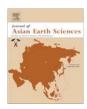
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# The rare earth element geochemistry on surface sediments, shallow cores and lithological units of Lake Acıgöl basin, Denizli, Turkey



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#### ABSTRACT

The sediments in Lake Acıgöl, located in SW Anatolia, Turkey, were formed under tectono-sedimentary events. REE geochemical investigations of the Lake Acıgöl sediments, from surface and shallow core sediments at different depths (0-10 cm, 10-20 cm and 20-30 cm) are presented to clarify the characteristics of REE and the nature of source rocks in the lake sediments' and to deduce their paleoenvironmental proxies. The chondrite-normalized REE patterns of these sediments are shown as light enrichment in LREE and flat HREE with a negative Eu anomaly that is close to the continental collision basin (CCB) in its profile; this is not comparable with PAAS and UCC. Inorganic detrital materials control the REE characteristics of the Lake Acigöl sediments and these sediments were accumulated in oxic and dysoxic depositional conditions and/or at passive margins derived from oceanic island arc rocks. They were affected by low chemical weathering, either at the original source or during transport, before deposition under arid or subtropical humid climatic conditions. In addition, we used GIS techniques (such as Inverse Distance Weighted (IDW) and Geographically Weighted Regression (GWR)) to investigate the spatial interpolation and spatial correlation of the REEs from the lake surface sediments in Lake Acıgöl and its surrounding lithological units. GIS techniques showed that the lithological units (e.g., Hayrettin Formation) north of Lake Acıgöl have high REE contents; however, Eu/Eu\* values were higher in some lake surface sediments than in lithological units, and that refers to a negative Eu-anomaly. Therefore, Lake Acıgöl sediments are derived from the weathered products, mainly from local, highly basic bedrock around the lake from the Archean crust. The chronology of Lake Acıgöl sediment was conducted using the Constant Rate of Supply (CRS) model. Using the CRS methods for the calculation of sedimentation rate, we obtained a 0.012 g/cm<sup>2</sup>/year value which is an average value for the first 20 cm depth of this lake. The core activity profiles of <sup>210</sup>Pb and <sup>137</sup>Cs were measured to estimate the age of the sediments; we observed activities of  $8.08 \pm 5.5$  Bq/kg for  $^{210}$ Pb and  $0.86 \pm 0.6$  Bq/kg for  $^{137}$ Cs.

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# 1. Introduction

In the last two decades, REEs have been widely used to study paleoenvironmental conditions and paleoclimatic changes (Bai et al., 2014; Ding et al., 2001; Domingo et al., 2011; Holser, 1997; Och et al., 2014; Yang et al., 2014) as well as sedimentary origin and tectonic settings (Chen et al., 2014; Cui et al., 2014). In addition, the distribution patterns of normalized-REE have received considerable attention in various geochemical studies due to their chemical properties of REEs. From La to Lu, REEs show limited variations in their physical and chemical properties which allow their fractionation and enrichment in different parts of the

earth surface (Das et al., 2006; Henderson, 1984; Johannesson et al., 1999; Taylor and McLennan, 1988; Wood, 1990).

Alkaline lakes provide a useful opportunity to investigate and improve the understandings of the mechanism of REE fractionation and behaviors in the aquatic systems (Wang et al., 2013). At SW Anatolia, Turkey, the crustal extension created several fluvio-lacustrine basins with active sedimentation in modern deep to shallow lakes (Helvaci et al., 2013). Lake Acıgöl is considered to be one of the largest hypersaline lakes in Turkey. It is located at the inner Aegean Region in a closed basin at the junction between three Provinces: Denizli, Afyonkarahisar and Burdur. Its sediments were formed under tectono-sedimentary events and its surface varies greatly due to seasonal drought with an active precipitation of sodium, calcium and magnesium salts (Helvaci et al., 2004). Lacustrine mineral sources of Lake Acıgöl include detrital,

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endogenic and authigenic-type materials (Helvaci et al., 2013). The mineralogical data demonstrate that the shallow core sediments of Lake Acıgöl show a distinct mineralogical sequence with increasing halite mineralization at the top and domination of gypsum and dolomite mineralization at the bottom (Helvaci et al., 2013; Tubitak110Y255, 2014).

Although a previous study has documented REE geochemistry of the Minoan tephra embedded in Holocene alluvial fan sediments in the northwestern part of Lake Acıgöl basin, presenting compatibility of these deposits in Greece ash deposits (Sulpizio et al., 2013), there have been no previous report about the REE distribution and fractionation in a whole Lake Acıgöl basin. Moreover, lakes generally have been formed by tectonic activity have often a long life, because the formed lake reservoir are not quickly silted as well

as Lake Acıgöl. While at Lake Acıgöl, the accumulated water volume increases in cm scale during the wet season by the effect of precipitations, and in mm scale by the deposition of some evaporates during dry seasons. Pioneer studies presented first useful methods for the long-term chronology of lake sediment cores using <sup>210</sup>Pb and <sup>137</sup>Cs radioisotopes (Goldberg, 1963; Krishnaswami et al., 1971). There are plenty ways from the conventional methods to the isotope traces (Appleby et al., 1986; Appleby and Oldfield, 1978, 1983) for the determination of sedimentation rates. Dating of sediment cores using <sup>210</sup>Pb and <sup>137</sup>C radioisotopes is the more acceptable way in the lakes if the accretion rates are relatively constant throughout the given period of time (Gharibreza et al., 2013).

This work deals with REE geochemical approach; distribution and fractionation of REEs in order to investigate their

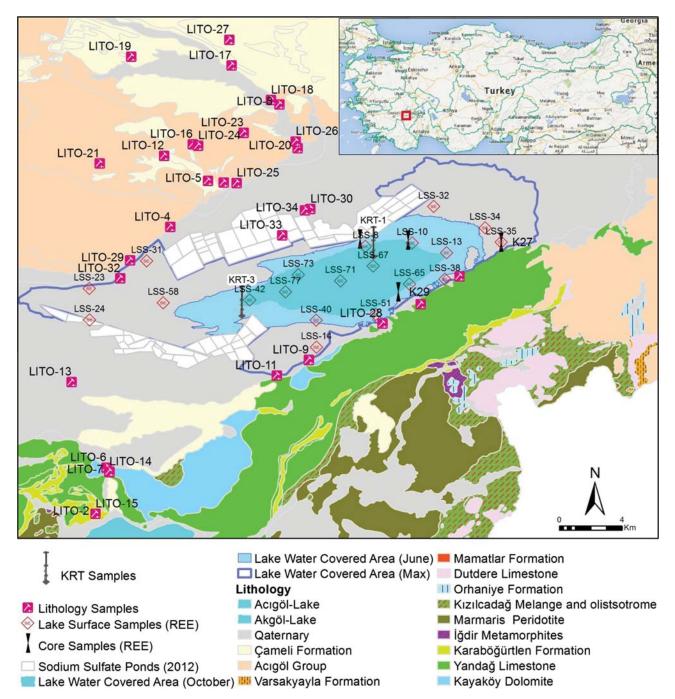


Fig. 1. Location and geological map of Lake Acıgöl and sedimentary and lithological sampling stations.

characteristics in Lake Acıgöl basin geomaterials (surface, shallow core sediments and lithological rock samples) to determine the nature of the source rocks in the lake sediments and also to deduce their paleo-environmental proxy. Moreover, the distribution patterns of REEs were also determined by performing a combination of geochemical studies, with spatial interpolation and spatial correlation analyses of the lake surface sediments and lithological sediments, using Inverse Distance Weighted (IDW) and Geographically Weighted Regression (GWR) techniques.

In addition, the evolutionary environmental history of Lake Acıgöl was also studied using the radioisotopes <sup>137</sup>Cs and <sup>210</sup>Pb to present the first estimates of the Lake Acıgöl sedimentation rates. <sup>137</sup>Cs horizons in the two studied cores showed a constant rate of <sup>210</sup>Pb supply along all distinctive layers in each core. Evaporative mineral layers, which are originated from saline water chemistry have been significantly affecting the variation of <sup>210</sup>Pb value with depth. Core dating was performed by measuring <sup>210</sup>Pb and <sup>137</sup>Cs specific activity profiles using low background gamma ray spectrometry to determine the sediment accumulation rates of this lake.

## 2. Material and methods

A total of 65 samples were collected from the surface and shallow core sediments of Lake Acıgöl and lithological units of the lake

drainage basin in October 2011. Sampling procedures were organized to collect oxic surface and anoxic subsurface sediments among these shallow depth intervals. While surface sediments were represented in the first 5 cm of the lake sediments, shallow core sediments were collected from three distinct sediment depths: 0–10 cm, 10–20 cm and 20–30 cm.

Geological samples, which were collected from the surrounding lithological units in order to determine geochemical background levels, were subdivided into two main categories, such as chemicals (salt and carbonate) and siliciclastic sediments (conglomerates and sandstones). High-density polyethylene sample boxes were cleaned with HCl for 24 h and then were triple washed with distilled water before transportation to the lake to maintain the integrity of the surface and surface sediment samples. Major elements in bulk sediments and rocks were determined using X-ray fluorescence (XRF) techniques with a Bruker S8 Tiger instrument; using pressed powder briquettes for all specimens following the method of Ogasawara (1987). Loss on Ignition (LOI) values for the calculation of total major oxide contents of the samples were determined using gravimetric methods at 950 °C. Approximately 50 mg of lake sediment was digested for the REE's and selected trace element analysis in two steps. The chemicals used for sample dissolution were all analytical grade. The first stage was completed with 6 ml 37% HCl, 2 ml 65% HNO<sub>3</sub> and 1 ml 38-40% HF in a

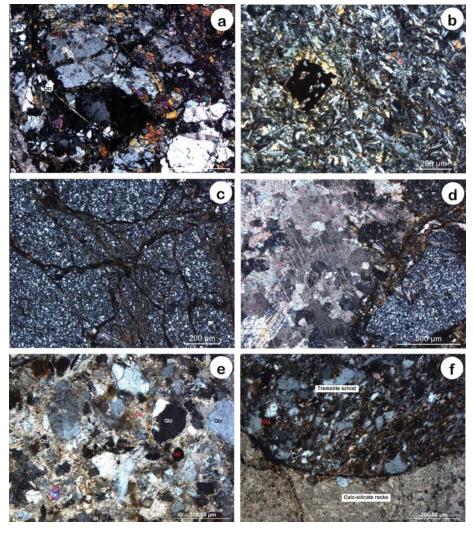


Fig. 2. (a) Mineral compositions of metagabbro rocks in the ophiolitic mélange in the study area, (b) intergranular texture with small granules of pyroxene in metabasaltic rocks, (c) small fibro-lamellar lathes of serpentine minerals in serpentinite rocks, (d) carbonate granules stained with iron surrounded by antigorite in serpentinite rocks, (e) mineral composition of calc-silicate rocks, (f) contact between tremolite schist and calc-silicate rocks.

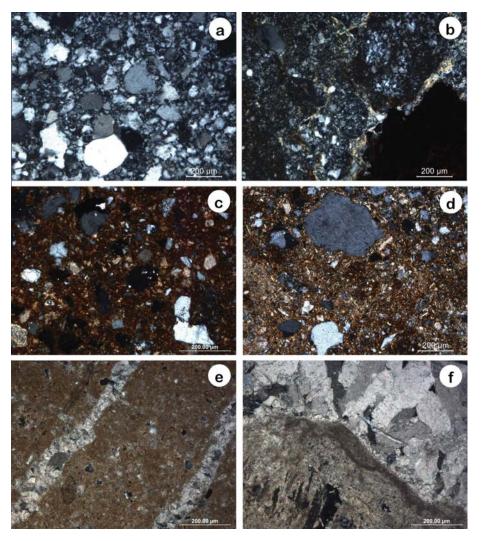


Fig. 3. (a) Quartz, feldspar and rock fragment grains in sublitharenite, (b) rock fragments composed of chlorite and hematite cemented with iron oxide in sublitharenite, (c) quartz and feldspar with the significant proportions of fine-grained matrix in Lithic graywacke, (d) microperthite enclosed in calcite cement stained with iron oxide in Lithic graywacke, (e) mudstone was crossed by fibrous calcite filled cracks, (f) Micritic Limestone associated with dolomitic matrix.

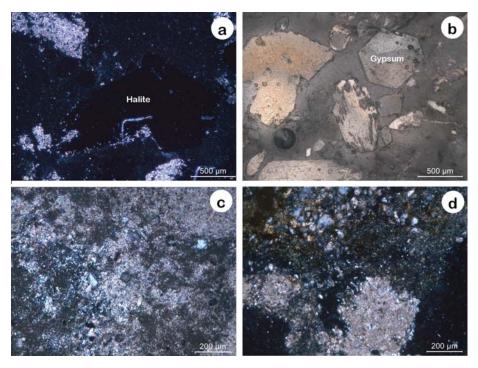
pressure- and temperature-controlled Teflon beaker, using a Berghoff Microwave™ at an average 135 °C. The digestion procedure was completed with the addition of 6 ml, 5% Boric acid solution. The Multi-element (REE) calibration standards of Perkin Elmer were used for the calibration and recovery test solution. The multi-element calibration standards were prepared for different concentrations employing 50 ml volumetric flasks and filling up to volume with% 1 HNO<sub>3</sub> and pure water. Digested bulk samples and standard solutions were instrumentally analyzed for REE by ICP-MS DRC-e 100 from Perkin-Elmer. High density (total dissolved solids 37 g/l) -lake water samples were analyzed with same ICP-MS instrument after the dilution of water samples. All instrumental analyses were carried out at Istanbul Technical University Geochemistry Laboratories (ITU/JAL; www.jal.itu.edu.tr). Spatial interpolation and spatial correlation of REE features were examined by IDW (Inverse Distance Weighted) interpolation and GWR spatial analysis methods, respectively.

Freeze-dried KRT-3 core samples were measured using an Ortec High Purity Germanium Gamma Spectrometer (Oak Ridge, TN, USA) in the LANSET facilities at the University of Ottawa. The GWL120230 detector has 1.92 keV resolution at 1.33 MeV line of Co-60 and the relative efficiency of 34.2%. Certified Reference Materials obtained from International Atomic Energy Association (Vienna, Austria) were used for efficiency corrections.

Sedimentation rate and chronological determinations were calculated using ScienTissiME (Barry's Bay, ON, Canada). The sedimentation rate for the <sup>137</sup>Cs dating model is constant based on the assumption of the date the core is collected and the maximum <sup>137</sup>Cs value, which is representative of the mid 1960s height of nuclear arms development and testing.

# 3. Geological and petrographical data

Lake Acıgöl basin is located in SW Anatolia (Fig. 1), NW of the left lateral strike-slip Fethiye-Burdur Fault Zone and trending parallel the Acıgöl Fault (Barka et al., 1995; Gürer et al., 2009). The southwest Anatolian extensional province is bounded by the Eskişehir Fault Zone in the north, and Fethiye-Burdur Fault Zone in the south. Additionally, it is a part of rotational mechanism of the Anatolian Block southwestward and Aegean extensional system (Bozkurt, 2001; Le Pichon and Angelier, 1979, 1981; McKenzie, 1978; Reilinger et al., 1997, 2010). Morphologically, the greatest rates of subsidence were observed near of the Acıgöl Fault scarp (Barka et al., 1995). Approximately NE–SW trending Acıgöl Lake and basin are located in front of south margin uplift in the study area and this basin is controlled by tectonic features as a normal fault (Barka et al., 1995).



**Fig. 4.** (a) Isotropic and low relief character of halite with less amount of dolomite in salt, (b) porphyroblasts of six-sided shaped gypsum replacing fine-grained anhydrite in gypsum rock, (c) silt-sized grains of dolomite, quartz and feldspars in dolomitic mudstone, (d) fine-grained matrix stained by iron oxide in dolomitic mudstone.

According to the geological studies of Lake Acıgöl area, lithological units are divided into two parts as basement and cover units. General geological map of the study area adapted from Şenel (1997) was given in Fig. 1. Acıgöl is a hyper-saline lake with a brine composition of Na–Cl–SO<sub>4</sub> (Budakoglu et al., 2014; Helvaci et al., 2013; Mutlu et al., 1999). Natural production started to be used in 1953 and raffination method was first applied in 1977. Many ponds have been established inside the lake to be used in the natural production process, and the pond area continues to expand to meet the requirements (Uca Avci et al., 2014). According to Karaman et al. (2015), the major effects on lake surface area changes are occurring due to the industrial, meteorological and hydrological events.

#### 3.1. Basement rock units

They were represented by allochthonous and para-allochthonous rock units at the southern and northern part of the lake basin, respectively. The allochthonous units include Late Triassic-Lias Kayaköy Dolomites, Toarcian Yandağ Limestones and Karaboğurtlen Formation, while the para-allochthonous units include Eocene-Oligocene basement rocks comprising ophiolitic conglomerates intercalated with sandstones, siltstones and limestones (Göktaş et al., 1989; Ozerdem et al., 2002; Şenel, 1997). Karaboğurtlen Formation was represented by Mesozoic ophiolitic mélange consisting of peridotites, amphibolitic schists, marbles, quartzites, metabasalts, serpentinites, serpentinized harzburgites, dunites, basic volcanic rocks, pelagic limestones, radiolarites, cherts and dolomites and diabase dyke systems, dated Cretaceous age (Parlak and Delaloye, 1999; Robertson, 2002). According to the petrographic studies, they contain metagabbros, metabasalts, tremoliteschists, serpentinite and calc-silicate rocks.

Metagabbros are dark greenish gray; medium to coarse-grained with hypidiomorphic and/or poikilitic or ophitic to subophitictexture. They consist mainly of plagioclase and tremolite-actinolite with quartz, relics of pyroxene minerals and opaques (Fig. 2a).

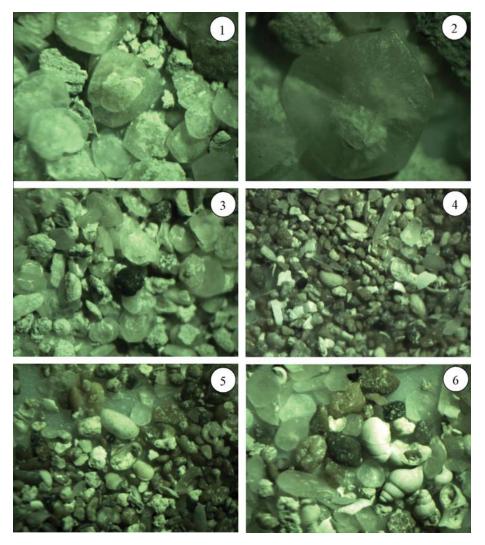
Plagioclase (andesine to labradorite in composition) forms subidiomorphic to xenomorphic crystal, locally laths and partly saussuritized (sericite and epidote), kaolinized and calcitized. Their alterations are either in the crystal core or on the peripheries causing masking for lamellar twinning (Fig. 2a). Tremolite–actinolite are main secondary amphibole minerals after pyroxene (Fig. 2a). Tremolite is colorless occurring as fibrous crystals with rare amount of actinolite which is greenish fibrous crystals. Quartz occurs as small amount of xenomorphic crystals recorded in the interspaces between the amphibole and plagioclase and sometimes scattered within the plagioclase.

Metabasaltic rocks are characterized by fine grained dark gray color containing calcic plagioclase lathes arranged in intergranular texture with small granules of pyroxene (Fig. 2b). Chromite and iron-oxide occurred as opaque minerals (Fig. 2b).

Serpentinite rocks associated with metagabbros and metabasalts. They are fine grained and varicolored including green, greenish gray and black varieties. Microscopically, they are formed mainly of serpentine minerals associated with variable amount of carbonate and picotite (Fig. 2c). They are mostly derived from peridotite and dunite as indicated by the presence of carbonate pseudomorph after olivine and/or pyroxene. The serpentine minerals are represented by mainly antigorite forming colorless small fibro-lamellar lathes (Fig. 2c). The exsolved red iron oxides are concentrated along the cracks and borders of the original olivine crystal and consequently forming the characteristic mesh structure (Fig. 2c). Carbonate forms fine to medium granules stained with iron and surrounded by colorless antigorite (Fig. 2d).

Calc-silicate rocks are medium to coarse grained with whitish gray color. The petrographic studies revealed that they are heterogeneous rocks, and are essentially consisting of about 80% as aggregate of carbonate minerals and quartz with biotite, muscovite, plagioclase, K-feldspar, chlorite and relics of pyroxene (Fig. 2e). Fe-oxide represents the opaque minerals and zircon occurred as

 $<sup>^{1}\,</sup>$  For interpretation of color in Figs. 2–4, the reader is referred to the web version of his article.



**Fig. 5.** Images of washed and sewed sediment samples under the binocular microscope image; 1 and 2 are images of separated tabular pseudo-hexagonal gypsum minerals from >1000 μm fraction of samples; 3, 4, 5 and 6 are general views of the >1000 μm fraction which clearly present dentritic carbonates (calcite, aragonite and dolomite), fossils, and lithogenic biotite contents of subsurface sediments.

accessory minerals. Carbonate is the main mineral constituent in the whole rock with quartz and forms fine to medium granules, and shows colorless, subhedral crystals and sometimes polysynthetic twinning. Quartz is irregular xenomorphic crystals which have oscillatory extinction denoting strain effect (Fig. 2e). Plagioclase forms tabular subidiomorphic and rarely xenomorphic crystals with albite twinning (Fig. 2e). The plagioclase crystals are completely altered to carbonate (calcite) as well as kaolinite. K-feldspar is represented by microperthite forming colorless tabular crystals. Muscovite and biotite are the mica minerals and formed small tabular crystals with colorless and brown color for muscovite and biotite respectively. Chlorite is greenish lathes crystal and is the alteration product after pyroxene.

Tremolite schist is usually metamorphosed from the ophiolitic rocks at the study area. This can be seen under microscope with the remnants of the primary minerals (e.g. pyroxene) that can be detected between the colorless tremolite where alteration is incomplete (Fig. 2f). Generally, this rock is medium-grained consisting essentially of bundles of small lathes of tremolite crystals associated with the minor amount of opaque minerals that occur as small clusters parallel to the general foliation (Fig. 2f).

#### 3.2. Cover rocks

These rocks are Miocene units and Quaternary sediments and contain three different rocks types; (1) the oldest units Upper Miocene age (Bilgin et al., 1990; Senel, 1997) formed of sandstone, mudstone, dolomitic stone, alternating of clayey dolomite, clayey marl and magnesite nodules; (2) the middle unit is Pliocene sediments consisting of lacustrine facies (such as mudstone and claystone, marl and sandstone) with gradation and cross-bedding features; (3) Quaternary deposits are siliciclastic and chemical sedimentary rocks that were seen around Lake Acıgöl. All siliciclastic rocks in the study area are represented by conglomerate, sandstone, and mudrocks, while the chemical sedimentary rocks composed of carbonate rocks and evaporates.

# 3.2.1. Siliciclastic rocks

Sandstone rocks are observed in Karabogurtlen Formation, Hayrettin Formation (Dazkiri member) and Cardik Formation (Maymundag member) in the study area. They were classified into two groups according to the classification of Pettijohn et al. (1987); sublitharenite and lithic graywackes. Sublitharenites are reddish



Fig. 6. Polarizan Microscope image of a prepared thin sections (0–10 cm) of subsurface sediments.

brown in color and have quartz more than 80% and the rock fragments, which exceed feldspar grains, are ranging from 5% to 15% (Fig. 3a). Quartz grains are subangular to subrounded monocrystalline to polycrystalline which show straight extinction (Fig. 3a). The rock fragments are composed of igneous and sedimentary lithoclasts; chlorite and hematite cemented with iron oxide (Fig. 3b). Lithic graywackes are reddish to brownish gray color contain quartz and feldspar with the significant proportions of fine-grained matrix ranging from 20% to 40%, which consists of an intergrowth of calcite, muscovite, biotite and opaques with

siltsized grains of quartz and feldspar (Fig. 3c). Also Quartz is represented by 35–45% and characterized by subangular to subrounded grains (Fig. 3c). Feldspar is ranging from 5% to 10% represented by microperthite (Fig. 3d). Cement is mainly calcite stained with iron oxide (Fig. 3d).

*Mudrocks* were classified during the field working and also based on Pettijohn's classification as mudstones. Reddish brown colored mudstones have been observed in Cameli Formation (Camurtasi-marn member). They have high amount of fine grained matrix (more than 75%). Silt-sized quartz grains ( $\sim$ 5%) are

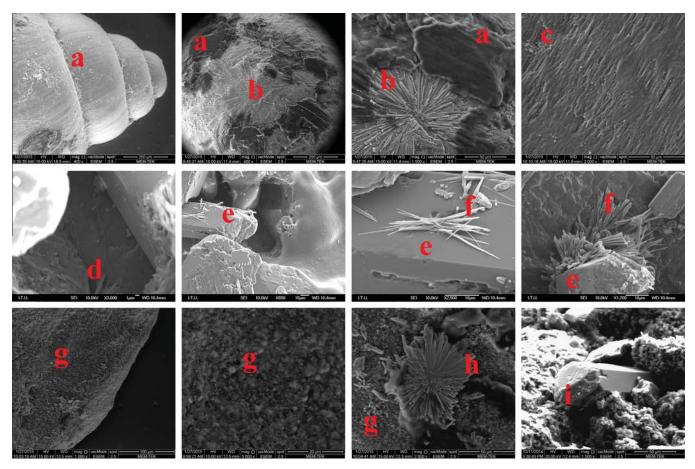


Fig. 7. Determined (a) carbonate fossils, (b) secondary gypsum (eugsterite) development on carbonate fossil, (c) surface of tabular gypsum, (d) remain of biogenic silica (algae) on gypsum surface, (e) lath gypsum, (f) eugsterite, (g) dendritic dolomite, (h) secondary gypsum development on dentritic dolomite, (i) lath gypsum via SEM studies.

presented in all samples with the significant amount of clay matrix stained with iron oxide (Fig. 3e). These rocks are crossed by fibrous calcite filled cracks (Fig. 3e).

#### 3.2.2. Chemical sedimentary units

These units are found in two locations at the study area; as a lithological unit around Lake Acıgöl and unlithified recent sediments of the lake.

3.2.2.1. Lithological units. Micritic Limestone generally are the products of calcium carbonate formed by inorganic precipitation in the water column in modern marine environments (Bathurst, 1975; Flugel, 1982; Tucker and Wright, 1990). In the study area, they are observed in Yandag kirectasi around the lake containing high amount of calcite (CaCO<sub>3</sub>; more than 70%) with carbonate mud (micrite) (Fig. 3f). It is also associated with dolomitic matrix (Fig. 3f).

3.2.2.2. Unlithified recent (subsurface) lake sediments. Acıgöl subsurface sediments are quite different from homogeneous siliciclastic shale type lacustrine sediments with their mixed lower and higher REEs components due to the nature of hypersaline environments. Major components of Lake Acıgöl sediment are mainly divided into non-biogenic and biogenic materials. Biogenic components of Lake Acıgöl sediment are primarily biogenic silica, authigenic carbonate precipitation, organic materials, fossil remains and other microbiological cycle products (e.g. Fe-oxides due to the magnetotactic and Fe(III) reducing bacteria activity; (Tubitak110Y255, 2014)). Determined bacteria and Archaea species in Lake Acıgöl sediments

related to sulfur, nitrogene and iron cycles have been probably supporting authigenic mineral occurrences in anaerobic subsurface lake sediment (Tubitak110Y255, 2014). As secondary carbonate minerals, authigenic carbonates have been occurring on and around gypsum minerals due to sulfate reducing bacteria (SRB) and Archaea activities (Tubitak110Y255, 2014). Non-biogenic materials consist mainly of siliciclastic, detrital, and endogenic chemical sediments (aragonite, calcite, Mg-calcite, halite, and gypsum). Therefore, elemental calcium has been originated from four distinct sources in the recent sediments; such as carbonates (mainly aragonite, Mg-calcite and calcite), Ca-sulfates (gypsum, anhydrite and bassanite), dentritic carbonate inputs (calcite and aragonite), and biogenic contributions that come from fossil remains.

Petrographically, surface and shallow core sediments of Lake Acıgöl contain evaporates and dolomitic mudstones. Evaporate sediments comprise salt and gypsum with dolomitic mudstone. These refers to in Lake Acıgöl the depositional environments are ranging from shallow subaqueous to subaerial which describe a gypsum-mudstone cycles (Garrison et al., 1978). Salt consists mainly of halite ( $\sim$ 80%) with less amount of dolomite (Fig. 4a). Halite is characterized by low relief and is isotropic mineral (Fig. 4a). Gypsum consists of porphyroblasts of gypsum replacing fine-grained anhydrite (Fig. 4b). Gypsum is characterized by six-sided shape with low relief and first order interference color (Fig. 4b). Dolomitic mudstone shows the silt-sized grains of sediment which is dolomite (calcium magnesium carbonate), quartz and feldspars with irregular bands of dark materials (Fig. 4c). Fine-grained matrix was stained by iron oxide (Fig. 4d). The mineralogical data demonstrate that the shallow core sediments of Lake

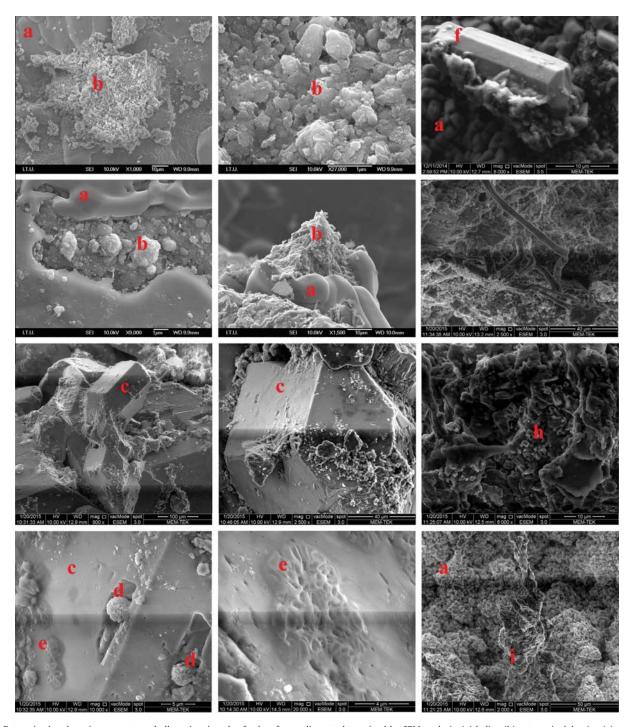


Fig. 8. Determined endogenic evaporate and allogenic minerals of subsurface sediments determined by SEM analysis, (a) halite, (b) autogenic dolomite, (c) gypsum, (d) spherical secondary gypsum development on gypsum surface, (e) Ca-carbonate development on gypsum surface, (f) K-feldspar, (g) calcified phytoplankton remains, (h) halite, (i) autogenic dolomite.

Acıgöl show a distinct mineralogical sequence with increasing halite mineralization and domination of gypsum and dolomite mineralization at the top (Tubitak110Y255, 2014).

The surface samples collected from Acıgöl closed basin mainly reflected the variations of elevated high endogenic mineral contribution, and allogenic fossil and the mineral contributions of the lithological units. While some carbonate shells (e.g. *Gastropod*) were well preserved and related to middle Miocene aged sandstones, diatom frustules are very seldom because of high alkaline lake water chemistry (Fig. 5). Endogenic gypsum as well as calcite,

dolomite and aragonite peloids in micritic matrix was observed in 10-cm length column of shallow core sediments (Fig. 6). According to this column based microscopic study, the shallow core sediments occur lamination of gypsum, calcite and dolomite with phytoplankton remains in micritic matrix. Individual fossils, secondary gypsum minerals, dentritic carbonates (Fig. 7) and endogenic evaporates, carbonates and dentritic alumina silicates (Fig. 8) were also examined with the Scanning Electron Microscope (SEM) studies. The total CaCO<sub>3</sub> percentage in the recent sediments could be controlled by mainly endogenic precipitation, inflow of detrital

(continued on next page)

LSS-77	13.4	2.0	7.9	24.8	7.5	1.0	0.7	0.1	0.0	0.0	18.5	4.9	1001			1.9	13.0	77.0	1.8		0.5	6.0	42.0	27.0	11.9	0.0	36.4	4.0	4.0	14.2	43.4	2.0	0.0	5.6	0.2	1.7	35.0	57.0	61.0	98.5	32.1	57.3	8.1	28.6	1.1	4.5	9.0
LSS-73	11.8	1.4	8.4	26.3	9.0	0.7	0.7	0.0	0.0	0.0	21.3	4.6	1000			2.2	11.0	0.09	1.4		0.2	3.0	3.1	17.6	9.2	0.0	27.9	3.0	5.0	120.6	30.6	3.0	0.0	4.5	0.1	0.0	26.0	37.4	57.0	96.6 14.0	23.9	45.7	9.9	23.0	0.8	3.4	7
LSS-71	12.7	1.8	7.1	30.0	3.1	0.9	0.7	0.1	0.0	0.0	25.6	2.4	1000	2		2.1	15.0	0.99	1.5		0.4	5.0	3.6	18.7	9.6	0.2	28.1	3.0	3.0	9.4	34.4	3.0	0.0	7.655	0.3	1.4	29.0	40.6	58.0	81.0	23.8	45.7	7.6	23.6	0.8	3.4	-
LSS-67	8.0	1.7	3.9	10.8	30.2	0.8	0.7	0.0	0.0	0.0	2.5	16.6	100.0			2.1	18.0	140.0	2.1		0.5	5.0	2.5	346	15.5	0.0	51.4	5.0	6.0	17.0	59.3	3.0	0.0	7.4	0.4	2.0	57.0	9.99	86.0	113.4	38.9	71.5	33.2	/3.1	1.3	6.1	0
TSS-65	7.6	1.0	3.4	39.7	1.6	0.5	0.1	0.0	0.0	0.0	22.4	1.0	20.3			4.2	15.0	23.0	1.4		0.2	0.9	2.0	15.3	6.7	0.0	16.4	2.0	2.0	6.60	20.6	0.0	0.0	3.2	0.1	1.3	21.0	62.4	0.49	10.8	15.0	28.9	3.6	13.6	0.6	2.2	0
LSS-58	6.0	0.6	21.2	20.2	9.4	0.5	0.1	0.0	0.0		24.3	7.5	9.0	0.9		1.5	12.0	50.0	0.9	0.1	0.1	9.0	0.9		4.0	0.0	21.2	3.0	2.0	7.8	7.9	4.0	2167.0	1.0	0.0	9.0	9.0	57.7	44.0	23.3	2.8	5.8	0.5	2.3	0.1	0.5	,
LSS-51	9.1	0.9	8.8	18.2	10.5	0.8	0.1	0.1	0.0	0.0	12.3	7.3	100.0			4.3	20.0	51.0	1.1	0.1	0.1	1.0	1.4	12.0	5.1	0.0	18.5	2.0	2.0	1/5.3	14.7	2.0	63063	1.4	0.1	1.2	20.0	47.2	71.0	26.4	5.2	10.0	0.0	4.3	0.2	0.9	-
LSS-42	8.6	1.1	6.7	29.0	2.7	0.6	0.1	0.1	0.0	0.0	19.6	2.5	26.5	1.8		2.1	15.0	37.0	1.5	0.0	0.3	1.0	1.7	13.3	9.7	0.0	40.0	5.0	3.0	32.0 6.1	17.2	ND	ND	1.7	0.1	1.4	24.0	26.0	56.0	12.6 3.6	5.4	8.6	1.1	4.5	0.2	6.0	,
LSS-40	10.0	1.0	11.3	26.2	2.6	0.5	0.1	0.0	0.0	0.0	8.2	1.8	35.4 90 6	1.4		2.2	19.0	58.0	1.0	0.0	0.1	1.0	0.70	12.2	8.7	0.0	46.3	2.0	2.0	5.3	18.1	2.0	1.0	1.7	0.1	1.4	26.0	44.9	75.0	33.8	8.7	16.0	1.8	6.6	0.2	1.0	,
TSS-38	37.5	4.7	4.6	11.2	3.7	1.9	0.5	0.2	0.2	0.0	3.8	2.2	1000	0.9		0.3	13.0	157.0	2.8	0.2	0.2	163.0	4.6	45.4	31.7	0.0	71.1	1.0	11.0	13.3	69.0	1.0	1.0	190.0	0.4	1.3	102.0	97.5	128.0	116.1	42.9	61.6	9.3	40.1	1.5	6.3	
LSS-35	23.8	3.1	16.6	13.8	8.0	1.2	0.4	0.1	0.1	0.0	Q.	ND	30.6	2.1		9.0	16.0	188.0	2.5	0.1	0.2	9.0	5.9	2.5	19.4	0.0	S	1.0	8.0	11.9	59.9	17.0	1.0	6.4	0.3	1.2	75.0	79.5	89.0	739	29.9	51.9	6.2	23.3	0.9	3.7	L
LSS-34	13.8	1.6	12.4	12.9	6.3	0.9	0.7	0.1	0.0	0.0	11.5	5.4	30.4	2.1		0.0	15.0	103.0	1.7	0.1	0.2	5.0	3.6	17.2	11.9	0.0	74.6	7.0	6.0	4.// 8.1	37.1	2.0	1.0	3.7	0.2	1.6	40.0	65.3	69.0	59.6 13.2	17.1	30.6	3.5	13.2	0.5	2.1	0.0
LSS-32	19.1	2.5	16.6	11.6	4.0	1.2	0.3	0.1	0.0	0.0	8.1	3.7	101 6	1.5		0.7	18.0	168.0	1.9	0.1	0.1	0.9	3.7	14.8	15.6	0.0	S	2.0	8.0	96.5 7.6	41.1	4.0	1.0	0./00	0.2	1.4	61.0	61.8	83.0	62.4 12.1	20.0	38.1	4.2	15.9	0.6	2.4	0.0
LSS-31	11.7	1.3	19.6	22.1	1.0	0.5	0.1	0.0	0.0	0.0	Q !	ND S S	38.8 07.8	1.1		1.9	19.0	65.0	1.2	0.0	0.1	1.0	2.4	11.8	8.8	0.0	68.3	2.0	4.0	2.00	21.2	3.0	1.0	2.3	0.1	1.3	32.0	56.4	67.0	7.2	11.0	21.0	2.3	8.6	0,3	1.3	0
LSS-24	9.9	1.1	12.2	14.2	5.0	0.8	0.1	0.1	0.0	0.0	13.3	6.3	34.7 99.0	0.3		0.5	16.0	84.0	S	0.0	0.1	4.0	2.8	116	5.0	0.0	160.5	2.0	4.0	5.7	26.0	3.0	1.0	0.4.0	0.1	6.0	23.0	39.8	56.0	45./ 8.6	11.2	21.1	2.3	2.7	0.8	1.4	0
LSS-23	13.8	1.5	18.9	16.8	2.7	9.0	0.7	0.1	0.0	0.0	7.6	2.3	32.8	1.6		0.8	19.0	119.0	S	0.0	0.1	4.0	3.0	13.5	12.7	0.0	328.0	1.0	6.0	8.0			1.0		0.1	1.3	33.0	49.3	63.0	50.9 9.4	13.4	26.0	2.9	10.6	6.0	1.7	
LSS-14	3.5	0.5	3.7	41.3	2.0	0.5	0.0	ND 0	0.0	ND	6.4	1.2	39.5	3.7		3.8	27.0	12.0	9.0	0.0	0.0	0.0	0.0	2 00	5.0	0.0	15.3	3.0	1.0	3.7	6.1	1.0	1.0	0.1800	0.1	1.0	13.0	27.7	/8.0	3.9	3.7	7.2	0.8	3.0	0.1	0.5	,
LSS-13	17.1	2.0	10.2	19.1	3.4	1.0	0.7	0.1	0.0	0.0	3.2	2.6	50.00 60.6	3.9		2.2	23.0	109.0	2.0	0.1	0.2	5.0	0.1.0	23.0	16.6	0.0	75.3	22.0	6.0	10.9	44.7	2.0	1.0	4.4	0.3	2.4	57.0	74.7	91.0	183	22.3	38.1	4.6	3.1	0.7	2.8	2
LSS-10	7.6	0.0	4.0	30.9	2.8	0.5	0.1	0.0	0.0	0.0	19.5	2.5	28.5 00.6	1.0		2.3	21.0	29.0	1.0	0.0	0.1	1.0	1.7	11.2	7.0	0.0	25.7	2.0	2.0	4.67	18.0	1.0	1.0	0414.0	0.1	1.0	22.0	43.0	67.0	30.3	8.3	15.8	1.7	6.3	0.7	1.0	,
ISS-8	6.3	0.9	4.3	32.5	1.6	0.4	0.1	0.0	0.0	ND	32.6	1.5	17.8	0.7	(maa) s	1.7	14.0	24.0	8.0	0.0	0.0	1.0	0.9	. «	5.5	0.0	16.6	3.0	3.0	2.5	9.7	1.0	1.0	0.6222	0.0	0.5	20.0	22.9	51.0	23.1 2.8	5.4.	8.5	6.0	3.4	0.1	0.5	,
SAMPLE_ID	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	1102	$P_2O_5$	MnO	$Cr_2O_3$	$50_3$	ت ا	LOI	TOC%	Trace elements	Ag 1.7	As	Ba	Be	Bi	Cd	S :	J (	3 5	r G	ll	Li	Mo	ND	N &	Rb	Sb	Sn	is E		n	>	Zn	Zr	× ×	La	Ce	Pr	DN S	Eu	. PS	Ē

SAMPLE_ID	FSS-8	LSS-10	LSS-13	LSS-14	LSS-23	LSS-24	LSS-31	LSS-32	LSS-34	LSS-35	TSS-38	LSS-40	LSS-42	LSS-51	LSS-58	TSS-65	LSS-67	LSS-71	LSS-73	LSS-77
Dy	0.3	9.0	1.9	0.4	1.1	6.0	0.8	1.5	1.4	2.5	4.7	0.7		0.7	0.4	1.5	4.0	2.1	2.2	3.1
Но	0.1	0.1	0.4	0.1	2.2	0.2	0.2	0.3	0.3	0.5	0.0	0.1		0.1	0.1	0.3	0.7	0.4	0.4	9.0
Er	0.2	0.3	1.1	0.2	9.0	0.5	0.4	0.8	0.8	1.4	2.7	0.4	0.4	0.4	0.2	0.8	2.2	1.2	1.1	1.7
Tm	0.0	0.0	0.1	0.0	0.1	0.1	0.1	0.1	0.1	0.2	0.4	0.1		0.1	0.0	0.1	0.3	0.2	0.2	0.2
Yb	0.1	0.3	0.0	0.2	0.5	0.5	0.4	0.7	0.7	1.2	2.4	0.3		0.3	0.2	0.7	1.8	0.9	0.9	1.4
Lu	0.0	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.1	0.2	0.4	0.1		0.1	0.0	0.1	0.3	0.2	0.2	0.2
Indices																				
>	19.2	37.2	93.6		61.7		48.0	87.7	72.9	126.5	180.6	37.2		24.2	13.5		240.2	113.9	112.5	144.4
\(\sum_{\text{LREE}}\)	17.9	34.6	85.9	15.3	55.2		44.7	81.6	67.3	116.3	162.0	34.4		21.5	12.0		224.1	105.2	103.8	132.0
> HREE	1.3	2.6	7.7		6.4		3.4	6.1	5.6	10.2	18.6	2.8		2.7	1.5		16.0	8.7	8.8	12.3
Eu/Eu*	0.7	1.7	0.7		0.7		0.7	0.7	0.7	0.7	0.7	0.7		0.8	0.8		0.7	0.7	0.7	0.7
(La/Lu) <sub>N</sub>	19.9	8.1	16.4	14.2	16.9	8.1	19.0	19.1	17.7	16.3	12.2	17.6		8.7	7.1		13.9	13.4	15.3	13.8
$(La/Yb)_N$	20.3	18.6	16.2	14.3	17.5		19.8	19.6	17.3	16.1	12.1	17.5		10.1	10.1		14.5	16.8	17.1	15.1
$(La/Sm)_N$	4.8	3.0	4.5	4.2	4.4		4.6	4.5	4.5	4.5	4.0	4.7		3.4	3.3		4.0	4.0	4.0	4.1
$(Gd/Yb)_N$	2.7	2.6	2.4	2.4	2.6		2.8	2.9	2.5	2.4	2.1	2.5		2.2	2.2		2.7	2.8	2.9	2.5
$(Tb/Yb)_N$	2.0	1.8	1.8	1.8	1.9		2.0	2.0	1.8	1.8	1.7	1.8		1.7	1.6		2.0	2.0	2.1	1.9
(Sm/Ho) <sub>N</sub>	3.4	5.3	2.9	5.6	0.3		3.4	3.5	3.1	2.9	2.4	3.1		2.6	2.7		2.9	3.3	3.2	2.8
"L,	14.1	13.5	11.2	10.6	8.6		13.3	13.3	12.1	11.4	8.7	12.5		8.0	8.3		14.0	12.0	11.8	10.7
Th/Sc	0.0	0.1	0.1	0.1	0.1		0.1	0.1	0.1	0.1	0.1	0.1		0.1	0.0		0.1	0.1	0.0	0.1
Zr/Sc	2.2	2.2	1.6	5.5	1.2		1.5	1.3	1.2	1.2	1.1	2.2		2.7	1.9		0.8	0.7	9.0	9.0
Th/U	1.6	1.7	1.8	8.0	2.2		1.7	3.4	2.4	5.3	6.4	1.2		1.1	1.8		3.7	5.3	4.9	3.3
$K_2O/Na_2O$	0.3	0.2	0.3	0.1	0.2		0.5	0.3	0.1	1.5	0.5	0.2		0.1	0.1		0.0	0.3	0.1	0.1
$\sum$ REE/TiO <sub>2</sub>	191.8	338.2	389.9	417.8	362.8		343.2	292.4	383.6	361.5	334.4	309.9		235.0	224.7	_	1366.9	9.099	682.9	661.3
$Fe_2O_3/TiO_2$	8.9	8.5	8.4	13.3	9.1		0.6	8.5	8.6	8.9	8.6	8.4		8.4	10.8		6.6	8.9	8.7	9.0
$MnO/TiO_2$	0.1	0.1	0.1	0.3	0.2		0.1	0.1	0.2	0.2	0.3	0.2		0.2	0.4		0.1	0.1	0.1	0.1
V/Cr	1.7	6.0	0.7	1.6	0.5	0.3	0.7	0.7	1.0	8.0	9.0	0.7		0.8	9.0		0.8	0.8	0.9	0.8
Al (ppm)	9528.9	11646.4	27104.3	4446.8	.8 16622.6	12440.4	13869.8	33456.9	23028.1	37744.8	55532.0	13075.7	12493.4	10958.2	5886.7	12210.7	11465.9	21249.9	19281.6	22616.7
CIW (molar)	2.8	3.5	11.4	1.1	8.3	6.5	5.9	18.8	11.5	21.8	29.5	4.6		4.0	2.1		3.0	6.3	5.6	7.0
CIA (molar)	2.8	3.5	11.1	1.1	8.2	6.4	5.9	18.1	11.3	21.0	27.6	4.5		3.9	2.1		3.0	6.2	5.5	6.9

 Table 2

 Selected trace elements, REE contents and calculated ratios of shallow core samples.

SAMPLE_ID	K1:0-10	K5:0-10	K27:0-10	K29:0-10	K1:10-20	K5:10-20	K27:10-20	K29:10-20	K1:20-30	K5:20-30	K27:20-30	K-29:20-3
	Shallow o	ore sedime	ents (0–10 cn	n)	Shallow co	re sediment	s (10–20 cm)		Shallow co	re sediments	s (20–30 cm)	
SiO <sub>2</sub>	21.8	11.7	19.6	9.9	19.4	13.8	20.5	7.3	22.4	11.6	20.9	4.8
$Al_2O_3$	7.6	3.7	5.4	3.1	7.4	4.3	6.2	1.9	9.1	3.1	7.4	1.1
$Fe_2O_3$	3.0	1.5	2.3	1.1	2.9	1.7	2.7	0.8	3.5	1.3	3.1	0.4
MgO	9.1	6.2	18.4	5.2	5.9	7.7	13.8	5.1	4.8	8.6	6.2	3.7
CaO	17.0	28.6	14.3	27.8	24.1	25.8	16.2	29.3	22.7	26.5	14.1	30.3
Na <sub>2</sub> O	3.6	3.6	2.1	3.8	2.9	3.4	3.6	3.6	2.5	3.7	11.7	4.5
₹ <sub>2</sub> 0	1.5	0.8	1.0	0.6	1.4	0.9	1.2	0.4	1.6	0.7	1.5	0.3
ΓiO <sub>2</sub>	0.3	0.2	0.3	0.1	0.3	0.2	0.3	0.1	0.4	0.2	0.4	0.1
$P_2O_5$	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0
MnO	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$Cr_2O_3$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	ND	0.0	0.0	0.0	ND
SO <sub>3</sub>	3.4	13.1	5.2	18.4	8.2	12.6	4.5	21.3	7.8	18.3	5.7	24.6
C1	2.9	3.3	1.6	2.9	2.2	3.0	2.4	2.5	1.8	3.1	5.5	2.7
.OI	30.2	26.8	29.5	26.7	24.9	26.1	28.4	27.4	23.1	22.5	23.2	27.1
Total	100.7	99.6	99.8	99.7	99.7	99.6	99.8	99.7	99.7	99.7	99.8	99.7
TOC%	2.1	1.3	1.0	0.8	0.9	1.6	1.1	1.0	1.0	1.6	0.6	1.0
Trace element	ts (ppm)											
Ag	1.0	1.8	0.9	1.6	1.1	1.3	1.0	2.0	1.0	1.1	0.9	2.2
As	17.0	16.0	16.0	16.0	19.0	19.0	29.0	13.0	20.0	13.0	28.0	11.0
Ba	160.0	73.0	147.0	48.0	124.0	76.0	137.0	29.0	155.0	58.0	175.0	12.0
Be	2.0	1.1	2.2	1.4	1.5	1.0	2.5	1.2	1.8	0.8	2.9	1.1
Bi	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.0	0.1	0.0	0.1	0.0
Cd	0.2	0.1	0.2	0.3	0.1	0.1	0.2	0.4	0.2	0.1	0.2	0.3
Co	7.0	1.0	4.0		4.0	1.0	5.0		7.0	1.0	7.0	
Cr Cr	102.0	38.0	57.0	25.0	92.0	50.0	70.0	16.0	115.0	29.0	79.0	6.0
Cs	4.0	2.5	4.5	1.6	3.4	2.2	4.7	1.2	4.1	1.7	5.4	0.7
Cu Cu	18.8	12.8	19.2	11.2	14.5	10.5	21.0	10.3	17.5	8.6	22.9	8.2
Ga	21.6	12.2	19.1	9.7	19.1	11.2	20.2	7.9	23.1	8.7	26.4	5.4
n	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
i	52.8	33.0	94.3	29.4	35.8	22.8	98.5	24.7	44.5	19.1	99.9	16.6
Лο	5.0	3.0	2.0	2.0	3.0	3.0	2.0	3.0	3.0	4.0	1.0	5.0
Νb	9.0	4.0	7.0	3.0	8.0	5.0	7.0	2.0	9.0	3.0	9.0	2.0
Ni	100.0	54.6	59.0	29.0	83.1	47.0	68.0	22.0	188.3	38.3	75.0	14.0
Рb	9.3	5.2	8.6	5.0	7.4	4.4	10.1	4.3	8.3	3.3	11.7	2.6
₹b	52.0	25.7	37.4	16.8	45.7	26.0	41.5	11.7	56.6	18.2	57.6	6.7
Sb	3.0	2.0	4.0	1.0	4.0	4.0	4.0	2.0	4.0	3.0	4.0	2.0
Sn									1.0			
Sr	1295.0	3236.0	1206.0	2484.0	1935.0	2845.0	1362.0	2831.0	1575.0	2420.0	1279.0	2827.0
Γh	6.2	1.6	3.3	1.4	5.3	2.4	3.4	1.1	6.5	1.6	5.2	0.5
ΓΙ	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.3	0.0
J	1.4	1.3	1.0	0.9	1.0	0.7	1.3	0.8	1.0	0.7	1.2	0.8
V	70.0	37.0	53.0	27.0	68.0	40.0	59.0	19.0	80.0	28.0	78.0	13.0
Zn	43.2	31.4	38.1	19.9	35.0	22.3	42.5	25.0	41.2	17.7	48.7	14.9
Zr	97.0	78.0	71.0	58.0	95.0	76.0	77.0	56.0	101.0	64.0	91.0	44.0
Sc	52.3	15.4	16.8	11.6	38.8	22.8	17.2	8.4	46.5	16.8	25.9	7.4
Y	12.6	6.1	7.6	3.3	11.7	6.8	7.8	2.2	14.4	5.4	10.1	1.1
a	19.6	7.3	11.6	5.3	17.8	9.7	12.4	3.7	21.5	7.4	17.7	1.9
Ce	38.6	12.3	21.5	9.9	35.2	19.3	23.5	7.1	42.4	14.4	33.5	3.6
Pr	4.4	1.6	2.4	1.1	4.0	2.2	2.6	0.8	4.8	1.7	3.7	0.4
Nd	16.8	6.9	9.7	4.4	14.9	8.2	10.2	3.1	18.0	6.3	14.5	1.6
Sm	3.2	1.1	1.8	0.8	2.8	1.5	2.0	0.6	3.4	1.2	2.8	0.3
u	0.7	0.3	0.4	0.2	0.6	0.3	0.5	0.1	0.7	0.3	0.6	0.1
Gd	3.1	1.1	1.9	0.9	2.6	1.4	2.0	0.6	3.2	1.1	2.8	0.3
Ъ	0.4	0.1	0.2	0.1	0.3	0.2	0.3	0.1	0.4	0.1	0.4	0.0
) У	1.9	0.7	1.3	0.6	1.7	0.9	1.4	0.4	2.0	0.7	1.8	0.2
ło	0.4	0.1	0.3	0.1	0.3	0.2	0.3	0.1	0.4	0.1	0.3	0.0
Er	1.1	0.4	0.8	0.3	0.9	0.5	0.8	0.2	1.1	0.4	1.0	0.1
ſm	0.2	0.1	0.1	0.0	0.1	0.1	0.1	0.0	0.1	0.0	0.1	0.0
'b	1.0	0.3	0.6	0.3	0.8	0.4	0.7	0.2	0.9	0.3	0.9	0.1
u	0.2	0.1	0.1	0.0	0.1	0.1	0.1	0.0	0.2	0.0	0.1	0.0
ndices												
REE	91.5	32.3	52.8	24.2	82.2	44.9	56.7	17.1	99.1	33.9	80.2	8.7
LREE	83.3	29.5	47.5	21.8	75.3	41.2	51.1	15.4	90.8	31.1	72.8	7.9
∑HREE	8.1	2.8	5.3	2.3	6.9	3.7	5.6	1.7	8.3	2.7	7.4	0.8
Eu/Eu*	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
(La/Lu) <sub>N</sub>	12.6	14.4	11.4	12.1	14.5	14.7	11.5	11.6	14.4	15.6	13.0	11.1
(La/Yb) <sub>N</sub>	13.6	15.0	12.0	12.9	15.1	15.7	12.4	12.5	15.2	16.2	13.8	12.8
(La/Sm) <sub>N</sub>	3.8	3.9	3.9	3.8	3.9	3.9	3.9	3.8	3.9	3.9	3.9	3.8
Gd/Yb) <sub>N</sub>	2.6	2.6	2.4	2.5	2.7	2.7	2.4	2.5	2.7	2.8	2.6	2.5
Tb/Yb) <sub>N</sub>	1.9	2.0	1.8	1.9	2.0	2.0	1.8	1.8	2.0	2.0	1.9	1.9
Sm/Ho) <sub>N</sub>	3.0	3.1	2.5	2.7	3.1	3.2	2.6	2.7	3.1	3.3	2.8	2.8
		٠	8.9	9.4	10.9	11.2	9.2	9.3	11.0	11.4	9.8	9.5

(continued on next page)

Table 2 (continued)

SAMPLE_ID	K1:0-10	K5:0-10	K27:0-10	K29:0-10	K1:10-20	K5:10-20	K27:10-20	K29:10-20	K1:20-30	K5:20-30	K27:20-30	K-29:20-30
	Shallow c	ore sedime	nts (0–10 cm	1)	Shallow co	re sediment:	s (10–20 cm)		Shallow co	re sediment:	s (20–30 cm)	_
Th/Sc	0.1	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.2	0.1
Zr/Sc	1.9	5.1	4.2	5.0	2.4	3.3	4.5	6.6	2.2	3.8	3.5	6.0
Th/U	4.4	1.2	3.3	1.6	5.3	3.4	2.6	1.4	6.5	2.3	4.3	0.7
$K_2O/Na_2O$	0.4	0.2	0.5	0.2	0.5	0.3	0.3	0.1	0.6	0.2	0.1	0.1
$\sum REE/TiO_2$	269.0	179.5	203.1	185.8	249.0	224.7	188.9	189.6	241.7	211.6	229.2	173.8
Fe <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	8.9	8.4	8.8	8.5	8.8	8.7	8.9	8.6	8.5	8.3	9.0	8.8
MnO/TiO <sub>2</sub>	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2
V/Cr	0.7	1.0	0.9	1.1	0.7	0.8	0.8	1.2	0.7	1.0	1.0	2.2
Al (ppm)	40232.9	19375.3	28798.3	16252.0	39068.3	22710.4	32556.9	10164.1	48385.4	16622.6	39227.1	5823.2
CIW (molar)	17.3	6.0	15.8	5.1	13.3	7.6	15.0	3.1	16.9	5.5	14.3	1.7
CIA (molar)	16.7	5.9	15.3	5.1	12.9	7.4	14.5	3.1	16.4	5.4	13.8	1.7

materials and secondary carbonate development on gypsum minerals. All of these data also indicate the difficulty of separation of carbonate contents exactly from other species.

## 4. Results and discussion

# 4.1. Rare earth element geochemistry

The concentrations of REEs in surface and shallow core lake sediments and lithological samples are shown in Tables 1, 2, 3a and 3b respectively. Box and whisker plots for REEs provide the summary statistics of the compositional range of each element in the distinct recent sediment intervals (Fig. 9a) and lithological units (Fig. 9b). As is evident in Fig. 9a, the REE concentrations ranged across nearly greater than median value of 5 ppm with the higher abundance of light REEs (La, Ce, and Nd) and showed a clear Oddo-Harkins rule with at La which is lower than Ce. The median value of each element in recent sediments (Fig. 9a) was slightly lower than the median value in lithological samples (Fig. 9b). Changes in the position of the box (percentiles 25 and 75), median, minimum and maximum elemental concentration values confirm the significant geochemical differences among surface and shallow core samples and lithological units.

There are large variations in SREE content between surface sediments (an average  $\Sigma$ REE = 78.7), shallow core sediments (an average  $\sum$ REE = 50.9), and lithological sediments (an average  $\sum$ REE of siliciclastic rocks = 195.9 and of chemical rock units = 144.5). Also, the  $\sum$ REE content decreased in shallow core sediment with increasing with high depth from 50.2 to 55.5 for 0–10 cm and 20–30 cm depth, respectively (Fig. 10a). Chondrite-normalized REE patterns of these sediments (Fig. 10a) show a generally high abundance of REE compared to chondritic concentrations, with particular enrichment in LREE. Also these samples showed nearly flat HREE normalized to Chondrite as (La/Sm)<sub>N</sub> ranging from 2.3 to 4.8 for surface sediments and for shallow core sediments from 3.7 to 3.9 (0-10 cm), 3.8 to 3.9 (10-20 cm) and 3.8 to 3.9 (20-30 cm) while  $(Gd/Yb)_N$  ranging from 2.1 to 2.9, from 2.4 to 2.6, from 2.4 to 2.7 and from 2.5 to 2.7 from the surface and different shallow core sediments, respectively. So, these rocks (surface and shallow core sediments) showed slightly light rare earth element (LREE) enriched and flat heavy rare earth element (HREE) patterns with negative Eu anomaly. Moreover, the REE profiles of these sediments are similar to profiles of the continental collision basin (CCB) (Fig. 10b) (Mclennan et al., 1990) and show that they have negative Eu anomalies [an average of Eu/Eu\* ratio is 0.8, 0.7 for the surface and shallow core sediments respectively].

The REE patterns of these sediments exhibit variations different from the average compositions of Post-Archean Australian average

shale (PAAS) and upper continental crust (UCC) (Taylor and McLennan, 1985) (Fig. 10c). These differences are clearly shown in Fig. 10d and e illustrating that Post-Archean Australian Shale (PAAS)-, and Upper continental crust (UCC)-normalized REE patterns of these sediments have generally low abundances of REE compared to the concentrations of PAAS (Taylor and McLennan, 1985) and UCC (Taylor and McLennan, 1985) with very slight enrichment of LREE and positive Eu\* anomalies. Therefore, there is no comparison between our samples of surface and subsurface sediments and these types of international sediments. The studied sediments have an average total REE content of 78.7, 50.2, 50.2 and 55.5 for surface and shallow core sediments (0-10, 10-20, 20-30 cm) respectively; which are not comparable to an average total REE content 165.8 for PAAS (data from Taylor and McLennan (1985)) and 143 for UCC (data from Taylor and McLennan (1985)). Also these incomparable are shown in the value differences of the chemical index of weathering (CIW) (Harnois, 1988) and chemical index of alteration values (CIA) (Nesbitt and Young, 1982) of the Lake Acıgöl sediments and PAAS and UCC. Lake Acıgöl surface and shallow core sediments from different depths are 8.0, 11.1, 9.7 and 9.6 CIW and 7.8, 10.7, 9.5 and 9.3 CIA; while the CIW of PAAS and UCC are 81.3 and 51.9 and their CIA is 71.9 and 46.2, respectively (see Fig. 10f).

Chondrite-normalized REE patterns of the studied lithological sediments (siliciclastic sediments; sandstone and conglomerate, and chemical sedimentary units; carbonate and salt) show that these rocks are enriched in light REE relative to heavy REE, and have negative Eu-anomalies (Fig. 11a). The carbonate contains significantly lower ∑REE (average 79.7) than sandstone (average 215.1), conglomerate (average 176.7) and salt (average 209.4). The REE profiles of these lithological sediments are slightly enriched in light REE [(La/Yb)n = 10.8, 14.1, 17.7 and 17.8 for carbonate, sandstone, conglomerate and salt, respectively] and are strongly depleted in the heavy REE [(Gd/Yb)n = 2.3, 3.1, 3.2 and 3.3 for carbonate, sandstone, conglomerate and salt, respectively and with a negative Eu anomaly [Eu/Eu\* = 0.8, 0.67, 0.7 and 0.66 for carbonate, sandstone, conglomerate and salt, respectively]. These ratios of Eu anomaly especially for sandstone and conglomerate are close to the Eu-anomaly ratio of upper continental crust (UCC) (Taylor and McLennan, 1985). Also, their REE profiles are similar to profiles of the continental collision basin (CCB) of Mclennan et al. (1990).

Primitive mantle-normalized incompatible element spider diagrams of the investigated lithological sediments (Fig. 11b) generally show the enrichment in Rb, Th, U, La, Pb, Nd and Y and slight depletion in Ce, Pr, Zr, Eu and Yb and strong depletion in Ba, Nb, P and Ti relative to the primitive mantle rocks. In particular, the mobile incompatible elements do not display strong differences among the types of these lithological sediments. Variations are more conspicuous in Nb, Ta, Ce, Sr, Nd, Sm, Zr and Hf. Also,

 Table 3

 a, b. Selected trace elements, REE contents and calculated ratios of lithological samples.

SAMPLE_ID	LITO-13	LITO-15	LITO-19	LITO-23	LITO-25	LITO-29	LITO-31	LITO-34	LITO-2	LITO-8	LITO-24
	Sandstone								Conglomera	te	
(a)									<del>-</del>		
SiO <sub>2</sub>	37.0	84.1	36.9	19.6	42.0	9.9	34.0	11.8	45.5	65.8	50.4
$Al_2O_3$	8.2	4.9	11.8	5.8	11.3	2.5	12.0	2.9	11.9	6.4	20.2
$Fe_2O_3$	4.1	2.9	5.2	3.6	5.7	1.5	5.2	1.3	9.1	1.8	7.3
MgO	5.0	1.6	1.6	3.0	1.4	10.4	3.9	6.3	6.6	2.1	2.1
CaO	19.4	2.5	23.7	37.0	19.9	36.0	20.8	10.0	13.4	12.4	5.4
Na <sub>2</sub> O	0.8	0.3	0.4	0.5	0.4	0.1	2.4	17.7	2.8	0.4	1.1
K <sub>2</sub> O TiO <sub>2</sub>	1.6 0.5	1.3 0.2	1.5 0.7	0.7 0.4	1.4 0.6	0.4 0.1	1.9 0.6	0.6 0.2	0.3 0.7	1.7 0.3	2.8 1.0
P <sub>2</sub> O <sub>5</sub>	0.3	0.2	0.7	0.4	0.5	0.1	0.0	0.2	0.7	0.3	0.1
MnO	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.0	0.2	0.0	0.0
Cr <sub>2</sub> O <sub>3</sub>	0.1	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SO <sub>3</sub>							2.9	14.5			
Cl								15.7			
LOI	23.1	1.9	18.2	29.3	16.6	39.0	15.9	19.0	9.6	9.1	9.6
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Trace elements											
Ag	1.9	0.0	0.4	0.8	0.4	0.2	0.7	0.3	0.3	0.0	0.5
As	7.0	2.0	14.0	14.0	11.0	1.0	12.0	10.0	3.0	6.0	6.0
Ba	213.0	69.0	189.0	336.0	195.0	7.0	212.0	67.0	46.0	112.0	67.0
Be	3.8	1.8	4.2	6.4	3.7	1.9	2.3	1.2	1.7	2.1	2.6
Bi Cd	0.4	0.1	0.2	0.1	0.2	0.1	9.4 0.3	0.3 0.2	0.1	0.1	0.1
Co	16.0	14.0	11.0	16.0	10.0	0.1	17.0	6.0	27.0	9.0	2.0
Cr	354.0	15.0	200.0	113.0	87.0	39.0	205.0	105.0	115.0	16.0	43.0
Cs	6.9	1.2	4.8	8.6	3.9	0.7	4.8	1.1	0.3	2.5	1.3
Cu	64.2	101.6	45.9	64.9	53.6	24.2	29.3	13.8	76.2	45.9	25.6
Ga	24.9	10.0	24.1	41.6	21.9	7.3	18.0	6.1	21.5	14.2	14.6
In							0.1	0.0			
Li	41.5	22.4	59.1	95.2	53.9	14.5	38.3	10.9	23.1	18.5	23.7
Mo	5.0	1.0	1.0	1.0	2.0	1.0	2.0	3.0	1.0	1.0	1.0
Nb	9.0	4.0	14.0	26.0	12.0	4.0	14.0	6.0	3.0	9.0	10.0
Ni	573.1	384.8	194.2	184.0	160.2	151.4	161.6	380.9	182.5	400.1	72.1
Pb	15.9	4.6	19.5	28.1	19.8	6.3	16.8	6.6	3.9	5.4	6.4
Rb Sb	52.0 3.0	22.0 4.0	52.0 4.0	112.0 6.0	51.0 4.0	11.0 6.0	73.6	17.5 6.0	5.0 3.0	43.0 5.0	23.0 3.0
Sn	5.0	4.0	4.0	1.0	4.0	0.0		0.0	5.0	1.0	5.0
Sr	1787.8	60.6	264.8	290.2	262.2	299.4	262.4	166.8	430.4	121.4	594.1
Th	14.2	3.8	19.7	31.5	17.2	3.4	8.8	2.7	1.5	13.6	17.0
T1	0.5	0.1	0.3	0.6	0.3	0.0	0.4	0.1		0.2	0.1
U	1.8	0.4	1.9	3.2	1.9	1.6	1.6	0.7	0.3	1.1	1.7
V	64.0	25.0	101.0	143.0	79.0	32.0	107.0	23.0	197.0	24.0	64.0
Zn	118.8	80.1	117.1	139.7	94.1	51.9	69.0	35.1	78.9	45.1	67.8
Zr	141.0	39.0	207.0	276.0	176.0	44.0	145.0	110.0	50.0	211.0	187.0
Sc Y	300.0 51.0	497.7 33.9	326.6 30.8	283.3 31.9	228.5 22.9	104.9 10.1	60.1 14.0	36.2 5.2	273.4 41.0	358.0 18.1	154.9 19.9
La	48.0	21.1	66.5	82.8	43.7	12.6	28.9	12.9	10.0	34.7	63.7
Ce	94.9	42.1	140.2	178.2	89.5	24.8	57.4	25.6	21.6	70.3	128.7
Pr	10.7	5.3	14.7	19.4	10.1	2.9	7.1	83.4	2.9	7.8	14.6
Nd	41.5	22.3	55.8	74.8	39.6	11.6	26.3	126.4	14.2	30.1	55.7
Sm	8.2	4.5	10.1	13.8	7.8	2.3	5.0	2.2	3.9	5.5	10.2
Eu	2.0	1.1	2.2	2.8	1.8	0.5	1.1	0.5	1.5	0.9	1.9
Gd	8.8	5.2	9.4	12.0	7.0	2.4	4.5	3.4	5.6	5.2	8.9
Tb	1.1	0.7	1.0	1.3	0.8	0.3	0.6	0.4	0.9	0.6	0.9
Dy	6.4	4.2	4.7	6.6	4.1	1.5	2.9	1.4	5.9	2.8	4.0
Но	1.3	0.9	0.8	1.1	0.7	0.3	0.6	0.2	1.2	0.5	0.6
Er	3.8 0.5	2.4	2.4	3.4	2.1	0.8	1.5	0.8	3.7 0.5	1.6	1.7
Tm Yb	3.5	0.3 2.0	0.3 2.0	0.5 3.1	0.3 1.9	0.1 0.6	0.2 1.3	0.1 0.5	3.3	0.2 1.3	0.2 1.4
Lu	0.5	0.3	0.3	0.5	0.3	0.0	0.2	0.1	0.5	0.2	0.2
Indices	221.2	112 5	210.7	400.2	200.7	60.0	127 5	2500	75.0	1616	292.8
∑LREE	231.2 205.2	112.5 96.5	310.7 289.6	400.3 371.8	209.7 192.5	60.9 54.8	137.5 125.7	258.0 251.0	75.8 54.1	161.6 149.3	292.8
∑HREE ∑HREE	26.0	16.0	21.1	28.6	17.3	6.1	11.8	6.9	21.7	12.3	17.9
Eu/Eu*	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.5	1.0	0.5	0.6
(La/Lu) <sub>N</sub>	9.5	7.1	22.3	18.5	15.3	13.4	12.1	14.4	2.1	18.6	32.4
$(La/Yb)_N$	9.0	6.9	21.7	17.6	15.1	13.0	14.3	16.8	2.0	17.7	31.1
(La/Sm) <sub>N</sub>	3.6	2.9	4.0	3.7	3.4	3.4	3.6	3.6	1.6	3.9	3.8
(Gd/Yb) <sub>N</sub>	2.0	2.0	3.7	3.1	2.9	2.9	2.7	5.4	1.4	3.2	5.2
(Tb/Yb) <sub>N</sub>	1.5	1.6	2.4	2.0	1.9	2.1	2.0	3.5	1.3	2.0	3.2
(Sm/Ho) <sub>N</sub> "r"	2.2 7.9	1.8 6.0	4.2 13.7	4.2 13.0	3.8 11.2	2.8 9.0	3.0 10.6	3.6 36.1	1.1 2.5	3.5 12.1	5.7 15.3

(continued on next page)

Table 3 (continued)

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SAMPLE_ID	L	ITO-13	L	JTO-15	LI	TO-19	I	ITO-23	3	LITO-2	25	LITO-2	9	LITO-31		LITO-34	. 1	LITO-2	I	LITO-8	L	JTO-24
	S	andstoi	ne														(	Conglon	nerate			
Th/Sc		0.0		0.0		0.1		0.1	1	0	.1	0	.0	0.1		0.1		0.0		0.0	)	0.1
Zr/Sc		0.5		0.1		0.6		1.0			.8		.4	2.4		3.0		0.2		0.0		1.2
Th/U		7.8		9.9		10.6		9.9		9	.0	2.	.1	5.5		3.7	7	5.9		12.7	7	9.9
K <sub>2</sub> O/Na <sub>2</sub> O		2.1		4.8		4.2		1.5	5	3	.4	3.	.5	0.8		0.0	)	0.1		4.3	3	2.6
$\sum$ REE/TiO <sub>2</sub>		513.9		562.6		463.8		1082.0	)	374	.6	468.	.6	213.1		1228.4	1	116.7		557.4	4	284.2
$Fe_2O_3/TiO_2$		9.1		14.6		7.7		9.8		10		11.		8.1		6.4		13.9		6.2		7.1
MnO/TiO <sub>2</sub>		0.2		0.7		0.1		0.2			.1		.3	0.1		0.1		0.3		0.		0.0
V/Cr	4	0.2		1.7	C	0.5		1.3			.9		.8	0.5		0.2		1.7		1.5		1.5
Al (ppm) CIW (molar		3462.1 18.8	2	25833.8 57.7	0.	2414.0 21.4		30915.8 8.0		59978 25		13181.	.6 .7	63631.6 22.7		15187.9 5.7		62731.6 29.3		33986.2 22.1		106881.9 64.8
CIA (molar)	)	18.1		49.5		20.8		7.9		24			. / .6	21.8		5.7		29.3		20.8		59.1
Chr (moiar)		10.1		43,3		20.0		/	,	27	. 1	٥.	.0	21.0		5.7		23.1		20.0	,	33.1
	LITO																					
	1	3	4	5	6	7	9	10	11	12	14	16	17	20	21	22	26	27	28	32	18	30
	Carbo	nate ro	cks																		Salt	
	carbo	ilute 10	CKS																		Suit	
(b)	240	0.0	2.4	1.7	0.1	0.0	2.0	0.2	0.2	0.1	0.1	147	112	22.0	1.0	0.1	20.2	<b>5</b> 4	0.1	0.0	242	25.2
SiO <sub>2</sub>	34.9 8.7	0.2 0.1	3.4 1.1	1.7 0.6	0.1 0.1	0.2 0.1	3.8 1.3	0.2 0.1	0.2 0.1	0.1 0.0	0.1	14.7 2.9	14.2 5.1	32.8 10.6	1.8 0.5	0.1 0.0	29.3 8.5	5.4 0.8	0.1	0.2 0.1	34.3 8.3	25.3 7.4
Al <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub>	4.8	0.1	0.6	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.0	1.8	2.2	4.5	0.5	0.0	3.4	0.5	0.0	0.0	3.8	3.7
MgO	3.9	0.5	4.9	0.9	3.7	0.9	17.3	0.4	0.5	0.7	3.5	3.7	1.3	2.9	3.8	0.4	3.2	0.8	0.4	0.6	2.3	3.8
CaO	24.0	55.9	47.4	53.2	54.1	56.9	31.5	55.6	56.2	55.6	52.2	41.4	42.6	24.7	49.7		28.9	52.2	57.1	55.6	28.2	20.0
Na <sub>2</sub> O	1.0			0.1			0.1					0.2	0.2	0.9			0.6	0.0		0.1	0.4	8.1
$K_2O$	1.9	0.0	0.3	0.1		0.0	0.1	0.0	0.0			0.6	0.7	1.3	0.1	0.0	1.1	0.1	0.0	0.0	1.1	1.2
TiO <sub>2</sub>	0.7		0.1	0.0			0.0					0.2	0.3	0.6	0.0		0.5	0.1			0.6	0.5
P <sub>2</sub> O <sub>5</sub>	0.4	0.0	0.0	0.0		0.0	0.0	0.3	0.0	0.0		0.2	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.1	0.1
MnO	0.1 0.0	0.0	0.0	0.0			0.0		0.0			0.1	0.0	0.0	0.0	0.0	0.0	0.0			0.1 0.0	0.1 0.0
Cr <sub>2</sub> O <sub>3</sub> SO <sub>3</sub>	0.0												0.0	0.0			0.0				0.0	13.9
Cl																						1.5
LOI	19.7	43.2	42.3	43.4	42.1	41.9	45.5	43.4	43.0	43.6	44.2	34.3	33.3	21.6	43.4	43.2	24.4	40.1	42.4	43.4	20.9	14.4
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Trace elemei	nts (nnn	1)																				
Ag	0.6	0.1	0.2	1.7	0.1	0.0	0.1		0.4	0.4	0.1	0.6	0.3	0.7	0.4	0.1	0.5	0.3	0.2	0.3	0.5	0.5
As	28.0		1.0	3.0								6.0	4.0	7.0	3.0		5.0	2.0			9.0	8.0
Ba	561.0											20.0	30.0	172.0			103.0	)			130.0	125.0
Be	5.4	1.2	1.2	1.3	1.4	1.4	1.4	1.4	1.4	1.3	1.3	2.1	2.7	4.0	1.4	1.2	3.4	1.4	1.3	0.8	3.4	1.8
Bi																				0.0		0.2
Cd	0.1	0.4	0.2	0.1	0.3	0.3	0.1	0.1	0.6	0.1	0.3	0.2	0.2	0.2	0.1	0.2	0.1	0.1	0.2	0.6	0.2	0.3
Co Cr	9.0 198.0						13.0					10.0	41.0	5.0 55.0	26.0	12.0	5.0 62.0	16.0			7.0 250.0	15.0 187.0
Cs	3.6	0.0	0.6	1.5			0.6	0.1	0.1	0.0	0.0	0.7	2.5	3.0	0.2	,	2.2	0.3		0.1	3.1	2.8
Cu	34.5	19.3	21.4	21.9	17.4	17.4	15.8	24.4	18.6	25.9	16.7	28.9	34.9	30.7	17.4	17.5	32.2	24.5	16.9	11.5	45.3	26.1
Ga	37.4	3.5	6.3	5.9	3.7	3.7	5.3	4.0	2.8	3.1	3.4	9.7	15.3	24.9	3.0	2.8	18.0	5.5	3.0	2.1	19.1	13.0
In																				0.0		0.0
Li	32.4	1.1	13.1	5.6	0.5	0.6	6.2	1.3	0.7	0.8	0.6	18.9	31.8	51.4	4.0	0.6	42.2	5.5	0.5	0.6	35.9	25.6
Mo	22.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	1.0	1.0	2.0	1.0	1.0	2.0	1.0	2.0	1.0	2.0
Nb	22.0	2.0	2.0	1.0	2.0	1.0	2.0	1.0	2.0	1.0	2.0	5.0	8.0	13.0	2.0	1.0	13.0	2.0	1/1-	1.0	13.0	10.0
Ni Pb	156.0 9.8	0.9	157.4	184.3	155.0 0.5	0.6	2.7	120.0 0.8	445.6 1.1	2.6	0.7	135.0 11.3	195.4 8.8	4 78.8 11.7	79.8 2.1	76.4 0.6	130.8 9.3	2.2	141.7 0.6	2.0	233.7 14.4	511.3 12.3
Rb	62.0	3.0	8.0	3.0	3.0	3.0	5.0	4.0	4.0	3.0	3.0	14.0	29.0	44.0	5.0	4.0	9.5 37.0	6.0	3.0	1.7	35.0	45.6
Sb	2.0		1.0	_,.	1.0		2.0		1.0	1.0		3.0	3.0	2.0	1.0		2.0	5.5	1.0	1.0	3.0	3.0
Sn	1.0												2.0									
Sr				2269.1									360.3			.3 268.8					359.1	396.7
Th	63.3	0.1	1.2	0.8	0.0	0.0	1.3	0.0	0.1	0.2	0.1	5.0	9.5	31.1	0.7	0.0	17.4	1.5	0.0	0.0	16.3	5.9
Tl	0.4			0.0	0.7	0 -	4.0	0.0	0.0	0.1		0.0	0.1	0.2	0.0		0.1			0.0	0.2	0.2
U	6.6	1.1	2.4	0.6	0.6	0.5	4.3	0.2	0.6	0.3	0.4	1.4	1.1	2.6	1.8	0.6	1.8	0.7	1.4	0.5	1.8	2.1
V Zn	102.0 88.2	5.0 23.4	21.0 75.7	7.0 33.2	5.0 23.2	4.0	17.0 33.8	2.0 27.2	6.0 33.7	2.0 47.6	5.0 21.6	34.0 60.4	58.0 60.6	88.0 104.3	12.0 31.2		78.0 80.2	16.0 27.8	2.0 22.6	3.0 34.5	71.0 82.4	62.0 49.7
Zr		15.0	23.0	29.0		14.0		15.0	15.0	17.0	15.0	63.0	86.0	237.0	18.0		219.0		16.0	16.0	227.0	49.7 167.0
Sc		48.1				52.4		52.6	47.9	46.9	56.5	186.6	181.6		61.8		179.9		45.7	14.4	334.3	51.5
Y	57.7	12.1		2.4	0.8	1.1	5.4	0.9	1.9	0.9	1.2	29.4	19.8	27.3	6.1	1.6	21.2	6.9	1.9	3.9	35.5	10.1
La	116.8		7.0	3.3	0.4	0.4	5.2	0.5	0.5	0.8	0.5	21.8	36.4	69.0	3.7	0.5	57.7	7.8	0.5	1.7	67.5	23.1
Ce	240.8	3.0		6.4	0.7	8.0	10.0	8.0	0.7	1.2	0.9	43.2	72.3	139.2	6.7	0.6	118.6		0.5	0.6	133.3	46.6
Pr	26.8	0.6	1.6	0.7	0.1	0.1	1.1	0.1	0.1	0.1	0.1	5.6	8.1	15.9	0.9	0.1	13.5	1.7	0.1	0.0	15.1	5.4
Nd	106.9		6.6	2.7	0.3	0.3	4.6	0.3	0.4	0.4	0.5	24.7	30.8	59.9	3.6	0.4	52.0	6.7	0.4	0.6	57.8	20.9
Sm	20.0	0.5	1.3	0.6	0.1	0.1	0.8	0.1	0.1	0.1	0.1	5.5	5.6	11.4	0.8	0.1	9.7	1.3	0.1	0.2	10.4	4.0
Eu Gd	4.5 17.8	0.1 0.8	0.3 1.5	0.2 0.5	0.0 0.1	0.0 0.1	0.2 0.8	0.0	0.0	0.0	0.0 0.1	1.4 5.9	1.1 5.3	2.4 10.0	0.2	0.0 0.1	1.9 8.6	0.3 1.3	0.0 0.1	0.1 0.2	2.1 10.0	0.9 3.6
Ga Tb	17.8 2.1	0.8	0.2	0.5	0.0	0.0	0.8	0.1	0.0	0.1 0.0	0.0	0.7	0.6	1.2	0.9	0.1	1.0	0.2	0.0	0.2	1.1	0.4
Dy	9.7	0.7	1.1	0.3	0.0	0.1	0.6	0.0	0.0	0.0	0.0	3.7	2.7	5.0	0.7	0.0	4.3	0.9	0.0	0.0	5.1	2.1
Но	1.8	0.2	0.2	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.7	0.5	0.9	0.1	0.0	0.7	0.2	0.0	0.1	0.9	0.4
Er	4.8	0.5	0.6	0.2	0.0	0.0	0.4	0.0	0.1	0.0	0.1	1.8	1.4	2.5	0.4	0.1	2.0	0.5	0.1	0.2	2.6	1.2

Tm	0.8	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.5	0.1	0.0	0.3	0.1	0.0	0.0	0.4	0.1
Yb	3.8	0.4	0.5	0.1	0.0	0.0	0.3	0.0	0.1	0.0	0.1	1.3	1.2	2.1	0.3	0.1	1.7	0.4	0.1	0.2	2.2	1.0
Lu	0.7	0.1	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.2	0.2	0.4	0.1	0.0	0.3	0.1	0.0	0.0	0.3	0.2
Indices																						
∑REE	557.3	13.6	34.6	15.0	1.7	2.0	24.4	2.0	2.2	2.8	2.5	116.7	166.5	320.3	18.6	2.3	272.3	32.5	2.0	4.1	308.9	109.9
$\sum$ LREE	515.7	10.7	30.5	13.8	1.6	1.7	21.9	1.8	1.8	2.6	2.1	102.2	154.4	297.8	15.8	1.8	253.5	28.9	1.6	3.1	286.3	100.9
$\sum$ HREE	41.6	2.9	4.1	1.2	0.2	0.3	2.5	0.2	0.3	0.2	0.4	14.5	12.1	22.5	2.7	0.5	18.8	3.6	0.4	1.0	22.7	9.0
Eu/Eu*	0.7	0.7	0.7	0.9	0.9	0.8	0.7	1.1	1.0	1.3	0.8	0.8	0.6	0.7	0.9	0.7	0.7	0.8	0.9	0.8	0.6	0.7
(La/Lu) <sub>N</sub>	17.1	5.5	11.1	15.0	9.5	6.2	10.7	7.9	4.8	17.2	5.2	12.5	20.6	16.1	7.2	4.3	23.6	12.5	4.4	4.5	21.0	14.7
$(La/Yb)_N$	20.6	5.5	10.4	16.8	10.2	7.8	10.7	10.4	5.7	17.8	6.2	11.0	20.1	21.9	7.0	4.9	22.1	12.7	5.0	6.6	20.0	15.9
$(La/Sm)_N$	3.6	4.1	3.3	3.6	3.6	3.8	3.9	3.2	3.5	4.8	3.4	2.4	4.0	3.7	2.8	3.4	3.6	3.6	4.1	6.2	4.0	3.6
$(Gd/Yb)_N$	3.8	1.4	2.6	2.9	2.3	1.8	2.1	2.1	1.1	2.1	1.5	3.6	3.5	3.8	2.0	1.2	3.9	2.6	1.3	1.0	3.6	3.0
$(Tb/Yb)_N$	2.6	1.2	1.9	2.0	1.7	1.4	1.6	1.5	1.2	1.5	1.2	2.6	2.2	2.7	1.7	1.1	2.6	1.9	0.9	0.9	2.2	2.0
$(Sm/Ho)_N$	3.8	1.1	2.3	3.5	2.7	1.8	2.3	2.6	1.5	3.1	1.8	2.9	4.0	4.2	1.9	1.1	4.7	2.6	1.1	1.0	4.0	3.5
"r"	12.4	3.7	7.5	11.4	8.0	6.5	8.9	7.9	5.2	12.6	5.9	7.0	12.8	13.2	5.8	3.9	13.5	8.0	3.9	3.1	12.6	11.2
Th/Sc	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.1
Zr/Sc	1.0	0.3	0.3	0.5	0.3	0.3	0.3	0.3	0.3	0.4	0.3	0.3	0.5	1.1	0.3	0.3	1.2	0.4	0.3	1.1	0.7	3.2
Th/U	9.5	0.1	0.5	1.2	0.0	0.0	0.3	0.1	0.1	0.5	0.1	3.6	8.8	11.9	0.4	0.0	9.9	2.2	0.0	0.1	8.9	2.9
$K_2O/Na_2O$	1.9			1.2			1.9					2.5	3.4	1.5			1.9	2.5		0.1	2.7	0.1
$\sum$ REE/TiO <sub>2</sub>	774.1		692.7	498.6			610.2					648.6	594.5	516.6	619.1		555.7	650.3			514.9	208.5
Fe <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	6.6		12.2	5.3			9.8					10.1	7.9	7.3	19.7		7.0	9.8			6.3	7.1
MnO/TiO <sub>2</sub>	0.2		0.6	0.0			0.3					0.3	0.1	0.1	0.7		0.1	0.0			0.1	0.1
V/Cr	0.5						1.3					3.4	1.4	1.6	0.5		1.3	1.0			0.3	0.3
Al (ppm)	46,109	371	5876	2912	265	424	6935	424	371	159	212	15,564	27,210	55,903	2859	212	44,839	4235	159	265	43,833	38,978
CIW (molai	16.8	0.1	1.3	0.6	0.1	0.1	2.2	0.1	0.1	0.0	0.0	3.8	6.2	18.8	0.6	0.0	13.9	0.8	0.0	0.0	13.9	13.0
CIA (molar)	16.2	0.1	1.3	0.6	0.1	0.1	2.2	0.1	0.1	0.0	0.0	3.8	6.2	18.4	0.6	0.0	13.6	8.0	0.0	0.0	13.6	12.7

the more immobile incompatible elements (Tb, Y, Tm and Yb) to the right side of the diagram show moderate depletion. Positive Th-anomalies in some samples of the lithological sediments combined with negative Sr-anomalies and strong negative Nb-anomalies in all samples of lithological sediments. It suggests that the derivation of these sediments is dominantly from rocks containing probably crystallized plagioclase and rocks resulted from the fractional or a magma contaminated by components added to the mantle source by subduction zone fluids (Wilson, 1989).

On the basis of the La–Th–Sc diagram, which distinguishes between the felsic and basic provenance (Cullers, 1994a, 1994b) Lake Acıgöl sediments (surface, shallow core and chemical lithological units) are derived mainly from highly basic rocks, except whether from amphibolites and/or metabasic rocks (Fig. 12a and b). Also, the sediment data grouped closer to Sc than to La along the La–Sc edge, refer to the entire sediment data plot far away UCC and PAAS. Thus, this also confirmed that there is no comparison to those of the international sediments (UCC and PAAS).

In addition, the characteristics of REE of Lake Acıgöl are defined by correlations between some parameters such as  $\sum$ REE/TiO<sub>2</sub> and Eu anomaly (log[Eu<sub>N</sub>/(Sm<sub>N</sub> × Gd<sub>N</sub>)]) as well as (La/Yb)<sub>N</sub>. Because the low concentrations of total REE of the sediment samples are diluted by biogenic silica, the  $\sum$ REE is normalized to TiO<sub>2</sub> (Tanaka et al., 2007). Also, biogenic silica does not contribute to bulk REE amounts of sediments. There is an intermediate negative correlation between  $\sum$ REE/TiO<sub>2</sub> and Eu anomaly and between Eu-anomaly and (La/Yb)<sub>N</sub> (Figs. 13a and 13b), and weak positive correlation between  $\sum$ REE/TiO<sub>2</sub> and (La/Yb)<sub>N</sub> (Fig. 13c) in all surface, shallow core and lithological samples.

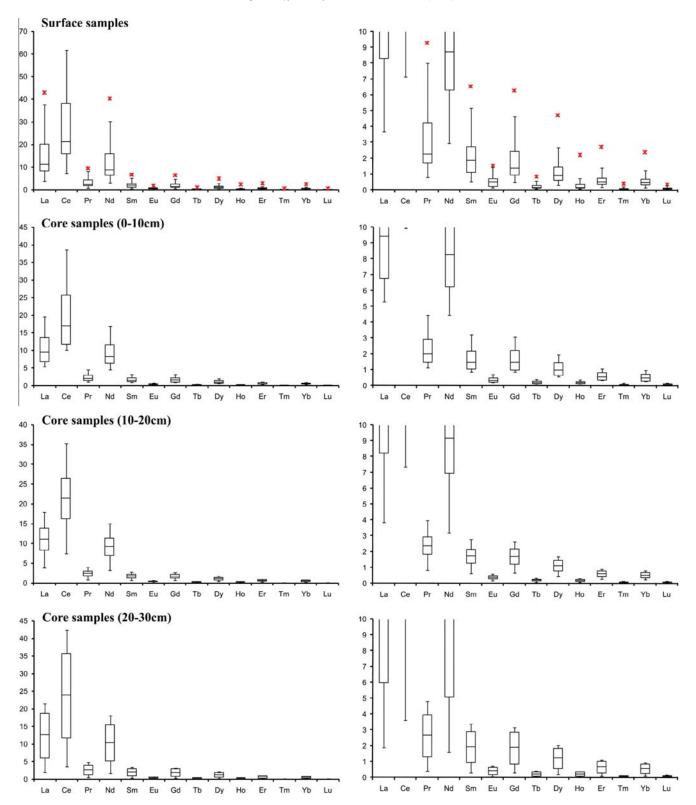
Also, the REE's potential is used to estimate the paleoenvironmental proxy. Low contents of TOC in surface sediments (an average 1.6) and subsurface sediments (averages 1.3, 1.2 and 1.0 for different depths 0–10 cm, 10–20 cm and 20–30 cm respectively) as well as the non-biogenic materials e.g., the oxides (Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and MnO/TiO<sub>2</sub>) has no and/or very weak correlation with  $\sum$ REE/TiO<sub>2</sub> (Fig. 13d and 13e) refer to these biogenic and non-biogenic materials do not control the characteristics of REE of Acıgöl sediments. Therefore, inorganic detrital materials predominantly may control their REE characteristics.

Moreover, many studies (e.g. Bjorlykke, 1974; Dill, 1986; Dill et al., 1988; Ernst, 1970) used the ratio as an index of paleooxygenation. Cr is mainly associated in the detrital fraction of sediments and it may substitute for Al in the clay structure (Bjorlykke, 1974). However, Vanadium is generally found in sediments deposited in reducing environments (Shaw et al., 1990) and may be restricted to organic matter by the incorporation of  $V^{4+}$  into porphyrins. Jones and Manning (1994) proposed that if V/Cr ratios are less than 2, these indicate the sediments were deposited in oxic conditions. While these ratios range from 2 to 4.25, they refer to dysoxic conditions, but if they are more than 4.25 it suggests suboxic to anoxic conditions. For Lake Acıgöl lake sediments, the V/Cr ratios of surface, shallow core (0-10 cm; 10-20 cm and 20-30 cm), sandstone, conglomerate, and salt sediments are 0.8, 0.9, 0.9, 1.2, 0.7, 1.5, and 0.3 respectively. Based on these ratios, below 2, the sediments were deposited in an oxic depositional environment. Also, the V/Cr ratios of lacustrine sediments (surface and shallow core) are close to that of sandstones.

In other words, the low values of CIA and CIW from the surface and shallow core sediments suggest low chemical weathering, either at the original source or during transport, before deposition, under arid or subtropical humid climatic conditions. These are shown in depletion and/or removal of alkali and alkaline earth elements with a slight increase in  $Al_2O_3$  (Fig. 14).

According to Liu et al. (2005), the concentrations of conservative lithophile elements "scandium (Sc) and aluminum (Al)" in sediments are not noticeably affected by biogenic cycles and anthropogenic contamination. The content of total REE of Lake Acıgöl sediment is positively correlated with Sc and Al with a correlation coefficient of 0.93 and 0.71, 0.84 and 0.92 and 0.69 and 0.76 for surface, shallow core and lithological sediments, respectively (Fig. 15). Therefore, the strong associations between REEs and Sc and Al indicate that the REE abundances in Lake Acıgöl sediments are derived from the weathered products from local bedrock around the lake.

McLennan et al. (1993) stated that the Th/U ratio is ranging between 3.5 and 4.0 in the upper crustal rocks, and if this ratio is higher than 4.0 in sedimentary rocks, it may indicate that the rocks were affected by intense weathering in source area or sediment recycling under oxidizing conditions resulting in oxidation of U<sup>4+</sup> to U<sup>6+</sup> and these cause the dissolution and loss of U (McLennan



**Fig. 9a.** Box-and-whisker plot of REEs concentrations (ppb) in 4 different lake sediments. The top and bottom of each box correspond to the 75th and 25th percentile values, respectively. The whiskers extending from the top and bottom of each box correspond to maximum and minimum values.

and Taylor, 1980; Taylor and McLennan, 1985). However, if the value of this ratio is lower than 3.5, it is due to sedimentary processes, which were accompanied by greater mobility and enrichment of U. Also, the observed moderate to high content of U in Lake Acıgöl sediments is mainly due to the enrichment of U in

the source rocks, which contributed more U to these sediments. Therefore, the Lake Acıgöl sediments have Th/U values averaging 2.7, 2.6, 3.2, 3.5, 7.3, 9.3, and 5.9 for surface sediments, shallow core sediments with different depths (0–10 cm), (10–20 cm) and (20–30), sandstone, conglomerate, and salt, respectively. Thus,

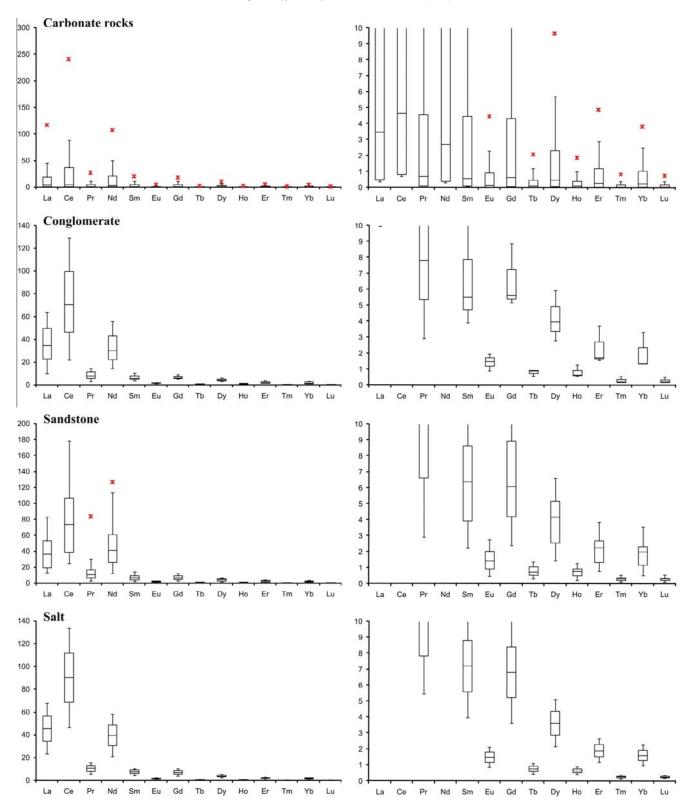


Fig. 9b. Box-and-whisker plot of REEs concentrations (ppb) in different lake basin lithological units. The top and bottom of each box correspond to the 75th and 25th percentile values, respectively. The whiskers extending from the top and bottom of each box correspond to maximum and minimum values.

the surface, shallow core and carbonate samples have Th/U ratios less than 3.5 more similar to the sediments from the mantle source that reflect the geochemically depleted nature (Newman et al.,

1984) (Fig. 16a), while sandstone, conglomerate and salt have a Th/U ratio more than 4.0 which indicates that they have a variable amount of old upper continental crust (Fig. 16b). Y/Ho weight

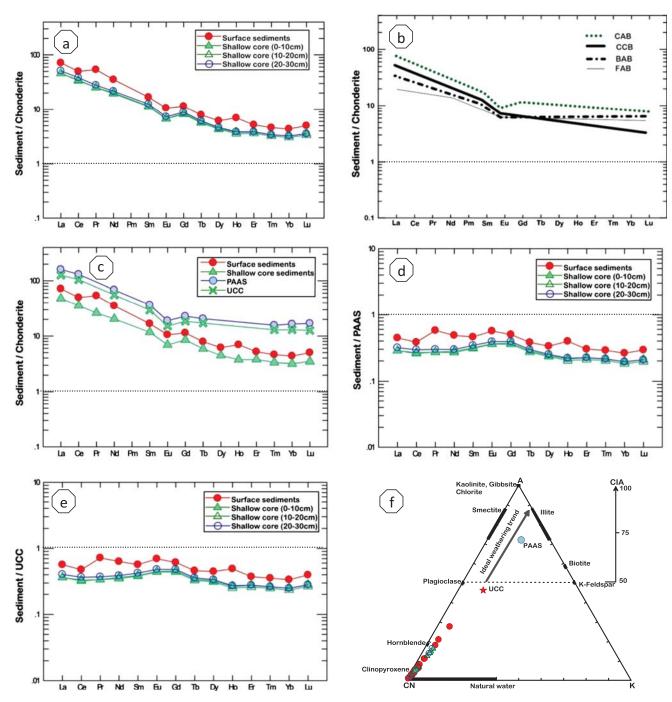


Fig. 10. Rare earth patterns of the surface and shallow core sediments (different depths) from Lake Acıgöl. Abundances normalized to (a) chondrites (Sun and McDonough, 1989), (b) typical chondrite-normalized REE profiles for clastic rocks in arc-related basins (after McLennan et al., 1990). CAB = continental arc basin, CCB = continental collision basin, BAB = back-arc basin, FAB = fore-arc basin, (c) comparison of REE patterns between the average of Lake Acıgöl sediments (surface and shallow core) and typical upper continental materials. Chondritic values by Sun and McDonough (1989). REE data of PAAS and UCC are quoted from (Taylor and McLennan, 1985), (d) Post-Archean Australian Shale (PAAS)-normalized REE profiles for surface and shallow core sediments (Taylor and McLennan, 1985), (e) upper continental crust (UCC)-normalized REE profiles for surface and shallow core sediments (Taylor and McLennan, 1985), and (f) A-CN-K (Molar Al<sub>2</sub>O<sub>3</sub>-CaO\* + Na<sub>2</sub>O-K<sub>2</sub>O) ternary diagram (Nesbitt and Young, 1982) of the samples from Lake Acıgöl surface and shallow core sediments.

ratios of the Lake Acıgöl sediments show 40–50, whereas chondrite and continental average shales such as NASC and PAAS have  $\sim\!\!28$  of Y/Ho weight ratio.

The  $(Gd/Yb)_N$  ratios are helpful in determining the nature of source rocks and the composition of the continental crust (Taylor and McLennan, 1985) which have recorded high values in the Archean crust. Also, the Archean crust has high U contents that are found in sediments from an oxygen minimum zone

(Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991; Sarkar et al., 1993; Somayajulu et al., 1994). The Lake Acıgöl sediments have slightly high values of U and (Gd/Yb)<sub>N</sub> and this interpreted in the Eu/Eu\* versus (Gd/Yb)<sub>N</sub> diagram (Fig. 17) which stated that Lake Acıgöl sediments are mostly derived from Archean crust, except carbonate rocks which are mostly derived from Post-Archean crust. Bhatia and Crook (1986) used some elements like Th, Sc, Zr, and La to determine the tectonic setting of

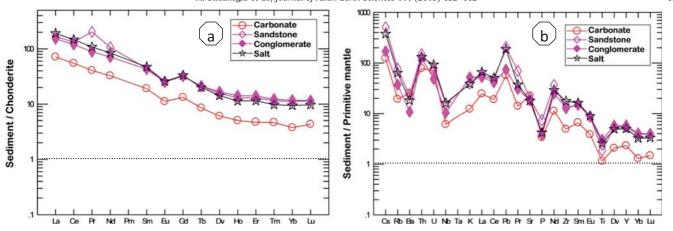


Fig. 11. (a) Chondrite-normalized REE patterns for the lithological samples. Normalizing values from Sun and McDonough (1989), (b) primitive mantle-normalized incompatible element spider diagrams of the studied; normalized values taken from Sun and McDonough (1989).

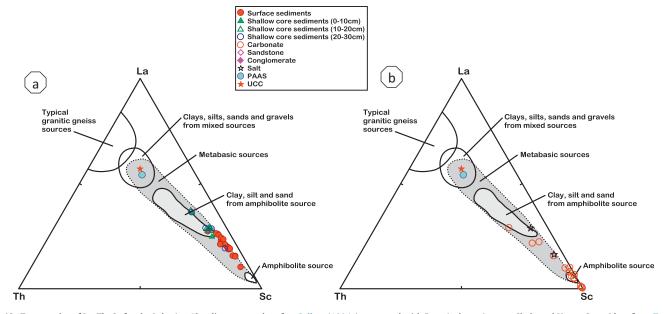


Fig. 12. Ternary plot of La–Th–Sc for the Lake Acıgöl sediment samples after Cullers (1994a) compared with Post-Archean Average Shale and Upper Crust (data from Taylor and McLennan (1985)), (a) surface and shallow core sediments, (b) chemical lithological units.

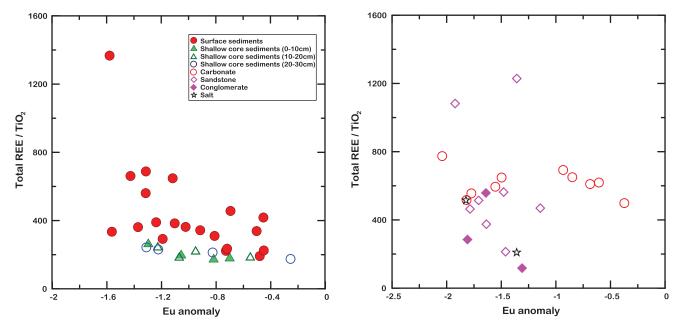


Fig. 13a. Correlation plots between  $\sum REE/TiO_2$  and Eu anomaly. Europium anomaly is defined as log  $[Eu_N/(Sm_N \times Gd_N)]$ .

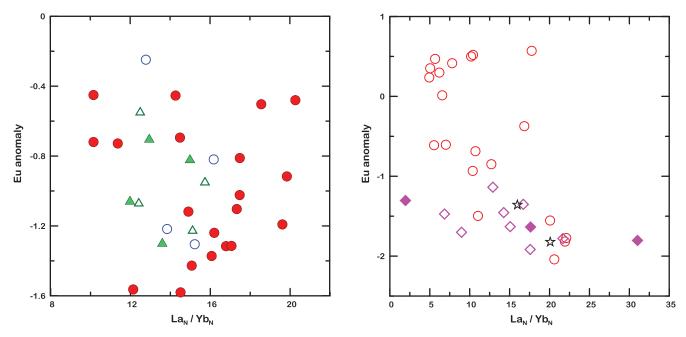
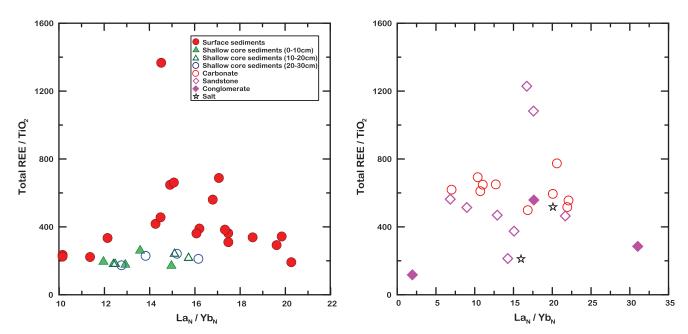


Fig. 13b. Correlation plots between Eu anomaly and (La/Yb)<sub>N</sub>.



**Fig. 13c.** Correlation plots between  $\sum REE/TiO_2$  and  $La_N/Yb_N$ .

the sedimentary rocks that they divided it into oceanic island arc, continental island arc, active continental margin and passive margin. Also, Mclennan et al. (1990) differentiated the recent deep-sea turbidities that derived from and deposited either at a passive margin, or at a continental arc margin, by using these elements. The two ternary diagrams e.g. Th–Sc–Zr/10 and La–Th–Sc show that most of the Lake Acigöl sediments derived from oceanic island arc rocks and deposited at passive margin (Fig. 18). This interpreted that the Lake Acigöl sediments were derived from highly basic rocks whether from amphibolites or metabasic rocks

(see Fig. 12). Because the oceanic island arc rocks are quartz-poor sediments, the Lake Acigöl surface and shallow core sediments are plotted in the field of quartz-poor sediments according to  $K_2O-Na_2O$  diagram of Crook (1974) (Fig. 19). However, sandstone and conglomerate rocks (Hayrettin Formation) around the lake basin are quartz-rich and quartz-intermediate fields and that refers to these lithological sediments are deposited at passive margin that is the transition between oceanic and continental crust and this enrichment in quartz may be derived from continental crust.

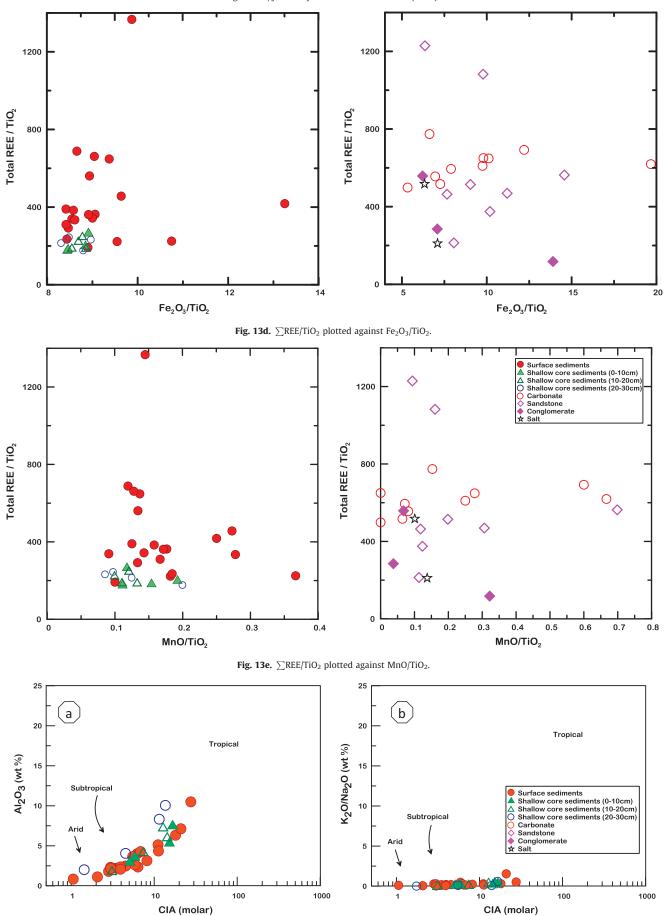


Fig. 14. Plotting of CIA (molar) versus Al<sub>2</sub>O<sub>3</sub> (a) and K<sub>2</sub>O/Na<sub>2</sub>O (b) of Lake Acıgöl surface and shallow core sediments (Goldberg and Humayun, 2010).

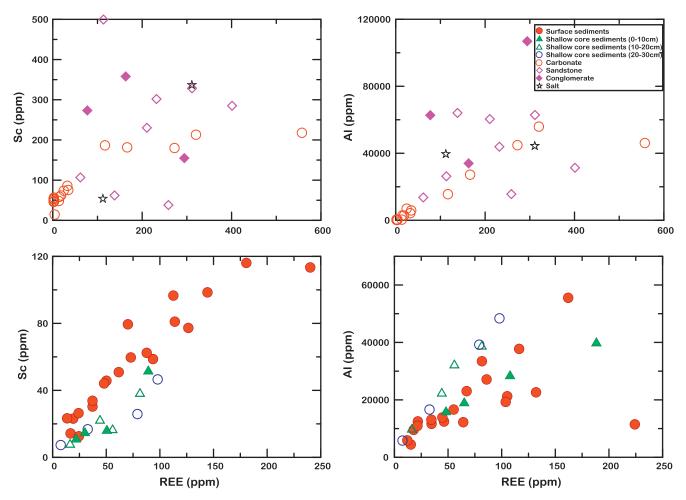


Fig. 15. Relationships between the contents of total REE and Sc and Al of the Acıgöl lake sediments.

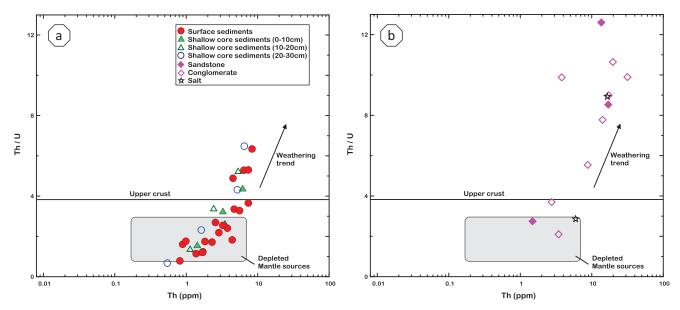


Fig. 16. Plots of Th/U versus Th for the Lake Acıgöl sediments (after McLennan et al., 1993), (a) surface sediments and shallow core sediments and (b) lithological samples.

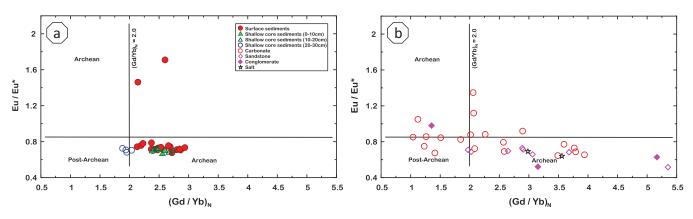
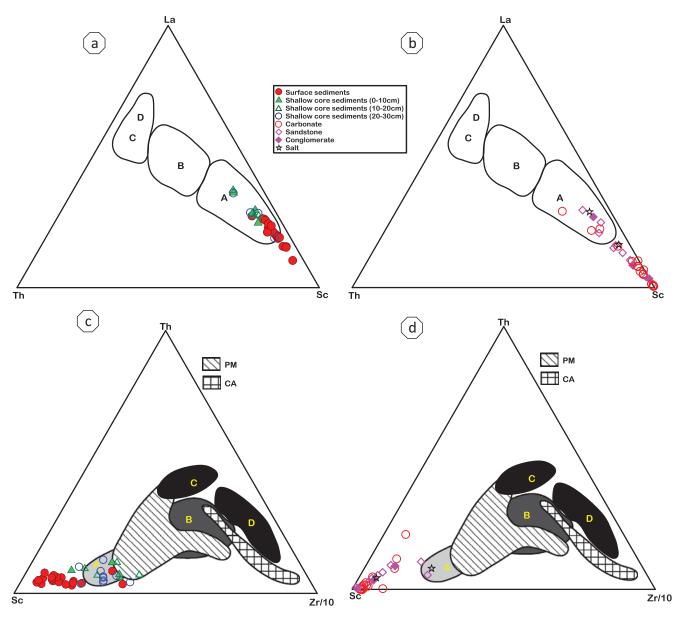


Fig. 17. Plot of Eu/Eu\* versus (Gd/Yb)cn for the Lake Acıgöl sediments, (a) surface and shallow core, (b) lithological sediments, fields after McLennan and Taylor (1991).



**Fig. 18.** Ternary diagrams La–Th–Sc and Sc–Th–Zr/10 of Lake Acıgöl sediments; (a) and (c) surface and shallow core sediments, (b) and (d) lithological sediments. Discrimination fields of tectonic setting are after Bhatia and Crook (1986). A: oceanic island arc; B: continental island arc; C: active continental margin; D: passive margin; PM: recent deep-sea turbidities derived from and deposited at a passive margin; CA: recent deep-sea turbidities derived from and deposited at a continental arc margin (data from Mclennan et al. (1990)).

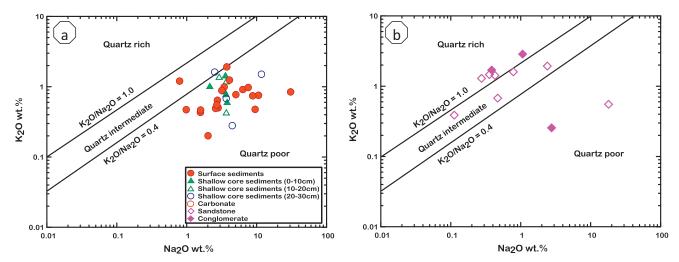


Fig. 19. Analyses of sediments to the richness of quartz of the Lake Acıgöl sediments after Crook (1974), (a) surface and shallow core, (b) lithological siliciclastic sediments.

REE element analyses of spring waters indicate that there are ppb level long term contributions of La Ce and Nd elements to the lake water (Table 4). Table also presents a few ppb level accumulation points in the lake water for the La and Ce elements.

#### 4.2. Spatial distribution of REE

Based on the Geographic Information System (GIS) techniques, the regression analysis was used to model the spatial relationship among the variable elements. Inverse Distance Weighted (IDW) is a type of straightforward and non-computationally intensive method that is used in geographic information science to determine multivariate spatial interpolation approach, in which the predicted value is more correlated with closer known points' values than far known points (Burrough et al., 1998; Longley, 2005; Ozelkan et al., 2013), while GWR is a statistical local regression technique (Foody, 2004) that calculates the regression model parameters varying in space and overcomes the non-stationarity problem (Fotheringham et al., 2003).

According to IDW technique, the spatial interpolation investigates high SREE contents of lithological units (Hayrettin Formation) that are located at north Lake Acigöl; and low contents of total REE of the surface lake sediments (Fig. 20a). Also, the contents of  $\sum$ LREE and  $\sum$ HREE are higher in the lithological units than in the lake sediments (Fig. 20b and c). A possible reason for the decrease in this parameter is the chemical sedimentary processes and the limited biogenic contributions on the recent Lake Acıgöl surface and shallow core sediments. However, the spatial interpolation of Eu/Eu\* ratio (calculated in accordance with REE normalized to chondrite of (Nakamura, 1974)) shows that this ratio is high in lake surface sediments and low in lithological units (Fig. 20d). This indicates that the Eu-anomaly is a negative anomaly because it has an opposite distribution for the total REE. Moreover, some trace element ratios e.g., V/Cr have been used to evaluate the index of paleo-oxygenation (Dill, 1986). The spatial distribution of V/Cr ratio (Fig. 20e) indicated that most of lithological units and lake sediments of the Lake Acıgöl area (<2 V/Cr), deposited in oxic conditions; except the conglomeratic rocks of Hayrettin Formation (>2 V/Cr), which were deposited in dysoxic

Based on the GWR techniques, the spatial correlation coefficient between  $\sum$ LREE and  $\sum$ HREE is high (0.92) in some lithological units (e.g. Hayrettin Formation and Cameli Formation) while the other lithological units and lake surface sediments are moderate (around 0.65) (Fig 21a). Also, in accordance with this technique (GWR), there is a matching and positive correlation between

∑REE and some conservative lithophile elements, like Sc and Al (Fig. 21b and c). The concentrations of these elements (Sc and Al) in sediments are not affected by biogenic and anthropogenic contamination (Liu et al., 2005). In addition, along the fault zone (directed NE−SW), the southern shores of the lake that are characterized alluvial fan deposits extended into lake, have moderate Al versus Total REE correlation based on GWR analyses. Therefore, the abundance of REE from Lake Acıgöl surface sediments weathered from the local bedrocks that surround the lake area.

# 4.3. Sediment accumulation rate

The determination of the sediment accumulation rate was calculated by using both Pb-210 and the Cs-137 methods in the two sediment core location. The distributed effect of industrial salt production ponds on recent sediment accumulation in lake basin was determined in the station 1 core (KRT-1 core) due to the difficulties on interpretation and modeling of sediment accumulation rates in this point. However we were able to measure sediment accumulation rates for station 3 (KTR-3) and concentration of <sup>210</sup>Pb, <sup>214</sup>Pb and <sup>137</sup>Cs radionuclides, <sup>137</sup>Cs dates according to CRS chronology, were given in Tables 5a, and 5b, respectively. The calculated sedimentation rate is 0.012 g/cm<sup>2</sup>/year according to CRS method for the first 20 cm depth of this lake. Sedimentation rate versus depth diagram (Fig. 22a), fallout radionuclides (Pb<sup>210</sup>, Pb<sup>214</sup>ve Cs<sup>137</sup> Bq/kg) concentration versus depth at the station K3 (Fig. 22b) and depth versus year diagram according to the model comparison of CRS, 137Cs and CIC (Fig. 22c) were also first time presented for the Lake Acıgöl Sediments.

At this point the lake must be experiencing significant mixing of the sediments due to the water pumping processes from the lake. Mixing can cause the redistribution of the <sup>137</sup>Cs throughout the profile as is evident from the measured activities. We would typically see almost no <sup>137</sup>Cs in the youngest sediments, followed by a single peak of <sup>137</sup>Cs in the core occurring in the mid 1960s due to the radiological fallout associated with nuclear arms testing and then a rapid drop to values of zero in older sediments. This is not the case with the station 1 core (KRT-1 core). The <sup>137</sup>Cs activities we measured do not provide us with confidence to apply the dating model based on this isotope. Mixing can also affect the <sup>210</sup>Pb (atmospheric = unsupported) and <sup>214</sup>Pb (watershed = supported) profiles. The <sup>210</sup>Pb profile should be highest at the surface and decreasing as we progress into older sediments. The <sup>214</sup>Pb profile should be relatively consistent throughout the core.

We see neither of the expected profiles for these 2 isotopes. The variability in the <sup>214</sup>Pb makes it impossible to establish a

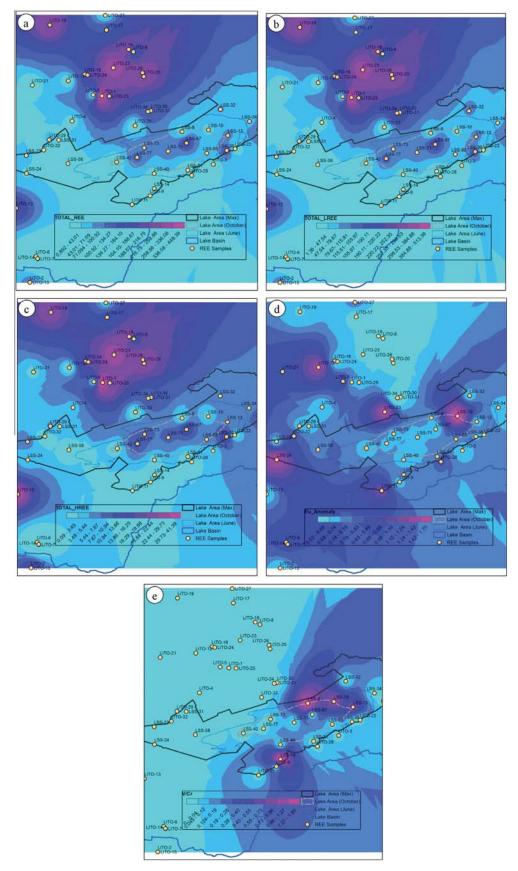


Fig. 20. Spatial interpolations by IDW techniques of Lake Acıgöl sediments and lithological units for (a) total REE, (b) total light REE, (c) total heavy REE, (d) Eu-anomaly, and (e) V/Cr ratio.

**Table 4**REE contents (ppb) of lake water and spring waters which are discharging to the lake.

		Station		Samp. ID.	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
		Long.	Lat.		(ppb)													
June 2013	SPRINGS	29.722	37.800	SPRNG-1	0.000	0.050	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.849	37.955	SPRNG-2	0.200	0.350	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.940	37.825	SPRNG-3	0.060	0.120	0.000	0.030	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.893	38.002	SPRNG-4	0.000	0.020	0.000	0.030	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.684	37.724	SPRNG-5	0.030	0.040	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.690	37.905	SPRNG-6	0.020	0.040	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.995	37.794	SPRNG-7	0.020	0.030	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.730	37.946	SPRNG-8	0.000	0.020	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		30.051	37.810	SPRNG-9	0.000	0.030	0.000	0.020	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.984	37.779	SPRNG-10	0.300	0.340	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
				Average	0.063	0.104	0.000	0.008	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Lake Water	29.898	37.844	LW-1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.855	37.863	LW-3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.898	37.844	LW-12	0.000	4.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.913	37.839	LW-13	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.934	37.832	LW-14	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.920	37.825	LW-15	4.000	6.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.920	37.825	LW-16	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.910	37.830	LW-17	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.899	37.835	LW-19	0.000	6.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		29.887	37.839	LW-20	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
				Average	0.400	1.600	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

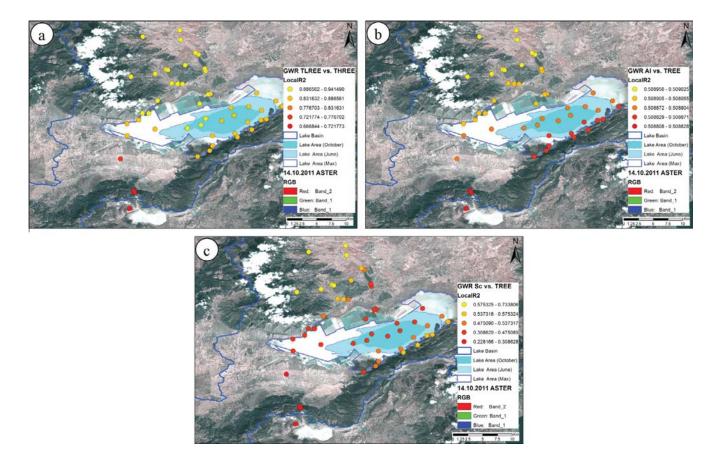


Fig. 21. Spatial correlation by GWR techniques of Lake Acıgöl sediments and lithological units, (a) correlation between total LREE and total HREE, (b) correlation between total REE and Sc, and (c) correlation between total REE and Al.

baseline of the watershed derived isotopes and thus we are unable to apply our statistical dating models to the <sup>210</sup>Pb and <sup>214</sup>Pb profiles. In the sediment cores of Arctic lakes/ponds where <sup>210</sup>Pb and sedimentation rates are very low (Muir et al., 1995; Rühland et al., 2003; Stern et al., 2005) and this case actually

happens. Researchers quite often have to extrapolate the data to the bottom of the core if they are unable to do any  $^{14}\text{C}$  dating. It is well know that  $^{210}\text{Pb}$  dating is only reliable to  $\sim$  1850s and as researchers approach that data the model fails due to the half-life of the  $^{210}\text{Pb}$  isotope.

**Table 5a** Cumulative dry mass  $(g/cm^2)$  values and concentration (Bq/kg) of  $^{210}Pb$ ,  $^{214}Pb$  and  $^{137}Cs$  radionuclides in station 3 (KRT-3).

Midpoint Depth (cm)	Cumul. dry mass (g/cm²)	210-Pb (Bq/kg)	214-Pb (Bq/kg)	137-Cs (Bq/kg)
0.5	0.5834	13.08	14.67	1.97
1.5	1.768	7.67	8.7	1.23
2.5	2.9496	5.65	7.23	1.22
3.5	4.1941	17.95	17.88	1.92
5	6.0108	6.63	6.05	1.16
7	8.1619	5.56	6.02	0.84
9	10.4519	21.51	17.1	1.69
11	12.9105	9.59	6.83	0.63
13	15.2586	8.19	9.66	0.63
16	18.7258	3.52	7.71	0
20	23.6869	7.68	5.8	0.37
24	28.8697	4.86	5.21	0.29
27	33.1354	1.95	4.13	0
29	36.0173	4.11	2.96	0.31
31	38.5475	3.31	2	0.68
	Total (Bq/kg) in core	121.26	121.95	12.94

**Table 5b** <sup>137</sup>Cs dates using the CRS chronology model for station 3 (KRT-3).

Depth		Chronology		Sedimentation rate
(cm)	(g/cm <sup>2</sup> )	Date (AD)	Age (yr)	(g/cm <sup>2</sup> )
0	0	2013.51	0	0.0279
0.5	0.5834	2000.34	13	0.5738
1.5	1.768	1998.65	15	0.9283
2.5	2.9496	1997.53	16	1.2169
3.5	4.1941	1995.32	18	0.3577
5	6.0108	1991.64	22	0.8634
7	8.1619	1989.26	24	0.9554
9	10.4519	1982.82	31	0.2022
11	12.9105	1972.55	41	0.3293
13	15.2586	1965.15	48	0.3064
16	18.7258	1955.84	58	0.5335
20	23.6869	1935.99	78	0.1317

#### 5. Conclusion

Lake Acıgöl is located at the inner Aegean Region of Turkey in a closed basin at the junction between three Provinces; Denizli, Afyonkarahisar and Burdur. This article studies the geochemistry and spatial geochemical modeling of REE contents of surface and shallow core sediments of this lake and the surrounding lithological sediments to examine REE characteristics and determine the nature of source rocks of the lake sediments with inferring their paleo-environmental proxy. The spatial REE geochemical modeling was carried out using Inverse Distance Weighted (IDW) and Geographically Weighted Regression (GWR) techniques. This modeling is distinguished into spatial interpolation and spatial correlation analyses of REE of lake surface sediments and lithological sediments. Generally, the Lake Acigöl surface sediments are oxidizing due to the shallow and well-mixed water columns while subsurface sediments take place in anoxic ooze zones with their negative ORP values. Recent sediments, REE distributions, fall into one group: this with LREE enrichment and fractionation, marked negative Eu anomalies and flat HREE at surface and shallow core sediments. These distributions are consistent with the varying composition of the respective source rocks. The  $\sum$ REE content decreased in shallow core sediment rather than the lake surface sediments and the lithological sediments surrounding. Chondrite-normalized REE patterns of the Lake Surface and shallow core sediments show high abundance of REE compared to chondritic concentrations with particular LREE enriched, nearly flat HREE and negative Eu anomaly. These REE profiles are similar to profiles of the continental collision basin (CCB) of Mclennan et al. (1990). However, there is no comparison between these sediments and the international sediments, e.g. PAAS (Taylor and McLennan, 1985) and UCC (Taylor and McLennan, 1985). Geologically, the lithological sediments are subdivided into carbonate, sandstone, conglomerate and salt. Their chondrite-normalized REE patterns show that they have LREE enrichment relative to HREE with negative Eu-anomalies. Also, their REE profiles are similar to profiles of the continental collision basin (CCB). Their primitive mantle-normalized multi-element patterns show positive Th-anomalies combined with negative Sr-anomalies and strong negative Nb-anomalies; this refers to these sediments derived dominantly from rocks containing possibly crystallized plagioclase and/or rock resulted from a magma contaminated by components added to the mantle source by subduction zone fluids (Wilson, 1989).

Moreover, all samples of the Lake Acigöl sediments are mainly derived from highly basic rocks; whether from amphibolites or metabasic rocks toward ultramafic/ophiolitic detrital end member. In addition, the strong associations between REEs and Sc and Al indicate that the REE abundances in Lake Acigöl sediments are derived from the weathered products from local bedrock around the lake (from Archean crust) except carbonate rocks mostly derived from Post-Archean crust, Low contents of TOC, as well as non-biogenic materials (authigenic Fe–Mn oxide), refer to the biogenic and non-biogenic materials do not control the REE characteristics; however, inorganic detrital materials control their REE characteristics of the Lake Acigöl sediments. Because the V/Cr ratio is an index of paleooxygenation, V/Cr ratios of Lake Acigöl sediments that are less than 2 showed that these sediments were

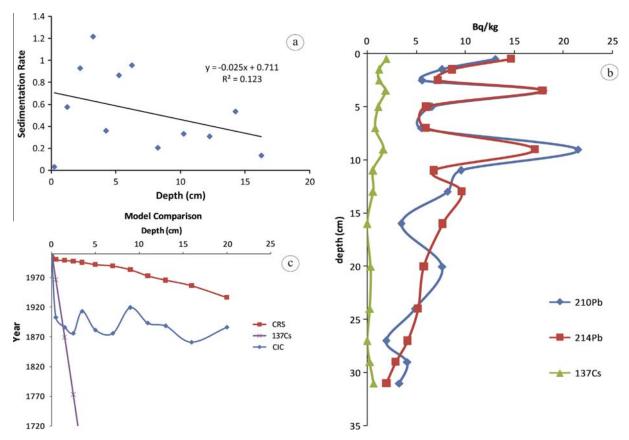


Fig. 22. (a) Sedimentation rate versus depth diagram for the first 20 cm at the station K3; (b) fallout radionuclides ( $Pb^{210}$ ,  $Pb^{214}$  and  $Cs^{137}$  Bq/kg) concentration versus depth at station 3 (KRT-3), (c) depth versus year diagram according to the model comparison of CRS,  $^{137}$ Cs and CIC.

deposited in an oxic depositional environment. Also these lake sediments were affected by low chemical weathering either of the original source or during transport before deposition under arid or subtropical humid climatic conditions. Low Th/U ratios (less than 3.5) values showed depleted mantle source rocks of most surface, shallow core and carbonate sediments, while high Th/U values (more than 4) of Hayrettin Formation (sandstone and conglomerate) show that they have variable amount of old upper continental crust. In accordance with Zr/Sc and Th/Sc values, Lake Acıgöl sediments are deposited at passive margins derived from oceanic island arc rocks particularly basic rocks either from amphibolites or metabasic rocks and this was caused by the ultramafic and ophiolitic rocks surrounding the study area. The source of the Lake Acıgöl sediments is not only detrital materials of siliceous rocks but also marine sediments such as carbonate rocks with higher Y/Ho ratios.

Determination of spatial interpolation of REE of Lake Acıgöl sediments, by using IDW method, refers to  $\sum$ REE,  $\sum$ LREE and  $\sum$ HREE contents that are higher in lithological units than the Lake surface sediments with negative Eu-anomaly. Also, this area is deposited in oxic and anoxic conditions based on V/Cr spatial distribution. By using the GWR method, the spatial correlation shows that the local bedrocks around the lake are the source of REE abundance.

Precipitation of La, Ce and Nd elements from lake water is probably controlled by negligible both evaporate and carbonate precipitation. The southern shores of the lake that are adjacent with basin-bounded fault (directed NE-SW), are characterized alluvial fan deposits extended into lake and have moderate Al versus Total REE correlation in lake sediments based on GWR analyses. All of these results strengthened massif effect of detrital materials on the REE accumulation process in the recent lake sediments.

Incredibly similar <sup>210</sup>Pb and <sup>214</sup>Pb activities indicate that there is a significant dilution effect occurring in this lake. There could be significant amount of deposition in the lake from the watershed, as well, the precipitation of the cations (calcium, sodium, potassium) related evaporate minerals to the lake bottom is causing the 210Pb and 214Pb to become diluted. We do not have to forget that industrial salt production in artificial salt pond around the lake shore directly effects natural dynamic of lake basin sediment accumulation conditions.

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