Geochemical characteristics of Kırka (Sarıkaya) borate deposit, northwestern Anatolia, Turkey

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The Kırka borate deposit was deposited in a Miocene lacustrine basin which is closely associated with volcanic activity which lasted from Paleogene to the beginning of Quaternary. Borate mineralization alternates with claystone, mudstone, tuff and fine-layered limestone and mostly shows a lenticular structure. The mineral paragenesis is composed of borax, tincalconite, ulexite, kurnakovite, probertite, tunellite, colemanite, dolomite, smectite group minerals, illite and some firstly reported minerals for the Kırka deposit including hydrochloroborite, brianroulstonite, hilgardite-4M and searlesite minerals. In comparison to average values of earth crust, concentrations of Cs, Sr, Li, As and Se were significantly enriched with respective rates of 21, 15, 14, 3 and 188 folds. Regarding KY, KS1 and KS2 locations, there are differences in both element abundances and their geochemical tendencies which are attributed to variations in discharge regime and physico-chemical conditions of the depositional environment. Independent behaviour of B₂O₃ might indicate that boron is not associated with clays and carbonates and, therefore, most part of boron must be derived from volcanic activity (hydrothermal solutions, gases). REE data indicate that the Kırka borate deposit was formed in a sedimentary environment where highly alkaline (high pH) hydrothermal solutions also took part in borate precipitation process.

1. Introduction

Kırka (Eskişehir), Kestelek (Bursa), Bigadiç (Balıkesir) and Emet (Kütahya) borate deposits in western Anatolia (figure 1a) comprise about 72% of world borate reserve. This work is related to Kırka borate deposit. Previous studies proposed that borate deposits in Turkey, including Kırka, were formed in lacustrine environments in association with volcanism started in Paleogene and continued to the beginning of Quaternary (Helke 1955; Özpeker 1969; Baysal 1972, 1973, 1974; Baysal and Ataman 1975; İnan 1975; Özpeker and İnan 1978; Ataman and Baysal 1978; Sunder 1980; Helvacı 1983; Yalçın 1988; Yalçın *et al.* 1989; Akyol and Akgün 1990; Yalçın and Baysal

1991; Palmer and Helvacı 1995, 1997; Floyd *et al.* 1998; Helvacı and Alonso 2000; Helvacı 2001, 2003; Helvacı and Orti 2004; Helvacı *et al.* 2004).

Various minerals are found in borate-zone in the Kırka deposit. Minerals display a mineralogical zonation consisting of Na, Na–Ca and Ca-borates including borax, kernite, tincalconite, ulexite, inyoite, meyerhofferite, colemanite, inderborite, hydroboracite, kurnakovite, pandermite, inderite and tunellite (Sunder 1980; Yalçın 1988; Yalçın and Baysal 1991; Palmer and Helvacı 1995). Among the deposits of Borate in Turkey, Kırka borate deposit is the only deposit that Na-borate minerals are dominant (Helvacı 2003). In these studies, only geology and borate mineral types in the deposit

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were investigated. However, major and trace element contents of the Kirka borates have not been studied before.

Major and trace element chemistry provide important information on the origin of ore deposits. Likewise, several trace elements may be more important than the major elements in a deposit. Also, it should not be ruled out that some elements that are not recently used or difficult to be exploited due to economic and technical conditions might be processed with improving opportunities. Similar studies were also carried out in the Kestelek (Koç *et al.* 2008a, b, c; Koçak and Koç 2011) and Bigadiç borate deposits (Koçak and Koç 2009, 2011, 2012).

Major and trace element contents of borate minerals, their enrichment levels and assessment by means of environmental conditions were first mentioned in Koç *et al.* (2008a, b, c); Koçak and Koç (2009, 2011, 2012) and it was found that Se, Sr, As, Cs, Li, Sb and Mo were enriched with respect to the average earth crust and andesite concentrations.

In the present work, major and trace element contents of the Kirka borates are studied. In this respect, recharge and depositional environment characteristics which were effective during the borate formation stage are evaluated with the use of geochemical data. For this aim, primarily major and trace element (including REE) concentrations of borate minerals and element enrichment levels were investigated. Based on inter-correlations, genetic affinity of elements, REE abundances and anomaly values, depositional environment conditions are discussed.

2. Materials and methods

Borate mineral samples collected from the Kirka borate deposit are the material of this work. Samples were taken from open pit surfaces and boreholes drilled by the Etibank Kirka Borate Exploitation Management which is nearly located at the center of borate basin. The borehole KS1 (BMK 2003/14) is at northwest of open pit, while borehole KS2 (BMK 2002/27) is at southwestern part. Surface samples (KY) were collected from certain levels showing variations from bottom to upper part of the Kirka open pit. Representative samples were collected from various parts of the basin to investigate major and trace element concentrations in borate minerals in central and marginal parts.

A total of 47 samples were taken; 8 (KS1) and 13 (KS2) from boreholes and 26 (KY) samples from the surface. Before the geochemical analysis, samples were cleaned with pressurized air and then washed to remove the clay particles.

In mineralogical studies, microscope, X-ray diffractometer (XRD) and confocal Raman method were used. XRD determinations of the samples were performed by X-ray diffraction (XRD) at the Turkish Petroleum Corporation (TPAO) laboratories in Ankara. A Rigaku-D model Max 2200 Ultima/Pc X-ray diffractometer with a Cu target was used in the analyses with 40 Kv, 20 mA, 1,54059 Å (CuK α 1) wave length and a scanning speed of 2° 2 θ /min. The Raman method was applied with Olympus BX41 model confocal Raman Spectrometer device at Petrography Research and Application Laboratory, Geology Department, Ankara University.

Chemical analysis was conducted at ACME (Canada) and Laboratories of the Eti Mine Works General Management. Major oxides were analyzed with Inductively-Coupled Plasma-Emission Spectrometry (ICP-ES) and trace and REE elements were determined with Inductively-Coupled Plasma-Mass Spectrometry (ICP-MS) method.

B₂O₃ analysis was performed with volumetric method at the Laboratories of the Eti Mine Works General Management.

3. Geologic setting

There are several studies concerning geology of the region stating that borate minerals were deposited in playa lakes within the Neogene units (Inan 1975; Sunder 1980; Yalçın 1988; Yalçın and Baysal 1991; Helvacı and Orti 2004).

Around the Kirka basin, pre-Miocene basement rocks (metamorphics consist of crystallized limestone, chloritic schist, metasandstone in Paleozoic; ophiolites in Cretaceous and carbonates in Eocene) and Neogene volcanic and sedimentary units are exposed. The Neogene units are represented by İdrisayla volcanites (andesite, rhyolite and volcanic breccia), Karaören Formation (zeolite-bearing tuffs), Sarıkaya Formation, Türkmendağı Basalt and Fetiye Formation (resedimented tuff) (figure 1b).

According to Yalçın and Baysal (1991), middle-upper Miocene Sarıkaya formation which hosts the borate deposits has a thickness of 150–300 m. The formation starts with 20–50 m thickened, massive thick-bedded limestones in travertine-like fibrous structure, alternating with claystone and tuff bands in centimeter scale and continues with 10–40 m thickened, thin-bedded dolomitic limestone. Laminated claystone/marl-dolomite level overlying the dolomitic limestone has a thickness of 5–40 m. Clayey-carbonaceous borate level of 20–160 m thickness is interlayered with tuffs in centimeter scale and contains altered, fibrous pumice particles. Above this zone, laminated claystone/

THICKNESS	LITHOLOGY	DESCRIPTION
20-50		Partly-banded limestones with abundant chert nodules
10-40		Dolomitic limestone
5-40		Laminated claystone/marl-dolomite
20-160		Clayey-carbonaceous borate level with tuffs
5-40		Laminated claystone/marl-dolomite level overlying the dolomitic limestone
10-40		Dolomitic limestone
10-50		Massive-thick bedded limestones in travertine-like fibrous structure alternating with claystone and tuff bands

Figure 2. Cross-section of the Sarıkaya Formation.

marl-dolomite alternation has a thickness of 5–40 m. This level is represented by hundreds of syn-sedimentary normal faults with slip rates in the range of millimeter to meter, interlayer folds and wrinkles or dislocations and load/slump structures. Upper part of formation is comprised by 10–40 m thickened dolomitic limestones and 20–50 m thickened, fibrous, partly banded limestones with abundant chert nodules (figure 2).

4. Analytical data and discussion

4.1 Mineralogy of borate deposit

Borate minerals in the Kirka deposit are borax, tincalconite, ulexite, kurnakovite, probertite, tunellite and colemanite and some firstly reported minerals for the Kirka deposit including hydrochloroborite,

brianroulstonite, hilgardite-4M and searlesite minerals (figure 3). In the assemblage, dolomite and smectite group minerals and illite are also found.

In the exploited part of deposit (KY), Na and Mg-borates are dominant, while western section (KS1 and KS2) is comprised by Ca-borates. In KY samples, deposition from bottom to the top is represented by Na-borate, NaCa-borate, Na-borate, Mg-borate + NaCa-borate, NaCa-borate, Mg-borate + NaCa-borate and Ca-borate + Sr-borate. The order of minerals in KS1 is NaCa-borate, Na-borate and NaCa-borate and that in KS2 is NaCa-borate, Ca-borate, NaCa-borate and Ca-borate.

Borax showing brecciated, banded and glassy textures is the main mineral in the Na-borate zone. The NaCa-borate zone composing of ulexite is just above the Na-borate zone. Ulexite is accompanied by kurnakovite, tunellite and probertite. Ulexite is

Figure 3. XRD diffractogram of first reported minerals for the Kurka: (a) hilgardite-4M and searlesite; (b) brianroulstonite; and (c) hydrochloroborite.

Figure 3. (Continued.)

massive, nodular and occurs as thin veins. Kurnakovite in NaCa-borate zone occurs in clay as prismatic single crystals of 1–20 cm size or crystal groups. Tunellites in platy texture and transparent appearance is found together with ulexite. Probertite is massive and transparent. Ca-borate zone comprises the upper-most part of borate deposition. Colemanite which is the main mineral occurs as transparent layers.

4.2 Geochemical properties of Kirka deposit

In this study, major, trace and rare earth element variations in a total of 47 samples from KY, KS1 and KS2 are examined. Element abundances and correlations are used to discuss deposition evolution of Kirka borates.

4.2.1 Major element abundances in Kirka borate deposit

The major element abundances, concentration ranges, their average values and average concentrations of earth crust (ECA), andesite (AA) and freshwater

(FWA) are given in table 1. Concentrations of all major elements are increased with respect to FWA. The B_2O_3 concentration in all samples is in the range of 26.42–44.89 wt% with an average of 37.3 wt%. The order of abundance of other elements with respect to average values is Na (7.27) > Ca (5.84) > Mg (2.35) > Si (1.30) > K (0.14) > Al (0.12) > Fe (0.09) (in %). When these values are compared to ECA and AA, Na content is enriched by 3.03–2.42 folds, Ca and Mg also slightly enriched while concentration of others (Si, K, Al and Fe) are significantly depleted (17–71 folds) (figure 4).

Comparison of element concentrations from KY, KS1 and KS2 samples (table 1) reveals different results for different parts of the depositional environment. For example, high Na and Mg concentrations are found in KY area indicating presence of Na–Mg borates. However, Ca concentrations in KS1 and KS2 samples are higher than those of KY. This might show westward increase of Ca-borates in Kirka borate deposit. Si, K, Al and Fe concentrations in samples are lower than those of ECA and AA and found to be higher in KY area.

Table 1. Major element contents of Kurka samples (%). (1) Krauskopf (1989), (2) Schroll (1975), (3) Abollino et al. (2004) (does not contain B_2O_3).

Sample	Depth (m)	B ₂ O ₃ (%)	Si (%)	Al (%)	Fe (%)	Mg (%)	Ca (%)	Na (%)	K (%)	TOT/C (%)	TOT/S (%)	LOI (%)	Sum (%)
KY26	1096.0	42.24	0.34	0.02	<0.03	1.06	7.84	3.82	<0.01	3.61	<0.02	N.A.	13.07
KY25	1094.5	37.01	0.97	0.18	0.04	5.26	4.22	2.42	0.12	2.47	<0.02	N.A.	13.20
KY24	1094.0	35.92	0.52	0.04	<0.03	8.20	1.24	0.51	0.03	3.43	<0.02	N.A.	10.54
KY23	1093.0	35.43	2.26	0.20	0.08	3.73	6.77	3.89	0.20	0.52	<0.02	N.A.	17.12
KY22	1092.0	39.21	0.72	0.01	<0.03	3.98	6.06	3.46	<0.01	0.32	<0.02	N.A.	14.23
KY21	1082.0	34.02	0.79	0.07	0.03	9.19	1.16	0.14	0.02	0.31	<0.02	N.A.	11.42
KY20	1081.0	33.25	2.79	0.09	<0.03	3.03	9.58	4.75	0.05	1.36	<0.02	N.A.	20.28
KY19	1080.0	32.73	1.65	0.25	0.09	7.84	2.90	1.14	0.20	0.04	<0.02	N.A.	14.07
KY18	1079.0	36.46	2.23	0.21	0.08	1.83	8.97	4.95	0.23	0.16	<0.02	N.A.	18.50
KY17	1078.0	37.78	0.93	0.10	0.03	4.24	0.99	6.48	0.06	0.25	<0.02	N.A.	12.83
KY16	1077.0	37.28	3.01	0.62	0.22	0.85	8.38	5.03	0.78	2.16	0.03	N.A.	18.90
KY15	1076.0	40.96	0.06	0.01	<0.03	0.04	0.04	12.36	<0.01	0.33	<0.02	N.A.	12.50
KY14	1075.0	37.58	0.54	0.02	<0.03	0.90	1.04	11.93	0.02	0.48	<0.02	N.A.	14.45
KY13	1071.0	41.83	0.23	0.02	<0.03	0.78	0.25	13.05	0.01	0.81	<0.02	N.A.	14.34
KY12	1070.0	39.50	0.89	0.18	0.06	0.54	0.58	12.06	0.17	0.04	<0.02	N.A.	14.47
KY11	1062.0	34.36	2.02	0.15	0.04	2.24	3.27	10.78	0.17	0.16	<0.02	N.A.	18.68
KY10	1061.5	39.46	0.51	0.09	0.03	0.39	0.39	11.77	0.10	0.11	<0.02	N.A.	13.28
KY9	1060.5	38.85	2.42	0.60	0.23	0.60	0.53	11.97	0.47	1.09	<0.02	N.A.	16.81
KY8	1060.0	36.35	3.13	0.87	0.14	0.27	0.09	10.97	1.19	1.26	<0.02	N.A.	16.66
KY7	1057.0	37.13	1.21	0.03	<0.03	2.00	2.22	11.15	0.02	1.94	<0.02	N.A.	16.63
KY6	1056.0	40.86	0.35	0.05	<0.03	0.51	0.34	11.97	0.02	0.79	<0.02	N.A.	13.25
KY5	1055.0	39.37	0.79	0.19	0.06	0.49	0.53	12.10	0.20	0.18	<0.02	N.A.	14.34
KY4	1054.0	39.91	0.38	0.04	<0.03	0.65	0.74	12.15	0.02	0.82	<0.02	N.A.	13.98
KY3	1053.0	28.71	2.10	0.06	<0.03	3.55	5.78	9.30	0.06	0.34	<0.02	N.A.	20.85
KY2	1052.0	33.42	1.99	0.03	<0.03	2.30	4.32	10.52	0.05	0.35	<0.02	N.A.	19.22
KY1	1050.0	28.03	2.54	0.04	<0.03	4.31	5.07	8.85	0.06	0.88	<0.02	N.A.	20.87
Average of KY samples		36.83	1.36	0.16	0.09	2.65	3.20	7.98	0.19	0.93	0.03	N.A.	15.62
KS1-1	90	41.10	0.36	0.01	<0.03	0.39	9.88	5.47	<0.01	0.3	<0.02	N.A.	16.10
KS1-2	105	43.97	0.50	0.02	<0.03	0.48	3.87	11.54	0.02	0.36	<0.02	N.A.	16.42
KS1-3	108.5	40.79	1.27	0.04	<0.03	2.09	2.30	13.56	0.04	1.58	<0.02	N.A.	19.30
KS1-4	110	27.51	2.74	0.09	<0.03	5.42	7.57	9.17	0.10	4.77	<0.02	N.A.	25.09
KS1-5	116	44.04	0.77	0.04	<0.03	0.72	3.04	12.70	0.04	0.54	<0.02	N.A.	17.31
KS1-6	139.3	38.08	1.00	0.02	<0.03	1.42	10.48	5.09	0.02	1	<0.02	N.A.	18.03
KS1-7	142.5	37.56	1.07	0.02	<0.03	1.51	10.33	4.99	0.02	1.08	<0.02	N.A.	17.94
KS1-8	145.3	26.56	4.39	0.33	<0.03	4.85	10.94	3.56	0.42	3.31	<0.02	N.A.	24.50
Average of KS1 samples		37.45	1.51	0.07	–	2.11	7.30	8.26	0.10	1.62	<0.02	N.A.	19.35

Table 1. (Continued.)

Sample	Depth (m)	B ₂ O ₃ (%)	Si (%)	Al (%)	Fe (%)	Mg (%)	Ca (%)	Na (%)	K (%)	TOT/C (%)	TOT/S (%)	LOI (%)	Sum (%)
KS2-1	163.1	43.74	1.06	0.02	<0.03	1.62	17.08	0.01	0.01	1	<0.02	N.A.	19.80
KS2-2	167	35.10	0.85	0.01	<0.03	2.37	10.86	4.78	0.02	1.95	<0.02	N.A.	18.88
KS2-3	175	39.21	0.48	0.03	<0.03	1.83	8.69	5.25	0.02	0.85	<0.02	N.A.	16.31
KS2-4	200	42.45	0.50	0.02	<0.03	2.03	3.15	11.79	0.02	1.05	<0.02	N.A.	17.50
KS2-5	210	44.89	0.43	0.08	<0.03	0.48	3.22	12.33	0.05	0.22	<0.02	N.A.	16.60
KS2-6	225	38.55	0.96	0.04	<0.03	1.22	10.03	5.25	0.03	0.81	<0.02	N.A.	17.53
KS2-7	235	40.02	0.91	0.24	<0.03	0.66	9.08	5.45	0.18	0.34	<0.02	N.A.	16.52
KS2-8	247	40.73	0.85	0.15	<0.03	0.34	9.33	5.62	0.15	0.09	<0.02	N.A.	16.44
KS2-9	255	31.37	1.60	0.20	<0.03	3.10	11.31	4.48	0.21	2.58	<0.02	N.A.	20.90
KS2-10	265	42.19	1.29	0.11	<0.03	1.92	16.92	0.15	0.10	1.49	<0.02	N.A.	20.48
KS2-11	295	29.50	1.04	0.01	<0.03	4.25	12.11	3.92	0.02	4.01	<0.02	N.A.	21.35
KS2-12	300	41.70	0.40	0.04	<0.03	0.21	9.71	5.47	0.05	0.16	<0.02	N.A.	15.88
KS2-13	312	26.42	3.09	0.18	<0.03	4.91	11.24	3.56	0.24	3.79	<0.02	N.A.	23.23
Average of KS2 samples		38.14	1.03	0.09	–	1.92	10.21	5.24	0.08	1.41	<0.02	N.A.	18.57
Average of all samples		37.30	1.30	0.12	0.09	2.35	5.84	7.27	0.14	1.18	0.03	N.A.	17.11
Standard deviation		4.84	0.98	0.17	0.07	2.22	4.64	4.20	0.22	1.22	–	N.A.	12.49
Various rates		26.42–	0.06–	0.01–	<0.03–	0.04–	0.04–	0.01–	<0.01–	0.04–	<0.02–	N.A.	16.91–
		44.89	4.39	0.87	0.23	9.19	17.08	13.56	1.19	4.77	0.03		38.76
Average (earth crust) (1)		0.0010	28.20	8.10	5.40	2.30	4.10	2.40	2.10	–	–	–	–
Average (Andesite) (2)		0.0015	26.00	8.85	5.85	2.18	4.65	3.00	2.30	–	–	–	–
Average (freshwaters) (3) * 10 ^{–4}		0.01	5.33	<30·10 ^{–3}	<30·10 ^{–3}	0.8–15.07; 3.64	1.8–49.29; 13.22	1.15– 36.78;5.28	0.51– 3.9;12.9	–	–	–	–

Figure 4. Bar diagrams of increase/decrease rates of elements of the Kirka.

4.2.2 Trace element abundances in Kirka borate deposit

Like in major elements, concentrations of trace elements (table 2) are also considerably increased with respect to FWA. However, concentrations of only five elements are increased, while others are decreased with respect to ECA and AA. The minimum–maximum concentrations (in ppm) of these elements are Se (<0.50–47.40), Li (45.20–791.80), As (<0.50–23.90), Cs (1.80–962.40) and Sr (22.60–50400.00). The difference between these values is large indicating that the amount of material transported to the environment is quite variable. Average concentrations and approximate increase rate (with respect to ECA) of these elements are Se (9.40 ppm – 187.96 folds), Li (282.92 ppm – 14.15 folds), Sr (5760.73 ppm – 15.36 folds), As (5.34 ppm – 2.97 folds) and Cs (1.80 ppm – 21.04 folds) (figure 4). The abundances, the increased concentrations of elements and minimum–maximum concentrations are similar for three different sampling sites (KY, KS1 and KS2).

Comparison of major and trace element contents of two other borate deposits in western Turkey yields similar results. For example Se, Li, Cs, Sb, Mo, As, Sr in the Kestelek deposit (Koç *et al.* 2008a, b, c; Koçak and Koç 2011) and Se, Li, Mo, Sb, As, Sr in the Bigadiç deposit (Koçak and Koç 2012) are found to be enriched with respect to ECA and AA. Regarding the degree of enrichment of trace elements, the Kirka, Kestelek and Bigadiç deposits resemble each other. Particularly, Se, Li, Sr and As are found to be enriched in each of these deposits. Only differences are Mo–Sb enrichment in Kestelek and Cs enrichment in Kestelek and Kirka.

The previous studies indicate volcanism in the region (Palmer and Helvacı 1995; Floyd *et al.* 1998; Helvacı and Orti 2004). These volcanic processes related to epithermal system have provided the participation of some elements into the environment. It is known that Se and As are associated with volcanism and epithermal systems and Cs and Sr are related to volatile-rich solutions formed after the solidification of magma. Lithium may replace aluminum in muscovite and other aluminosilicates

(Elkin and Margrave 1968; Bürküt 1977; Akçay 2002; Halilova 2004). Therefore, in the study area, (a) Miocene volcanism and related hydrothermal solutions and volatiles, as well as, (b) clays transported from terrestrial regions, might be the source of these elements. This will be discussed in detail in the next section of correlation analysis.

4.3 Correlation analysis

Correlations between elements in borate samples yield some important information regarding formation conditions. Data given in table 3 show that there are strong–very strong positive correlations between Si, Al, Fe and K. Regarding trace elements, Cs, Nb, Rb, Zr, Ni, Pb, As and REE also positively correlated with each other and major elements as well. Si shows strong positive correlation with Li and Mo, which are not included to the above-mentioned trace element group, and weak positive correlation with Mg, Ca and U. This indicates that Si may be derived from two different sources. Considering that Si together with Al is resistant to chemical alteration and indicative of detrital origin (Boggs 2009; Fu *et al.* 2011), it can be stated that they are transported from terrestrial environment to the lake basin in association with clays. If this is the case, Cs, Nb, Rb, Zr, Ni, Pb, As and REE should have also been transported by the clays. Elements can be transported as absorption on the surface of clay and easily be released in the borate depositional environment and thus become a part of the borate crystal structure. Furthermore, it is possible to release the depositional environment appropriate conditions in the clay structure (Krauskopf 1989). Some part of Si might be brought to the lacustrine environment in the form of silicic acid as an alteration product of silicates (Krauskopf 1989).

Mg and Ca display different behaviours. Mg is weakly positively correlated with Si (0.29) and negatively correlated with Na (−0.57). Ca is very positively correlated with Se and strongly negatively correlated with Na (−0.67). Ca is also weakly positively correlated with Sr, U and Mo. The lack of relation between detrital group and Ca–Mg pair might indicate the later elements differ in transport mechanism to the depositional site compared to the former. Weak positive correlation with Si shows that some part of Mg has a silicate origin.

Na is the only major element which shows positive correlation (slightly weak) with B_2O_3 (0.27). Regarding trace elements, sodium shows strong positive correlation only with Cu. In addition to negative correlations with Ca and Mg, Na generally shows very weak negative correlations with other major and trace elements.

B_2O_3 is strongly negatively correlated with Si, Mg and Li, very weakly correlated with Ca and K, weakly correlated with U and Mo and very weakly positively correlated with Na. These correlations reveal that Na and B_2O_3 are not associated with clays and carbonates and in fact they are derived from hydrothermal solutions and exhalations.

TOT/C (total carbon) is strongly correlated with none of the elements. It shows weak positive correlation with Si, Mg, Ca, Ba and Sr and weak negative correlation with B_2O_3 and Na. The weak positive correlation of C with Ca and Mg indicates that some part of carbon in TOT/C is associated with carbonates. The weak positive correlation of Si with TOT/C and Ca and strong positive correlation with Al might yield that Si has multiple origin, both clays and carbonates.

Correlations of Se, Li, As, Cs and Sr which display significant enrichment with respect to ECA and AA indicate that they are derived from a similar source. Very strong correlation of Se with Ca, strong correlation of Li with Si, strong–very strong correlation of As and Cs with clay group elements (e.g., Si, Al, Fe and K) and very strong correlation with Ba are noticeable (table 3). Considering negative correlations of these elements and groups determined in the cluster analysis (figure 5), it can be stated that As and Cs are associated with clay group, Se and Sr are associated with carbonates and Li is associated with Si.

The cluster analysis (Pearson) performed using the correlation coefficients yielded three different element groups (figure 5). The first group is comprised of Al, Fe, K, Cs, Nb, Rb, Zr, Ni, Pb and As which are accompanied by REE, Y, Th and Cu. Ca, Se, Ba and Sr form the second group and Si, U, Mo and Li form the third group.

4.4 Rare earth elements

Although all REEs are determined in all KY and KS2 samples, La, Ce and Pr were detected only in KS1 samples. Averages of REE concentrations (in ppm) in all Kirka samples are La (0.95), Ce (1.85), Pr (0.22), Nd (1.30), Sm (0.28), Eu (0.08), Gd (0.25), Tb (0.05), Dy (0.27), Ho (0.08), Er (0.18), Tm (0.03), Yb (0.23) and Lu (0.03).

Considering that studied borate deposit was formed in a sedimentary (lacustrine) environment, REE concentrations were normalized with respect to PAAS (Post-Archean Australian Shales). Normalization was made taking into account that REE patterns of PAAS, average shale and upper crust are almost parallel (Taylor and McLennan 1985).

KS2 with complete REE data reflects a significant negative Eu anomaly as also shown in curves and average values representing KY area

Table 2. Trace element contents of Kırka samples (ppm). (1) Krauskopf (1989), (2) Schroll (1975), (3) Abollino et al. (2004), (4) Şahinci (1991).

Sample	Se	Li	As	Cs	Sr	Ba	Co	Nb	Rb	Th	U	Zr	Y	Mo	Cu	Pb
KY26	7	45.2	6	6.4	50400	626	0.3	<0.1	1.3	<0.2	<0.1	0.8	0.4	<0.1	0.5	0.2
KY25	5.7	126.8	7.1	46.5	8562	7	0.9	0.8	23.8	2.1	0.2	2.3	8.3	<0.1	0.5	1.6
KY24	1	95.6	<0.5	17.2	1355	3	3.9	0.1	7.2	<0.2	<0.1	1.8	0.2	<0.1	0.2	0.4
KY23	6.1	426.1	4	76.6	9047	6	4.9	0.6	34.6	1	0.2	1.7	1.2	0.7	0.9	1.8
KY22	7	155.9	<0.5	12	839.2	<1	0.5	<0.1	2	0.5	0.3	0.8	0.3	0.1	0.3	<0.1
KY21	1.6	133.7	3	32.5	1437	10	0.9	0.3	8.9	0.2	0.2	1.8	0.2	0.1	0.3	0.4
KY20	10.3	617.8	4.2	58.1	11967	44	<0.2	0.3	14.4	0.6	0.3	0.6	0.6	1	0.8	0.7
KY19	3.7	263.2	7.8	79.7	4254	19	2	0.9	34.2	1.3	0.2	2.6	1.5	0.6	0.9	2.2
KY18	9.5	411.4	5.8	66.4	12979	45	0.5	0.8	37.8	0.9	0.3	1.9	1.4	0.7	<0.1	1.7
KY17	1.1	176.9	1.5	40.6	1997	3	<0.2	0.4	13.8	0.3	<0.1	1.2	0.5	0.2	0.8	0.6
KY16	10.1	329	23.9	163.6	9610	16	0.7	1.9	137.7	2.3	0.2	9.3	11.2	0.4	1.9	3.1
KY15	<0.5	154.1	<0.5	1.8	22.6	<1	<0.2	<0.1	0.8	<0.2	<0.1	2.2	0.1	<0.1	1.3	<0.1
KY14	1.8	274.1	<0.5	30.6	953	6	<0.2	<0.1	6.2	<0.2	<0.1	0.9	0.2	<0.1	1.1	<0.1
KY13	<0.5	205.1	<0.5	7.7	727.9	5	<0.2	<0.1	2.3	<0.2	<0.1	<0.1	0.2	<0.1	1.3	0.2
KY12	0.8	257.8	10	52.3	1211	8	0.3	0.7	28.5	1.1	0.2	2.8	1	<0.1	1.4	1.3
KY11	5.3	583.8	5.7	62	2414	17	0.3	0.6	35.6	0.4	0.2	4.2	0.5	0.2	1.6	1.2
KY10	0.6	209.9	3.3	33.4	455	8	0.2	0.4	19.3	0.3	<0.1	0.9	0.5	<0.1	1.4	0.6
KY9	1	415.4	22.7	962.4	450.9	23	1	2	133.7	0.8	0.1	7	1.4	0.1	2.9	3.7
KY8	0.5	309.2	16.6	52.5	39	52	0.4	0.9	129.8	<0.2	<0.1	12.9	0.4	0.1	1.7	1.4
KY7	3	428.3	2.3	37.2	2067	6	<0.2	0.2	7.4	0.3	0.2	0.7	0.3	<0.1	1.1	0.2
KY6	0.6	210.5	3	34.7	453.8	4	<0.2	0.1	5.8	<0.2	<0.1	1.7	0.3	<0.1	1.3	0.3
KY5	0.8	222.8	5.5	57.9	299.5	10	0.3	0.6	37.1	0.7	<0.1	2.6	1	0.1	1.2	1.2
KY4	1.1	227.4	2.2	16	1196	7	<0.2	0.1	6.6	0.3	<0.1	0.6	0.3	<0.1	1.3	0.1
KY3	6.5	693.4	3.9	62.3	2983	12	<0.2	0.3	15.9	0.2	0.2	3.4	0.4	0.2	1.1	0.4
KY2	5.3	667.5	3.2	74.9	2528	17	0.2	0.2	16.4	<0.2	<0.1	0.4	0.4	0.2	1.1	0.4
KY1	6.6	791.8	5.5	101.4	3024	14	<0.2	0.3	20.3	<0.2	0.3	0.9	0.4	0.7	1.1	0.4
Average of KY	4.04	324.33	7.01	84.10	5048.92	40.33	1.08	0.60	30.05	0.78	0.22	2.64	1.28	0.36	1.12	1.05
KS1-1	17.1	74.8	<0.5	12.6	7603	3	2	<0.1	1.4	<0.2	<0.1	3.2	0.2	0.1	0.4	0.1
KS1-2	9.8	133.5	0.7	20.1	1393	3	0.7	<0.1	5.3	<0.2	<0.1	1.7	<0.1	<0.1	0.7	0.2
KS1-3	6.2	346	1.6	66.2	813.3	10	10.8	0.2	10.6	<0.2	<0.1	5.8	0.2	0.1	0.9	0.5
KS1-4	16.4	615.7	8.4	153.4	5207	24	3.3	0.4	28.4	0.4	<0.1	2.7	0.4	0.3	1	0.4
KS1-5	7.8	162.5	3	25.8	1632	6	2.7	0.1	9.4	0.2	<0.1	4.3	<0.1	<0.1	1	0.4
KS1-6	23.7	218.5	<0.5	38.7	2518	9	1	0.1	7.3	<0.2	<0.1	2.1	0.1	<0.1	<0.1	<0.1
KS1-7	18.5	256.7	0.6	41.7	4201	40	0.8	0.2	7.7	0.2	<0.1	3.6	0.3	0.1	0.4	0.2
KS1-8	26.2	234.5	16.4	126.2	6349	125	0.7	0.9	57.6	1.7	<0.1	10.9	1.1	0.7	0.8	1.9
Average of KS1	15.71	255.28	5.12	60.59	3714.54	27.50	2.75	0.32	15.96	0.63	—	4.29	0.38	0.26	0.74	0.53

Table 2. (Continued.)

Sample	Se	Li	As	Cs	Sr	Ba	Co	Nb	Rb	Th	U	Zr	Y	Mo	Cu	Pb
KS2-1	47.4	176.7	5.3	3.4	20261	125	2.1	0.1	1.9	0.2	0.2	4.4	0.6	0.2	0.4	0.4
KS2-2	27.9	166.2	1.6	5.4	10273	7	0.3	0.1	2	<0.2	0.2	2.7	0.6	<0.1	0.4	0.2
KS2-3	7.4	105.6	1	20.1	12172	10	0.9	<0.1	5.9	<0.2	0.1	1.4	0.8	0.2	0.9	0.4
KS2-4	4.8	258.1	1	17.6	4996	14	0.4	0.2	6.6	<0.2	<0.1	1.5	0.4	0.3	1.6	0.3
KS2-5	3.1	245.8	3.5	21.9	4145	10	<0.2	0.3	12.1	0.3	0.2	2.1	0.8	0.2	1.5	0.5
KS2-6	13.4	169.8	1.4	4.6	9305	19	<0.2	0.2	5	0.3	0.1	1.4	0.6	<0.1	0.6	0.4
KS2-7	9.9	91.6	5	26.3	13389	22	0.8	0.5	24.5	1	0.2	3.6	3.3	0.2	1.2	1.3
KS2-8	9.9	103.7	4.5	20.1	10271	44	0.5	0.3	16.2	0.3	0.1	3.9	3.3	0.2	0.9	1.4
KS2-9	13	221.5	5.2	31.8	7563	26	<0.2	0.5	24.9	1	0.2	3.2	1.5	0.2	0.7	2
KS2-10	28.5	227.1	2.4	33.7	5412	22	1	0.4	18.5	0.4	0.2	2.4	0.6	0.1	1.2	0.5
KS2-11	13.1	300.7	0.9	23.3	5317	41	<0.2	<0.1	2.7	<0.2	0.2	1	0.4	<0.1	0.3	0.1
KS2-12	8.6	80.3	0.5	10.6	1949	5	0.2	0.1	7.1	<0.2	<0.1	1.1	1.8	<0.1	0.4	0.3
KS2-13	13.2	675.4	3.5	76.5	4713	32	<0.2	0.5	30.9	0.8	0.4	4.1	0.9	0.7	0.8	1.1
Average of KS2	15.40	217.12	2.75	22.72	8443.54	29.00	0.78	0.29	12.18	0.54	0.19	2.52	1.20	0.26	0.84	0.68
Average of all samples	9.40	282.92	5.34	63.12	5760.73	34.78	1.42	0.46	22.71	0.69	0.21	2.89	1.14	0.31	0.98	0.85
Standard deviation	9.42	186.93	5.51	138.92	8047.13	93.85	2.06	0.43	31.91	0.57	0.07	2.62	2.03	0.26	0.52	0.83
Various rates	<0.5– 47.4	45.2– 791.8	<0.5– 23.9	1.8– 926.4	22.6– 50400	<1– 626	<0.2– 10.8	<0.1– 1.9	0.8– 137.7	<0.2– 2.1	<0.1– 0.4	<0.1– 4.4	<0.1– 11.2	<0.1– 0.7	<0.1– 2.9	<0.1– 3.1
Average (earth crust) (1)	0.05	20	1.8	3	375	500	22	20	90	8.5	2.7	165	35	1.5	50	12.5
Average (Andesite) (2)	0.05	20	1.9	2.3	800	714	10	20	72	7	1.8	260	25	0.9	35	15
Average (fresh-waters) (3)	0.1·10 ⁻³	1·10 ⁻³	2·10 ⁻³	1.8·10 ⁻³ (4)	50·10 ⁻³	10·10 ⁻³	0.05 ·10 ⁻³	–	–	–	0.05 ·10 ⁻³	–	–	1·10 ⁻³	1.8 ·10 ⁻³	0.2 ·10 ⁻³

Table 2. (Continued.)

Sample	Ni	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
KY26	<0.1	0.1	0.2	0.04	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KY25	1.3	3.8	8.2	0.97	3.6	0.91	0.09	0.93	0.19	1.14	0.24	0.74	0.12	0.88	0.12
KY24	0.2	0.2	0.4	0.05	<0.3	<0.05	<0.02	<0.05	0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KY23	0.9	1	2.2	0.24	1	0.18	<0.02	0.19	0.03	0.17	0.04	0.1	0.02	0.11	0.02
KY22	0.6	0.2	0.4	0.05	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KY21	0.2	0.6	1	0.13	0.6	0.12	<0.02	0.09	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KY20	0.8	0.5	1.1	0.11	0.4	0.07	<0.02	0.07	0.02	0.07	0.02	0.05	<0.01	0.06	0.01
KY19	1.1	1.2	2.4	0.3	1.3	0.27	0.03	0.24	0.04	0.22	0.05	0.14	0.02	0.15	0.02
KY18	0.2	1.7	3.2	0.37	1.4	0.27	0.03	0.24	0.04	0.19	0.04	0.13	0.02	0.11	0.02
KY17	0.4	0.4	0.8	0.09	0.4	0.08	<0.02	0.08	0.01	0.08	<0.02	0.04	<0.01	<0.05	<0.01
KY16	4.9	10.4	23.8	2.48	9.6	2.06	0.29	2.05	0.33	1.86	0.38	1.08	0.15	0.92	0.14
KY15	0.1	<0.1	0.2	<0.02	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KY14	0.3	0.1	0.2	<0.02	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KY13	0.2	0.1	0.2	<0.02	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KY12	1.6	0.8	1.6	0.17	0.8	0.16	<0.02	0.15	0.02	0.12	0.02	0.09	0.02	0.11	0.02
KY11	0.8	0.5	0.9	0.09	0.4	0.08	<0.02	0.07	0.01	0.05	<0.02	0.04	<0.01	<0.05	<0.01
KY10	0.7	0.4	0.9	0.08	0.5	0.07	<0.02	0.08	0.01	0.07	<0.02	0.04	<0.01	<0.05	<0.01
KY9	5.4	1.9	3.5	0.38	1.5	0.26	0.03	0.23	0.04	0.25	0.06	0.18	0.02	0.13	0.02
KY8	1.8	0.6	1	0.1	0.6	0.07	<0.02	0.07	0.01	0.06	<0.02	<0.03	<0.01	<0.05	<0.01
KY7	<0.1	0.2	0.3	0.02	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KY6	0.4	0.3	0.5	0.04	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KY5	1.5	0.8	1.8	0.17	0.7	0.14	<0.02	0.16	0.02	0.11	0.03	0.06	0.02	0.07	0.01
KY4	0.3	0.4	0.5	0.04	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KY3	0.5	0.4	0.6	0.05	0.3	<0.05	<0.02	0.06	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KY2	0.2	0.2	0.4	0.03	<0.3	<0.05	<0.02	0.06	<0.01	0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KY1	0.7	0.3	0.4	0.04	<0.3	<0.05	<0.02	0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
Average of KY	1.05	1.08	2.18	0.26	1.54	0.34	0.09	0.28	0.06	0.32	0.10	0.22	0.05	0.28	0.04
KS1-1	<0.1	0.2	0.3	0.02	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KS1-2	<0.1	0.1	0.1	<0.02	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KS1-3	0.2	0.3	0.4	0.02	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KS1-4	0.4	0.5	0.8	0.08	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KS1-5	<0.1	0.3	0.4	<0.02	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KS1-6	<0.1	0.2	0.3	<0.02	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KS1-7	0.4	0.4	0.6	0.06	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
KS1-8	0.8	2.1	3.8	0.34	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01
Average of KS1	0.45	0.51	0.84	0.10	—	—	—	—	—	—	—	—	—	—	—

[illegible]

Figure 5. Cluster dendrogram for elements of Kirka samples.

Figure 6. REE distributions for Kirka borate samples (normalized according to Taylor and McLennan 1985).

(figure 6). Except for this anomaly, curves show a flat pattern. Concentrations of heavy rare earth elements (HREE) are higher than those of light rare earth elements (LREE). The negative Eu anomaly is detected in many sedimentary rocks. In order to have more information on environmental conditions, concentrations of rare earth elements in natural waters and hydrothermal solutions are to be known. McLennan (1989) who classified

hydrothermal waters as oceanic and terrestrial types, divided terrestrial hydrothermal waters into two categories: low-pH and high-pH waters. Waters showing a negative Eu anomaly was described by McLennan (1989) as high-pH hydrothermal waters of terrestrial environment. Based on this, REE concentrations of Kirka borate deposit indicate that high-pH hydrothermal waters contributed to borate formation process.

Alternatively, negative Eu anomaly is thought to represent anoxic reducing environment (Constantopoulos 1988; Henderson 1984). Hydrothermal solutions (Sverjensky 1984; Bau 1991) and leaching (Bence and Taylor 1985) give rise to reducing of Eu^{3+} to Eu^{2+} and as a result a strong negative Eu anomaly appears.

This negative Eu anomaly needs to be explained considering that borates formed in an oxygenated lacustrine environment. In oxygenated environments, Eu^{2+} is easily oxidized to Eu^{3+} which contributes to borate formation. Since its ionic radius is similar to that of Ca and Na, this should result in a positive Eu anomaly (Weil and Drake 1973; Bau 1991; Ehinola *et al.* 2010). Therefore, there must be some explanation for the negative Eu anomaly in Kirka borates. First, it can be suggested that sufficient amount of Eu was not transported to the lake environment by hydrothermal waters and due to reduced nature of the fluid or early precipitation of feldspar (retention in feldspar) before the REEs became a part of the lacustrine geochemical environment. In addition, H_2S -bearing hydrothermal solutions make the environment to have a partly reducing character. Considering all these data and suggestions, it is proposed that the Kirka borate deposit was formed in a sedimentary environment with contribution from high-pH hydrothermal waters, and during the leaching of country rocks, Eu^{3+} was reduced to Eu^{2+} which caused a negative Eu anomaly.

5. Conclusions

- The Kirka borate deposits were formed in Miocene lacustrine basins which are associated with volcanic activity which lasted from Paleogene to the beginning of Quaternary. Borate mineralization generally shows a lenticular structure and is interlayered with claystone, mudstone, marl, tuff and thin-layered limestone (Helvacı 2003).
- The mineral paragenesis is composed of borax, tincalconite, ulexite, kurnakovite, probertite, tunellite, colemanite, dolomite, smectite group minerals, illite and some firstly reported minerals for the Kirka deposit including hydrochloroborite, brianroulstonite, hilgardite-4M and searlesite minerals.
- Based on major element abundances, Ca-borates occur at western part of the deposit, while Na- and Mg-borates are dominant at the area of management.
- Most of major and trace elements (e.g., Si, Al, Fe, K, Cs, Nb, Rb, Zr, Ni, Pb, As) are mobilized as a result of alteration of silicate rocks and transported to the lake environment in association with detrital clays. Li and Mo which have an affinity for Si rather than Al, can be included to this group. Other elements (Ca, Ba, Sr, Se) are associated with carbonates.
- Among the trace elements Se, Li, As, Cs and Sr are much more enriched than ECA and AA. These elements are derived from volcanism continued through the Miocene and related hydrothermal solutions and volatiles as well as clays transported from terrestrial regions.
- It was noticed during the exploitation that Se, Li, As, Cs and Sr could be produced as byproducts which are important results with regard to economic value of the deposit. However, exploitation of these elements is still neglected.
- There is a great difference between minimum and maximum concentrations indicating that conditions of deposition environment is quite variable, particularly, regarding element input and the amount of material transported varied with respect to climate and volcanic activity. The variation in element concentrations is almost the same in different parts of the deposition environment (three different sampling sites).
- In Kirka deposit, independent behaviour of B_2O_3 indicates that boron is not associated with clays and carbonates, and thus, most part of boron must have been derived from volcanic activity (hydrothermal solutions, gases). Based on REE data, high-pH hydrothermal waters also contributed to formation of Kirka borate deposit.

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