Major Ion and Rare Earth Element Concentrations in Rainwaters from Ajdabiya, Benghazi and Al Marj, NE Libya: Natural and Anthropogenic Sources

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Abstract

Rainwater samples collected from Ajdabiya, Benghazi and Al Marj, NE Libya have been analyzed for their rare earth elements (REE) and major ions. The major ion compositions of these samples show the contributions of oceanic, crustal, and anthropogenic sources, and suggest the relative importance of these sources. The studied samples have distinctly high SO_4 and NO_3 contents. The rainwater samples also have variable REE compositions with various enrichment of light REE over heavy REE. Rainwater samples from Ajdabiya and Benghazi are significantly enriched in light REE, whereas those collected in Al Marj have loess or shale-like REE composition. The enrichment of light REE in the Ajdabiya and Benghazi rainwater samples corresponds to the typical signature of an anthropogenic source. The Y/Ho ratios in the studied samples are all higher than average crustal values, and in general, increase with increasing enrichment of light REE. This indicates that physical mixing of crustal and oceanic sources of the REE cannot account for the variations of the Y/Ho ratios. Furthermore, although the anthropogenic source of the REE is generally characterized by a high

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Y/Ho ratio, factors such as particle/rainwater interactions, pH, and speciation of REE may also be responsible for the variable abundance and fractionation of REE and Y/Ho in the studied rainwaters.

Keywords: *Rainwater; Rare earth elements; Major ions; natural source; anthropogenic source; Ajdabiya; Benghazi; Al Marj; NE Libya*

Introduction

The rare earth elements (REE) form a chemically coherent group of elements. Because of the systematic variation of their behavior due to the lanthanide contraction, the relative abundances of the REE are widely used to study geochemical processes. In addition, the REE have also been found to be a potential indicator of environmental pollution (Olmez and Gordon, 1985; Olmez *et al.*, 1991; Zhang *et al.*, 2001; Zhang *et al.*, 2012), because anthropogenic inputs show characteristic signatures of REE composition. Olmez and Gordon (1985) studied the REE compositions of particles released by coal-fired plants and refineries, and recognized that the particles released from these sources were strongly enriched in light REE (LREE) due to the zeolite cracking catalysts. Fly ash, bottom ash, and waste waters from oil-fired power plants also show enrichment of the LREE over heavy REE (HREE) (Olmez, 1989). Olmez *et al.*, (1991) were the first to report the anthropogenic REE signal of oil-refined petroleum products in aquatic sediments, and they reported that the sources of the LREE enrichment were petroleum-cracking catalysts and their products. Zhang *et al.*, (2001) found that distribution of REE in various waste ashes from Japan differ significantly. Although these studies did not involve the measurement of REE in rainwater, rainwaters contaminated by certain industries such as the oil-fired power plants and refineries are expected to show dissolved REE signatures of contaminants because of water-or cloud-particle interactions. In addition to achieving a better understanding of the distribution of the major ions and REE in rainwater, the compositions of the major ions and REE in samples collected from urban and non-urban areas have been studied.

The present work focuses on the major ion and REE concentrations in rainwaters from three cities, Ajdabiya, Benghazi and Al Marj, NE Libya (Fig. 1).

Materials and methods

Rainwater samples were collected from three locations (Ajdabiya, Benghazi and Al Marj, four samples of each city). The rainwater samples were collected during the same rain event (November 2013). The rainwater samples were collected manually on a roof of a building with a Teflon funnel that was located approximately 1 m above the roof. The roof-top sampling locations were chosen to avoid contamination from local sources.

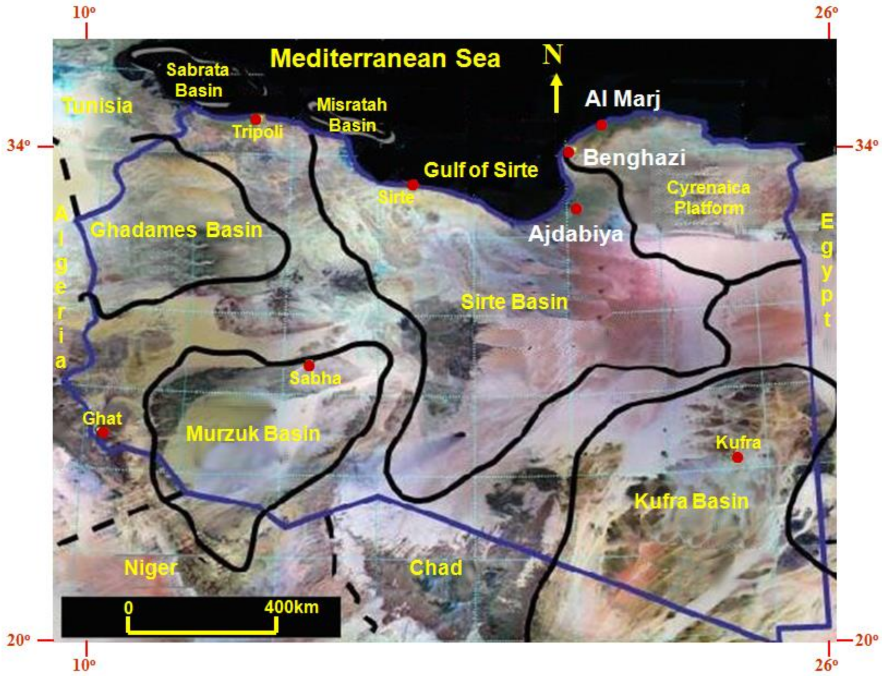

Fig. 1: Location map showing the location of the studied cities

Prior to use, the sampler was cleaned with acid (2–3N HCl), rinsed with Milli-Q water, and dried. Within 4 h after collection, all samples were filtered through 0.22 im membrane filters. An aliquot of about 50 ml was used to measure major ion compositions, and the remainder was acidified to pH=1.5 for REE determination. Major cations were determined with an Inductively Coupled Plasma-Association Emission Spectrometer (ICP-AES), and the major anions were measured by ion chromatograph. REE were determined with an Inductively Coupled Plasma-Mass Spectrometer, PMS2000 quadruple mass spectrometer (ICP-MS). Before measurement, samples were concentrated by using solvent extraction and back extraction with a mixture of 65% HDEHP (2-etheylhexyl hydrogen phosphate) and 35% H_2MEHP (2-ethylhexyl dihydrogen phosphate) in heptane. By using this pre-concentration method, the concentrations of the REE and Y in solution for the ICP-MS can be made about 200 times higher than in rainwater. The internal standard, indium, was added to the rainwater samples to control the recovery rate of the REE during the solvent extraction/back extraction procedure, whereas the internal standard, cadmium, was added as a monitor of the equipment stability before ICP-MS analysis. The analyses were done in the ACME analytical laboratories of Vancouver, Canada.

Results and discussions

Major ions

The concentrations of major ions and REE in the studied rainwaters are given in Table 1.

Table 1: Chemical analysis data (major ions in μeq/kg, REE in ppm) of the studied rainwaters

City	Ajdabiya				Benghazi				Al Marj			
Sample	**A1**	**A2**	**A3**	**A4**	**B1**	**B2**	**B3**	**B4**	**M1**	**M2**	**M3**	**M4**
pH	5.50	5.80	5.50	5.70	6.10	6.00	6.00	6.10	5.80	5.80	5.70	5.50
Ca	13.49	6.41	6.40	3.32	2.83	6.59	6.49	6.98	30.50	25.61	28.11	28.00
Mg	4.20	4.61	4.55	2.80	12.70	4.44	4.32	4.85	26.30	68.30	136.00	135.11
Na	6.48	6.66	6.33	2.44	17.10	6.48	6.40	6.48	117.00	243.00	563.00	562.90
K	5.88	8.34	7.22	7.47	31.50	3.38	3.33	7.52	14.00	38.20	15.60	15.54
Cl	3.95	11.91	11.12	11.29	9.41	22.11	22.00	18.30	109.00	275.00	734.00	733.87
NO_3	7.37	14.30	14.09	3.35	14.41	32.50	32.15	28.22	9.93	58. 7	3.93	3.55
SO_4	6.60	17.10	17.00	4.54	12.82	35.21	35.00	23.12	14.07	58.60	72.50	72.34
PSS%	6.17	4.67	4.54	6.42	7.60	2.21	2.19	3.36	79.70	48.40	92.80	92.53
nss-SO_4	6.18	16.30	16.11	4.25	11.80	34.51	34.42	22.30	2.54	29.40	5.51	5.44
Y	40.55	65.51	65.00	31.48	145.36	76.73	76.23	46.05	41.87	18.37	80.74	80.66
La	386.30	402.50	402.10	381.20	259.10	88.19	88.00	83.00	25.29	11.46	55.98	55.87
Ce	1043	986.30	985.90	1056	571.10	192.00	191.93	190.90	28.95	24.57	81.79	81.68
Pr	61.87	62.53	62.33	57.28	41.65	16.35	16.13	13.47	3.74	2.86	11.19	11.00
Nd	159.00	170.80	170.00	147.09	137.03	60.33	60.00	42.57	13.96	11.79	40.94	40.73
Sm	23.28	24.94	24.77	19.91	22.97	10.95	10.67	7.38	2.89	2.36	7.55	7.54
Eu	3.40	3.84	3.61	2.68	4.64	2.48	2.33	1.74	0.73	0.41	1.72	1.69
Gd	14.97	15.83	15.67	11.85	18.29	9.68	9.53	6.52	3.45	2.18	9.30	9.22
Tb	1.22	1.40	1.31	0.80	2.35	1.44	1.23	0.86	0.44	0.31	1.13	1.11
Dy	4.25	5.86	5.00	2.41	11.84	7.45	7.43	4.51	2.57	1.72	6.26	6.21
Ho	0.75	1.06	1.00	0.42	2.19	1.30	1.21	0.79	0.54	0.33	1.27	1.13
Er	2.41	3.34	3.11	1.36	7.12	4.10	4.00	2.51	1.46	0.96	3.39	3.34
Tm	0.33	0.48	0.39	0.17	0.99	0.59	0.55	0.34	0.20	0.14	0.48	0.39
Yb	2.22	3.21	3.09	1.08	6.68	3.87	3.56	2.21	1.16	0.92	3.21	3.00
Lu	0.37	0.55	0.49	0.18	1.09	0.58	0.55	0.33	0.16	0.14	0.46	0.41

The pH values range from 5.5 to 6.1. None sea salt sulfate (nss-SO_4) and percent sea salt (PSS) values were calculated based on equations as follows:

1)If Cl/Na equivalent ratio>1.17, nss-$SO_4=[SO_4]_{sample}-[Na]_{sample}\times[SO_4/Na]_{seawater}$, $PSS\%=100\times(SO_4/Na)_{seawater}/(SO_4/Na)_{sample}$

2) If Cl/Na equivalent ratio<1.17, nss-$SO_4=[SO_4]_{sample}-[Cl]_{sample}\times[SO_4/Cl]_{seawater}$, $PSS\%=100\times(SO_4/Cl)_{seawater}/(SO_4/Cl)_{sample}$

In the equations, [SO_4/Na] stands for the equivalent ratio, whereas (SO_4/Cl) is for a weight ratio.

There are three main origins for dissolved solids in rainwaters: marine, anthropogenic and terrigenic. The most important anthropogenic sources in the study area include petroleum contamination, cement industry and combustion of garbage. The presence of nitrate can be attributed to an input of various gaseous nitrogen oxides and be used as a tracer of anthropogenic pollution (Ezcurra *et al.*, 1988; Sanusi *et al.*, 1996; Lu *et al.*, 2011). However, the source of sulphate is complicated, as it also has a marine origin (Han and Liu, 2006; Wu *et al.*, 2012). Na is generally considered as a tracer of the marine source, although a small contribution of terrigenic origin arises due to the input of crustal aerosols (Negrel and Roy, 1998; Han *et al.*, 2010). Consequently, these elements are used to identify the sources of the dissolved solids in the studied rainwater samples.

Differences in chemical composition of the rainwater samples suggest different sources of the major ions. Samples from Ajdabiya and Benghazi had clearly land-derived sources. Samples from these cities show high nss-SO_4/Na and Cl/Na ratios (Table 2), suggesting the existence of abundant nss-SO_4 and Cl. Equivalent ratios of none sea salt nss-SO_4/Na are plotted against Cl/Na in Fig. 2. The Cl/Na ratio generally increases with increasing nss-SO_4/Na ratio. As can be seen from this figure, rainwater samples collected from Ajdabiya and Benghazi have higher nss-SO_4/Na ratios, but the Cl/Na ratios bracket the average seawater value of 1.17. Since the existence of the abundant nss-

SO_4 indicates an anthropogenic origin, rainwaters with a Cl/Na ratio larger than 1.17 may have not only marine but also anthropogenic origins.

Table 2: Ratios of major ions in the studied rainwater samples

Ratios	**Ajdabiya**				**Benghazi**				**Al Marj**			
	A1	**A2**	**A3**	**A4**	**B1**	**B2**	**B3**	**B4**	**M1**	**M2**	**M3**	**M4**
K/Na	0.91	1.25	1.14	3.06	1.84	0.52	0.52	1.16	0.12	0.16	0.03	0.03
Cl/Na	0.61	1.79	1.76	4.63	0.55	3.41	3.44	2.82	0.93	1.13	1.30	1.30
nss-SO_4/Na	0.95	2.45	2.55	1.74	0.69	5.33	5.38	3.44	0.02	0.12	0.01	0.01
NO_3/Na	1.14	2.15	2.23	1.37	0.84	5.02	5.02	4.35	0.08	0.24	0.01	0.01

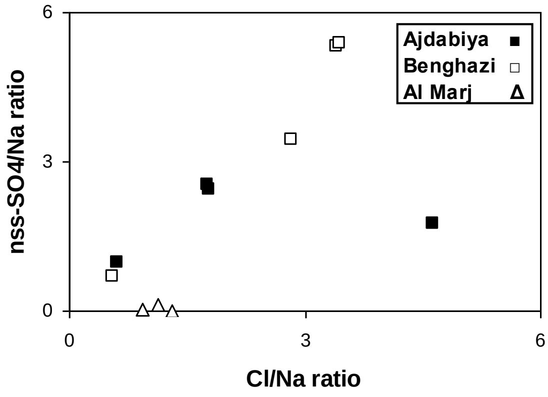

Fig. 2: Variations of Cl/Na vs. nss-SO_4/Na equivalent ratios of the rainwaters

Noteworthy is that K does not vary with Na in these samples, suggesting a different origin. However, K is correlated with NO_3 and SO_4, as is observed from the co-variations of NO_3/Na and nss-SO_4/Na when plotted against K/Na (Figs. 3-4). NO_3/Na and nss-SO_4/Na both increase with increasing K/Na and this suggests the same or similar origin of K, SO_4 and NO_3. Accordingly, K in these rainwater samples, like NO_3 and SO_4, may originate from human activity. Rainwaters from Ajdabiya and Benghazi show the highest NO_3/Na, nss-

SO_4/Na and K/Na ratios. This is a clear indication of atmospheric pollution over these densely populated areas.

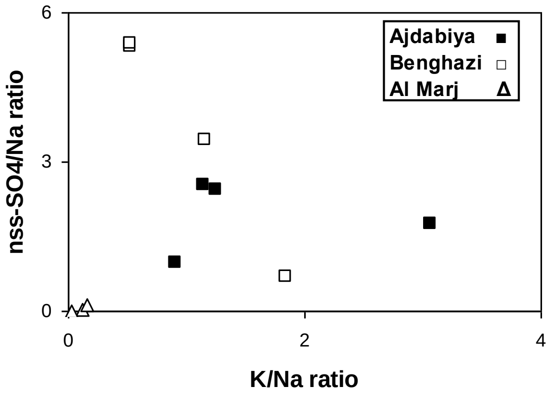

Fig. 3: Variations of K/Na vs. nss-SO_4/Na equivalent ratios of the rainwaters

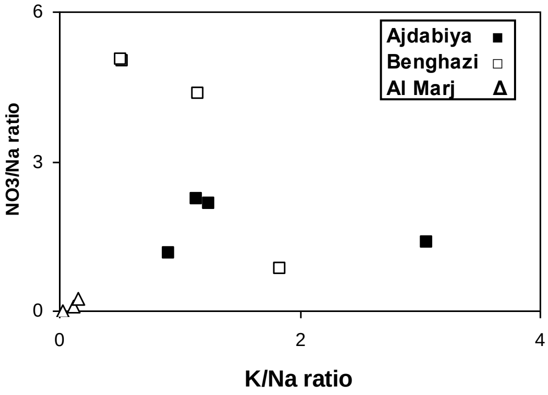

Fig. 4: Variations of K/Na vs. NO_3/Na equivalent ratios of the rainwaters

Rare earth elements

The analyzed elements include the 14 REE and Y. The data of these elements are quoted in table 1. The REE in the studied rainwater samples show significant differences in composition. The contents of total REE are the highest in the rainwater samples from Ajdabiya (1703ppm) and lowest in samples from Al Marj (60.15ppm, Table 3). The studied samples from different locations exhibit an order of magnitude variation in LREE concentrations yet the variations in HREE concentrations are smaller.

Table 3: REE parameters and Y/Ho ratio in the studied samples

REE parameters	Ajdabiya				Benghazi				Al Marj			
	A1	A2	A3	A4	B1	B2	B3	B4	M1	M2	M3	M4
LREE	1676.85	1650.91	1648.71	1664.16	1036.49	370.30	369.06	339.06	75.56	53.45	199.17	198.51
HREE	26.52	31.73	30.06	18.27	50.55	29.01	28.06	18.07	9.98	6.70	25.50	24.81
∑REE	1703.37	1682.64	1678.77	1682.43	1087.04	399.31	397.12	357.13	85.54	60.15	224.67	223.32
LREE/HREE	63.23	52.03	54.85	91.09	20.50	12.76	13.15	18.76	7.57	7.98	7.81	8.00
La/Yb	174.01	125.39	130.13	352.96	38.79	22.79	24.72	37.56	21.80	12.46	17.44	18.62
Y/Ho	54.07	61.80	65.00	74.95	66.37	59.02	63.00	58.29	77.54	55.67	63.57	71.38

In the present study, the REE are normalized to Post-Archean Australian Shale (PAAS) values (Taylor and McLennan, 1985). PAAS-normalized REE patterns of the studied samples are shown in Fig. 5. The rainwater samples collected in Al Marj have flat REE patterns, indicating a shale-like composition, whereas samples from Ajdabiya have the highest enrichment of LREE.

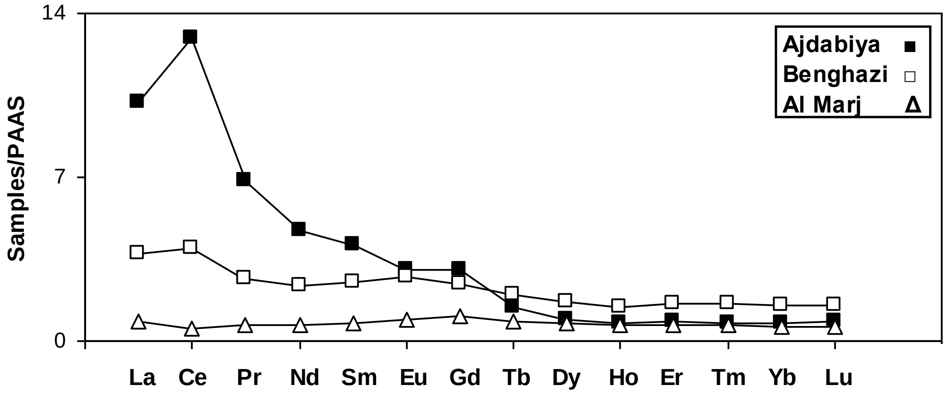

Fig. 5: PAAS normalized REE diagram in the studied samples

Sources

The REE in rainwater are most likely derived from the washout or dissolution of aerosols. Like trace metals such as Cu, Zn, and Pb (Lim and Jickells, 1994; Roy and Negrel, 2001; Honorio *et al.*, 2009), the REE in aerosols may also have three main sources, which are low temperature crustal weathering (crustal sources), a variety of high temperature anthropogenic processes (anthropogenic sources) and sea-salt or sea-spray generation (oceanic sources).

Rainwaters from Benghazi and Ajdabiya all have high concentrations of anthropogenic components such as NO_3 and nss-SO_4 and the same PAAS-normalized REE patterns. This suggests that major ions and REE in rainwaters may originate from the same sources. Anthropogenic sources of the REE to the atmosphere include particles produced during crude oil cracking, combustion of oil and gasoline products, which are highly enriched in the LREE (Olmez and Gordon, 1985, Olmez *et al.*, 1991; Chudaeva *et al.*, 2006; Suzuki *et al.*, 2011; Bai and Wang, 2014). Rainwaters of Ajdabiya and Benghazi have significant enrichment of LREE over HREE. It could be concluded that the enrichment of LREE is due to anthropogenic inputs. Particle/cloud water interactions may also be a control over the fractionation between LREE and HREE in rainwater, but we have not analyzed particulate materials in rainwaters.

Acidity of rainwaters

Adsorption of trace metals on aerosols of various soil components shows strong pH dependence, and the scavenging rate of the REE in aerosols by rainwater is considered to be largely dependent on its pH (Spokes *et al.*, 1994; Herut *et al.*, 2000; Celle-Jeanton *et al.*, 2009; Heimburger *et al.*, 2013). However, rainwaters often have a complex pH history. Cloudwaters can be very acidic because of oxidation of SO_2 and uptakes of H_2SO_4 and HNO_3. During a raining event, the pH of rainwater is often higher at the beginning due to interactions with alkaline dust (Chen *et al.*, 1994; Verma *et al.*, 2000; Chatterjee and Singh, 2012). The pH values measured for rainwaters, therefore, may not reflect the pH condition to which the aerosols were exposed prior to its removal. Our measured pH values do not show significant difference among the different samples. However, the Benghazi and Ajdabiya rainwater samples do have significantly higher NO_3 and SO_4 concentrations and the highest NO_3/Na and nss-SO_4/Na ratios, indicating that these rainwaters have absorbed more H_2SO_4 and HNO_3 during their earlier stages of rain-formation processes.

Y/Ho ratio

Fractionation between Ho and Y in the oceanic basin and during water/rock interaction has intrigued many researchers in recent years (e.g. Kawabe *et al.*, 1991; Zhang *et al.*, 1994; Moller *et al.*, 2003; Iwashita *et al.*, 2011). Y has a similar chemistry as the lanthanides, especially that of Ho, because these two elements have almost the same ionic radius and valences. These two elements behave geochemically similar in most magmatic systems, and hence the Y/Ho ratio is very constant in the lithosphere of the Earth, and even in planetary materials. However, there is much evidence to show that these two elements are significantly fractionated in aqueous systems (Zhang *et al.*, 1994), indicating that Y has a different aqueous chemistry than that of the lanthanides. However, the mechanism that fractionates these two elements has not yet been well documented.

The Y/Ho ratios in the studied rainwaters range from 54 to 77.54, all higher than the average value (Y/Ho=52) of the continental crust and the chondritic ratio (Y/Ho=28), but significantly lower than the average ratio of seawater (Y/Ho=105). I am not aware of any report on the factors controlling the fractionation mechanism of these two elements in rainwater. However, the high Y/Ho ratios in rainwater compared with that of the crust may be inherited from anthropogenic and/or oceanic sources, and may suggest the fractionation between these two elements due to aerosol/rain interactions. If Y/Ho fractionation does take place during aerosol/rain interaction, the particulate-scavenging mechanism suggested by several authors (e.g., Zhang *et al.*, 1994; Moller *et al.*, 2003; Iwashita *et al.*, 2011) may also account for this fractionation in rainwaters. It should be noted that, although mixing of sea spray characterized by high Y/Ho ratios in the studied rainwaters could have resulted in the Y enrichment over Ho, generally, an increase of Y/Ho with increasing La/Yb ratio does not support this interpretation because surface seawaters have a very low La/Yb ratio (Fig. 6). Accordingly, I conclude that the high Y/Ho ratio in rainwaters most likely is the result of anthropogenic input of the REE in addition to the Y/Ho fractionation during the rain-formation processes.

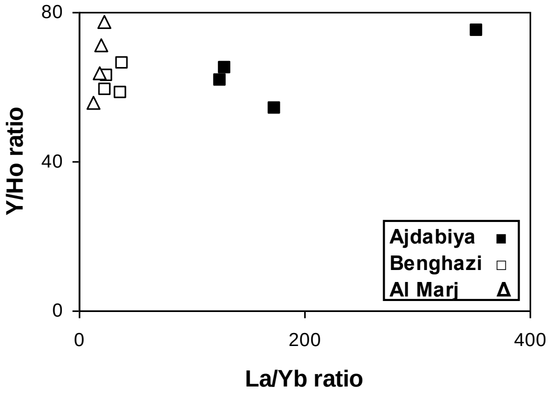

Fig. 6: Variations of La/Yb vs. Y/Ho ratios of studied rainwaters

Conclusions

Rainwater samples collected from Ajdabiya, Benghazi and Al Marj, NE Libya show large differences in major ion compositions. Variations in anion and cation compositions reflect mixing of oceanic, crustal, and anthropogenic sources. Rainwaters of Ajdabiya and Benghazi contain more anthropogenic anions such as NO_3 and SO_4, as well as more cations from crustal sources. Major ions of rainwaters collected over Al Marj are dominated by oceanic sources. The REE compositions in the studied rainwaters are highly variable, and are characterized by various degrees of LREE enrichment, which cannot be accounted for by mixing with oceanic or crustal sources. The largest LREE enrichment is in rainwater of Ajdabiya and Benghazi. When coupled with the highest NO_3/Na and nss-SO_4/Na ratios, it implies that anthropogenic sources of the REE may be enriched in LREE. The rainwater samples collected in Al Marj have flat REE patterns, indicating a shale-like composition. The Y/Ho ratios in the studied rainwaters are all higher than those of the crust, and, in general, increase with increasing LREE enrichment. Physical mixing of crustal and oceanic sources of the REE cannot account for these variations. Although the fractionation of these two elements during the rain/particle reaction cannot be ruled out, we favor the conclusion that the anthropogenic REE input is generally characterized by a high Y/Ho ratio.

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الملخص العربي

تهدف الدراسة إلى معرفة تركيز الايونات الرئيسية والعناصر الارضية النادرة في مياه الامطار من ثلاثة مدن ليبية هي بنغازي واجدابيا والمرج وبالتالي معرفة مصادر هذه العناصر. من خلال الدراسة نجد أن الايونات الرئيسية اتية من ثلاثة مصادر مختلفة هي القارة والمحيط والصناعة. تحتوى مياه الامطار فى بنغازي واجدابيا والمرج تحتوى على نسبة كبيرة من ايونات الكبريتات والنترات. تحتوى مياه الامطار المدروسة على نسب مختلفة من العناصر الارضية النادرة, حيث تحتوى عينات مياه الامطار في بنغازي واجدابيا على نسبة كبيرة من العناصر الارضية النادرة الخفيفة أكثر من عينات المرج. هذه النسبة الكبيرة من العناصر الارضية النادرة الخفيفة في بنغازي واجدابيا يدل على أن مصدرها ليس طبيعي بل صناعي. نسبة الايتيريوم إلى الهولميوم فى كل العينات المدروسة أكبر من متوسط القشرة الارضية ولكن أقل من متوسط مياه البحر. نسبة الايتيريوم إلى الهولميوم بزيادة نسبة العناصر الارضية النادرة الخفيفة.