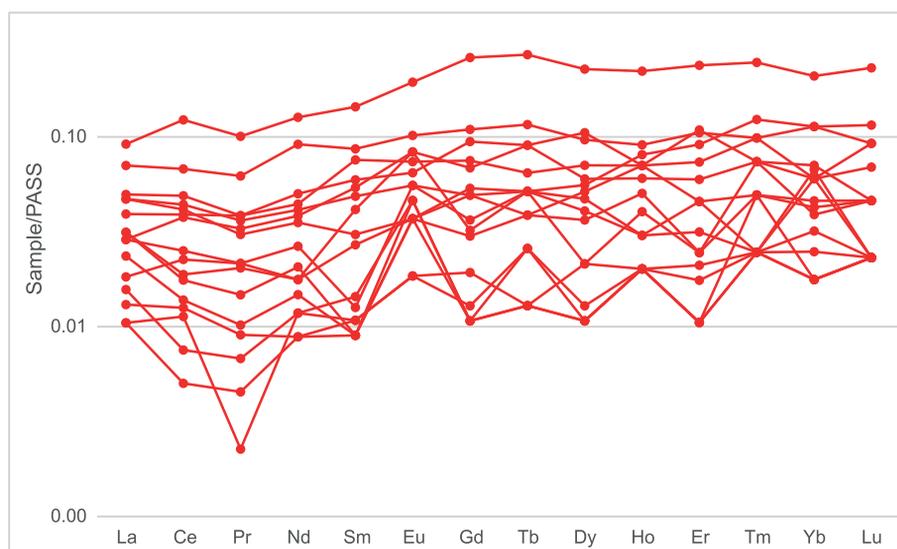

Fig. 6. REE distribution for the Igdekoy-Doganlar deposit (normalized with Taylor and Mclennan, 1985)

Igdekoy-Doganlar borates. The presense of a positive Eu anomaly indicates dissolution of Ca-plagioclase (Weill and Drake, 1973). If the Ca-plagioclase content of volcanic rocks in the study area was high and the alteration was sufficient, Eu would be increased in the lacustrine environment where the Igdekoy-Doganlar borates were deposited. The presence of negative Eu anomaly may arise from low degrees of hydrothermal alteration (Usui and Mita, 1995; Sasmaz et al., 2014).

Ho is expected to show a positive anomaly in Ca-borate samples because its ionic radius is identical to that of Ca. Indeed, a slightly positive Ho anomaly was recognized.

The average Y/Ho value of borates in the Igdekoy-Doganlar area is 30 (5 to 44). Modern sea water has notably high Y/Ho ratio (44) with respect to chondrite (26–28) (Kamber and Webb, 2001). Most geological materials (including all volcanic rocks and clastic deposits) have Y/Ho ratio close to chondritic value (Nozaki et al., 1997). The average Y/Ho of the Igdekoy-Doganlar borates is very similar to the chondritic ratio.

Low REE contents (<6.4 ppm), LREE depletion in PAAS-normalized patterns and positive Eu anomaly probably indicate a hydrothermal source (Sant'anna et al., 2006).

In general, the Igdekoy-Doganlar borate samples are characterized by LREE and medium rare earth element (MREE) enrichments. LREE enrichments may indicate a hydrothermal source. MREE enrichment is also characteristic of high temperature acidic hydrothermal fluids (Fee et al., 1992; Johannesson et al., 1996). REE compounds originating from moderately acidic rocks also show MREE enrichment and positive Eu anomaly (Johannesson et al., 1996).

The REE contents and elemental anomalies provided the following information:
– low REE contents and LREE depletion indicate a hydrothermal source;
– Ce values and negative anomalies show that the borates were deposited in an oxygenated environment. However, the absence or weak negative Ce anomalies in some samples show a partly oxygenated environment (Kato and Isozaki, 2009), and H_2S-bearing hydrothermal fluids are thought to had emanated from some parts of the lake, which is supported by the presence of realgar, orpiment and native sulphur minerals in borate deposits at Igdekoy-Doganlar;
– samples with a positive Eu anomaly indicate a magmatic origin and a CO_2 contribution from volcanic exhalations;
– the weak negative Eu anomalies in four samples is explained by a high pH, low degrees of hydrothermal alteration and low Eu contributions to the lake environment.

In western Anatolia, a low REE content is a common feature in all deposits. Negative Eu anomalies were found in Kırka, Hisarcık (Emet) and Şeyhler (Emet) borate deposits and posi-tive Eu anomalies were found in Kestelek, Espey (Emet) and Şeyhler (Emet) deposits as well. Small Ce anomalies are common in all deposits in western Anatolia (Kocak and Koc, 2016, 2018; Koc et al., 2017; Kocak, 2017). As seen in previous studies, both positive and negative Eu anomalies are observed in all deposits with a low Ce anomaly.

CONCLUSIONS

In the Igdekoy-Doganlar deposit, colemanite, ulexite, hydroboracite and probertite were found to be the major borate minerals. In addition, halite, anhydrite, glauberite, smectite and illite were also found.

B, Li, Se, As, Sb, Sr and Cs are concentrated in these deposits and can be used as indicator elements for exploration of borate deposits. B and Sr are particularly useful for exploration of borate deposits.

Among the elements that are enriched in the Igdekoy-Doganlar region, such as Sr, As, Cs, Se, Li and Sb, some of them, especially Li and Se may be produced as by-products.

Low concentrations of Sc, Hf, and low Th and a very weak correlation between Zr and Y/Ho indicate exceptionally low terrestrial contributions.

In the Igdekoy-Doganlar region, Ce and Eu show both negative and positive anomalies, but positive Ce and Eu anomalies are dominant. This data indicates that the sedimentary environment of the Igdekoy-Doganlar borate deposit was oxygenated and high-pH hydrothermal waters contributed to borate formation processes. Due to a continental crust contribution and low temperature conditions, the interaction between volcanic rocks and groundwater was limited which resulted in a negative Eu anomaly in some samples.

Geological data, evidence of hydrothermal contributions, the presence of minerals forming in alkaline conditions, and REE anomalies all suggest that the Emet Igdekoy-Doganlar borate deposits formed in high-pH playa lakes. The water was sourced from volcanic and terrestrial environments and concentrated under evaporative conditions due to the effect of an arid to semi-arid climate.

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