

## INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF SOIL AND SEDIMENT SAMPLES FROM THE SIWA OASIS, EGYPT

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Instrumental Neutron Activation Analysis (INAA) was used to study geochemical peculiarities of the Siwa Oasis in the Western Desert of Egypt. A total of 35 elements were determined in soil and sediment samples (Na, Mg, Al, Cl, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Br, Rb, Sr, Zr, Sb, I, Cs, Ba, La, Ce, Nd, Eu, Tb, Dy, Tm, Yb, Hf, Ta, Th, and U). For data interpretation Cluster Analysis was applied. Comparison with the available literature data was carried out.

Инструментальный нейтронный активационный анализ использовался для изучения геохимических особенностей оазиса Сива в Западной пустыне Египта. В целом были определены 35 элементов в образцах почв и донных отложений (Na, Mg, Al, Cl, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Br, Rb, Sr, Zr, Sb, I, Cs, Ba, La, Ce, Nd, Eu, Tb, Dy, Tm, Yb, Hf, Ta, Th и U). Для интерпретации данных применялся кластерный анализ. Было проведено сравнение с имеющимися литературными данными.

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### INTRODUCTION

The Siwa Oasis, almost unique on its own, is located about 560 km west of Cairo and 300 km south of the Mediterranean Sea, in the homonymous depression on the Marmarica Plateau [1]. The Siwa Depression is about 82 km long and 21 km wide with a total area of about 1000 km<sup>2</sup>. It lies at about 18 m below the sea level being completely surrounded by the Sahara Desert (Fig. 1).

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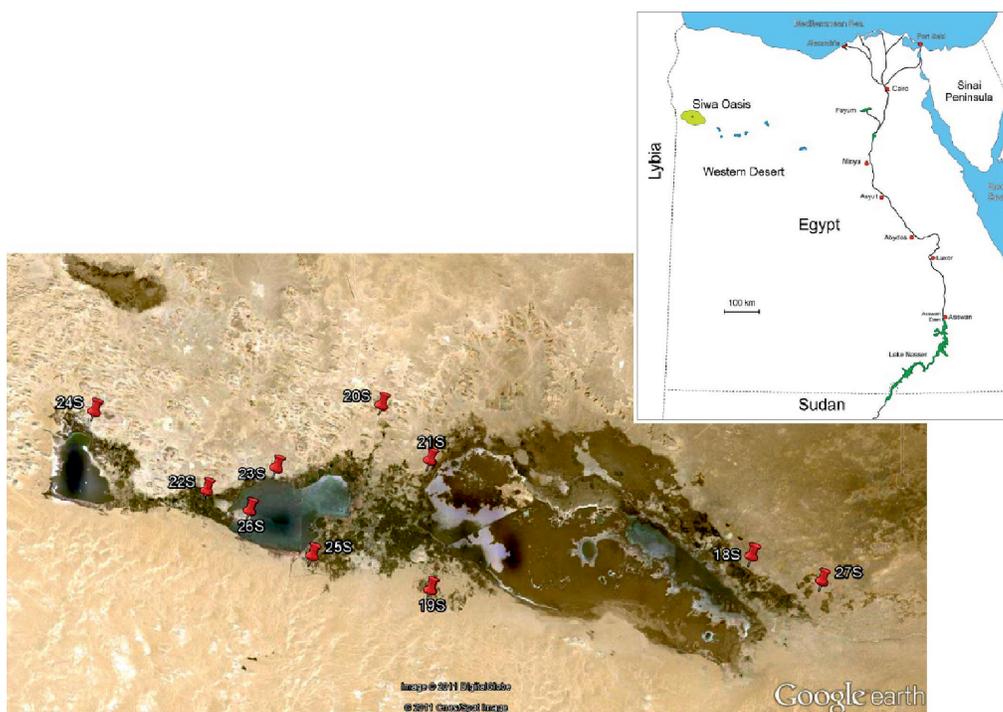


Fig. 1 (color online). Location of the Siwa Oasis in the Western Desert and sampling sites (red pins)

The Marmarica Plateau consists of shallow marine limestone of Miocene age, clastic marine shale, and banded carbonates with marl intercalation [4]. According to Said [1], the Siwa Depression longest axis is oriented in the east-west direction, while five significant lakes (“birket”) and about five smaller basins populate the Siwa Depression floor. All contain highly mineralized waters whose level seasonally fluctuates, some of them drying up exposing significant deposit of evaporates (halite, gyps, etc.).

Although surrounded by desert, the Siwa Oasis, due to the existence of about 200 fresh water springs and more than 1800 artesian springs, which provide the necessary water to irrigate the entire fertile zone of 3800 ha, is inhabited since ancient times [5].

The coexistence of an arid to semiarid climate with the presence of a significant volume of highly mineralized lakes and reservoirs together with more than 2000 sources of fresh water, intensively used for irrigation, create some local pedologic conditions which should be reflected in the soil geochemistry.

A better description of the Siwa Oasis soils and water, including more data regarding the presence of both major and trace elements, is presented in [2]. It was shown that the Siwa Oasis soil is of a loamy and sand-loamy type, a characteristic reflecting the Oasis position in the Sahara Desert. To assess contamination of the environment with heavy metals and other toxic elements, as well as to continue collecting data regarding the geochemistry of the Siwa Oasis, seven soil samples, one sediment sample, and two samples from the salt deposit were collected in summer of 2012 to determine both major and trace elements by multielement instrumental neutron activation analysis. The analysis of the results obtained is presented in this paper.

## MATERIALS AND METHODS

**Samples Collection and Preparation.** A total of 10 samples one kg each were collected randomly [6] from different around the Siwa Oasis beaches within 5 cm from the earth crust. Figure 1 shows their corresponding coordinates and labeled codes. The samples were dried in air and cleaned from roots of plants and other wastes. The samples were then dried in an oven for 6 h at 95 °C, meshed with non-tool and sieved. Finally, the samples were packed in zipped bags.

**Neutron Irradiation and Samples Analysis.** Samples irradiation was performed at the Frank Laboratory of Neutron Physics of the Joint Institute for Nuclear Research (JINR), Dubna, Russian Federation, at the IBR-2 pulsed reactor using epithermal neutrons. Samples of about 100 mg of soil or sediment were wrapped in polyethylene and aluminum foils for short and long-term irradiations, respectively. The analytical scheme used has been described in detail elsewhere [7] and only a brief account is given here. To determine short-lived isotopes, the samples were irradiated for 60 s and measured for 15 min. In case of long-lived isotopes, the samples were irradiated for 4 d, repacked and measured twice using high purity germanium detectors, after 4–5 d and 20–23 d of decay for 30 min and 1.5 h, respectively. Data processing and determination of element concentrations were performed using software developed at FLNP JINR [8]. Element contents were determined on the basis of certified reference materials: the total error in the determination of 37 elements varied between 5 and 30%.

The accuracy of the analyses was checked by simultaneous analysis of the following standard reference materials: 2709 (NIST, Soil, San Joaquin), 2710 (NIST, Montana Soil, Highly Elevated Trace Element Concentrations), 2711 (NIST, Soil, Moderately Elevated Trace Elements Concentrations), 433 (IAEA, Marine Sediment), 1633b (NIST, Constituent Elements in Coal Fly Ash), 1632c (NIST, Trace Elements in Coal).

**Statistic Assay.** For a most comprehensive statistical analysis of our data, in spite of the reduced number of samples, we have used Cluster Analysis (CA) [9]. For a better description of investigation elements with respect to different average rocks, we have also used Sc–La–Th and Co–Hf–Sc ternary diagrams of incompatible elements [10, 11], as well as other 2D plots of incompatible, low soluble elements, such as La vs. Th or Th/Sc vs. Zr/Sc. All calculations were done by means of StatSoft TM Statistica 11, OriginLab TM Origin 7.5, and LibreOffice 4.1.0.

## RESULTS AND DISCUSSION

A total of 35 elements were determined in seven samples of soil, two samples of salty soil (22S and 26S), and one of sediments (21S) (see sampling sites in Fig. 1). Figure 2 shows a typical spectrum for sample 25S as obtained by gamma spectrometer with HPGe detector, while the Table contains the obtained results compared to the content of the same elements in the Upper Continental Crust (UCC) [10], Post Archaean average-Australian Shale (PAAS) [10], North American Shale Composite (NASC) [12], as well as the Average Soil Composition (ASC) as compiled by Vinogradov [13].

**Major Elements.** By INAA we could determine only the content of six elements: Na, Mg, Al, Ca, Ti, and Fe — too few to obtain a complete description of the geochemistry of considered samples, but enough to compare them (see the Table). In this regard, we have

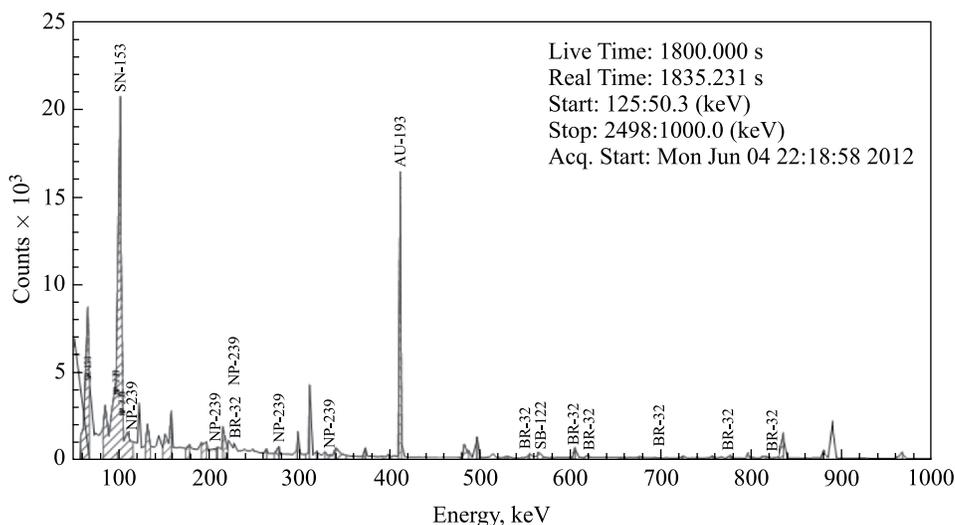


Fig. 2. Typical spectrum for sample 25S as obtained by gamma spectrometer with HPGe detector

noticed the most important variation in the case of Na, Mg, and Ca; this peculiarity allows us to evidence the existence of at least three different subtypes of soil, on the one hand, and to prove the existence of a considerable amount of NaCl, on the other.

The first assertion is sustained by the results obtained by UCC and illustrated in Fig. 3, *a*. Here one can see the existence of at least three clusters, one of them corresponding to

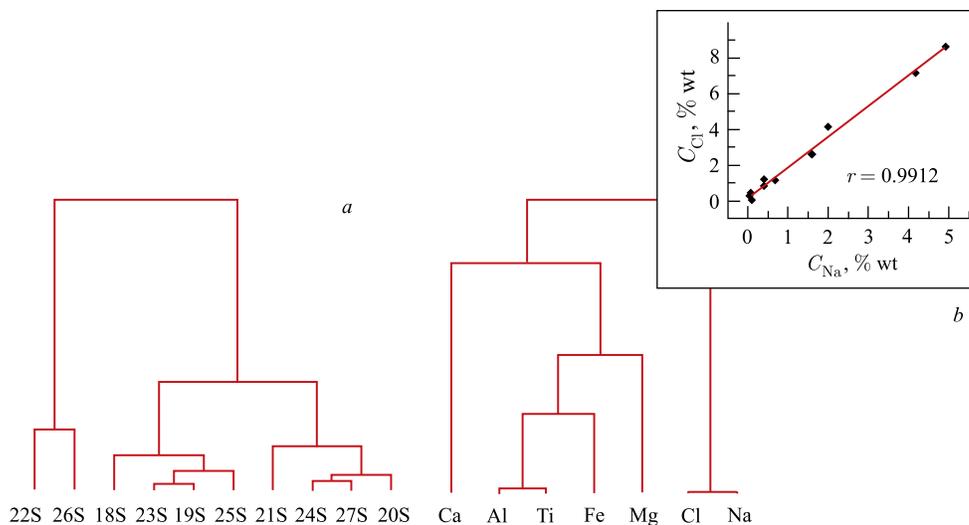


Fig. 3. Two tree diagrams illustrating the existence of three subtypes of soils from the point of view of Na, Mg, Al, Cl, Ti, Ca, and Fe distributions (*a*) and the presence of NaCl in all investigated soil and sediment samples (*b*). The inset illustrates the existing perfect correlation ( $r = 0.9912$  at  $p < 0.01$ ) between sodium and chlorine in all Siwa Oasis samples

**Minimum, maximum, average, and standard deviation (in mg/kg) of the content of all 35 elements in the Siwa Oasis samples together with the content of the same elements in UCC [10], NASC [12], and in average soil [13]**

Element	Min.	Max.	Aver.	St. Dev.	UCC [9]	NASC [11]	Soil [12]
Na	2500	48000	8229	6900	25400	1370	6300
Mg	1000	33900	11376	11318	11600	1334	6300
Al	2530	21500	12715	6758	78300	67000	71300
Cl	2440	85000	14903	13303	150	nd	100
Ca	30800	396000	163313	114355	31500	25900	13700
Sc	0.62	5.5	2.8	1.7	14	30	7
Ti	243	2250	1303	707	3300	4196	4600
V	2.52	39.9	22.35	12.23	140	130	100
Cr	8	35.3	19.61	9.37	69	125	200
Mn	40	730	255	122	770	nd	850
Fe	1480	15300	9031	5145	41700	14100	38000
Co	0.85	6.47	3.9	2.17	17	26	8
Ni	1.69	12.6	8.27	4.13	55	58	40
Zn	3.11	48	16.57	9.74	67	2.7	50
As	2.47	13.1	4.78	1.37	1.6	nd	5
Br	73.6	229	176	50	2.1	70	5
Rl	6.7	27.2	15.73	7.12	110	125	100
Sr	42.2	1760	246	169	350	142	300
Zr	57.6	527	268	127	170	200	300
Sb	0.06	0.23	0.13	0.05	0.2	7.3	0.5
I	7.16	59.6	17.08	9.67	0.5	nd	5
Cs	0.19	1.37	0.59	0.29	3.7	8.5	7
Ba	42.9	153	110	37	570	636	500
La	4.51	14.3	10.38	3.8	30	31	44.5
Ce	7.44	26.7	19.47	7.55	58	10.8	88.2
Nd	4.12	37	19.39	11.42	2.6	27.4	37.3
Eu	0.26	0.83	0.66	0.11	1.1	0.7	1.2
Tb	0.09	0.37	0.27	0.11	0.6	0.5	0.9
Dy	0.28	4.38	1.72	1.22	3.5	nd	5.3
Tm	0.1	0.46	0.29	0.1	0.32	0.41	0.45
Yb	0.28	1.84	1	0.41	2	1.9	3
Hf	1.78	16	7.21	4.41	4	6.3	5
Ta	0.18	0.76	0.38	0.19	1.5	0.41	1
Th	1.19	3.66	2.58	0.88	11	12.3	6
U	0.44	2.42	1.38	0.62	2.8	2.7	1

samples 22S and 26S being completely different from the other two. At a careful analysis of the Table, these two samples confirm an increased content of sodium chloride with respect to the other ones.

Regarding NaCl, it is worth mentioning its presence in all samples as the tree diagrams reproduced in Fig. 3, *b* show; this fact is in good agreement with the literature data [2]. Here, Na and Cl form a single cluster, while the other four elements form another. But at a careful analysis one can notice that the second cluster could be divided into two subclusters, one consisting of Mg, Fe, and Al and the other one, only of Ca. This observation confirms the

presence of calcium carbonate, on the one hand, and of the clay, which is in good agreement with the previous observations regarding the Siwa Oasis soils [2].

Data reproduced in the Table document a significant increase of Cl content, of about two to three orders of magnitude, with respect to other sedimentary average samples such as UCC, NASC, and ASC. According to [2], this peculiarity consist in the high content of table salt present in the water of springs as artesian sources.

A similar enrichment, but with a lower magnitude, was noticed in the case of calcium, whose average content is about four times higher than in UCC or NASC and ten times higher than in ASC. In this case, the source of such a high content of calcium could be attributed to the marine limestone — the main constituent of the Marmarica Plateau [2–4].

This peculiarity could also be an explanation of the reduced content, with respect to UCC of the majority of trace elements, as will be discussed in the next section.

**Trace Elements.** By INAA we have determined the content of 29 trace elements: Sc, Ti, V, Cr, Mn, Co, Ni, Zn, As, Br, Rb, Sr, Zr, Sb, I, Cs, Ba, La, Ce, Nd, Eu, Tb, Dy, Tm, Yb, Hf, Ta, Th, and U (see the Table). As in this study we have investigated both soils and sediments, we have used the UCC contents to normalize our results (see Fig. 4).

Using this approach, we were able to evidence that, with some exception, the content of all considered elements is below UCC. The only remarkable exceptions are I and at a lesser extent As, Zr, and Hf. In the case of I, we have noticed the average content 37 times higher than UCC, but only about four times higher than ASC.

However, in the absence of any industrial activity, it is less probable that As has anthropogenic origin, rather it appears as a natural element. Even its highest content of about 13 mg/kg was recorded once and in the soil sample 26S was highly enriched in salt and

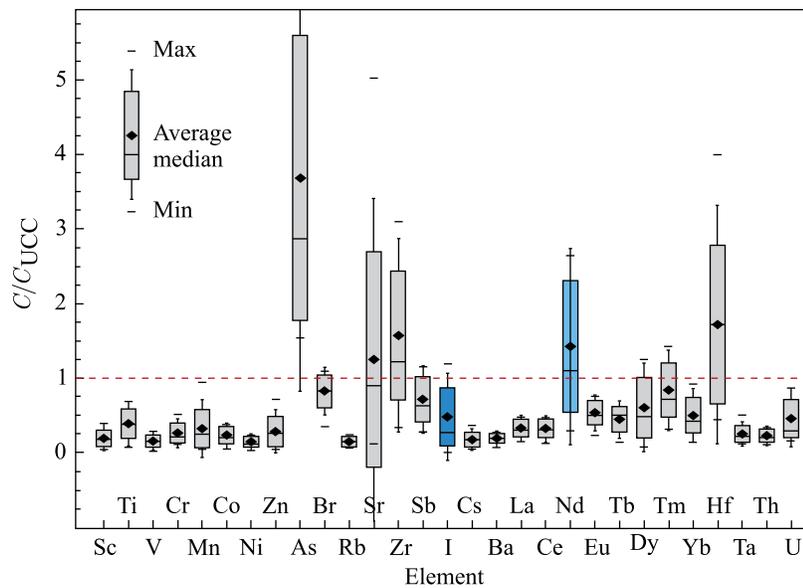


Fig. 4. Box and whiskers diagram of the content of 29 trace elements in ten samples of soil and sediments of the Siwa Oasis. To be more illustrative, all contents are normalized to UCC. Iodine and neodymium contents are divided by 100 and five, respectively

collected in the vicinity of one of the few salted lakes which populate the Oasis (see Fig. 1). Moreover, we have previously noticed the same relative increased content of As for an entire set of soil and sediment samples collected along the Nile River [12], so we could consider that in the case of the Siwa Oasis, As appears as a natural element as well.

Iodine represents another element whose content in almost all Siwa samples is significantly higher than that in UCC or in average soil [13]. Again, we have noticed the same peculiarity in the case of above-mentioned study [14]. Additionally, we have noticed an almost perfect correlation between iodine and sodium ( $r = 0.9819$ ), on the one hand, and between iodine and chlorine ( $r = 0.9926$ ) contents, on the other, for all Siwa samples. By taking into account the distance between the Nile River and the Siwa Oasis, the increased content of iodine seems to be a characteristic for the entire Egypt, assertion of which would need future studies to be confirmed. But, by taking into account the iodine tendency to accumulate in brine, it is quite possible that its presence in all Siwa soils is due to the salt accumulated on the bed of seasonal dry lakes and transported at great distances by wind during dry seasons.

INAA allows one to determine the content of incompatible Sc, Co, Zr, REEs, Hf, and Th whose relative low mobility during sedimentation permits to be used as good indicators of sediments origin as well as the degree of weathering [10, 15–17].

Zirconium and hafnium are two elements whose content is higher than that of corresponding one in UCC. We have also noticed that the average Hf to Zr ratio of 0.027 is very close to UCC value of 0.024, but higher than 0.016, the ASC value. As we have previously observed the same peculiarity for sediments and soils along the Nile River, from Aswan to the Nile Delta [12], we can interpret it as a general characteristic of the investigated area.

In this regard, we have remarked that the Zr/Sc ratio is, in the majority of samples, higher than the corresponding values reported for UCC [9], NASC [12], or PAAS [10] (Fig. 5).

This great dispersion could be explained by a possible coexistence of local sedimentary material, rich in carbonates, with some detrital material transported from the Nile valley, whose sediments showed an increased Zr/Sc ratio [16].

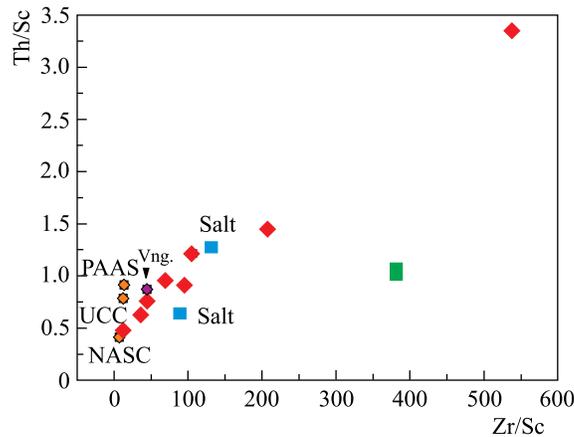


Fig. 5 (color online). The Th/Sc versus Zr/Sc plot of all Siwa Oasis samples. Green square corresponds to 19S sample, rich in organic material, while the purple ones represent the salt rich 22S and 26S samples

The La versus Th diagram [10] reproduced in Fig. 6 shows that all samples form a cluster characterized by an average value of  $4.1 \pm 1.1$ , closer to corresponding values of 2.73, 2.52, and 3.05 reported for UCC, NASC, and PAAS, but significantly lower than 7.4, the value of ASC. These data could sustain the same hypothesis regarding the presence of some Nile valley detrital material of continental origin, most probably from the Nile valley.

Finally, in Fig. 7 we have reproduced two ternary diagrams which illustrate the relative complex origin of Siwa soils and sediments. While in the Sc–Th–La diagram [18] (Fig. 7, a), the points corresponding to all samples form a cluster around the average sedimentary rocks UCC, NASC, as well as PAAS, in the Co–Hf–Th diagram reproduced in Fig. 7, b the same points are spread far away with respect to the average sedimentary rocks. By taking into account that all soil samples are enriched in NaCl whose exact composition was not enough

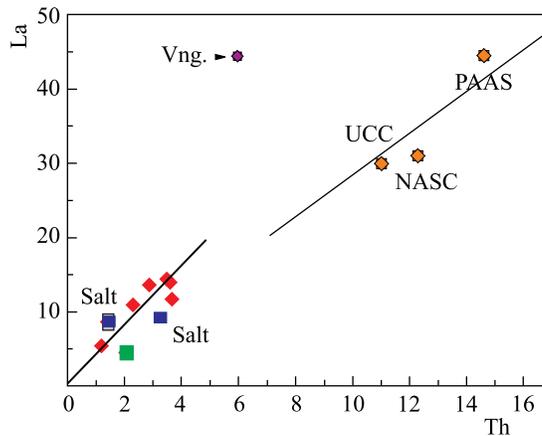


Fig. 6. The La versus Th plot of all Siwa samples. By their average value  $4.1 \pm 1.4$  Siwa soils and sediments seem to be closer to average UCC, NASC, and PASS than to average soil

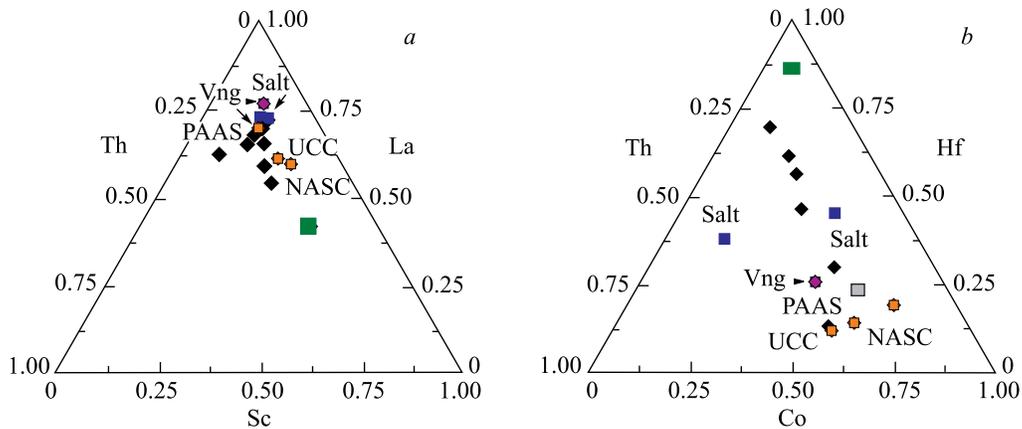


Fig. 7 (color online). Two ternary diagrams illustrating the possible relationship between Siwa soils and sediments and the average sedimentary UCC, NASC, PAAS, as well as ASC

investigated, this fact can possibly influence the relatively significant dispersion of data as illustrated in the diagram. This assertion could be sustained by the position of the points corresponding to the 22S and 26S samples, rich in salt, which also occupy some eccentric positions (see the purple squares in Fig. 7, *b*).

While in the Sc–La–Th diagram (Fig. 7, *a*) all points are more or less grouped around average sedimentary rocks, in the Co–Hf–Th diagram these points are dispersed which could be a consequence of the elevated salt content. In both diagrams, the sample 19S, rich in organic material, occupies different positions, with respect to the other one, most probably due to its increased content of organic matter. It should also be remarked that in both diagrams, ASC appears in the vicinity of average sediments.

## CONCLUSIONS

The content of five major rock forming and 29 trace elements determined by Instrumental Neutron Activation Analysis in 10 samples of soil and sediments collected from the Siwa Oasis evidences for some peculiarities related to its remote location in the Western Desert of Egypt.

In addition to an increased content of sodium chloride, we have noticed a higher amount of iodine, arsenic, zircon, hafnium, and neodymium.

In the case of major elements, Cluster Analysis (CA) evidences for similarities not only within samples but also between elements themselves and allows evidencing the presence of some clay minerals, whose exact nature needs further investigation.

In the case of trace elements, we have noticed a good correlation between chlorine and iodine, signifying a common origin of these elements, obviously originating from the salt contained by the Oasis lakes.

Although the arsenic content was in some samples higher than reported for the average soil, the total absence of any industrial activity enabled us to consider arsenic as a natural occurring element.

The content of other incompatible and low soluble elements, such as Sc, Zr, La, Hf, and Th showed for the majority of soil and sediment samples common traits to continental rocks but also to the Nile sediments.

In view of this, as well as the relatively limited number of studies devoted to the Siwa Oasis, we consider it to be an excellent place for further detailed investigations regarding both soil and sediment geochemistry.

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