# Mineralogy and Geochemistry of Major, Trace and Rare Earth Elements in Sediments of the Hypersaline Urmia Salt Lake, Iran

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Abstract: Urmia Salt Lake (USL) is a hypersaline lake located at the NW corner of the Iran platform. The lake area is estimated to have been over 5000 km<sup>2</sup> at one point, but has now decreased to <1000 km<sup>2</sup> in the last two decades. It contains 4.6×10<sup>9</sup> tons of halite and other detrital and evaporative minerals such as calcite, aragonite, dolomite, quartz, feldspars, augite and sylvite. This study examined the mineralogy and geochemistry of bed sediments along the mid-east toward NE bank sediments collected from 1.5 meters depth and nearby augite placer. Due to the diverse lithology of the surrounding geology, bed sediments vary from felsic in the mid-east to mafic in the northeast. Weathering of tephrite and adakite rocks of the Islamic Island at the immediate boundary has produced a large volume of augite placer over a 40 km length, parallel to the shoreline. Based on the study result, weathering increases from south to north and the geochemistry of the sediments shows enrichment of MgO, CaO, Sr and Ba associated with Sr deployment in all samples. Rare earth elements (REE) patterns normalized to the upper continental crust (UCC) indicated LREEs enrichment compared to HREEs with an elevated anomaly of Eu, possibly due to surface absorbance of Mn and Fe minerals, associated with Sr elevation originating from adakites in the lake basin vicinity.

Key words: mineralogy, geochemistry, augite placer, Urmia Lake, Iran

# **1** Introduction

Urmia Salt Lake (USL) is an internationally recognized salt lake which has been recognized as a world heritage site (Birkett and Mason, 1995) by the United Nations. It is located between west and east Azarbayedjan in the northwest corner of Iran. It was previously 5200-6000 km<sup>2</sup> in area, which has now decreased to <1000 km<sup>2</sup> in the last two decades, effected by dry climate and unsuitable agricultural management. Up to 4000 km<sup>2</sup> area is covered by sediments and 65×108 tons of dissolved salt, now almost precipitated and exposed to the air (Alipour, 2006). USL, as one of the largest supersaturated hypersaline lakes in the world, lacks enough information on its bed sediment composition. Many interested researchers over the past 200 years have conducted some studies, but almost all of them concentrated on water quality, ecology, hydro-geochemistry and history of the lake (e.g. Abich, 1856; Kelts and Shahrabi, 1986; Asemet al., 2012; Asem et al., 2012; Touloie et al., 1997; Jamshidi, 2002; Asem and Mahmoudi, 2013).

Recently some new research has been published (Eimanifar and Mohebbi, 2007; Hassanzadeh et al., 2011; Alipour and Olya, 2015; Tourian et al., 2015) that discusses only the management and desiccation of USL. A few publications based on bed sediment research are limited to scarce M.Sc. theses, which have been supervised by authors investigating mineralogy and geochemistry of major and trace elements of USL bed sediments (Hosseni, 2012; Haseli, 2014; Aslanpour, 2015; Mosavi-onlaghi, 2016; Alipour et al., 2012).

Geochemical characteristics of lake sediments are affected by source rock, basin evolution and watershed weathering, particle sorting, geochemical processes during transportation, and diagenetic phenomena. Therefore, lake sediments play an important role in revealing composition, weathering of watersheds, ecology and past climatological regimes (Last and Smol, 2001; Jin et al., 2003; Laird et al., 2003; Rose et al., 2004).

Geochemical behavior and differences of trace elements such as Sc, Ga, Th, Pb, Cr, Zr, Rb and REEs in lake sediments during transportation, weathering and sedimentation are appropriate geochemical indices to

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determine geology and tectonics of the lakes basins (Jin et al., 2003; Das and Haake, 2003; Rose et al., 2004). Major element geochemistry of surface sediments moved to lake basins also could display their essential geochemically controlled factors (Bianchi et al., 2002).

Major and trace element geochemistry and mineralogy in various water bodies are fully described (Knappe et al., 2005; Dupre et al., 1990; Elderfield et al., 1990), but the study of the composition of the lake bed sediments, especially of the REEs, is limited compared to the rocks ) Taylor and McLennan, 1985) and this very obvious in USL. REEs unique characters such as low solubility, immobility and absorbance by oxides and hydroxides (Koeppenkastrop et al., 1993; Bau, 1993) are vital in determination of weathering, erosion, transportation, sedimentation and clarifying the geochemistry of lake sediments. Using these criteria may help to characterize the sediments of Urmia salt lake (USL) and their origin. Therefore, due to lack of research on lake bed sediments, this paper has focused on the mineralogy and geochemistry of major, trace and REEs of USL.

# **2** Geological Setting

Geological formations surrounding the Urmia Lake

consist of Jurassic limestone and Eocene volcanic rocks (Alipour, 2006) (Fig. 1). The Eslami peninsula contains Eocene Lucite dikes, trachyte, tephrite, phenolite, basanite and synite (Alizadeh and Jangjo, 2017). A tremendous diversity of rocks and permanent water flow controls the composition of the lake bed in different parts.

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The Islamic peninsula in the northeastern part of USL is a unique geological character of the area. It occupies up to  $500 \text{ km}^2$  of tephritic rocks with agglomeratic texture. Varieties of intermediate to mafic rock types consisting of tephrite, basanite with pyroclastic interlayer agglomerate and weathered tuffaceous materials (Fig. 1) are present at this island (Moayyed et al., 2008). The large volume of volcanic layered rocks may have formed either by frequent flowing lava or rapid collection of pyroclastics after volcanic activity (Fig. 2a,b). Most of these rocks consist of feldspars and large pyroxenes (up to one centimeter in diameter) which have easily exhumed due to weathering and interactions between volcanic rocks with the salty water of the lake (Fig. 2c). Short distance transportation of these minerals has formed a placer deposit parallel to the bank, and also contributed to the bed sediment composition, which is well reflected in XRD analysis (Fig. 3, Table 1).



Fig. 1. Geological map of the USL with sample location (GIS modified, 1993-2006).

1, Gravel plain; 2, Clay flat; 3, Granite and rhyolite; 4, Shale, acidic volcanic rock, sandstone and basalt; 5, Congolomerate, sandstone and marn; 6,Sandstone, limestone and dolomite; 7, Lucite and trachyte; 8, Alteration of shale, sandstone and conglomerate; 9, Igneous rocks; 10, Salt flat; 11, Lahar deposits.



Fig. 2. Volcanic flow structure of the Islamic Island nearby the Kalantary causeway (a) and Agh-Gonbad village (b).



Fig. 3. Main rivers flowing into the Urmia Salt Lake.

# **3** Methodology

This study is based on field investigation and the

 Table 1 Major and minor mineral phases of lake bed

 sediments by XRD analysis

Samples	Major phase	Minor phase
LE-1	halita	aragonite, calcite,
	liante	muscovite-illite ,chlorite
LE-4	augite	hornblende,
	augne	carbonate-hydroxide-apatite
LE-5	ankerite Halite Quartz	aragonite, albite, gypsum,
	ankenne, mante, Quartz	montmorillonite
LE 15	halite, aragonite,quartz,	calcite, muscovite-illite, chlorite,
LE-15	calcite	dolomite, albite

sampling is based on exposed sediments 50 m from bank and a geological map prepared from the surrounding rock types. Subsequently, mineralogical and geochemical analyses were performed on 17 samples taken with an auger (Netherlands) from the bottom part of 1.5 meters depth. Samples were air-dried and milled to a -200 mesh. Ten samples were analysed by ICP-MS for trace and rare earth elements. In two samples major elements were determined using XRF at the Geological Survey of Iran. Four samples were studied by XRD for mineral identification. Some samples were floated in balsam and dried to prepare polished thin sections for microscopic mineral identification. The Pearson correlation coefficient and SPSS10 is used for data processing and interpretations.

# 4 Results and Discussion

It has been shown that lake sediments depend on the geochemical origin of the material, physical and chemical weathering of the basin, tectonic activity, wind activity, transportation, sedimentation and diagenetic processes (Fralick and Kronbergi, 1997). The same factors control the different types of sediments but in various intensity at the USL, which are discussed as bellow:

### 4.1 Mineralogy

Four samples from the bank of the eastern and northeast part of the Urmia Lake were analysed by XRD (Table 1). XRD results show a remarkable difference from mid-east to north, nearby Agh-Gonbad village toward to Taymorloo (Fig.1). Augite is the main mineral forming a large volume of the placer (Figs. 4b, 5) due to remarkable presence of mafic volcanic tephritic rocks alongside the lake at the mid-east bank in the Agh-Gonbad area (Fig. 1). From Teymorloo to the north, augite decreases while pyroclastics and halite with clastic materials increase around the Aji-Chay river (Fig. 3). From the eastern part toward the northeast, mineralogical composition of the sediments changes to halite as the main mineral phase, due to the increased distance from tephrite (Fig. 4a) and entering the Aji-Chay paleodelta (Fig. 3), forming very large, thick, dried flood plain sediments, where Aji-Chay has completely ceased to flow into the lake. Minor minerals in these parts consist of aragonite, calcite, muscovite-illite, chlorite, quartz, albite, hornblende, and carbonate-hydroxide-apatite (Table 1).

The present distribution of minerals indicates that the local geology is the main controlling factor of lake sediment composition. Similar works in the southeast (Haseli, 2014) and southwest (Hoseyni, 2012) have demonstrated the main influence of the local geology in



Fig. 4. Augite placer (Left) and picture of Augite crystals under microscope STME SV8 (Right).



Fig. 5. Microscopic pictures of placer minerals in thin sections. Cal, calcite; Cpx; clinopyroxene; Arg, aragonite; Qtz, quartz; Oo, Ooid.

forming the chemical composition of the lake bed sediments, compared to diagenetic chemical and biochemical mineral precipitations in the lake.

Overall sediment compositions could be grouped in thre categories: clastic; chemical; and biochemical minerals. Similar mineralogical composition of sediment types have been reported from the southwest (Hoseyni, 2012) and southeast of the salt lake (Haseli, 2014), indicating similar mineral formation and weathering processes governing the USL.

Clastic sediments are normally carried by rivers (Alipour, S., 2006). These sediments include volcanic silicates such as augite, hornblende, quartz, and albite, and clays including chlorite, muscovite and illite. Chlorite in this region may have formed as an alteration product from volcaniclastic minerals such as hornblende or pyroxenes (More and Reynolds, 1989). Illite is an abundant clay mineral in the sediments and may have formed from feldspathoids or muscovite (Nelson, 2006) of Islamic Island rocks. Dolomite and calcite possibly precipitated insitu in the lake, as well as being carried by rivers to the lake. Dolomite may form as Mg concentration has increased (Sinha et al., 2004) in the lake, especially during the last two decades, as the water level in USL has decreased. Chemical and biochemical minerals increase towards the northeast while the amount of clastic

sediments decreases.

Toward the north major minerals such as ankerite, aragonite, halite and calcite are associated with minor phase such as albite, gypsum, montmorillonite, dolomite, chlorite and muscovite (Table 1; Fig. 6a, b).

## 4.2 Geochemistry

### 4.2.1 Geochemistry of major elements

The various lithologies along the sampling profile and the diversity of sediments entering the lake create diversity in the context of major elements in analysed samples (Table 3). For example, the amount of  $SiO_2$  varies from 22.37% up to 47.29%, which is lower than what is reported for UCC (Upper Continental Crust) (Taylor and McLannan, 1985), PAAS (Archaen Australian Shale) (Taylor and McLannan, 1985; Gromet al., 1984) and NASC (North American Shale) (Table 3).

Major elements were normalized to PAAS (Taylor and MacLenna, 1985) (Fig. 7). The plot shows strong enrichment of Ca, Na and Mg, indicating mafic composition, in accordance with the mafic source rocks of Islamic Island. This type of composition emphasizes local geology in controlling the major composition of the lake bed sediments compared to chemical and biochemical mineral forming processes.

Table 2 Pearson	correlation betwee	n maior element	ts of lake bed	sediments of	the NE	profile
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			3				I			
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	MnO	Na <sub>2</sub> O	$P_2O_5$	TiO <sub>2</sub>
SiO <sub>2</sub>	1		_							
Al <sub>2</sub> O <sub>3</sub>	0.263	1								
CaO	-0.395	-0.964**	1		_					
Fe <sub>2</sub> O <sub>3</sub>	0.840**	0.093	-0.237	1		_				
K <sub>2</sub> O	-0.013	0.940**	-0.886**	-0.075	1		_			
MgO	0.55	-0.417	0.297	0.608	-0.553	1		_		
MnO	0.61	-0.162	0.032	0.783**	-0.338	0.772**	1			
Na <sub>2</sub> O	-0.255	-0.127	0.126	0.159	0.005	-0.29	0.101	1		
$P_2O_5$	0.299	-0.558	0.44	$0.690^{*}$	-0.573	0.597	$0.718^{*}$	0.445	1	
TiO <sub>2</sub>	$0.750^{*}$	-0.162	0.004	0.940**	-0.324	0.639*	0.833**	0.231	0.830**	1

\* Correlation is significant at the 0.05 level (2-tailed). \*\* Correlation is significant at the 0.01 level (2-tailed).



Fig. 6. XRD mineralogy (C& D) diagrams of Lake Sediments



Fig. 7. Major oxides normalized to PAAS (after Taylor and MacLenna, 1985) variations in sampling profile of USL sediments.

# 4.2.1.1 Pearson correlation coefficient of major elements

Correlation coefficients of major elements (Table 2) show negative correlation between  $Al_2O_3$  and CaO (r=-0.96), which could be due to the inadequate feldspars or the  $Al_2O_3$  introduced to the lake by river transportation. The positive correlation between  $Al_2O_3$  and  $K_2O$  (r=0.93) can be related to the presence of muscovite, illite and chlorite in the area. Positive correlation between  $Fe_2O_3$  with TiO<sub>2</sub> (r=0.94) and TiO<sub>2</sub> with MgO (r=0.63) in sediments might be due to the similar geochemical behavior in this environment and the mafic minerals such as hornblende and augite produced by mafic volcanic rocks and weathered gabbro intrusions in north of the lake.

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rable 5 Major oxide (we /o) and trace element (ppm) concentration in the sediments of Orimia Sait Lake																
	LE-1	LE-3	LE-4	LE-6	LE-7	LE-8	LE-13	LE-14	LE-15	LE-17	MAX	MIN	Average	PAAS	UCC	NASC
SiO <sub>2</sub>	31.09	42.82	47.3	32.04	33.6	22.37	41.41	44.51	24.65	46.29	47.29	22.37	36.609	62.8	66	64.8
$Al_2O_3$	8.96	7.49	3.53	7.75	9.64	6.78	12.95	13.07	6.71	10.79	13.07	3.53	8.767	18.9	15.2	16.9
CaO	12.71	16.48	22.3	16.36	11.8	18.95	7.59	7.04	21.57	10.16	22.31	7.04	14.492	1.3	4.2	3.56
Fe <sub>2</sub> O <sub>3</sub>	3.1	4.96	4.32	3.59	3.1	2.1	3.8	3.9	2.06	3.4	4.96	2.06	3.433	7.23	5	6.33
$K_2O$	1.99	1.58	0.53	1.8	2.42	1.67	2.71	2.66	1.55	1.92	2.71	0.53	1.883	3.7	3.4	3.99
MgO	5.35	9.9	14.6	6.01	5.7	8.52	7.91	8.28	4.07	6.03	14.58	4.07	7.635	2.2	2.2	2.85
MnO	0.08	0.12	0.11	0.09	0.06	0.09	0.09	0.09	0.05	0.09	0.12	0.05	0.087	0.11	0.08	0.06
Na <sub>2</sub> O	8.23	13.11	0.78	6.66	6.09	4.51	3.15	2.27	6.05	3.62	13.11	0.78	5.447	1.2	3.9	1.15
$P_2O_5$	0.31	1.13	0.88	0.8	0.28	0.26	0.18	0.18	0.1	0.14	1.13	0.1	0.426	0.16		0.11
TiO <sub>2</sub>	0.51	1	0.87	0.72	0.55	0.39	0.6	0.61	0.32	0.69	1	0.32	0.626	1	0.5	0.78
V	83	126	96	101	89	65	105	107	56	88	126	56	91.6	150	60	130
Cr	103	190	369	117	112	64	109	124	52	411	411	52	165.1	110	35	125
Co	12.7	24	27	16.2	14.6	10.5	16.5	16.9	8.3	18.8	27	8.3	16.55	23	10	25.7
Ni	70	49	78	54	98	68	111	127	49	190	190	49	89.4	55	20	58
Cu	39	63	45	58	48	36	48	44	27	34	63	27	44.2	50	25	
Rb	50	23	8	36	73	50	65	66	37	42	73	8	45	160	112	125
Sr	882	878	548	1132	554	1095	223	259	1291	222	1291	222	708.4	200	350	142
Y	14.5	28.5	26.1	20	15.9	11.8	17.3	18.7	10.9	16.7	28.5	10.9	18.04	270	22	35
Zr	80	189	92	135	84	122	88	97	47	54	189	47	98.8	210	190	200
Nb	9.2	14.6	3.7	13	10.6	7	11	11.5	5	10	14.6	3.7	9.56	19	25	13
Cs	4.8	4.6	1.2	4.2	4.9	3.4	5.5	5.2	3	2.2	5.5	1.2	3.9	15	3.7	5.2
Ba	497	1224	444	1268	387	323	454	537	235	385	1268	235	575.4	650	550	636
Hf	1.51	4.23	2.51	2.67	1.6	1.25	1.75	1.82	0.94	1.04	4.23	0.94	1.932	-	-	-
Та	0.39	0.6	0.12	0.46	0.5	0.25	0.73	0.71	0.21	0.62	0.73	0.12	0.459	-	-	-
TH	7.23	10.94	5.45	9.89	7.05	5.23	7.75	7.56	4.52	4.95	10.94	4.52	7.057	-	-	-
U	2.2	2.6	1.1	2.7	1.9	2	2.1	2.7	2.4	1.22	2.7	1.1	2.092	-	-	-
LOI	25.58	8.02	1.36	21.59	24.6	32.8	16.97	14.72	31.39	14.4	32.8	1.36	19.146	-	-	-

Table 3 Major oxide (wt%) and trace element (ppm) concentration in the sediments of Urmia Salt Lake



Fig. 8. Plots of Log ( $Na_2O/K_2O$ ) and Log ( $Fe_2O_3/K_2O$ ) vs. Log ( $SiO_2/Al_2O_3$ ) from USL sediments, following the geochemical classification diagrams from (after Pettijohn et al., 1972) (a) and from (after Herron, 1988)(b).

# 4.2.1.2 Maturity and weathering determination of sediments

Mobility of major elements during weathering and transportation and diagenetic processes can be used to determine the maturity of the sediments (Mclenann et al., 1993). Some chemical equations can be used to differentiate mature from immature sediments (Pettijohn et al., 1972; Herron, 1988; Vital and Stattegger, 2000).

Plotting the analytical results in logs of  $SiO_2/Al_2O_3$  versus log (Na<sub>2</sub>O/K<sub>2</sub>O) (Pettijohn et al., 1972; Herron, 1988) show most of the samples fall in graywacke (Fig. 8a) and shale catagories (Fig. 8b). Unaltered sandstone and shale with detrital feldspars and quartz indicate that

the sediments are immature, which again highlights the control of the local geology as the main mineral source input to the lake bed sediments. The LOI content of analysed sediment samples (Table 3) increase from south to north due to the abundance of augite in the south and elevation of hydrous minerals such as montmorillonite in the north.

## 4.2.1.3 Weathering

The ternary plot of  $Al_2O_3$  - (Fe<sub>2</sub>O<sub>3</sub>+MgO) - (CaO+Na<sub>2</sub>O+K<sub>2</sub>O) (Nesbitt and Young, 1989a, 1996b) (Fig. 9a) and of (Nesbitt et al., 1996) (Fig. 9b) were used for clay weathering intensity in the studied area. The





Fig. 9.  $Al_2O_3$ -(CaO + Na<sub>2</sub>O)-K<sub>2</sub>O plot of sediment samples (Nesbitt and Young, 1989a, 1996b) compared to data for Post-Archean Average Shale (PAAS) and Upper Crust (UC) given by (after Taylor and McLennan, 1985) and North American Shale Composite (NASC) given by (after Gromet et al., 1984) (a). Triangular  $Al_2O_3$ -(CaO+Na<sub>2</sub>O+K<sub>2</sub>O)-Fe<sub>2</sub>O<sub>3</sub>+MgO plot of sediment samples (after Nesbitt and Young, 1989a, 1996b) in comparison with Post-Archean average shale and upper crust (after Taylor and McLennan, 1985) and North American Shale Composite (after Gromet et al., 1984) (b).

results of both plots indicated that weathering in the sampling profile is increased toward the north, with data points tending toward the  $Al_2O_3$  vertex. Samples close to the  $Al_2O_3$  vertex are depleted from elements such as Ca, Na, and K due to longer transportation distances, while samples toward the south are enriched in elements such as  $Al_2O_3$  (Fig. 8). Increase of  $Al_2O_3$  toward the north (Fig. 9a,b), indicates that weathering increases from south to north, with increasing distance from Islamic Island fresh rocks. The highest value is close to Islamic Island tephritic rocks, while lower values move towards the north, which is pointing sedimentary clays of Aji-Chay delta sediments at these parts (Fig. 3).

### 4.2.2 Trace Element Geochemistry

The concentration of trace elements is an effective guide for determining the source of sediments and their weathering processes and sedimentation (Taylor and McLennan, 1985; Last and Smol, 2001). Based on trace elements patterns normalized to UCC values, the mean of trace elements show enrichment of Ba, Sr and depletion of Rb, Ta and Hf with Sr for samples that contained more augite (Fig. 10).

Sr in the study area varies between 222–1291 ppm with a mean value of 716 ppm (Table 3). The amount of Sr in UCC is 350 ppm and 200 ppm in PAAS, while strontium in the southwest of the lake and south of the causeway is 704 ppm (Hoseyni, 2012). In the southeast of the lake and north of the causeway it is 1560 ppm (Haseli, 2014), which shows that the enrichment of this element is up to 3.5 times of PAAS and twice of UCC all around the USL banks.

Enrichment of Sr may be referred to the presence of abundant Ca-feldspathoids toward the north and may be



Fig. 10. Normalized trace elements distribution of northeast USL sediments to UCC (after Taylor and McLennan, 1985).

due to abundant adakitic volcanic rocks around the USL basin. Adakites are rocks with Sr>400 ppm, SiO2>56%,  $Al_2O_3>15\%$ , MgO<3% and enriched in LILE (large ion lithophile elements) and LREE, while they are depleted in Y<18 ppm HREE, Yb<1.9 and have a high ratio of La/Yb>20 and Sr/Y>40 (Defant and Drummond, 1990). Sr enrichment therefore, reflects the priority of local geology in the sediments of the lake.

Rb and Sr behave contradictorily when feldspars are weathered (Goldstein, 1988; Chen et al., 1999). Rubidium tends to replace K in minerals such as muscovite and Kfeldspars, while Sr replaces Ca in minerals such as plagioclase, pyroxene and carbonate (Yan Zeng et al., 2013). Weathering products in the lake basins that finally find their way to lake carry strontium derived from soils and deposits in the lake, while Rb remains in the soil. As a result the ratio of Rb/Sr always decreases in the lake sediments over time (Yan Zeng et al., 2013). The ratio of Rb/Sr in the study area varies between 0.1–0.29 with a mean value of 0.1. This amount is less than the Rb/Sr mean in UCC (0.32) and of PAAS (0.8). The low ratio of Rb/Sr could be attributed to the abundance of Sr transportation from Sr rich tephrite and adakite from surrounding rocks of the watershed, rather than reflecting weathering intensity. Positive correlation between Rb with  $K_2O$  (r=0.92) may perhaps be attributed to replacement in muscovite and illite (Fig. 11a), while a positive correlation between Sr and CaO is indicative of Sr in calcite, aragonite and other Ca-minerals (Fig. 11b). Enrichment of Ba may be due to attraction by hydrous manganese oxide concentrated at the bottom the lake (Masahito et al., 1992).

### 4.2.3 Geochemistry of Rare Earth Elements

The presence of similar patterns of REEs in sediments are either the result of similar lithology or the consequence of strong weathering (McLennan, 1989). In the NW of the Urmia Lake, the concentration of REEs ranges from 67.75 –218.38 ppm with a mean of 123.62 ppm (Table 4), which is close to UCC (146.39 ppm) but less than the 184.5 ppm of PAAS (Taylor and McLennan, 1985). Normalized REE patterns to chondrite show the enrichment of LREEs in respect to HREEs in this part of the lake (Fig. 12).

REEs normalized to UCC (Fig. 13) show an enrichment of LREEs  $(La/Sm)_n=0.47-0.90$  compared to HREEs  $(Gd/Yb)_n=0.73-1.93$  and positive Eu anomaly  $(Eu/Eu^*=0.64-3.18)$ . REEs prefer to remain in organic phases as



Fig. 11. Correlation equations between Sr and Ca (a) and Rb with K (b).



Fig. 12. Chondrite normalized REE diagram of the USL sediments. All samples are showing very similar patterns characterized by LREEs enrichment.



Fig. 13. REEs pattern of northeast USL sediments normalized to UCC (Taylor and McLennan, 1985) with distinctive Eu anomaly in augite abundant samples, originated from tephritic rocks.

allochthonous compounds or attraction by oxides, clay minerals and organic materials (Ohta and Kawabe, 2001; Coppin et al., 2002; Haley et al., 2004).

Positive correlation between REEs and Fe<sub>2</sub>O<sub>3</sub> (r=0.80-0.97), MnO (r=0.65-0.72) is due to surface absorbance by Fe<sub>2</sub>O<sub>3</sub> and MnO. A similar trend of REEs with TiO<sub>2</sub> (r=0.80-0.97) and P<sub>2</sub>O<sub>5</sub> (r=0.97-0.93) (Table 5) may relate to the presence of hydroxyapatite and augite as hosts for these elements in the USL sediments.

The flattened Eu anomaly in a chondrite normalized REEs diagram (Fig. 12) designates depletion of LREEs during weathering progressions, while the elevated Eu in UCC normalized REEs of USL (Fig. 13) reveals LREEs differentiation compared to HREEs in the continental crust.

### **5** Conclusion

(1) The mineralogy of the lake sediments in the NE part

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Sample	Sample LE-17 LE-15 LE-14 LE-13 LE-8 LE-7 LE-6 LE-4 LE-3 LE-1											
La	18	14	24	23	17	22	34	31	41	21		
Ce	35	28	46	44	36	43	66	67	84	41		
Pr	4.32	3.21	5.33	5.14	3.86	5.12	8.39	9.82	11.31	4.97		
Nd	17.1	12.6	20.5	19.8	15.3	20.2	33.8	43.9	48.2	19.9		
Sm	3.37	2.35	3.98	3.81	2.85	3.86	6.72	9.84	10.26	3.81		
Eu	0.95	0.58	0.98	0.97	0.73	0.98	1.81	2.56	2.68	0.97		
Gd	3.05	1.97	3.38	3.29	2.33	3.2	5.26	7.95	8.09	3.09		
Tb	0.48	0.32	0.52	0.52	0.36	0.49	0.72	1.1	1.08	0.45		
Dy	2.92	1.75	3.13	2.98	1.94	2.72	3.8	5.59	5.84	2.52		
Er	1.65	1.14	1.97	1.84	0.97	1.51	1.77	2.29	2.55	1.29		
Tm	0.24	0.17	0.28	0.27	0.16	0.22	0.24	0.27	0.31	0.2		
Yb	2.3	1.5	2.7	2.6	1.5	2.1	2.2	2.4	2.8	1.9		
Lu	0.24	0.17	0.27	0.25	0.16	0.21	0.22	0.25	0.27	0.19		
TREE	89.62	67.76	113.04	108.47	83.16	105.61	164.93	183.97	218.39	101.29		
(La/Sm) <sub>N</sub>	0.801	0.893	0.904	0.905	0.894	0.854	0.758	0.472	0.599	0.826		
(Gd/Yb) <sub>N</sub>	0.774	0.767	0.731	0.739	0.907	0.890	1.39	1.93	1.687	0.950		
(Eu/Eu <sup>*</sup> )	0.870	0.646	0.837	0.847	0.747	0.856	1.21	1.41	1.45	0.861		

I able 5 Pearson correlation between major element	s with REES of lake hed sediments of the NE profile
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			J					r r		
	$SiO_2$	$Al_2O_3$	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	MnO	Na <sub>2</sub> O	$P_2O_5$	TiO <sub>2</sub>
La	0.458	-0.235	0.118	0.845**	-0.271	0.529	0.743*	0.431	0.934**	0.890**
Ce	0.452	-0.333	0.212	0.832**	-0.373	0.607	0.772**	0.407	0.964**	0.898**
Pr	0.494	-0.414	0.283	0.832**	-0.478	$0.663^{*}$	0.772**	0.349	0.973**	0.916**
Nd	0.493	-0.469	0.336	0.814**	-0.539	$0.699^{*}$	0.772**	0.321	0.973**	0.909**
Sm	0.512	-0.498	0.363	$0.807^{**}$	-0.58	$0.734^{*}$	0.774**	0.279	0.962**	0.906**
Eu	0.515	-0.5	0.363	0.804**	-0.586	$0.721^{*}$	0.779**	0.282	0.965**	0.914**
Gd	0.555	-0.478	0.339	0.826**	-0.574	$0.752^{*}$	0.785**	0.246	0.947**	0.919**
Tb	0.598	-0.452	0.312	0.843**	-0.561	0.775**	0.789**	0.196	0.925**	0.927**
Dy	$0.665^{*}$	-0.36	0.218	0.893**	-0.489	$0.756^{*}$	0.814**	0.209	0.903**	0.959**
Er	0.828**	-0.018	-0.094	0.974**	-0.19	$0.658^*$	$0.755^{*}$	0.118	$0.722^{*}$	0.937**
Tm	0.873**	0.252	-0.356	0.972**	0.069	0.537	$0.706^{*}$	0.071	0.554	0.868**
Yb	0.881**	0.399	-0.504	0.940**	0.215	0.464	$0.658^{*}$	0.021	0.433	0.802**
Lu	0.930**	0.347	-0.445	0.926**	0.129	0.505	0.651*	-0.068	0.416	0.807**
Y	0.718*	-0.238	0.098	0.939**	-0.375	0.724*	0.821**	0.209	0.869**	0.974**

\*. Correlation is significant at the 0.05 level (2-tailed). \*\*. Correlation is significant at the 0.01 level (2-tailed).

of the USL, in spite of abundance of evaporative minerals, reflects the local geology. It is dominated by chemical and biochemical precipitates in the northern zone, while clastic minerals increase toward the southern part. Augite, as the main mineral forming the large placer, controls most of the trace and REEs in the sediments.

(2) Lake sediments are enriched in Ca, Mg, Sr and Ba, but depleted in Rb, Ta and Hf with Sr depletion from augite-bearing –bearing samples. Sr in lake sediments is 3.5 time higher than of PAAS and twice of UCC. Strong correlation between Sr with CaO is due to replacement of Sr for Ca in carbonate minerals. Strong correlation between Rb with K is due to replacement of Rb for  $K_2O$  in illitemuscovite.

(3) Based on the lake bed mineralogical compositions, their present petrological nature resemble graywacke and shale.

(4) Weathering intensity is increased from the east toward Aji-Chay river delta and towards the north.

(5) In the reddish clay sediments of the Aji-Chay vicinity unstable elements such as Ca, Na and K decrease while Al as a stable element is increased.

(6) Among trace elements SR compared to UCC (350 ppm), PAAS (200 ppm), NASC (114 ppm) with mean

value of 716 ppm is highly elevated. This reflects the role of Sr rich adakitic rocks of the Islamic Island and local geology in controlling the composition of the sediments.

(7) Rb/Sr (0.29–0.1) mean ratios in the profile is 0.1, which is less than that of UCC (0.32) and PAAS (0.8) and indicates the concentration of more Sr transported from Sr rich tephritic and adikitic rocks and probably intensive weathering.

(8) REEs normalized to chondrite and UCC indicate enrichment of LREEs compared to HREEs, associated with a positive Eu anomaly. The Eu anomaly is controlled by the presence of augite and apatite, while REEs are controlled by iron and manganese oxide surface attraction.

(9) The local geology is the main control on forming the lake sediments rather than chemical precipitation of minerals from the lake water.

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