

Rare metal mineralization (Zr, U, Th, REE) associated to El Seboah Acidic Peralkaline Rocks, South Western Desert of Egypt: Recovery technique

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Abstract

El Seboah acidic mass represent one of peralkaline volcanic activity phenomena in the South Western Desert of Egypt. The mass covering an area about 0.25 km² and consists of peralkaline granites (slightly and highly altered) intruded in Nubian sandstones and cutted by peralkaline rhyolite dyke which runs in NNE-SSW trend. Petrographical study indicated that, slightly altered peralkaline granite consists of quartz, aegirine, cryptocrystalline silica, potash feldspar perthites and alkali amphibole. The accessories are opaques and zircon while carbonate, hematite and secondary uranium minerals are secondary products. Iron oxides being heterogeneous in intensity and distribution in highly altered peralkaline granite. The original textural characteristics for highly altered peralkaline granite under the ferrugination process obliterated and essential minerals affected by different degrees. Also new mineral formed as subsolidus albite clots, eudialyte mineral and REE composite grains. Peralkaline rhyolite dyke characterized by spherulitic texture, fine - to medium-grained greenish color and composed mainly of radiated aegirine-augite, quartz, anorthoclase and opaques. Extreme enrichments in rare metals such as (Zr, Nb, U and Th, REEs and Y) characterize these peralkaline acidic rocks. The highest concentrations (Zr up to > 1%, 0.1% Nb, 0.5% total REEs, Y up to 0.49%, eU up to 54 ppm and eTh up to 685 ppm). The rare metals bearing minerals are zircon (a single crystals and composite grains), thorite, uranothorite, bastnaesite and amorphous secondary uranium. The chondrite normalized pattern in slightly, highly altered peralkaline granites and peralkaline rhyolite indicated that, higher LREEs enriched pattern, alterations of granites took place under open system and these rocks evolved from magma of lithospheric rifting, Slightly enriched LREEs pattern in peralkaline rhyolite dyke, due to the presence of aegirine-augite mineral. Strong negative $\Delta Eu < 1$ indicated that the nature of residual peralkaline melts: (a) it was extremely rich in fluorine, H₂O, and thus very low viscosity, despite its low temperature (<650°C); (b) it was strong depleted in feldspar - compatible elements, as indicated by strong negative Eu anomalies; and (c) it had abundances of HFSE cations. Redistribution of elements took place by post magmatic hydrothermal solutions. Negative $\Delta Ce < 1$ anomaly, means that the alteration fluids were oxic for altered granite (open system) and slightly oxic for emplaced peralkaline rhyolite. Extraction of $\Sigma REEs + Y$ from sample of highly altered peralkaline granite applied. The leaching efficiency exceeding 80%.

Keywords

Peralkaline Granites, Thorite, Amorphous Secondary Uranium, Compatible Elements, Lithospheric Rifting

1. Introduction

South of Egypt is located in the eastern extension zone of Central African lineament and Trans African lineament (Schandelmeier and Pudlo, 1990). Black *et al.* (1985) and Bowden (1985) reported that, the occurrences of alkaline provinces in North Africa (including Egypt) controlled by major lithosphere weaknesses represented by the Trans African Lineament and the Central African lineament megashears. The REE- mineralized alkaline granites are widespread along these tectonic lineaments (Abdallah, 2006).

The peralkaline granites appear to be part of the anorogenic group of granites (A-type) identified by Loiselle and Wones (1979) and Collins *et al.* (1982). They originated from alkaline magmas, such magmas may have been formed in the upper mantle either by fractional crystallization of basic magma, partial fusion of continental crust, or by contamination with a peralkaline fluid phase and were emplaced as dykes and small stocks.

El-Reedy (1979): studied the anorogenic alkaline rocks in the South Eastern Desert geochronologically and proposed three phases of igneous activity according to the Rb/Sr and K/Ar dates, they are 250-200 Ma, 155-125 Ma, and 110-70 Ma. They were emplaced along a large scale zone and deep-seated Tectonic fractures trending N30°W and N60°E that were supposed to be related the rifting and opening of the Red Sea Garson and Krs (1976) or ENE (Central African lineament) Hashad and El Reedy(1979) Serencits *et al.* (1979) and El Agami and Abdalla (2003).

The peralkaline igneous rocks in South of Egypt are the extreme enrichment in HFSE, notably Zr, Nb, Y and REEs (Abu Elatta, 2007 and Abu Elatta *et al.*, 2013).

El Seboah acidic peralkaline mass locates in the Southwestern Desert of Egypt at the intersection of Lon. 31° 53' 56" E and Lat. 22° 45 '48" N, (Fig. 1a).

The present study deals with petrography of peralkaline rocks in El Seboah area. Throw some lights on their mineralogy and the comparison between slightly altered granite and highly altered one occur in the study area, indicate the role of post magmatic hydrothermal alterations in redistributions and the concentrations of rare metals in these rocks.

2. Materials and Methods

2.1. Field Observations and Spectrometric Measurements

El Seboah granites occur as a small stock extends in WSW-ENE direction, intruded into Nubia sandstones from the most northwest part, and surrounded by Windblown recent sand from other all sides (Fig. 1b). El Seboah granitic magma occurs as isometric mass, which is comparable to alkaline rocks of El Ramly *et al.* (1971). These granites thought to be a ring complex of alkaline syenite (Egyptian geologic Survey and Mining Authority (1981). Peralkaline rhyolite dyke dissects them and three

strike slip faults, one of them running in ENE- WSW direction with right lateral movement while the two other running in NNW-SSE direction with left lateral movement and intensive alterations occur along these faults (Fig. 2a). These granites divided according to the degree of alterations into slightly altered and highly altered one. The slightly altered granite is medium to coarse - grained and brown greenish color while the highly altered one is brick red color, due to the impregnation of microfractures and cleavage planes of minerals by red iron oxides. The alterations processes include silicifications, Fe oxy-hydroxides, sericitizations, carbonatizations and kaolinitizations. It has hardly separates these processes of alterations in the field because the alteration processes are highly superimposed. In addition, hydrothermal pegmatite veins and pockets are developed and are variable in width and length. The peralkaline rhyolitic dyke is greenish color, width 1.5 m, running in NNW-SSE direction with dipping angle 60° toward SW (Fig. 2b).

The equivalent of both uranium (eU) and thorium (eTh) measured in field in ppm by using a portable gamma-ray spectrometer (RS-230). Fifteen samples collected (seven from highly altered granite, four from slightly altered granite and four from peralkaline rhyolite dyke) for different purposes.

2.2. Laboratory Methods

Twelve thin sections of the studied rocks are prepared for the petrographical studies and photomicrographs using a Nikon (optical – pol) polarizing microscope equipped with a full automatic photomicrograph attachment (Microflex AFX – II).

Fifteen representative samples chosen from the studied rocks for chemical analysis in the laboratories of the Nuclear Materials Authority (N M A), for some trace element (Zr, Nb and Y) by X – ray fluorescence method (Philips – PW 1480 X – ray) spectrometer X unique II with automatic sample changer (PW – 1510). The uranium and thorium contents were chemically measured through Arsenazo (III). The results of chemical analyses presented in Table (1). Three samples (the first sample from highly altered granite (sample 4), the second sample from slightly altered granite (sample 11₁) and the third sample from peralkaline rhyolite dyke (sample 10₂)) analyzed for REE in the chemical warefare laboratories by ICP MS Egilant Technologist 7700 serial Japan. The sample 4 contains approximately 0.76% ΣREEs +Y, for that rich in ΣREEs +Y and the more uses and important of rare earth elements in the entire world. Thus, we trials to recovery of pure rare earth elements from that sample, where REEs + Y was analyzed in the different working aqueous phases using the spectrophotometric method (Marczenko, 1986) by using Arsenazo III as complexing agent and the absorbance was measured at 650 nm against proper standard solutions using a Lambada UV/VIS spectrophotometer (Perkin-Elmer, USA). The obtained REEs +Y sulphate leach liquor was then subjected directly to treatment by 80% oxalic acid,

where REEs precipitated as Re-oxalate followed by ignition at 900°C to obtain the RE₂O₃+Y₂O₃ product or by IX recovery of the leaded RE from El Seboah working sample. A proper solution of RE sulphate subjected to Dowex50W-X8 cation exchange resin was used by packing 15 ml wsr in a glass column of 1.5 cm diameter and after saturation, the loaded resin column was eluted using 4 N HCl acid. From the obtained eluate, the RE chloride were precipitated as their oxalates followed by ignition at 900°C

to obtain the RE₂O₃+Y₂O₃ product.

Mineralogical investigation of the heavy minerals and precipitate Rare earth oxides carried out by using ESEM/EDX technique to identify different minerals in the chemical welfare laboratories also.

3. Results and Discussion

3.1. Petrography

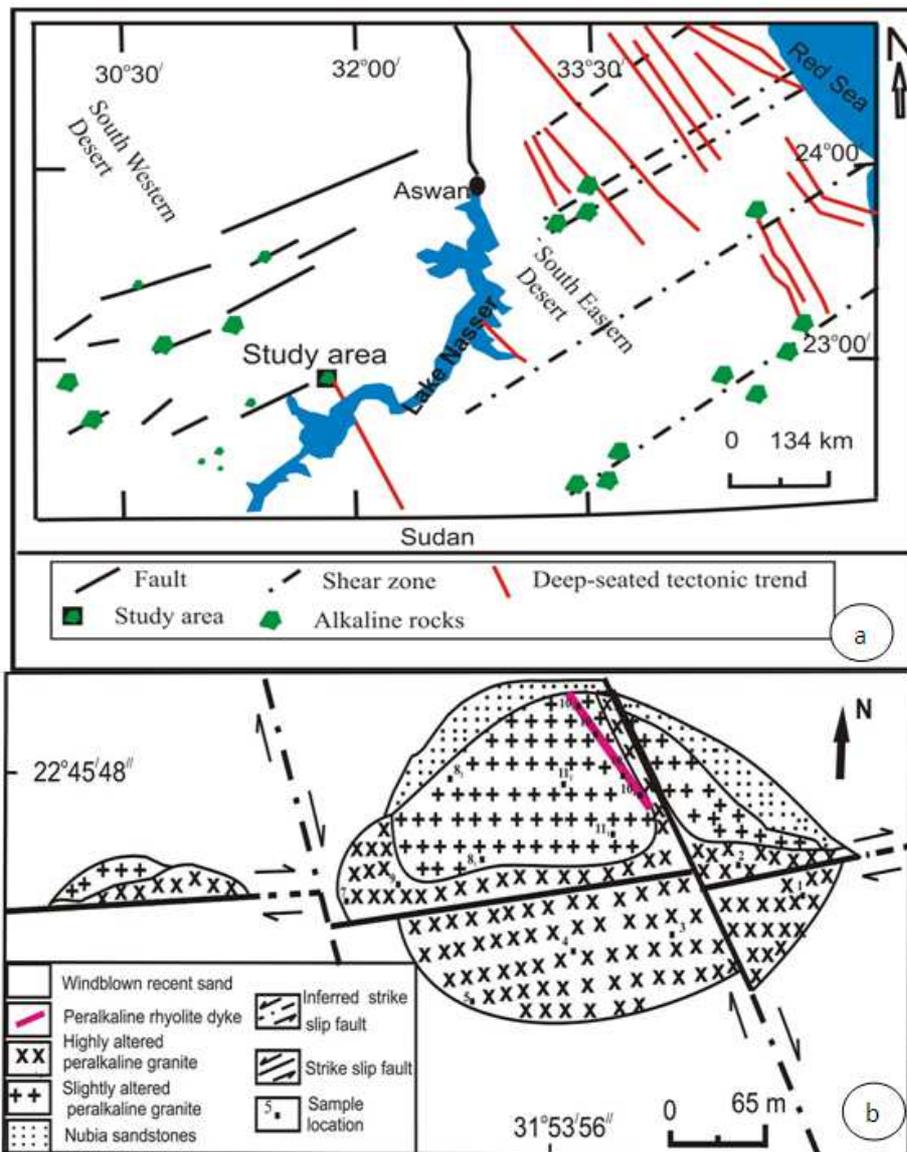


Fig.1. a. Location and b. Geological map of the study area.

The slightly altered peralkaline granite consists of quartz, aegirine, cryptocrystalline silica, potash feldspar perthites and alkali amphibole. The accessories are opaques and zircon while carbonate, hematite and secondary uranium minerals represent the secondary products. Quartz occurs as coarse-grained subhedral to anhedral crystals or as fine to medium intestinal crystals and globular masses (spherulites). Spherulite types develop through devitrification, by helping slower rates of cooling, higher temperatures and more water.

All of these factors permit more extensive nucleation and growth. Spherulite types based on the arrangement of fibers relative to the nucleus are axiolites type or two-axiolitic spherulite banded. Axiolites type where fiber aggregates of crystals radiating from a common plane (McArthur et al., 1998) (Fig. 2c). Two-axiolitic spherulite banded, where the first band from core consists of sheaf-like spherulites nucleating on phenocrystal of aegirine but the second band consists of sheaf-like spherulites nucleating on a circular of

iron oxide grains (Fig. 2d).

Aegirine crystals range in size from medium to long prismatic shapes with columnar or eight sided cross sections, also it occurs as fine to medium acicular habit. Aegirine crystals partially altered to arvedsonite and riebeckite (Fig. 2e) or along the cleavage to iron oxides. Opal occurs mainly as cavity filling or lining in colloform. Tridymite occur as spherulites forming pockets, microveinlets or as medium to coarse anhedral crystals. Potash feldspar perthites occur as subhedral to anhedral crystals of orthoclase perthite or string perthite. They are highly altered to kaoline; also, they occur as fine to medium crystals forming spherulites with quartz. Zircon occurs as subhedral to euhedral crystals as inclusions within aegirine crystals (Fig. 2f). Opaques occur as euhedral to subhedral crystals, in general associated with associated with alkaline minerals and constituent about 7% of the whole rock. Carbonate occurs as patches where secondary uranium mineral occurs as rose-like shape (Fig. 2g).

In highly altered peralkaline granite, although iron oxides being heterogeneous in intensity and distribution in studied thin sections, the original structural characteristics of peralkaline granite under this ferrugination process are slightly preserved. The essential minerals affected by different degrees. Aegirine stained partially or wholly by invading iron oxides and changed nearly too opaque. Perthites also stained by iron oxides by different degrees.

Patches and tectonic wedge of zoelitized occur frequently and partially stained by iron oxides. Some carbonate patches or crystals and veinlets were developed. Fine-grained subsolidus albite clots developed within quartz (Fig. 2h). This indicates a Na-rich fluid associated with ferruginated process. Eudialyte occur as rose-red material colors. It in immersion media are pale yellow in transmitted light have a poorly developed basal cleavage (Fig. 2i). Secondary uranium also found as undefined shape (Fig. 2j).

Peralkaline rhyolite dyke are fine-grained greenish color and composed mainly of radiated or patches aegirine-augite, quartz, potash feldspar (anorthoclase) and opaques. This dyke characterized by spherulitic texture represented by a fan spherulite type (Fig. 2k) of radiated aegirine-augite. Aegirine-augite also occurs as patches contain inclusions of opaques and some patches decomposed to iron oxides. Anorthoclase occurs as euhedral phenocrysts, show ophitic, and subophatic texture with aegirine - augite. They partially altered (Fig. 2l) to kaolinite due to the low temperature alteration, which causes release of potassium and could form kaolinite and opal. Quartz occurs as well defined phenocrysts contain opaques as inclusions or as undefined shape contain mainly aegirine-augite as inclusion. Opaques constituent about 7% of the whole rock and occur as fine irregular crystals distributed through the rock.

3.2. Concentrations of Rare Metals in El Seboah Peralkaline Acidic Rocks

3.2.1. Uranium and Thorium

The equivalent (eU) up to 54 ppm and the equivalent (eTh) up to 685 ppm in highly altered peralkaline granite while eU up to 24 ppm and eTh up to 76 ppm in slightly altered one, but eU up to 32 ppm and eTh up to 84 ppm in the peralkaline rhyolite dyke. Uranium and thorium minerals in the studied area are represented by (a) secondary uranium minerals, (b) uranothorite (Th, U) SiO₄ and (c) thorite (ThSiO₄).

- (a) *Secondary uranium minerals* are rare and occurring as pale yellow radiated acicular or filling the fractures in crystals of the altered granites as reported in petrography study. The most of secondary uranium minerals in the ferruginated peralkaline granite are absorbed on iron oxides and clay minerals as well as they occur in amorphous state, so that it is so difficult to examine by XRD.
- (b) *Uranothorite* usually occurs in the late stage of acidic and alkaline rocks. Also occurs in pegmatitic formations and in aureoles of contact alteration of the host rocks penetrated by the intrusive. Occasionally found in high-temperature hydrothermal formations. These mineral crystallize in tetragonal system and usually occur as impregnated grains. Uranothorite contains 10% to 16% of UO₂. Uranothorite in the study area occur as yellowish brown or orange color crystals in the altered granites of the area and its volcanic rocks as examined ESEM/ EDX (Fig. 3a) and contains U 9.7% and Th 71.7%. It crystallized in cubic system with hexagonal form.
- (c) *Thorite* occurs as black to brownish black grains associated with silica and iron oxides in altered granite and volcanic rocks of the study area. Thorite grain is less often massive.

The value of eU/U ratios (Table 1) are used to deduce whether U was added or leached from rock; where if these ratios are greater than one indicate recent U loss, while the ratios are less than one indicate recent U addition.

The studied alkaline rocks show eU/U ratios ranging among 0.1 to 0.67, indicated addition of uranium and the daughters of addition uranium, which emit gamma ray, not produced yet or the equilibrium state has not yet achieved by the decay series. The Th/U ratio in upper crustal is 3.8 (Taylor and McLennan, 1985). The most Th and U enriched rocks have lower Th/U ratio, in the studied rocks we found all samples have ratios between 3.4 and 0.45 (Table 1), so that they affected by post magmatic processes. The eU/ eTh ratios range from 0.07 to 0.38 (Table 1), so that they are not fertile granites, where eU/ eTh ratio for fertile granites is greater than 0.4 (Hall and Walsh, 1969).

Table (1). Concentrations of some trace elements (ppm) in El Seboah altered peralkaline granites and peralkaline rhyolite dyke as well as their radiometric ratios.

No.	Rock type	Zr	Y	Nb	Eu	eTh	U	Th	eU/eTh	eU/U	eTh/Th	Th/U
1		>10000	4865	1933	33	120	50	109	0.3	0.66	1.1	2.2
2		3623	1071	583	24	200	65	191	0.12	0.36	1	2.9
3		7761	3465	1359	54	241	80	232	0.22	0.67	1	3.4
4	Highly altered peralkaline granite	4995	2626	874	27	128	60	131	0.21	0.45	1	2.2
5		9484	4255	1661	50	685	205	664	0.07	0.25	1	3.2
7		2039	907	356	7	30	66	30	0.23	0.1	1	0.45
9		3179	1422	558	21	76	80	79	0.3	0.26	1	1
	Av.	5180	2601	1046	31	211	87	205	0.20	0.4	1	2.2
8 ₁		2277	1018	398	24	80	77	78	0.3	0.31	1	1
8 ₂	Slightly altered peralkaline granite	2249	1008	393	20	74	75	70	0.3	0.26	1	0.93
11 ₁		2732	1220	477	15	64	55	63	0.23	0.27	1	1.1
11 ₂		3049	1362	534	19	70	55	65	0.3	0.34	1	1.2
	Av.	2577	1152	451	20	72	66	69	0.28	0.3	1	1
10 ₁		6670	2955	1166	27	77	61	74	0.33	0.44	1	1.2
10 ₂	Peralkaline rhyolite	5508	2449	963	30	78	62	82	0.38	0.48	0.95	1.3
10 ₃		7023	3114	1229	28	81	66	86	0.34	0.42	0.94	1.3
10 ₄		5595	2484	978	32	84	65	79	0.38	0.49	1	1.2
	Av.	6199	2751	1084	29	80	64	80	0.36	0.46	0.97	1.25

3.2.2. Zirconium

Zircon crystals, nominally $ZrSiO_4$, are much more complex than their formula implies where zircon structure has two possible sites for cation substitution, a tetragonal (Si) and a triangular dodecahedral site (Zr), (Speer, 1980). The chemistry of zircon is relatively simple; usually ZrO_2 , HfO_2 , and SiO_2 compose more than 99% of the total oxides. The Y, REEs, Th and U elements are predominantly involves replacement of Zr in the larger triangular

dodecahedral sites. Coupled substitution of REEs and PO_4 into the zircon structure ($Y, REE)^{3+} + P^{5+} = Zr^{4+} + Si^{4+}$) (Speer, 1980; Romans et al., 1975) can lead to substantial enrichment in the REEs. Also Hoskin et al. (2000) reported that coupled substitution of REEs and PO_4 into the zircon structure at an interstitial site, where $(Mg, Fe)^{2+} + 3(Y, REE)^{3+} + P^{5+}$ replaced by $3Zr^{4+} + Si^{4+}$ or $(Al, Fe)^{3+} + 4(Y, REE)^{3+} + P^{5+}$ replaced by $4Zr^{4+} + Si^{4+}$.



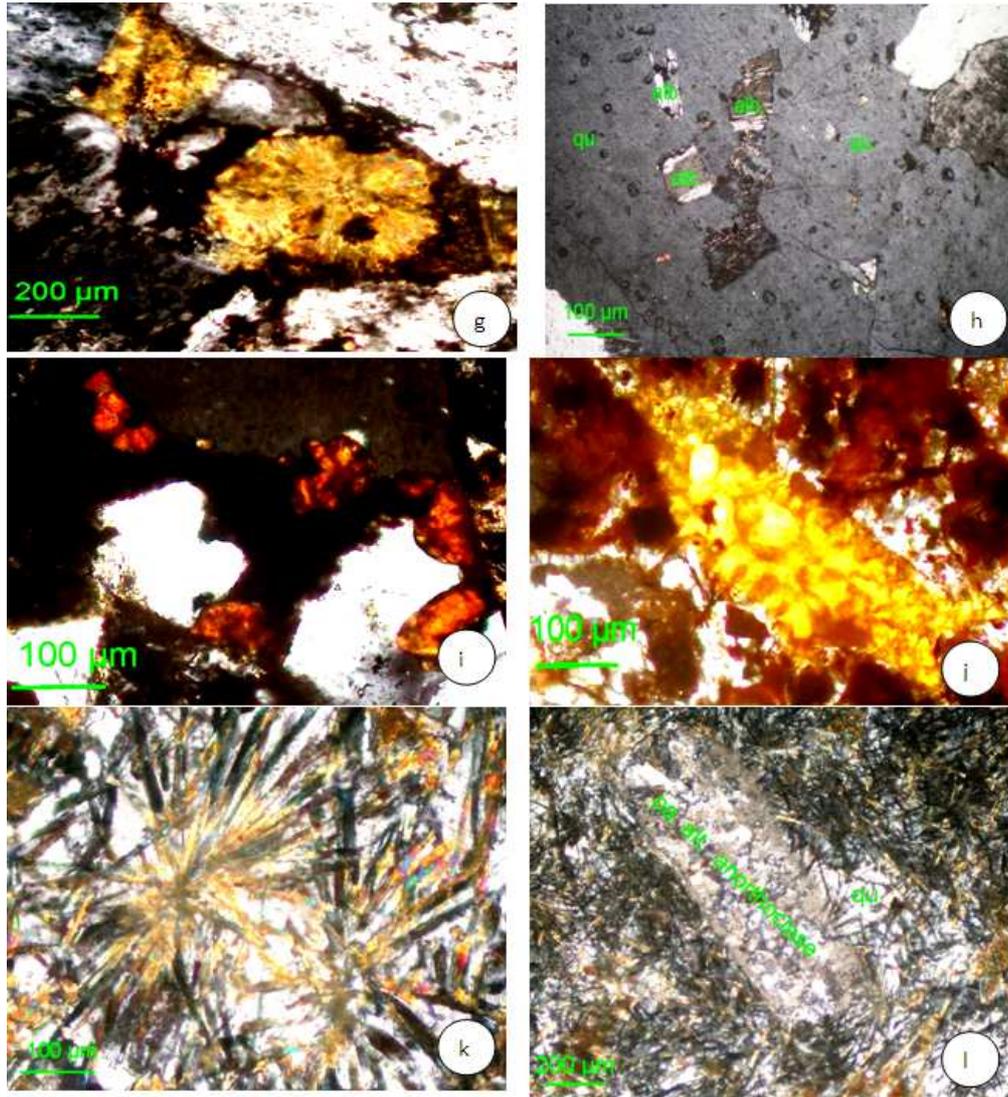


Fig. 2. Field photographs show El Seboah highly and slightly peralkaline altered granites (a) and peralkaline rhyolite dyke cutted slightly peralkaline granite (b). Photomicrographs (c, d, e, f, g, h, i and j) show axiolites , two axiolitic spherulite banded, aegirine altered to riebeckite, euhedral zircon crystal occurs as inclusion within aegirine crystal, secondary uranium mineral occurs as rose-like shape , albite clots were developed within quartz , eudialyte occur as rose-red material color and undefined shape of secondary U in altered peralkaline granites respectively. Photomicrographs (k) and (l) are fan spherulite texture and partial altered anorthoclase in peralkaline rhyolite dyke respectively.

The REE substitution into zircon can be clearly related to the size of the REE ion. The Zr^{4+} , which normally occupies the triangular dodecahedral site, is smaller than the Lu^{3+} ion. Since the ionic radii of the REEs decrease from La^{3+} to Lu^{3+} (lanthanide contraction), the substitution into the zircon lattice becomes progressively easier for the higher atomic number REEs. This effect illustrated in the analyses of zircon and other coexisting phases from igneous rocks (Fujimaki, 1986; Sawka and Chappell, 1988; Heaman et al., 1990). Experimental studies have also demonstrated zircon's preference for the HREEs (Watson, 1980). However, the measured variations in the partition coefficients between the HREEs and the LREEs are much lower than those observed in the natural samples, and the experimental studies suggest that significant partitioning of the LREEs into zircon is possible. It had shown that Ce could be anomalously high in zircon compared to other

measured LREEs (Murali et al., 1983). Heaman et al. (1990) stated that all the elements analysed increase systematically from the least to most magnetic fraction. The most dramatic increase is observed for Sm (83% change) suggesting that the light rare earth elements (LREEs) are preferentially enriched compared to the HREEs in the more magnetic fractions. Assuming that the zircon/magma partition coefficients for the REEs remain constant during crystallization, the preferred interpretation for this change in the REE profile is an external influence (alteration?) on the trace element abundance of the more magnetic zircon crystals. The alternative interpretation is that the LREEs are stronger zoned in this zircon population than the HREEs. Also stated that LREE-enriched, suggests that they underwent metamorphic reworking by replacement recrystallization in the presence of metamorphic fluid. The LREE enrichment is due to the presence of micro scale

LREE-bearing mineral inclusions (such as apatite, monazite or epidote) in the zircons. Also reported that increased trace element substitution, especially the LREEs, during rapid, late-stage crystallization from a mafic magma.

Zirconium concentrations in the studied slightly and highly altered peralkaline granites range from 2249 ppm to 3049 ppm with an average 2577 ppm and from 2039 ppm to more than 1% with an average 5180 ppm respectively. Zr occurs mainly in the form of the zircon mineral and composite grains enriched REEs.

Zircon mineral in the study area occurs as a single crystal range in shape from anhedral to euhedral (Fig. 3b) as indicated by ESEM/ EDX and contains Zr 60.91% and Si 28.54%. In addition, Na 5% and Cl, but the most common occurrence in highly altered granite occurs as aggregates and/or a single contains inclusions (as in petrographical study). Composite grains enriched REEs are consist of fluorapatite and zircon as indicated by ESEM/ EDX (Fig. 3c) and contain F 2.5%, Ca 3%, P 1.5 %, Zr 6 %, and Si 11%. It is enriched LREEs (Fig. 3d) or monazite and zircon as indicated ESEM/ EDX (Fig. 3e) and contains P 8.5 %, Ca 1.5%, Zr 37 %, and Si 6.3%. It is enriched LREEs (Fig. 3f).

Zirconium concentrations in the peralkaline rhyolite dyke range from 5508 ppm to 7023 ppm with an average 6199 ppm. It rarely finds in a form separate minerals in this studied rock, but may find in the crystal structure of alkali mineral.

3.3. REEs

Measured REEs for three samples (11₁, 4 & 10₂) are 5000 ppm, 2100 ppm and 1600 ppm in highly altered peralkaline granite, slightly altered peralkaline granite and fresh peralkaline rhyolite dyke respectively. REEs bearing minerals in these studied rocks are (a) bastnaesite (CeCO₃) (OH, F), (b) composite grains enriched REEs and (c) alkali mineral.

3.2.3.1a. Bastnaesite (CeCO₃) (OH, F)

Bastnaesite mineral is cerium fluoro- carbonate. Cerium is the dominant metal ion, but various rare earth metals substitute for cerium in the formula. Bastnaesite mineralogical divided into three minerals, cerium rich (Ce one), lanthanum rich (La one) and yttrium rich (Y one) forms. Bastnaesite ranges in color from honey-yellow to reddish brown and crystallized in hexagonal system. It shows vitreous luster from transparent to translucent. Bastnaesite found in carbonate and alkaline igneous intrusive rocks as well as hydrothermal sources in metamorphic zones. Bastnaesite mineral is cerium rich one, which identified by EMES/EDX (Fig. 3g) and contains F 2.45%, Si 11% and ΣLREEs 77%. It found in the study area in altered peralkaline granites and enriched in LREEs (Fig. 3h)

3.2.3.1c. Alkali Mineral

Alkali mineral (aegirine-augite) is main source of REEs in El Seboah peralkaline rhyolite dyke, where we not found separate minerals for REEs during mineralogical study. Marks et al. (2004) reported that clinopyroxenes and amphiboles show a continuous development from LREEs-enriched patterns in the calcic minerals via wave-shaped pattern in the Ca–Na minerals towards a more pronounced HREEs enrichment in the most Na-rich minerals and an increase in Zr, Hf, Sn and HREEs concentrations with increasing Na/Ca ratio. These features appear to be related an increasing preference of these elements for the mineral structure as the magmatic evolution proceeds. Calculations of clinopyroxene melt partition coefficients based on a theoretical model after Wood and Blundy (1997) shows that HREEs relative to LREEs are easier incorporated into the crystal structure, as the system becomes more Na–Fe³⁺ rich, which is in qualitative agreement with the observed mineral (aegirine- augite) during petrographical study of this dyke.

3.3. Chondrite- Normalized REEs Pattern

To understand of the physo-chemical conditions prevailed during the late magmatic process and hydrothermal alterations in El Seboah peralkaline acidic rocks, the chondritic values given by Taylor and McLennan (1985) used for the REEs normalization in the present work. In a chondrite, normalized REEs values diagram, samples (11₁, 4 & 10₂) of slightly, highly altered peralkaline granites and peralkaline rhyolite dyke respectively (Fig. 4) are similar and indicated that:

Two samples of altered peralkaline granites are enriched LREEs pattern. (La/Gd = 5.4 and 7.2) means (1) the alteration processes took place under open system (Irber, 1999) and (2) the peralkaline granites are evolved from magma of lithospheric rifting. The peralkaline rhyolite dyke is slightly enriched LREE relative HREE, where La/Gd = 0.66 due to the presence of aegirine-augite mineral.

Three samples show strong negative - ΔEu < 1, Table (3.5). This means the nature of residual peralkaline melt: (1) it was extremely rich in fluorine, H₂O, and thus very low viscosity (Baker and Vaillancourt, 1995), despite its low temperature (<650°C); (2) it was strong depleted in feldspar – compatible elements, as indicated by strong negative Eu anomalies; and (3) it had abundances of HFSE cations. Redistribution of elements took place by the hydrothermal solutions (Bau and Dulski (1999).

Three samples show - ΔCe < 1 anomaly (Table 2), this means that the alteration fluids were oxic (open system) (Abu Elatta, 2007) for altered peralkaline granites and the very low - ΔCe for peralkaline rhyolite dyke indicated, this dyke emplaced in slightly oxic condition.

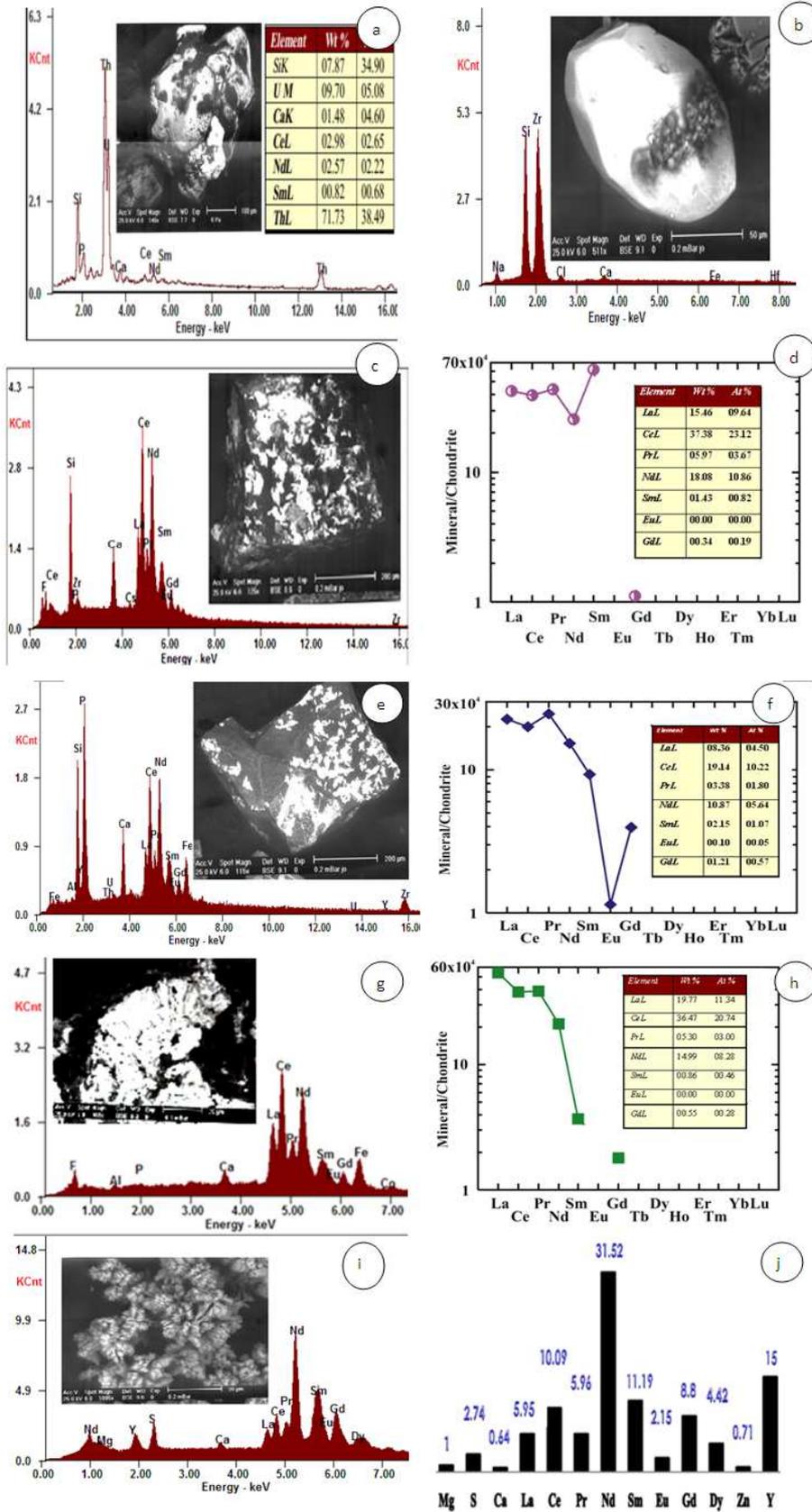


Fig.3. a. ESEM/ EDX of uranothorite, b. ESEM/ EDX of zircon mineral, c. & d. ESEM/ EDX, chondrite normalized LREE pattern and the percentage of REES obtained by EDX for composite grain (zircon and fluorapatite), e. & f. ESEM/ EDX, chondrite normalized LREE pattern and their percentages obtained by EDX for composite grain (zircon and monazite), g. & h. ESEM/ EDX, chondrite normalized LREE pattern and their percentages obtained by EDX for bastnaesite mineral and i. & j. ESEM/ EDX and the percentages of rare earth oxides obtained from EDX for sample 4.

3.4. Extraction of REEs from sample 4

3.4.1. Selection of the Acid Leaching of REEs

The exploratory leaching experiments were performed at different H₂SO₄, HCl concentrations (100, 200, 300, 400 and 500 g/l), and determine ΣREEs (REEs+Y) content in the mixed ore sample approximately 7600 ppm (0.76%) and the weight of ore sample equal 50 g at an S/L ratio of 1/4 and a temperature of room temperature for 0.5 h. The obtained leaching efficiencies of ΣREEs (REEs+Y) show in Table (3). From the obtained results, it is clear that sulphuric acid gives the best leaching efficiency than hydrochloric acid, further we can use sulphuric acid 500g/l which gives 60% leaching efficiency, thus used in all leaching experiments.

Table (2). Concentrations of REEs (ppm) and their ratios in El Seboah peralkaline acidic rocks as well as crustal abundance

Element/sample	Sample 11 ₁	Sample 4	Sample 10 ₂	*Crustal abundance
La	470	980	255	30
Ce	895	1970	495	64
Pr	100	240	55	7.1
Nd	380	930	210	26

Element/sample	Sample 11 ₁	Sample 4	Sample 10 ₂	*Crustal abundance
Sm	60	180	40	35
Eu	9	26	6	0.88
Gd	65	180	385	3.8
Tb	9	31	6	0.64
Dy	50	155	35	3.5
Ho	10	39	7	0.8
Er	29	125	21	2.3
Tm	4	17	3	0.33
Yb	37	80	37	2.2
Lu	3	13	3	0.32
La*	1281	2670	695	
Ce*	935	2059	517	
Pr*	730	1752	401	
Sm*	260	779	173	
Eu*	103	299	69	
Gd*	212	588	1258	
ΔCe = 2Ce*/La*+Pr*	0.93	0.93	0.58	
ΔEu = 2Eu*/Gd*+Sm*	0.42	0.44	0.096	
La/Gd	7.23	5.44	0.66	

La* = La in sample / La in chondrite
 *Crustal abundance = Taylor and McClennan (1985)
 Sample 11₁ = slightly altered peralkaline granite
 Sample 4 = highly altered peralkaline granite
 Sample 10₂ = peralkaline rhyolite dyke

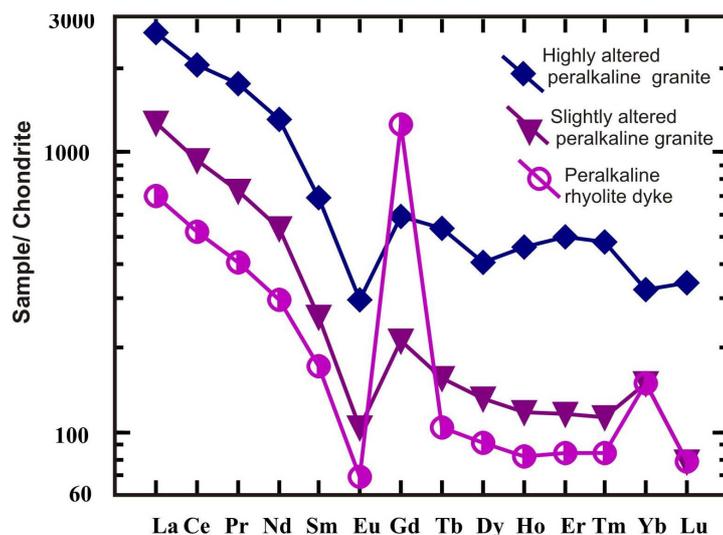


Fig.4. Normalized REEs pattern for El Seboah peralkaline acidic rocks.

Table (3). Effect of acid concentration upon leaching REEs.

Acid Conc., (g/l)	Leaching efficiency of ΣREEs, %	
	H ₂ SO ₄	HCl
100	22	8
200	34	14
300	45	18
400	52	22
500	60	30

3.4.2. Effect of Agitation Time

A series of leaching experiments at varying agitation times ranging from 0.5 to 6h was performed. In these experiments, the other leaching conditions fixed at 500g/l acid at a solid /liquid ratio of 1/4. The leaching temperature fixed at room temperature and an ore sample weight 50 g.

The obtained leaching efficiencies of ΣREEs (REEs+Y) show in Table (4). From the obtained results, it is clear that an agitation time is quite important due to the increasing rate of dissolution of ΣREEs (REEs+Y) from 60 to 70% at 2h, after 2h reaches to 6h the leaching efficiency of ΣREEs (REEs+Y) steady constant to reaches at 68%.

Table (4). Effect of time upon acid leaching of Σ REEs.

Agitation time, h	Leaching efficiency, % Σ REEs
0.5	60
1	69
2	70
4	68
6	68

3.4.3. Effect of Solid/ Liquid Ratio

A series of leaching experiments performed to study the effect of S/L ratio (from 1/4 through 1/8). Other leaching conditions fixed at an acid concentration of 500g/l, 2h agitation time, and using an ore sample ground to -200 mesh size at room temperature. The obtained results tabulated in Table (5). It is clear from that the best solid liquid ratio is 1/4 because after that the results nearest from other, for that we prefer the lowest cost as 1/4.

Table (5). Effect of solid/ liquid ratio.

Solid/Liquid ratio	Leaching efficiency, % Σ REEs
1/4	70
1/5	72
1/6	74
1/8	74

3.4.4. Effect of Leaching Temperature

The work oriented towards increasing the leaching temperature. Thus, another leaching series of experiments performed at temperature room temperature to 200°C with fixed conditions of 500g/l acid concentration for 2h agitation at S/l ratio of 1/4 and results shown in Table (6).

Table (6). Effect of temperature on the leaching efficiency of Σ REEs.

Leaching temperature °C	Leaching efficiency, % Σ REEs
Room Temperature	70
60	75
100	77
150	80
200	80

It is well know that in most chemical reactions, the rate of dissolution of Σ REEs (REEs+Y) increased by increasing temperature. For ores containing difficulty soluble minerals, the improvement in extraction at elevated temperature may be very marked. The increased extraction usually obtained at the expense of higher acid consumption due to increased solubilization of other gangue minerals in the ore. From the obtained results, the leaching efficiencies of Σ REEs (REEs+Y) greatly improved from 70 to 80% by increasing the temperature from room temperature to 150°C respectively and steady constant at 200°C.

From the above studied leaching factors of the working El Seboah ore sample, it can be concluded that the

optimum leaching conditions for dissolving 80% of its rare earth elements content would be summarized as follows:

- i- Sulphuric acid concentration: 500 g/l.
- ii - Agitation time : 2hr.
- iii - Solid-to-liquid ratio (wt. /sulphuric acid vol.) : 1/4.
- iv - Leaching Temperature : (150°C).

3.4.5. Potentialities of Recovery of Rare Earth Elements

3.4.5.1. Direct Precipitation of REEs

For the recovery of rare earth elements from El Seboah sulphuric acid leach liquor, a proper 2-liter leach liquor was prepared from 0.5 Kg of the worked sample using the above-mentioned determined optimum leaching conditions. Chemical analysis of the leached Σ REEs (REEs+Y) in this liquor found to assay 1.52 g/l. For this purpose, the obtained eluate samples in the form of Σ REEs (REEs+Y) collected and subjected to precipitation by oxalic acid followed by filtration and proper washing. The washed precipitate ignited at 900°C to obtain 4.8 g of Σ RE₂O₃ + Y₂O₃. The latter analyzed by ESEM/EDX (Fig. 3i & j).

3.4.5.2. Ion Exchange Recovery of REEs

The cation exchange resin Dowex 50W-X8 was used where a 15 ml wsr volume was packed in 1.5 cm diameter glass column. The theoretical capacity of the working resin is equivalent to 1.7 meq/ml (Bakry, 2013).

a. REEs Adsorption

The prepared 2 liter of leach liquor 1.52 g/l REEs then subjected to adsorption by resin at flow rate of about 0.5 ml/min. The effluent was collected every 100 ml and determine REEs, all results are tabulated in Table (7).

Table (7). REEs in the effluent of the working resin column

Effluent sample no. (100ml)	Effluent REEs, conc., g/l	REEs adsorption efficiency, %
1-14	Nil	100
15	0.19	87.5
16	0.44	71.1
17	0.58	61.8
18	0.97	36.2
19	1.1	27.6
20	1.5	1.3

Total adsorbed REEs \approx 2.6 g

The adsorbed REEs on the resin is 2.6 g/15ml wsr of Dowex 50W-X8 indicating that the capacity amounted to 173.3 g/l of the working wsr.

b. REEs Elution

The loaded resin column was first washed with 2 N HCl to remove all impurities adsorbed, then using 4 N HCl to eluate REEs, the obtained eluate sample (10 ml) as shown in Table (8).

Table (8). REES elution curve of loaded resin column

Eluate sample no. (10 ml)	REEs conc. gl^{-1}
1	10.60
2	17.20
3	20.91
4	26.73
5	82.11
6	25.01
7	23.65
8	18.43
9	14.97
10	9.98
Toal eluted REEs \approx 2.5 g	

C. Preparation of $RE_2O_3 + Y_2O_3$ Product

The obtained eluate samples in the form of rare earth chloride were collected and subjected to precipitation by oxalic acid followed by filtration and proper washing. The washed precipitate was ignited at $900^\circ C$ to obtain 6.3 of $\Sigma RE_2O_3 + Y_2O_3$.

Finally, all the results concerning, the studied procedure of $\Sigma RE_2O_3 + Y_2O_3$ recovery from El Seboah working sample using sulphuric acid are schematically represented in the overall flow sheet shows in (Fig. 5).

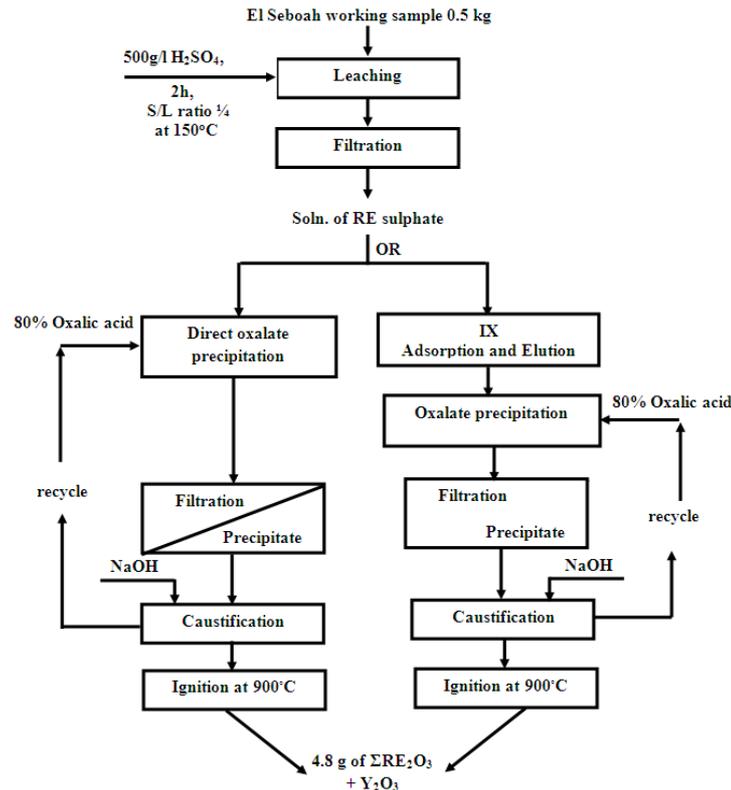


Fig. (5). Proposed flow sheet for $RE_2O_3+Y_2O_3$ recovery from El Seboah highly altered peralkaline granite.

4. Conclusion

El Seboah acidic mass represent one of peralkaline magmatic activity phenomena in the south Western Desert of Egypt. It emplaced along ENE – WSW shear zone in South Egypt (central African shear zone (Schandelmair and Pudlo, 1990)) as Nusab El Balgum mass complex (Abu Elatta et al., 2013) and Gara El Hamara (Abdallah, 2006). El Seboah acidic mass located at intersection Lon. $31^\circ 53' 56''$ E and Lat. $22^\circ 45' 48''$ N, formed after late Cretaceous and consists of peralkaline granites intruded in Nubian sandstones and cutted by peralkaline rhyolite dyke (width 1.5) which runs in NNE-SSW trend with dipping angle 60° toward SW.

Peralkaline granites are dissected by three strike slip faults, one of them running in ENE- WSW direction with right lateral movement, which represents the reactivation of old ENE- WSW trend, while the two other running in

NNW-SSE direction with left lateral movement with intensive alterations occur along these faults. These granites divided according to the degree of alterations into slightly altered and highly altered one. The slightly altered granite is medium to coarse - grained and brown greenish color while the highly altered one is brick red color; due to the impregnation of microfractures and cleavage planes by red iron oxides. The alterations processes include silicification, Fe oxy-hydroxides, sericitization, carbonatization and kaolinitization. It has hardly to separate these processes of alterations in field because the alteration processes are highly superimposed.

Petrographically, slightly altered peralkaline granite consists of quartz, aegirine, cryptocrystalline silica, potash feldspar perthites and alkali amphibole. The accessories are opaques and zircon while carbonate, hematite and secondary uranium minerals represent the secondary products. They characterized by two type of spherulite

textures according to the arrangement of fibers relative to the nucleus. Axiolites type, where fiber aggregates of crystals radiating from a common plane (McArthur *et al.*, 1998) or by two axiolic spherulite banded, where the first band from core consists of sheaf-like spherulites nucleating on phenocrystal of aegirine but, the second band consists of sheaf-like spherulites nucleating on a circular of iron oxide grains.

In highly altered peralkaline granite, although iron oxides being heterogeneous in intensity and distribution in studied thin sections, the original structural characteristics of peralkaline granite under this ferrugination process obliterated and essential minerals were affected by different degrees. Aegirine stained partially or wholly by invading iron oxides and changed nearly too opaque. Perthites also stained by iron oxides by different degrees. Patches and tectonic wedge of zoelitized occur frequently and partially stained by iron oxides. Some carbonate patches or crystals and veinlets were developed. Fine-grained subsolidus albite clots developed within quartz. This indicates a Na-rich fluid associated with ferruginated process. Eudialyte occur as rose-red material colors. It in immersion media are pale yellow in transmitted light have a poorly developed basal cleavage. Secondary uranium also found as undefined shape.

Peralkaline rhyolite dyke are fine - to medium-grained greenish color and composed mainly of radiated aegirine-augite, quartz, potash feldspar (anorthoclase) and opaques. This dyke characterized by spherulitic texture, which formed because of radiating needles of aegirine-augite and represented by a fan spherulite type where, conical arrays of crystal fibers radiating from a single point.

Extreme enrichments in rare metals such as Zr, Nb, U and Th, REEs and Y characterized these peralkaline acidic rocks. The highest concentrations (Zr up to > 1%, 0.5% Nb and 0.5% total REEs, Y up to 0.49%, eU up to 54 ppm and eTh up to 685 ppm). The rare metal bearing minerals are thorite, uranothorite, amorphous secondary uranium, zircon (a single crystals and composite grains), bastnaesite and alkali minerals. The REEs concentrations associated to El Seboah mass are mainly LREEs and they are less than LREEs found in Nusab El Balgum highly altered peralkaline granites (up to 2.6% , Abu Elatta *et al.*, 2013) and different from El Garra El Hamra mass complex which is enriched HREEs (up to 2%, Abdallah, 2006).

The value of eU/U ratios (Table 1) used to deduce whether U added or leached from rocks. The studied peralkaline rocks show eU/U ratios ranging among 0.1 to 0.67, indicated addition of uranium and the daughters of addition uranium, which emit gamma ray, not produced yet or the equilibrium state has not yet achieved by the decay series. The most Th and U contents in the enriched rocks have lower Th/U ratio. In the studied rocks, all samples have ratios between 3.4 and 0.45 (Table 1), which indicated that they affected by post magmatic processes. The eTh/Th ratios are equal one or approximately equal one for all samples, On the other hand eU/ eTh ratios range from 0.07 to 0.38 (Table 1), so that they are not fertile granites, where

eU/ eTh ratio for fertile granites is greater than 0.4 (Hall and Walsh, 1969).

A chondrite, normalized REEs values diagram, samples (11₁, 4, & 10₂) of slightly, highly peralkaline granites & peralkaline rhyolite dyke respectively are similar and indicate that:

- i. The altered peralkaline granites are enriched LREEs pattern, (La/Gd = 5.4 and 7.2). This means that the alteration processes took place under open system and the peralkaline granites evolved from magma of lithospheric rifting. The peralkaline rhyolite dyke is slightly enriched LREE relative HREE, where La/Gd= 0.66 due to the presence of aegirine-augite mineral.
- ii. All the studied samples show strong negative - Δ Eu < 1, Table (2). This means the nature of residual peralkaline melt was extremely rich in fluorine, H₂O, and thus very low viscosity, despite its low temperature (<650°C); and it was strong depleted in feldspar – compatible elements, as indicated by strong negative Eu anomalies. In addition, it had abundances of HFSE cations. Redistribution of elements took place by the hydrothermal solutions.
- iii. All the studied samples show - Δ Ce < 1 anomaly (Table 2), this means that the alteration fluids were oxic (open system) for altered peralkaline granites. The slightly oxic for the peralkaline rhyolite dyke due to that dyke extruded peralkaline granites (not open system).

An alternative procedure for the recovery of the (RE₂O₃+Y₂O₃) from highly altered peralkaline granite has 0.76% Σ REEs +Y successfully applied. In this procedure, a leaching efficiency exceeding 80% for the Σ REEs + Y has achieved using sulphuric acid. The relevant leaching factors have been properly optimized 500g/l of sulphuric acid, 2h agitation time, 1/4 SL ratio at 150°C. From the above all results, which indicated that 80% leachability of Σ REE+Y from 0.5 kg of the El Seboah working sample, we can obtain 4.8 g of (RE₂O₃+Y₂O₃) and the best extraction in this method is Nd₂O₃.

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