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The rare metal deposits of the El Garra El Hamra syenites, South Western Desert, Egypt

ABSTRACT



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Keywords: The El Garra El Hamra complex is a small high-level plug (with associated volcanics) that was emplaced along an El Garra El Hamra ENE-WSW trending dextral strike-slip fault corresponding to the Guinean-Nubian lineament. Owing to continued Guinean-Nubian lineament movement along this fault, the intrusion split into two parts that were displaced horizontally by approximately Peralkaline 580 m. The intrusion consists mainly of syenites (fresh and altered) and granites (altered) that are locally Trans-African shear zone overlain by alkaline trachyte and rhyolite and are hosted by Nubian sandstones. The fresh syenites are composed of perthitic K-feldspars, albite, alkali pyroxenes (aegirine-augite and aegirine) and secondary alkali amphiboles (arfvedsonite and riebeckite). Accessory minerals include opaques, apatite, zircon, xenotime-(Y) and bastnäsite-(Ce). Calcite and hematite are alteration products. Geochemically, the syenites are peralkaline; their CIPW norms classify them as ranging between syenite and quartz syenite in compositions. They were emplaced in a withinplate tectonic setting along the Guinean-Nubian lineament (Kalabsha), close to the extension of the Chephren-Kom Ombo trend (a branch of the Trans-African Shear Zone). They were evolved from a magma compositionally similar to Ocean island basalt (OIB). Numerous dextral and sinistral strike-slip faults cut the intrusion and may have facilitated the circulation of fluids that altered them hydrothermally. These faults developed during or shortly after emplacement of the intrusion or perhaps during subsequent reactivation of the Guinean-Nubian and Trans-African shear zones and were accompanied by dykes that range in compositions from intermediate to acidic composition; most of which strike ENE-WSW. Hydrothermal alteration of the syenites locally led to extreme enrichment in rare metals (e.g. LREE, HREE, Zr, Hf, Th, U, Nb and Be) as the minerals zircon, gittinsite, bastnäsite-(Ce), parisite-(Ce), monazite-(Ce), REE-rich fluorapatite, chevkinite-(Ce), xenotime-(Y), pyrochlore,

columbite-(Fe), Nb-rutile and thorite. Fluorite and barite are important gangue minerals.

1. Introduction

The rare metal province of South Western Egypt is associated with altered peralkaline rocks localized along the eastern extension zone of the Central African lineament and the Trans-African lineament (Shandelmeier and Pudlo, 1990). Black et al. (1985) and Bowden (1985) concluded that the alkaline provinces in North Africa (including that discussed here) are related to major weaknesses in the lithosphere represented by these two megashears and related Riedel faults (Fig. 1a). Hashad and El Reedy (1979), Serencits et al. (1979) and Abu Elatta et al. (2013), concluded that in Egypt emplacement of peralkaline rocks along the ENE-WSW trending of the Guinean-Nubian lineament and the NNW-SSE trending of The Trans-African shear zone were associated with the rifting and the opening of the Atlantic Ocean and the Red Sea. The Trans-African shear zone, which extends from the Niger Delta in Nigeria to the Nile delta in Egypt (Nagy et al., 1976) (Fig. 1a), has been

active since the Jurassic and was particularly active during the Late Mesozoic when peralkaline rocks were interpreted to have been emplaced. The most important branches of the Trans-African shear zone in Egypt are Uweinat-Baharia-Port Said trend, Tarfwai-Qena South Sinai trend and Chephren-Kom Ombo trend (Issawi et al., 2009) (Fig. 1c). In addition, there is another dextral trend related also to the Equatorial Atlantic fractures, which extends from Gulf of Guinea to the Red Sea in South of Egypt (Guiraud et al., 1985, 2000; Fig. 1b). This trend is called the Guinean-Nubian lineaments (Fig. 1b and c) and the most important branch of this lineament in Egypt is Kalabsha fault (Issawi, 1968; Issawi et al., 2009) (Fig. 1c). The Guinean-Nubian lineament has been reactive until very recent times; e.g., in 1983, an earthquake took place along the Kalabsha fault.

El Garra El Hamra (Fig. 2) is one of a small number of peralkaline intrusions that are exposed in Southwestern Egypt. However, it is very likely than others lie hidden beneath late Cretaceous Nubian

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Fig. 1. a-Compiled geologic map (after Nagy et al. (1976), Black et al. (1985), Bowden (1985), Shandelmeier and Pudlo (1990)) showing the distribution of alkaline provinces in North Africa and its relation with major shear zones, b-Major shear zones and apparent Archean and Paleoproterozoic cartons from Guiraud et al. (2000), (G.N.L., Guinean–Nubian lineament; H, Hodna; Hog, Hoggar; N Taoud, North Taoudenni Lineament; Tib, Tibesti; T. L., Tibesti Lineament. Apparent curvature of the Tibesti Lineament is due to projection) and c-Location of the studied area, major trends of the trans-African shear zone and the Guinean Nubian lineament in Egypt (Nagy et al., 1976; Issawi et al., 2009).

sandstones, based on the occurrence of numerous dykes of peralkaline composition, which cut the Nubian sandstone in areas where large intrusions have not been observed (e.g., El Seboah; Abu Elatta et al., 2014).

The El Garra El Hamra complex comprises peralkaline volcanics (peralkaline rhyolite and trachyte) and intrusions (peralkaline granites and syenites) (Issawi, 1968; Fig. 2a). The latter was emplaced in Nubian sandstones. Although the age of the complex is unknown, the host rocks and the occurrence of numerous xenoliths of Nubian sandstones in the complex are constrained to be no older than late Cretaceous age (Hegazy, 2009). Three periods of peralkaline igneous activity have been recognized in Southern Egypt, namely at 250–200 Ma, 155–125 Ma,

and 110–70 Ma (El Reedy, 1979; El Sayed et al., 2014). We, therefore, conclude that El Garra El Hamra was emplaced during the youngest of these periods; the late Cretaceous is defined by the International Commission on Stratigraphy as the time interval 100.5–66 Ma (International Commission on Stratigraphy, 2015).

Locally, the El Carra El Hamra complex hosts high concentrations of rare metals (e.g., Th, U, Zr, Hf and Nb) and is of particular interest because of its concentration of rare earth elements (REE) and the high proportion of heavy REE (HREE) relative to light REE (LREE). The purpose of this article is to present information on the primary nature of the syenites, their hydrothermal alteration and related rare metal mineralization and on the major-and trace element geochemistry of the



Fig. 2. a-Geologic map of El Garra El Hamra (after Issawi (1968)), b and c-Field photographs showing a general view of a dextral ENE-WSW branch (Kalabsha fault) of the Guinean-Nubian lineament that split El Garra El Hamra into two parts.



Fig. 3. El Garra El Hamra structural map.

bulk rocks and minerals. These data are used to make inferences regarding the genesis of the El Garra El Hamra syenites and related mineralization with a special emphasis on the processes that concentrated the REE to potentially economic levels.

2. Geological setting

The El Garra El Hamra complex is a small, high-level plug (with associated volcanics) hosted by Nubian sandstones. It was emplaced along an ENE-WSW trending dextral strike-slip fault of the Guinean-Nubian lineament (Figs. 1c and 2), namely the Kalabsha fault (Issawi, 1968). The El Garra El Hamra complex is also located close to the Chephren-Kom Ombo trend, a branch of the Trans-African shear zone (Issawi et al., 2009). Owing to continued movement along the Kalabsha fault, however, the complex was split into two parts with a horizontal displacement of approximately 580 m (Hegazy, 2009) (Fig. 2). The main intrusive rock types are peralkaline syenites (relatively fresh and hydrothermally altered) and hydrothermally altered granites, which are locally overlain by alkaline trachyte and rhyolite. A number of the NEE-SWW sinistral strike-slip faults of the Chephren-Kom Ombo trend also cut the complex and were cut, in turn, by E-W and N-S trending dextral strike-slip faults (Fig. 3). The faults referred to here and above range in width from 0.5 m to 40 m, containing fault gouge, breccias and they were the focus of ferrugination (Fig. 4a). Dykes varying in width from $20\,\mathrm{cm}$ to 1.5 mare common and most of them were altered and are intermediate to acidic in composition. Veins are frequently observed



Fig. 4. Field photographs showing a-fault breccias cemented by hydrothermal solutions, b-fluorite and barite veins, c-a red jasper vein and d-a mineralized vein.

and represent the filling of tension fractures parallel to faults, especially those trending ENE-WSW. They vary from 5 cm to 50 cm in width and the main vein minerals are barite and fluorite (Fig. 4b). The veins recorded are barite, fluorite (Fig. 4b) and jasper (yellow and red) (Fig. 4c). In addition, some veins contain quartz and high proportions of rare metal mineral (Fig. 4d).

3. Methodology

A total number of 20 thin sections (six from relatively fresh syenite and 14 from hydrothermally altered syenites) were studied petrographically using an optical microscope and a scanning electron microscope attached to a JEOL JXA-8900L electron microprobe equipped with a Si(li) energy dispersive spectrometer (EDS) and five wavelength dispersive spectrometers (Department of Earth and Planetary Sciences, McGill University). All, except the main rock-forming minerals, were identified from compositional data using the EDS. Quantitative analyses were conducted in WDS mode with a beam current of 50 nA, an acceleration voltage of 20 kV and a dwell time of 60 ms. A total of 13 representative samples (four weakly altered and nine strongly altered syenites) were analyzed for their major and trace element bulk rock compositions by Acme Labs., Canada using ICP-OES and ICP-MS methods.

4. Syenites mineralogy

The relatively fresh syenites are medium- to coarse-grained, pinkish grey in color and equigranular. Perthitic K-feldspar, plagioclase, aegirine-augite, aegirine, arfvedsonite and riebeckite are the main rockforming minerals, the main accessory minerals are zircon, bastnäsite-(Ce) and apatite. Perthitic K-feldspar crystals (Fig. 5a) make up ~65% of the rock by volume; the crystals are subhedral to anhedral and commonly display Carlsbad twinning. The exsolution takes the form of albite stringers and blebs, with the stringers generally extending across twin boundaries crystals. Perthites usually interlock with adjoining crystals of perthite or quartz. Subhedral to anhedral plagioclase crystals (albite) form ~7% of the rock by volume and display polysynthetic twinning. Alkali pyroxenes (aegirine-augite and aegirine) comprise ~18% of the rock volume and commonly are interstitial to quartz and K-feldspars. They were partially replaced by alkali amphibole as well as by iron oxides and calcite, especially along their peripheries and cleavages. Inclusions of zircon and bastnäsite are common (Fig. 5b). Arfvedsonite (deep blue to pale violet grey pleochroism) replaced aegirine. Riebeckite is pleochroic (varying shades of blue) and developed on aegirine-augite or aegirine crystals, where the crystal wholly changed into riebeckite (Fig. 5c). Opaques are about 4-5% of the rocks by volume and are associated with mafic minerals, which they partially replaced. Bastnäsite occurs as reddish brown to dark brown crystals (Fig. 5c) that have granular, slender prismatic habit and are distributed over the rocks or as inclusion in aegirine crystals. Zircon occurs as fine prisms enclosed within alkali pyroxene and potash feldspars. Apatite is rare and enclosed within feldspars as single long, thin, slender crystals (Fig. 5d).

The strongly altered syenites and granites are red to brick red in color and are cut by numerous hydrothermal veins up to 10 cm in thickness containing barite, fluorite, or jasper (red and yellow). These veins are parallel to the dominant strike-slip faults. Veins composed of aegirine and K-feldspar ranging in thickness from a few centimetres to 50 cm in thickness are also observed and maybe magmatic in origin. Many perthitic K-feldspar crystals in the syenite and granite have been fractured and, where this was the case, the fractures were filled by hematite (Fig. 6a) and/or fluorite. Aegirine-augite and aegirine were partially or wholly altered to hematite and, as noted above, they were also altered to arfvedsonite and/or riebeckite, which, in turn, were altered to calcite; the calcite occurs in patches and as microveinlets.

Quartz becomes richer and occurs as anhedral crystals or microveinlets containing radioactive minerals and iron oxides (Fig. 6b). Numerous miarolitic cavities were recorded in these rocks (Fig. 6c). Accessory minerals comprise up to 30 vol% of the rock. These minerals are zircon (ZrSiO₄), gittinsite (CaZrSi₂O₇), bastnäsite-(Ce) [(Ce,-La)CO₃F], parisite-(Ce) [Ca(Ce,La)₂ (CO₃)₃F], monazite-(Ce) [Ce,-La,Nd,Th)PO₄], apatite [Ca₅(PO₄)₃(F,OH)] with LREE and Na chevkinite-(Ce) [Ce₄(Ti,Fe²⁺,Fe³⁺)₅(Si₂O₇)O₈], xenotime-(Y) [YPO₄], pyrochlore [(Na,Ca)₂Nb₂O₆,Ca)₂Nb₂O₆(OH,F)], columbite-(Fe)



Fig. 5. Photomicrographs showing a-perthitic orthoclase, b-aegerine crystal contains inclusions of bastnäsite and iron oxides, c-aegirine crystal altered to riebeckite and d-a slender crystal of apatite.

[(Fe,Mn)Nb₂O₆], Nb-rutile, rutile, thorite (ThSiO₄), barite (BaSiO₄), fluorite (CaF₂) and sphalerite [(Zn,Fe)S].

Zircon crystals are different in size and color. These crystals occur as altered large crystals (Fig. 6d), zoned (Fig. 5e) or metamict (Fig. 6f). Some crystals have spongy interiors, indicative of the interaction with or growth from hydrothermal fluids. Other crystals form a cluster (Fig. 7a) and yet others have been brecciated and re-cemented (Fig. 7b). Locally, it is associated with or surrounded by xenotime-(Y) (Fig. 7c), consistent with the fact that the two minerals share the same structure. The association also indicates that xenotime-(Y) crystallization postdated that of zircon. Elsewhere zircon contains numerous inclusions of columbite, feldspar (Fig. 7d), Ta minerals, fluorite (Fig. 7e), xenotime and hematite (Fig. 7f). Gittinsite occurs as fibrous masses (Fig. 8a). It is colorless in thin sections in polarized light and shows first order interference colors under crossed Nicols.

Bastnäsite-(Ce) occurs as subhedral to anhedral orange to reddish brown crystals of variable size. It contains inclusions of fluorite and hematite. Bastnäsite-(Ce) is usually accompanied by parisite-(Ce) and commonly is intergrown with it (Fig. 8b and c). Locally, bastnäsite-(Ce) rims parisite-(Ce) (Fig. 8d) and is rimmed by monazite-(Ce) (Fig. 8e). Monazite-(Ce) is observed in some thin sections as large colorless crystals with good cleavage. In addition, it is found as inclusions in apatite (Fig. 8h). Apatite occurs as yellow, hexagonal crystals (Fig. 8i), which are commonly prismatic and stubby. It also occurs as tabular plates and globular masses. Based on its EDS spectra, apatite contains LREE and Na in addition to Ca and phosphate (Fig. 8h). Chevkinite-(Ce) occurs as dark brown euhedral prismatic crystals and in some cases shows evidence of having replaced earlier quartz (Fig. 8k). Inclusions of bastnäsite-(Ce) are common (Fig. 8k and 1).

Xenotime-(Y) is the principal HREE mineral. It occurs as yellowish brown to greyish bipyramidal (Fig. 9a) or prismatic crystals. As mentioned above, it is commonly associated with zircon.

Pyrochlore is the dominant Nb-Ta mineral and occurs as yellowish brown rounded grains (Fig. 9b), black euhedral crystals (Fig. 9c) or microveinlets (Fig. 9d and e). Columbite, the next most important NbTa mineral, occurs as short black prisms and contains inclusions of barite (Fig. 9f). The niobian rutile mineral occurs as black subhedral to anhedral prismatic crystals (Fig. 10). Commonly, the crystals have been fractured and contain inclusions of hematite (Fig. 10b).

Thorite occurs as black or brown crystals of variable shapes and sizes (Fig. 10c and10d). Some crystals show evidence of radiation damage (Fig. 10c).

Barite occurs as yellowish to blue microveinlets (Fig. 10d and e). It also occurs along the cleavages of arfvedsonite and aegirine (Fig. 10f). Locally, the crystals are skeletal although elsewhere euhedral crystals are observed. Fluorite occurs as violet stringers (Fig. 10g and h) or is disseminated through the rocks (Fig. 10i). Sphalerite is rare and occurs as light to dark-brown euhedral to subhedral crystals (Fig. 10j).

5. Bulk rock geochemistry

5.1. Least altered syenites (fresh)

5.1.1. Major and trace elements

The syenitic rocks of the El Garra complex (Table 1) have SiO_2 contents in the range of 60.31–66.07 wt%. Alumina contents vary from 10.47 to 15.7 wt% and the alkali contents are high (9.14–11.61 wt%). As expected from the high alkali contents, the rocks are also iron-rich (FeOt of 6.77–9.94 wt%) and the MgO (0.09–0.13 wt%) and CaO (0.81–1.54 wt%) contents are low; the FeOt/(FeOt + MgO) ratio is 0.987–0.998 (Table 1). Such compositions are typical of A-type magmas (Whalen et al., 1987). The fresh syenitic samples have CIPW normative aegirine (Table 1), which is consistent with their enrichment in alkalis and the presence of alkali mafic minerals.

The least altered El Garra El Hamra syenites are highly enriched in HFSE (e.g., REE up to 90 ppm, Th up to 103 ppm, Zr up to 2485 ppm and Nb up to 469 ppm). They also have high Ga (40–44 ppm) and Be (7–28 ppm) contents. Of particular importance is the high content of HREE, up to 485 ppm. The chondrite-normalised REE profiles (Fig. 11) are variable and range from those with a distinct fractionation of HREE



Fig. 6. a-Photomicrograph showing cracks in a K-feldspar crystal that filled by iron oxides (under normal light), b-Photomicrograph showing a microveinlet of quartz contains a radioactive mineral (under crossed nicols), c-Photomicrographs showing a miarolitic cavity (under crossed nicols), d-Back-scattered electron image of an altered large crystal of zircon has a pongy interior, e-Photomicrograph showing zoned crystals of zircon (under crossed nicols) and f-Photomicrographs showing metamict zircon (under crossed nicols).

 $[(Gd/Yb)_N=\sim2]$ and LREE enrichment $[(La/Yb)_N=10.87-11.37]$ except sample 4, which shows $(La/Yb)_N=2.49$, indicating this sample is rich in both LREE and HREE. A negative Eu anomaly in studied samples, Eu/Eu $^*=0.53-0.57$ (Table 1) implies fractionation of Cabearing plagioclase.

The Rb content (89–99 ppm) is relatively low, which gives the rocks a high K/Rb ratio (205.6–555.5) relative to the continental crustal average (~240; Shaw, 1968). By contrast, igneous rocks derived mainly from upper mantle materials have K/Rb ratios from 700 to 1500 (Heier, 1973). In agreement with previous studies of A-type igneous rocks, this suggests that the El Garra El Hamra magma originated in the mantle but incorporated a substantial proportion of crustal material. Sr content is also very low (23–56 ppm). Indeed, relative to the primitive mantle, it is the most strongly depleted of the trace elements typically shown on a spidergram (Fig. 12). The strong depletion of both Eu and Sr is most plausibly attributed to fractionation of plagioclase (Figs. 11 and 12). In contrast to Sr, Ba is strongly depleted in samples 2 and 3, weakly depleted in samples 1 and 4. This behavior likely reflects fractionation of K-feldspar (Ba substitutes for K).

5.1.2. Geochemical classification, magma type and tectonic setting

On the Zr/TiO₂ versus SiO₂ diagram (Fig. 13), the syenitic rocks have a composition comparable to the volcanic equivalent of syenite, except sample 4, which lies on contact between syenite and granite field. To some extent, the same conclusion is reached using the R1 versus R2 diagram of De La Roche et al. (1980) (Fig. 14). It should be noted, however, that this diagram depends on elements such as Na, K, and Ca that are easily mobilized during hydrothermal alteration, and, as mentioned earlier, all the rocks that were analyzed had undergone some alteration. Thus, samples plotting outside the fields of syenite, quartz syenite and alkali granite or with anomalously high values of R1 may not properly represent their unaltered equivalents. On the ferroan/ magnesian discrimination diagram of Frost et al. (2001), the rocks are all classified as ferroan types (Fig. 15). Batchelor and Bowden (1985) classify the El Garra El Hamra rocks as anorogenic, despite the questionable applicability of this diagram for the reasons given above. Based on the behavior of Hf, Rb and Ta (Harris et al., 1986), they are formed in a within-plate setting (Fig. 16), within the volcanic zone of the Guinean-Nubian lineament (Kalabsha fault) based on the Ta/Yb versus



Fig. 7. a-Photomicrograph showing a cluster of zircon (under crossed nicols), b-Back-scattered electron image of a brecciated zircon, c-Back-scattered electron image showing an association of zircon and xenotime, d-Back-scattered electron image of zircon contains inclusions of columbite, e-Back-scattered electron image of zircon contains inclusions of tantalite and fluorite and f-Back-scattered electron image of zircon contains inclusions of xenotime and hematite.

Th/Yb diagram of Schandl and Gorton (2002; Fig. 17). The same conclusion is reached from the concentrations of TiO₂, Zr and Hf using the criteria of Müller et al. (1992) that rocks containing 1.5 wt% TiO₂, > 350 ppm Zr and > 10 ppm Hf are formed in a within-plate environment. By comparison, the least altered El Garra El Hamra intrusive rocks contain 0.53–0.78 wt%TiO₂, 569–2835 ppm Zr and 14–57 ppm Hf clearly reflecting 'within-plate' tectonic setting.

5.2. Hydrothermally altered syenites

5.2.1. Major elements

The hydrothermally altered intrusive rocks of El Garra El Hamra (Table 1) show distinct compositional variations from their least altered equivalents, which provide insights into the mineralogical changes accompanying alteration. The change in mineral compositions and in elements during hydrothermal alteration of El Garra El Hamra syenite is due to acid-basic interaction of hydrothermal fluids and their general evolution as they cool through time from an early alkaline to an acidic and then to a late alkaline substage (Korzhinskii, 1953; Zharikov, 1976). The hydrothermal process involves a mass balance change

because of input/loss of acid (SiO₂, F, Cl, SO₃, CO₂, etc.) and alkaline/ basic (K₂O, Na₂O, CaO, MgO, etc.) components. The acidic metasomatic rocks (or the products of acid leaching) show common enrichment with acid components and depletion of alkalis and alkali earth relative to the initial rocks. Alkaline and basic metasomatism produces the opposite mass exchange. Each of the metasomatic families has been related to specific T-pH fields (Zharikov et al., 2006). Moreover, the metasomatic families can be divided into two general groups, namely: those with and those without quartz (acidic and neutral-alkaline) (Zharikov et al., 2006).

On the diagram of Zr/TiO₂ versus SiO₂ (Fig. 13), the altered syenitic rocks range in composition from phonolite (silica-deficient) to trachyte (intermediate in silica) and peralkaline rhyolite (pantellerite and comendite, which are silica-oversaturated, and rich in total alkalis). In Fig. 18, we apply Q-P diagram of Debon and LeFort (1988) that relates changes in SiO₂, Na₂O, K₂O and CaO contents to changes in the quartz content (Q parameter) and K-feldspar and plagioclase contents (P parameter) during alteration. From this diagram, it is evident that the altered rocks experienced appreciable leaching of silica and a modest addition of plagioclase (Fig. 18). This diagram helps to study the effects



Fig. 8. a-Back-scattered electron image showing an association of gittinsite and xenotime, b-Photomicrograph showing an association of bastnäsite and parisite (under normal light), c-Back-scattered electron image showing the same association of bastnäsite and parisite in Fig. 8b, d-Back-scattered electron image of parisite rimed by bastnäsite, e-Back-scattered electron image of bastnäsite rimed by monazite, f-Photomicrograph showing a large crystal of monazite (under crossed nicols), g-Back-scattered electron image of monazite, h-Back-scattered electron image of monazite occurs as an inclusion in apatite which contains LRRE&Na, i-Photomicrograph showing the cracked crystal of apatite (under normal light), j-Back-scattered electron image of apatite contains inclusions of monazite and hematite, k-Photomicrograph showing subhedral to anhedral crystals of chevkinite contain inclusions of bastnäsite (under normal light) and l-Back-scattered electron image of chevkinite contains bastnäsite as inclusions.

of the secondary processes on the major element compositions of the rocks. The compositional trends indicate two stages of post-magmatic and hydrothermal alteration evolution. The variations of the K-feld-spar/albite (P-parameter) versus quartz contents (Q parameter) show that the first stage of alteration (the horizontal arrow) (Cuney and Kyser, 2008) includes, at lower temperatures, the K-feldspars will separate from the albite in a process called exsolution. This process takes place at constant quartz content, followed by the second stage (the vertical arrow), where exsolution process is accompanied by silicification leading to quartz-oversaturated compositions (positive Q values). More specifically, silicification led to the formation of the silicified syenites, which are generally, enriched in rare metals (Nb, Ta, Th, U, Zr, Hf and REE).

To make a comparison between fresh and hydrothermally altered syenites in major oxides, we used MacLean's (1990) method of calculating mass change for hydrothermally altered syenites (Table 2). The

hydrothermally altered syenites are enriched in SiO₂, FeOt, K₂O, CaO, slightly in P_2O_5 and TiO₂ as well as depleted in Na₂O, with no significant differences in MgO and MnO relative to fresh syenites (Fig. 19a).

5.2.2. Trace elements

The alteration also leads to the modification of trace elements, where hydrothermal fluids, led to a significant enrichment in rare metals (e.g., REE up to 34,939 ppm, Th up to 5686 ppm, U up to 197 ppm, Zr up to 40,741 ppm, Hf up to 952 ppm, Nb up to 3552 ppm and Ta up to 429 ppm). As for REE abundances, LREE are high up to 31,925 ppm, HREE up to 9549 ppm. This fact is obvious, using MacLean's (1990) method to make a comparison with fresh syenites (Table 2) and Fig. 19b. Hydrothermally altered syenites show a strong enrichment in LREE, HREE, Zr, Nb, Th, Hf, with a significant enrichment in U and Be. In addition, they show an increase in Ba. The shapes



Fig. 8. (continued)

of the chondrite-normalised REE profiles (Fig. 20) are variable and range from those that show unfractionated HERE where $(Gd/Yb)_N$ ratios (0.61–0.75) with enrichment in LREE or HREE where $(La/Yb)_N$ ratios range from 1.14 to 41.62. $(La/Sm)_N$ ratios (0.69–15.38) indicate unfractionated to fractionated LREE. Chondrite-normalised patterns show negative Eu anomaly (Eu/Eu^{*} = 0.43–0.49). Additionally, slightly positive Ce anomalies in samples 5 and 8, and a strongly positive anomaly in sample 13.

The hydrothermally altered syenites of El Garra El Hamra either plot outside of the fields for anorogenic syenites (Fig. 14) or show a significant dispersion on the diagram of Schandl and Gorton (2002) using the trace elements generally considered to be immobile during the alteration processes (Fig. 17). In addition, we note no change using the trace elements that are immobile during alteration processes (Fig. 16).

6. Mineral chemistry

Electron microprobe analyses have been carried out for some investigated minerals (bastnäsite, monazite, zircon, xenotime and Nbrutile) in El Garra El Hamra hydrothermally altered syenites.

Bastnäsite (19 crystals) (Table 3) is characterized by a high Ce_2O_3 contents (mean 33.51 wt%), followed by La_2O_3 (mean 20.89 wt%), Nd_2O_3 (mean 10.62 wt%) and Pr_2O_3 (mean 3.53 wt%).

Accordingly, it is bastnäsite-(Ce). Unlike bastnäsite in many other deposits, the El Garra El Hamra bastnäsite also contains elevated concentrations of Gd_2O_3 (mean 1.43 wt%), Dy_2O_3 (mean 0.14 wt%) and Y_2O_3 (mean 0.69 wt%). Indeed, the mean Σ HREO content is 1.98 wt%. The average chondrite-normalised pattern (Fig. 21a) shows a pronounced negative Eu-anomaly (mean Eu/Eu^{*} = 0.11) and a significant negative Ce anomaly (mean Ce/Ce^{*} = 0.81).

Monazite (5 crystals) (Table 3) also contains Ce₂O₃ as its principal REE oxide (mean 33.26 wt%) followed by La₂O₃ (mean 21.45 wt %),Nd₂O₃ (mean 8.83 wt%), and Pr₂O₃ (mean 3.09 wt%) classifying it as monazite-(Ce). Like bastnäsite-(Ce), it also contains significant Gd₂O₃ (mean 0.10 wt%) and Y₂O₃ (mean 0.45 wt%). However, the mean Σ HREO content (0.55 wt%) is significantly lower. As in the case of bastnäsite, the chondrite-normalised pattern of average monazite-(Ce) (Fig. 21b) has a pronounced negative Eu-anomaly (mean Eu/Eu^{*} = 0.31). in addition, a positive Pr anomaly.

Data for 14 xenotime crystals (Table 4) indicate that the mineral is dominated by Y_2O_3 (mean 40.14 wt%). The next most important REE oxide is Dy_2O_3 (mean 7.085 wt%) followed by Er_2O_3 (mean 5.04 wt%), Gd_2O_3 (mean 3. 88 wt%) and Yb_2O_3 (mean 3.342 wt%). The average chondrite-normalised REE profile pattern for xenotime-(Y) is characterized by a very strong negative Eu anomaly (mean Eu/Eu^{*} = 0.02) and a relatively flat distribution of the HREE (Fig. 22a).



Fig. 9. a-Photomicrograph showing xenotime crystals (under crossed nicols), b-Back-scattered electron image of pyrochlore grains, c-Photomicrograph showing euhedral crystals of pyrochlore (under normal light), d-Photomicrograph showing a pyrochlore microveinlet, e-Back-scattered electron image of a pyrochlore microveinlet and f-Back-scattered electron image of columbite crystals contain inclusions of barite.

Zircon (6 crystals and 12 spots) (Table 4) has an unusually high content of Σ REO (mean 7.84 wt% with 4.31 wt% Y₂O₃). The chondritenormalised REE pattern for average zircon (Fig. 22b) has a pronounced negative Eu-anomaly (mean Eu/Eu^{*} = 0.33). The main mechanism for the incorporation of REE in zircon is commonly assumed to be through a coupled substitution, in which (Y + REE)³⁺ + P⁵⁺ = Zr⁴⁺ + Si⁴⁺, maintaining charge balance (Hoskin et al., 2000; Finch et al., 2001; Hoskin and Schaltegger, 2003). Moreover, oxidized hydrothermal solutions cause the positive Tb anomaly (Fig. 25b), where these solutions oxidized Tb³⁺ to Tb⁴⁺ that substitutes Zr⁴⁺, Hf⁴⁺ and Th⁴⁺ (Hansen et al., 1996).

Data for Nb-rutile (six crystals) indicate that on average it contains 7.37 wt% Nb_2O_3 and 0.25 wt% Σ REO, dominantly HREE (Table 4). The chondrite-normalised pattern for average Nb-rutile crystals (Fig. 22c) displays pronounced positive Ce and Tb anomalies; this mineral was formed from oxidized hydrothermal solutions.

7. Petrogenesis

El Garra El Hamra fresh syenites belong to perakaline rocks. Crustal

contaminations in these rocks will be reflected in the geochemistry of trace elements. Scarrow et al. (2009) mentioned that melts derived from the mantle with little crustal contamination are reflected by their mantle like Th/U ratio ~4, low Cs (< 5 ppm) and high Rb/Cs ratio (> 40). In the present geochemical data, El Garra El Hamra fresh syenites have low Cs concentrations (0.7-1.6 ppm) and high Rb/Cs ratios (74.17–242.68) reflecting mantle origin. Moreover, Zhang et al. (2008) mentioned that low Th/Ce ratios and lack of negative Eu anomalies suggest that crustal contamination does not play a significant role in the modification of magmas, whereas the continental crust has relatively high Th/Ce ratios (~0.15) and negative Eu anomalies (Taylor and McLennan, 1995). Additionally, mantle-derived magmas have low Th/ Ce ratios (0.02-0.05, Sun and McDonough, 1989). In the present work, negative Eu anomalies in studied peralkaline syenites as well as markedly low Th/Ce ratio (0.08, 0.09 and 0.14) in samples1, 2 and 3, respectively and its value of 0.42 in sample 4, reflect that crustal contamination had an effect on the magma modification in samples of 1, 2 and 3 but a higher effect in sample4. The same result also was obtained from the Zr versus Zr/Nb discrimination diagram (Fig. 23), in addition to a higher effect of the fractional crystallization on sample 4



Fig. 10. a-Back-scattered electron image of Nb-rutile, b-Back-scattered electron image of rutile contains inclusions of hematite, c & d-Back-scattered electron images of thorite e-Photomicrograph showing a microveinlet of barite (under normal light), f-Back-scattered electron image of the same microveinlet of barite in (e), g-Back-scattered electron image of barite crystals occur along cleavage of the aegirine and/or arfvedsonite, h-Photomicrograph showing a network of the fluorite mineral (under normal light), i-Photomicrograph showing crystals of fluorite (under normal light) and j-Back-scattered electron image of an euhedral sphalerite crystal.

Table 1

Chemica	l analyses	for El	Garra	El Hamra	fresh and	hydrothermall	y altered syen	ites.
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Rock unit Fresh syenites Hydrothermally altered syen				ed syenites									
Sample	1	2	3	4	5	6	7	8	9	10	11	12	13
SiO ₂	61.14	60.31	60.51	66.07	75.02	69.54	69.94	58.34	65.66	65.42	62.76	67.96	75.1
Al_2O_3	15.7	13.71	13.87	10.46	6.34	6.09	7.19	6.95	4.82	10.03	5.93	7.45	3.07
Fe ₂ O ₃	6.77	9.8	9.72	9.94	8.58	8.58	8.09	20.11	13.5	11.03	10.82	11.25	6.71
MgO	0.11	0.13	0.12	0.09	0.03	0.06	0.07	0.05	0.04	0.06	0.03	0.02	0.05
CaO	1.13	1.54	1.42	0.81	1.86	0.36	2.62	0.9	0.93	0.36	6.37	1.3	0.27
Na ₂ O	6.12	6.81	6.82	4.93	2.03	1.54	1.13	4.93	2.59	3.63	1.69	0.75	0.11
K ₂ O	5.49	4.55	4.59	4.21	2.43	4.52	4.26	5.45	3.88	6.44	4.32	6.44	2.12
TiO ₂	0.53	0.62	0.78	1.01	0.52	0.23	0.78	0.43	0.38	0.45	1.88	1.65	1.18
P_2O_3	0.2	0.17	0.16	0.06	0.1	0.18	1.12	0.06	0.83	0.1	0.37	0.25	0.82
MnO	0.2	0.18	0.17	0.09	0.02	0.04	0.02	0.08	0.06	0.04	0.05	0.04	0.08
L.O.I	2.3	1.9	1.5	1.4	2.2	2.4	2.7	1.8	2.6	1.6	3.7	1.7	2.2
Total	99.68	99.69	99.67	99.08	99.05	93.55	97.86	99.11	95.71	99.3	97.94	98.84	90.75
CIPW													
Qz	3.8	4.53	4.53	23	-	-	-	-	-	-	-	-	-
Or	32.44	26.89	27.13	24.88	-	-	-	-	-	-	-	-	-
Ab	50.19	45.19	45.79	30.36	-	-	-	-	-	-	-	-	-
An	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
С	0.0	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-
Ac	1.4	10.69	10.5	10	-	-	-	-	-	-	-	-	-
Di	0.59	0.67	0.65	0.36	-	-	-	-	-	-	-	-	-
Wo	1.09	1.75	1.3	0.0	-	-	-	-	-	-	-	-	-
Hy	0.0	0.0	0.0	0.09	-	-	-	-	-	-	-	-	-
11	0.49	0.39	0.36	0.19	-	_	_	-	-	-	-	-	-
Не	6.28	6.01	6.09	6.48	-	_	_	-	_	-	-	-	-
Tn	0.75	1.03	1.45	2.23	_	_	_	_	_	_	_	_	_
Ru	0.0	0.0	0.0	0.0	_	_	_	_	_	_	_	_	_
An	0.47	0.4	0.40	0.14	_	_	_	_	_	_	_	_	_
np	0.17	0.1	0.10	0.11									
Trace elements													
Ва	817	86	98	2407	471	1411	2728	1976	5117	581	1860	624	269
Be	7	14	10	28	19	19	66	12	39	29	26	24	65
Cs	1.6	1.1	1.2	0.7	0.9	0.7	0.5	0.7	0.6	1.9	0.7	0.5	0.6
Со	1	1	1	1	1	1	1	2	3	1	1	1	1
Ga	41	40	40	44	29	21	33	44	31	54	31	41	11
Hf	14	18	19	57	49	156	52	57	63	25	116	58	952
Nb	122	227	225	469	451	1966	637	340	502	327	1194	792	3552
Rb	99	91	89	170	97	195	182	268	175	258	155	22	87
Sn	4	6	6	20	15	32	17	35	33	22	50	253	129
Sr	40	23	24	56	46	212	528	41	217	28	168	72	105
Та	6	13	12	16	34	114	39	26	25	21	99	62	423
Th	15	36	28	103	744	5686	2883	144	4609	1411	1115	1165	429
U	4	9	9	9	40	100	76	12	77	26	57	42	197
Zr	569	806	845	2835	2363	8449	2436	2672	3038	1204	6585	2877	40,741
RFF													
Y	70	92	98	231	448	1872	1148	231	1304	389	747	682	5669
La	103	141	153	119	414	8797	1578	164	6455	579	872	478	932
Ce	192	259	298	247	1125	15 375	2809	412	9369	891	1573	804	11 283
Pr	24	31	33	28	99	1515	286	36	831	95	183	90	467
Nd	88	119	121	102	349	4978	950	132	2485	299	616	297	2310
Sm	17	23	23	24	72	675	149	32	264	50	123	56	852
F11	3	4	4	4	10	86	22	5	33	7	20	9	131
Gd	15	21		25	67	499	145	35	192	40	120	66	1016
ть	2	3	3	5	13	74	32	7	34	11	24	15	182
Dv	14	19	19	41	90	/ 7	228	16	251	Q1	161	120	1166
Цо	2	2	2	10	20	432	230	10	231	10	22	20	241
Fr.	3	10	10	22	20 61	250	145	20	150	10 E1	00	29	680
EI T	1	10	10	52	01	230	105	29	136	51	96	94	089
1 III V1	1	1	1	5	9	39	24	4	21	/	15	15	9/9
i D	0	9	9	32	33 7	230	152	24	105	35	91	89 10	551
LU	1	1	1	4	/	30	15	3	12	4	12	12	72
ZKEE	546	/35	/9/	909	2839	34,936	//4/	1170	21,569	2566	4688	2856	20,540
LIKEE	427	5/7	032	524	2096	31,426	5/94	/81	19,437	1921	3387	1/34	15,975
ZHKEE	119	158	108	485	//0	3510	1953	389	2131	645	1301	1122	10,565
Geochemical ratios													
Na ₂ O/K ₂ O	1.12	1.5	1.49	1.17	0.85	0.31	0.27	0.9	0.67	0.56	0.39	0.12	0.05
$Na_2O + K_2O$	11.61	11.36	11.41	9.14	4.46	6.06	5.39	10.4	6.47	10.07	6.01	7.19	2.23
FeOt/(FeOt + MgO)	0.998	0.987	0.988	0.99	-	-	-	-	-	-	-	-	-
A. In	1.02	1.18	1.17	1.21	0.94	1.23	0.9	2.02	1.76	1.29	1.26	1.1	0.81
K/Rb	554.5	500	515.7	205.57	-	_	_	_	_	-	_	_	_
Rb/Cs	165	82.73	74.17	242.86	-	_	-	-	-	-	-	-	-
Th/U	3,75	4	3.11	11.44	18.6	56.86	37.93	12	59,86	24.75	19.56	27.74	2.18
Th/Ce	0.08	0.14	0.09	0.42	_	-	-	_	-	0	_		_
	0.00	0.11	0.00	5									

(continued on next page)

 Table 1 (continued)

Rock unit	Fresh syenites			Hydrothermally altered syenites									
Sample	1	2	3	4	5	6	7	8	9	10	11	12	13
Th/U Nb/Ta	3.75 20.33	4 17.46	3.11 21.25	11.44 28.19	18.6	56.86	73.93	12	59.86	54.27	19.56	27.74	2.33
Eu/Eữ (La/Yb)N (La/Sm)N	0.57 10.87 3.5	0.54 10.95 3.86	0.53 11.37 4.21	0.44 2.49 3.19	0.45 5.06 3.63	0.45 25.75 8.19	0.46 8.08 6.66	0.46 4.53 3.23	0.44 41.62 15.38	0.43 11.06 7.23	0.49 6.44 4.48	0.47 3.64 5.33	0.43 1.14 0.69

-= Not calculated, FeOt = Total iron and 0 = not found, HREE include Y.

In addition to all of the above, enrichment in LILE and LREE, as well as the lack of Nb depletion in these rocks, reflect within-plate and rifting environment sources (Li et al., 2000; Deng et al., 2012). Depletion also in Sr, P and Ti (Fig. 12) indicates a strong mantle source for these rocks similar to alkaline volcanic rocks derived from alkali basalt magmas of Chad (Mbowou et al., 2012). Strong depletion of Ba in samples 2 and 3, slight depletion in sample1 with the lack of depletion in sample 4, reflected the crustal contamination in these samples (Fig. 12).

The El Garra El Hamra studied fresh syenites show enrichment in LREE, Zr, Nb, Th and U, like many alkaline rocks of the world, e.g., high concentrations of LREE, Zr, Nb, Th and U in pantellerite of Lake Chad (Mbowou et al., 2012), high concentrations in REE, U and Th in nepheline syenites of Kvanefjeld deposit at Ilímaussaq, South Greenland (Sørensen et al., 2006, 2011) and colossal concentrations of Nb + REE in Kola Peninsula, Russia (Kogarko et al., 2002).

Nb/Ta ratios in the studied peralkaline range from 17.46 (sample 2) to 28.19 (sample 4), whereas Taylor and Mclennan (1985) and Green (1995) stated that the crust has lower Nb/Ta values (10–12) compared with the mantle (17.5), so that the studied peralkaline syenites originated from the mantle.

Finally, the diagram La–Y–Nb (Fig. 24) of Cabanis and Lecolle (1989), shows that fresh syenites originated from alkaline intracontinental magma likes OIB magmas according to Pearce (2008; Fig. 25).

El Garaa El Hamra fresh syenites have a quite similar origin as alkaline rocks in Egypt. De Gruyter and Vogel (1981) suggested that alkaline melts formed in asthenosphere by shear heating caused by the acceleration in the plate motion. These melts were emplaced along reactivated Pan-African fractures and pre-existing zones of weakness. The same model was also reported by El-Ramly and Hussein (1982), who suggested that, under certain favorable geotectonic conditions (e.g., intracontinental mantle plumes), magmas are produced, due to partial fusion of deeper levels in the upper mantle this could produce enough heat and volatiles (Lameyre et al., 1984 and Black et al., 1985) and through differentiation resulted in the variety of rocks taking part in the formation of these complexes. Moreover, those syenites have a mantle source as syenites of Kerala Khondalite belt of South India that signified crystallization of the rocks at shallow levels of the crust and originated from enriched mantle source magma (Sreejith and Ravindra Kumar, 2009). In addition to the similar hypothesis, it has also been put for the syenite and associated rocks of Elagiri complex of South Indian granulite terrain (Mukhopadhyay et al., 2011).

8. Radioactivity

The fresh syenites have U and Th contents ranging from 4 to 9 ppm and from 15 to 103 ppm, respectively. The contents of U and Th compare with alkali-rich syenites (up to 100 ppm for both of U and Th) of IAEA (1979) and Boyle (1982). TheTh/U ratios for fresh syenites (Table 1) are the same for peralkaline granite and peralkaline syenites and close to the crustal average (3.8, Taylor and McLennan, 1985), but quartz syenite sample 4 has a higher ratio (11.44). The higher ratio in the quartz syenite may due to enrichment in Th relative to U, because some U enters into an aqueous phase as uranyl ions and deposited in fractures, faults and/or open space filling during the final stage of magmatic differentiation (Gabelman, 1970), where Th remains mainly in the form of the thorite minerals.

On the other hand, hydrothermally altered syenites are marked by U contents ranging from 12 to 197 ppm with an average of 70 ppm, whereas Th ranges from 144 to 5686 ppm with an average of 2021 ppm, so that altered syenites appear to be Th-rich (thoriferous). The Th/U ratios range from 2.18 to 59.86 with an average of 28.83. The anomalously high Th contents suggest that altered syenitic rocks are enriched in Th-bearing minerals such as thorite, monazite and zircon as well as uranothorite. In addition, U in altered syenites is oxidized to U^{6+} , which is soluble in solutions, so that uranium migrated out of the altered syenites.

In both fresh and altered syenitic rocks, Th and U show a positive correlation (Fig. 26a). This means that U is associated with Th in the same minerals. In addition, altered samples are enriched in Th relative to U as aforementioned and some other incompatible trace elements, such as Y (Fig. 26b).



Fig. 11. REE distribution patterns for the El Garra El Hamra fresh syenites (Boynton, 1984).











Fig. 14. R1 versus R2 for El Garra El Hamra studied syenites. This binary R1-R2 diagram of the compositional fields of de la Roche et al. (1980) and tectonic discrimination fields (Batchelor and Bowden, 1985). Symbols as Fig. 13.



Fig. 15. SiO_2 versus FeOt/(FeOt + MgO) for the El Garra El Hamra studied syenites (Frost et al., 2001). Symbols as Fig. 13.



Fig. 16. Hf-Rb/30-3Ta for the El Garra El Hamra studied syenites (after Harris et al. (1986)). Symbols as Fig. 13.



Fig. 17. Ta/Yb versus Th/Yb for the El Garra El Hamra studied syenites (after Schandl and Gorton (2002)). Symbols as Fig. 13.



Fig. 18. Q-P chemical-mineralogical diagram of Debon and LeFort (1988) showing the variations (in millications) of quartz content (Q parameter) relative to the K-feldspar/plagioclase (P-parameter), green Arrows (after Cuney and Kyser, 2008) for the El Garra El Hamra studied syenites. Symbols as Fig. 13.

9. Discussion

The alkaline metallogenic province of Southwest Egypt contains altered and fresh peralkaline rocks localized along the ENE-WSW trending of the Guinean-Nubian lineament at its intersecting with the trends of the Trans-African shear zone (Fig. 1). Only a small number of peralkaline intrusions are currently exposed [e.g., Nusab El Balgum (Abu Elatta et al., 2013), El Garra El Hamra and El Seboah (Abu Elatta et al., 2014); Fig. 1). However, it is very likely than others lie hidden beneath the older sandstones. This interpretation is supported by field observations that have documented large numbers of dykes of peralkaline composition that cut the older rocks (Nubian sandstones) in areas where large intrusions have not been observed (Abu Elatta, 2016).

Multistage emplacement of peralkaline rocks in Southwest Egypt (including that discussed here) along the Guinean-Nubian lineament, especially along the ENE-WSW trending dextral strike-slip fault (Kalabsha fault), which is the most important branch of this lineament in Egypt (Issawi, 1968; Issawi et al., 2009; Fig. 1c) were due to the reactivation of the Guinean-Nubian lineament for long period times. The Guinean-Nubian lineament has been activated since the Jurassic and was particularly active during the Late Mesozoic when peralkaline rocks interpreted to have been emplaced. Three periods of peralkaline igneous activity have been recognized in South Egypt, namely at 250–200 Ma, 155–125 Ma, and 110–70 Ma (El Reedy, 1979; El Sayed et al., 2014). Although the age of the El Garra El Hamra peralkaline complex is unknown, the host rocks and the occurrence of numerous xenoliths of Nubian sandstones in the complex are constrained to be no older than late Cretaceous age (Hegazy, 2009). Accordingly, we can conclude that El Garra El Hamra that comprises peralkaline volcanics (peralkaline rhyolite and trachyte) and intrusions (peralkaline syenites and granites) was emplaced during the youngest of these periods.

Owing to continued movement along the Guinean-Nubian lineament (ENE-WSW Kalabsha fault) and the faults of the Chephren-Kom Ombo trend as opening the Atlantic Ocean led to emplace many igneous objects that appeared in the the El Garra El Hamra complex in form of mineralized dykes as well as hydrothermal veins. The solutions that were associated with dykes that have been intruded into syenites and faults that have been cut El Garra El Hamra complex mass may have facilitated the circulation of fluids that caused the hydrothermal alterations for the alkaline syenites are enriched in SiO₂, FeOt, CaO and slightly enrichment in the both of P_2O_5 and TiO₂ as well as depleted in Na₂O with no significant changes in both of MgO and MnO relative to the fresh syenites (Fig. 19a). They are also strongly enriched in these elements (LREE, HREE, Zr, Nb, Th, Hf and Ba). In addition to a significant increase in U compared to the fresh syenites (Fig. 19b).

On the other hand, the chondrite-normalised REE patterns for hydrothermally altered syenites (Fig. 20) are variable and range from those showing unfractionated HREE where $(Gd/Yb)_N$ ratios (0.6-1.75) with enrichment in LREE or HREE where $(La/Yb)_N$ ratios range from 1.14 to 41.62. $(La/Sm)_N$ ratios (0.69-15.38) indicated unfractionated to fractionate LREE. All samples show a negative Eu anomaly (0.43-0.49). This result suggests that hydrothermal solutions (1) were of low temperature (< 650 °C) and (2) had abundant HFSE cations. Redistribution of elements took place by the hydrothermal solutions (Bau and Dulski, 1999). Slightly positive Ce anomalies in samples 5 and 8 and a strongly positive anomaly in sample 13 are due to this fact; these samples are rich in Zr (Table 1), where Ce⁴⁺ is incorporated into zircon because Ce⁴⁺ has the same charge as Zr^{4+} and a similar ionic radius (Ce⁴⁺ = 0.97 Å; $Zr^{4+} = 0.84$ Å). Ce⁴⁺ is incorporated into zircon more easily than the larger Ce³⁺ (ionic radius = 1.143 Å), according to Thomas et al. (2003).

Moreover, the chondrite-normalised patterns (Figs. 22 and 23) show a positive Ce anomaly for average bastnäsite crystals, and a positive Pr anomaly for average monazite crystals, in addition to a positive Tb anomaly for average zircon and Nb-rutile crystals which are due to the oxygenated environments. According to Bao and Zhao (2008) where they reported that, under chemical weathering, cerium (Ce) tends to behave differently from other REE, as cerium in oxidizing environments occurs as Ce⁴⁺ and is highly insoluble as CeO₂ whereas the other REE maintain their 3+ ionic states and are leached by circulating water (Marsh, 1991). A positive Ce anomaly suggests that Ce is fixed as Ce⁴⁺ in the oxidizing hydrothermal solutions after having been dissolved initially as Ce³⁺. Authigenic phases precipitating from solutions such as bastnäsite are also rich in Ce and display positive Ce anomaly. The Ce⁴⁺ was scavenged by the bastnäsite crystals that were found in these rocks led to depletion of Ce in oxic hydrothermal solution (Elderfield and Greaves, 1982). Accordingly, the authigenic phases that were precipitated from Ce-depleted in oxidizing hydrothermal alterations such as monazite crystals are also depleted in Ce and display negative Ce anomalies. This can be done prior to a positive Pr anomaly. Moreover, oxidized hydrothermal solutions caused the positive Tb anomaly, where these solutions oxidized Tb^{3+} to Tb^{4+} that substitutes Zr^{4+} , Hf^{4+} and Th⁴⁺ (Hansen et al., 1996).

From the previous data, we can conclude the main factors controlling

Table 2								
MacLean's (1990)	method of	calculating n	nass and	elemental	change of	of hydrotheri	nally alter	ed syenites.

Oxide or element	Least altered	Altered	Changes without mass correction	EF (Al ₂ O ₃)	RC	MC
SiO ₂	62.01	67.75	5.74	2.0886	141.503	79.49
Al ₂ O ₃	13.43	6.43	-7		13.301	0.00
Fe ₂ O ₃	9.06	10.96	1.9		22.891	13.83
MgO	0.11	0.04	-0.07		0.083	-0.03
CaO	1.22	1.66	0.44		3.467	2.247
Na ₂ O	6.17	1.04	-5.13		2.172	-4
K ₂ O	4.71	4.42	-0.29		9.232	5.52
TiO ₂	0.73	0.83	0.10		1.733	1
P_2O_3	0.15	0.42	0.27		0.877	0.73
MnO	0.16	0.05	-0.11		0.104	-0.06
L.O.I	1.77	2.3	0.53		4.804	3.03
Total	99.53	96.90	-3.62		200.17	101.76
Ba	852	1670.78	818.78		3489.59	2637.59
Be	29	33.22	4.22		68.66	39.66
Hf	27	169.77	142.77		354.58	327.58
Nb	260.75	1084.22	823.47		2264.5	2003.75
Th	45.5	2020.67	1975.17		4220.37	4174.87
U	7.75	69.67	61.92		145.51	137.76
Zr	1263.75	7818.33	6554.83		16329.36	6554.58
LREE	540.0	9172.33	8632.33		19157.33	18617.32
HREE	232.5	2487.33	2254.83		5195	4962.5

EF = M precursor/M altered, M = some immobile, like Al_2O_3 , RC = EF * wt% or ppm of component in altered sample, MC = RC - precursor.



Fig. 19a. Enrichment and depletion in major oxides of El Garra El Hamra hydrothermally altered syenites.



Fig. 19b. Enrichment and depletion in the trace elements of El Garra El Hamra hydrothermally altered syenites.

the deposition of extreme enrichment of REE and HFSE minerals in hydrothermally altered syenites. These factors are the decreasing temperature, the increasing pH, the oxygenated solutions and the activities of the transporting and depositional ligands (Migdisov and Williams-Jones, 2002, 2007; Williams-Jones et al., 2012; Gysi and Williams-Jones, 2013; Migdisov and Williams-Jones, 2014). In addition to the common association of hydrothermal fluorite with HFSE deposits in these rocks, this indicated that fluoride has long been considered as the most likely transporting ligand of these elements (Wood, 1990; Haas et al., 1995). Moreover, Williams-Jones et al. (2012) suggest instead that F acts as a binding ligand promoting precipitation and that the bulk of REE transportation in hydrothermal fluids is achieved through the complexation

with chloride. The natural systems that are highly enriched in HFSE as the studied hydrothermally altered rocks are very common also highly enriched in F. It is evident that solution mechanisms for the REE and HFSE in El Garra El Hamra are exceptionally complex and likely involve the interplay between volatile content and peralkalinity of the melt. Fiege et al. (2011) also, suggest that low fo_2 of the melt can enhance HFSE solubility. The extreme enrichment in HREE in some samples but the extreme enrichment in LREE and HREE in the others may be due to the deposition of HREE and LREE minerals near the source, from which orthomagmatic fluid came out according to ligand types and an increasing temperature. The other samples that show extremely enrichments in LREE may be due to the deposition of LREE minerals more distal from their source as a result of the increase in pH and the decrease in temperature. In addition, the decreasing activity of ligands was illustrated by the recent experimental data and thermodynamic modelling by Migdisov and Williams-Jones (2014) indicating that, in most geological settings, REE are transported mainly as chloride complexes. The experimental data showed also chloride complexes of the LREE are considerably more stable than those of the HREE, and are transported mainly as chloride complexes that this difference in stability increases with increasing temperature. Thus, hydrothermal fluids in which the REE that are transported as chloride complexes have the capacity to strongly fractionate the REE by preferentially mobilizing the LREE to locations that are considerably more distal from their source than those in which the HREE are concentrated. On the other hand, the deposition of the REEs as bastnäsite-(Ce) from chloride complexes according to Williams-Jones et al. (2012) can be described by the reaction:

 $REECl^{2+} + HF + HCO^{3-} = REECO3F + 2H^{+} + C^{-}$

In general, El Garra El Hamra hydrothermally altered syenites are associated with hematitisation, silicification (silicate + quartz), carbonatization (carbonate minerals), argillic (clay minerals), Fe-Mn-oxyhydroxide particles, fluorite, barite, Fe-rich amphibole and enrichment in REE and HFSE minerals. It resembles many localities in the world that are enriched in rare metals deposits as a result of hydrothermal alterations, such as Olympic Dam in South Australia and Bushveld complex in South Africa (Pirajno, 2008). Moreover, it is similar to peralkaline rocks elsewhere, notably at Strange Lake Canada, where pervasive hematisation has obliterated primary igneous textures and caused low temperature mobilization of the REE and other field strength elements (Gysi and Williams-Jones, 2013).



Fig. 20. REE distribution patterns of El Garra El Hamra hydrothermally altered syenites (Boynton, 1984).

Table 3

Average electron microprobe analyses of hy	drothermal bastnäsite and monazite
crystals.	

Mineral	Bastnäsite n = 19	Monazite n = 5
Composition		
SiO ₂ %	0.325	0.091
Al ₂ O ₃ %	0.028	0.002
MgO%	0.997	u.d.
CaO%	0.029	1.195
Na ₂ O%	1.336	U.d.
P ₂ O ₅ %	Not found	29.746
CO ₂ %	19.14	Not found
PbO%	0.03	0.296
BaO%	0.061	0.133
SrO%	0.274	0.062
ThO ₂ %	1.305	0.383
UO2%	0.033	0.017
La ₂ O ₃ %	20.887	21.54
Ce ₂ O ₃ %	33.315	33.258
Pr ₂ O ₃ %	3.524	3.089
Nd ₂ O ₃ %	10.617	8.321
Sm2O3%	1.365	0.232
Eu ₂ O ₃ %	0.07	u.d.
Gd ₂ O ₃ %	1.143	0.101
Dy ₂ O ₃ %	0.139	u.d.
Y ₂ O ₃ %	0.693	0.453
F	7.611	0.288
Cl	0.025	u.d.
Total	102.622	99.207
ΣREO	71.753	66.882
ΣLREO	69.778	66.44
ΣHREO	1.975	0.554
ΣLREO/ΣHREO	35.331	119.928

HREO including Y₂O₃.

10. Conclusions

- 1. The El Garra El Hamra complex is a small, high-level plug that was emplaced along the Kalabsha fault. It has been split into two parts, due to continuous movement along this fault. The El Garra El Hamra complex comprises peralkaline syenites (most of them hydrothermally altered but the rest is still relatively fresh) and hydrothermally altered granites, which are locally overlain by alkaline trachyte and rhyolite.
- 2. The fresh syenites are composed essentially of perthitic K-feldspar, plagioclase, aegirine-augite, aegirine, arfvedsonite and riebeckite, while the main accessory minerals are zircon, bastnäsite-(Ce) and apatite. They are enriched in the REE and HFSE (e.g., Zr, Nb and Th).
- 3. The fresh syenites have alkali affinity, belonging to ferroan types



Fig. 21. Chondrite normalised REE plots for hydrothermal minerals from altered syenites of El Garra El Hamra (Boynton, 1984), a-average bastnäsite crystals and b-average monazite crystals.

and ranging in composition from syenites to quartz syenites. They were formed in a within-plate tectonic setting from magma batches uprising along the branch of the Guinea-Nubian lineament from the lithospheric mantle. Fractional crystallization and crustal contamination processes led to the magma modification to syenites and quartz syenites.

4. The extreme enrichment in rare metals (REE and HFSE) in

Table 4

Average electron microprobe analyses of hydrothermal xenotime, zircon and Nb-rutile crystals.

Mineral	Xenotime N = 14	Zircon n = 12	Nb-rutile n = 6
Composition			
SiO ₂	0.759	26.167	0.412
Al_2O_3	0.684	0.989	0.164
FeOt	0.684	1.492	2.488
CaO	u.d.	0.142	0.028
Na ₂ O	0.018	u.d	u.d.
TiO ₂	0.543	3.202	89.128
P_2O_5	35.126	3.458	0.009
ZrO ₂	0.543	48.425	0.004
Nb ₂ O ₃	0.034	0.928	7.371
Ta ₂ O ₃	0.075	u.d.	u.d.
ThO ₂	0.976	0.206	0.0562
UO ₂	0.016	0.897	0.005
Ce_2O_3	0.048	0.391	0.0833
Nd ₂ O ₃	0.192	0.259	0.066
Sm ₂ O ₃	0.351	0.179	u.d.
Eu ₂ O ₃	0.016	0.028	u.d.
Gd ₂ O ₃	3.879	0.381	0.066
Tb ₂ O ₃	0.699	0.262	0.047
Dy ₂ O ₃	7.084	0.695	0.042
Ho ₂ O ₃	1.493	0.134	0.004
Er ₂ O ₃	5.043	0.631	u.d.
Yb ₂ O ₃	3.342	0.576	0.002
Y_2O_3	40.143	4.313	0.004
Total	101.748	93.755	99.98
ΣREO	62.289	7.844	0.252
ΣLREO	0.607	0.857	0.0893
ΣHREO	61.683	6.992	0.165
ΣLREO/ΣHREO	0.01	0.123	0.541

HREO including Y₂O₃.

hydrothermally altered syenites is due to first, the nature of residual peralkaline melts which are indicated by negative Eu anomalies, which means it had abundances of HFSE cations. Second, related to reactivation of Guinean-Nubian lineament (Kalabsha fault) for long



Fig. 23. Zr versus Zr/Nb diagram for the El Garra El Hamra peralkaline syenites (Davidson and Wilson,1989). Symbols as Fig. 13.

period of times where other batches from evolved magmas emplaced and appear as mineralized dykes and veins on the surface today. Additionally, the different rare metal concentrations in the studied samples indicate that the minerals occur in zones of hydrothermally altered syenites.

- 5. The main factors controlling the deposition of extreme enrichment of REE and HFSE minerals in hydrothermally altered syenites are the decreasing temperature, the increasing pH, the oxygenated solutions and the activities of the transporting and depositional ligands.
- 6. Fluoride is considered the main transporting ligand of REE and HFSE cations, beside chloride in the hydrothermal solutions that caused the extreme enrichment in REE and HFSE minerals of hydrothermally altered symptome.
- 7. The LREE and HREE enrichments observed in some samples may be due to the deposition of HREE and LREE minerals near the source



Fig. 22. Chondrite normalised REE plots for hydrothermal minerals from altered syenites of El Garra El Hamra (Boynton, 1984), a-average xenotime crystals and baverage zircon crystals and c-average d-average Nb-rutile crystals.



Fig. 24. La/10-Nb/8-Y/15 diagram for the El Garra El Hamra studied syenites (Cabanis and Lecolle, 1989). Symbols as Fig. 13.







Fig. 26a. The relation between Th and U for the El Garra El Hamra studied syenites. Symbols as Fig. 13.



Fig. 26b. The relation between Th and Y for the El Garra El Hamra studied syenites. Symbols as Fig. 13.

according to ligand types and an increasing temperature.

- 8. The extreme enrichment in LREE observed in some other samples may be due to the deposition of LREE minerals more distal from their source according to the increase in pH, the decrease in temperature. In addition, they were transported as chloride complexes.
- 9. According to the study, El Garra El Hamra hydrothermally altered syenites are petrologically and economically important rocks in terms of the geochemical characteristics of the hydrothermally altered rocks and their enrichments in rare metal deposits. Further detailed studies may reveal the exact potential of the magmatic rocks in the El Garra El Hamra area.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.oregeorev.2018.08.001.

References

- Abu Elatta, S.A., 2016. Rare metal (Nb, Ta, Zr, Hf, Th, U and REEs)-Bearing Minerals in Peralkaline Igneous Rocks from the South Western Desert of Egypt. Internal Report. Nuclear Materials Authority, Egypt.
- Abu Elatta, S.A., Assran, H.M., Ahmed, A.A., 2013. Preliminary study on HFSE mineralization in the peralkaline granites of Nusab El Balgum Area, South Western Desert, Egypt. Geomaterials 3, 90–101.
- Abu Elatta, S.A., Ali, G.M., Rabea, A.B., 2014. Rare metal mineralization (Zr, U, Th and REE) associated to El Seboah acidic peralkaline rocks, South Western Desert of Egypt: recovery technique. Am. J. of Earth Sci. 1 (3), 73–85.
- Bao, Z.W., Zhao, Z.H., 2008. Geochemistry of mineralization with exchangeable REY in the weathering crusts of granitic rocks in South China. Ore Geol. Rev. 33, 519–535.
- Batchelor, R.A., Bowden, P., 1985. Petrogenetic interpretation of granitoid rock series using multicationic parameters. Chem. Geol. 48, 43–55.
- Bau, M., Dulski, P., 1999. Comparing yttrium and rare earths in hydrothermal fluids from the Mid-Atlantic Ridge: implications for Y and REE behaviour during near-vent mixing and for the Y/Ho ratio of Proterozoic Sea water. Chem. Geol. 155, 77–90.
- Black, R., Lameyre, J., Bonin, B., 1985. The structural setting of alkaline complexes. J. Afr. Earth Sci. 3, 5–16.
- Bowden, P., 1985. The geochemistry and mineralization of alkaline ring complexes in Africa (a review). J. Afr. Earth Sci. 3, 17–39.
- Boyle, R.W., 1982. Geochemical Prospecting for Thorium and Uranium Deposits. Elsevier, Amsterdam and New York, pp. 498.
- Boynton, W.V., 1984. Geochemistry of the rare earth elsements: meteorite studies. In: Henderson, P. (Ed.), Rare Earth Element Geochemistry. Elsevier, pp. 63–114.
- Cabanis, B., Lecolle, M., 1989. Le diagramme La/10-Y/15-Nb/8; un outil pour la discrimination des sériesvolcaniques et la mise en évidence des processus de mélange et/ oude contamination crustale (The La/10-Y/15- Nb/8 diagram; a tool for distinguishing volcanic series and discovering crustal mixing and/or contamination): ComptesRendus de l'Academie des Sciences, Série 2, Mécanique, Physique, Chimie, Sciences de l'Univers. Sciences de la Terre 309 (20), 2023–2029.
- Cuney, M., Kyser, T.K., 2008. Deposits related to magmatic differentiation. In: Cuney, M., Kyser, K. (Eds.), Recent and Not-so Recent Developments in Uranium Deposits and its Implications for Exploration. MAC Short Course, pp. 55–77.
- Davidson, J.P., Wilson, I.R., 1989. Evolution of alkali basalt trachyte suite from Jebel

Marro volcano, Sudan, through assimilation and fractional crystallization. Earth Planet. Sci. Lett. 95, 141–160.

- Debon, F., Lefort, P., 1988. A cationic classification of common plutonic rocks and their magmatic associations: principles, method, applications. B. Mineral. 111, 493–510.
- De Gruyter, P., Vogel, T.A., 1981. A model for the origin of the alkaline complexes of Egypt. Nature 291, 571–574.
 De La Roche, H., Leterrier, J., Grandclaude, P., Marchal, M., 1980. A classification of
- volcanic and plutonic rocks using R1R2-diagram and major element analyses its relationships with current nomenclature. Chem. Geol. 29, 183–210.
- Deng, J., Yang, X., Sun, W., Huang, Y., Chi, Y., Yu, L., Zhang, Q., 2012. Petrology, geochemistry, and tectonic significance of Mesozoic shoshonitic volcanic rocks, Luzong volcanic basin, eastern China. Int. Geol. Rev. 54 (6), 714–736.
- Elderfield, H., Greaves, M.J., 1982. The rare earth elements in seawater. Nature 296, 214–218.
- El-Ramly, M.F., Hussein, A.A., 1982. The alkaline ring complexes of Egypt. Geological Survey of Egypt, Paper No. 63, 16p.
- El Sayed, R.A., Hassan, M.A., Abu Elatta, S.A., 2014. Petrographic, radiometric and paleomagnetic studies for some alkaline rocks, south Nusab El Balgum mass complex, South Western Desert, Egypt. Geomaterials 4, 27–46.
- El Reedy, M.W.M., 1979. Geochronological and geochemical studies on the alkalic rocks in the South Eastern Desert, Ph. D. Thesis, Faculty of Science, Cairo University, 290p.
- Fiege, A., Kirchner, C., Holtz, F., Linnen, R.L., Dziony, W., 2011. Influence of fluorine on the solubility of manganotantalite (MnTa₂O₆) and manganocolumbite (MnNb₂O₆) in granitic melts - an experimental study. Lithos 122, 165–174.
- Finch, R.J., Hanchar, J.M., Hoskin, P.W.O., Burns, P.C., 2001. Rare-earth elements in synthetic zircon: Part 2. A single crystal X-ray study of xenotime substitution. Am. Mineral. 86, 681–689.
- Frost, B.R., Barnes, C.G., Collins, W.J., Arculus, R.J., Ellis, D.J., Frost, C.D., 2001. A geochemical classification for granitic rocks. J. Petrol. 42, 2033–2048.
- Gabelman, J.W., 1970. Speculations on the uranium ore fluid. Uranium Exploration Geology, pp. 315–330.
- Green, T.H., 1995. Significance of Nb/Ta as an indicator of geochemical processes in the crust-mantle system. Chem. Geol. 120 (3–4), 347–359.
- Guiraud, R., Issawi, B., Bellion, Y., 1985. Les Lineaments Guineo-Nubiens, un trait
- structural majeur à l'échelle de la plaque Africaine. C.R. Acad. Sci. Paris 300, 17–20. Guiraud, R., DoumnangMbaigane, J.C., Carretier, S., Dominguez, S., 2000. New evidence for a 6000 km length NW–SE-striking lineament in northern Africa: the Tibesti Lineament. J. Geol. Soc. (Lond.) 157, 897–900.
- Gysi, A.P., Williams-Jones, A.E., 2013. Hydrothermal mobilization of pegmatite-hosted REE and Zr at Strange Lake, Canada: a reaction path model. Geochimica et Cosmochimica Acta 122, 324–352.
- Haas, J.R., Shock, E.L., Sassani, D.C., 1995. Rare-earth elements in hydrothermal systems -estimates of standard partial molal thermodynamic properties of aqueous complexes of the rare-earth elements at high pressures and temperatures. Geochim. Cosmochim. Acta 59, 4329–4350.
- Hansen, S., Mosel, B.D., Müller-Warmuth, W., Fielding, P.E., 1996. EPR studies of Tb⁴⁺ in single crystals of zircon and scheelite structure silicates and germanates. Z. Naturforsch. 51a, 885–894.
- Harris, N.B.W., Pearce, J.A., Tindle, A.G., 1986. Geochemical characteristics of collisionzone magmatism. In: Coward, M.P., Ries, A.C. (Eds.), Collision Tectonics. Geological Society London, Special Publication, pp. 67–81.
- Hashad, A.H., El Reedy, M.W.M., 1979. Geochronology of anorogenic alkalic rocks. Southeastern Desert, Egypt. Ann. Geol. Surv. Egypt 9, 81–101.
- Hegazy, M., 2009. Geochemical and Mineralogical studies of Rare Metal Mineralization in Garra El Hamra Granite Syenite Complex and the Surrounding Environ, South Western Desert, Egypt. M.SC. Thesis, Faculty of Science, Mansour University, Egypt, 74p.
- Heier, K.S., 1973. Geochemistry of granulite facies rocks and problems of their origin. Philos. R. Soc. Lond., Ser. 273, 429–442.
- Hoskin, P.W.O., Kinny, P.D., Wyborn, D., Chappell, B.W., 2000. Identifying accessory mineral saturation during differentiation in granitoid magmas: an integrated approach. J. Petrol. 41, 1365–1396.
- Hoskin, P.W.O., Schaltegger, U., 2003. The composition of zircon and igneous and metamorphic petrogenesis. In: Hanchar, J.M., Hoskin, P.W.O. (Eds.), Zircon. Reviews in Mineralogy and Geochemistry, pp. 27–62.
- IAEA (International Atomic Energy Agency), 1979. Gamma ray surveys in uranium exploration, Technical Report. Vienna, Series, paper no. 186, 90p.
- International Commission on Stratigraphy, 2015. Divisions of Geologic Time-Major Chronostratigraphic and Geochronologic Units USGS Retrieved 10 March 2013. Issawi, B., 1968. The Geology of Kurkur Dungul Area, Paper No. 46, Geological Survey of
- Egypt. Issawi, B., Francis, M., Youssef, A., Osman, R., 2009. The Phanerozoic of Egypt: a geodynamic approach. Geol. Surv. Egypt, Spec. Publ. 81, 589p.
- Kogarko, L.N., Williams, C.T., Woolley, A.R., 2002. Chemical evolution and petrogenetic implications of loparite in the layered, agpaitic Lovozero complex, Kola Peninsula, Russia. Mineral. Petrol. 74, 1–24.
- Korzhinskii, D.S., 1953. Outline of metasomatic processes (in Russian, German edition, 1965.Abriss der metasomatischen Prozesse, Akad.Verl., Berlin) In: Raja, S. (Ed.), Main Problems on the Science of Magmatogenic Ore Deposits. Acad. Sci. Publishing, Moscow, pp. 334–456.
- Lameyre, J., Black, R., Bonin, B., Giret, A., 1984. Les provinces magmatiques de l'EstAméricain, de l'OuestAfricainet des Kerguelen. Indications d'un contrôletectoniqueetd'une initiation superficielle du magmatism intraplaque et des processusassociés. Annal. Geol. Soc. Nord Lille C3 (45), 101–114.

- Li, Xianhua, Zhou, Hanwen, Lee, Chi-yu, Sun, Min, Chen, Chenhong, 2000. Shonshonitic intrusive suite in SE Guangxi: petrology and geochemistry. Chin. Sci. Bull. 45, 653–659.
- MacLean, W.H., 1990. Mass change calculations in altered rock series. Miner. Deposita 25, 44–49.
- Marsh, J.S., 1991. REE fractionation and Ce anomalies in weathered Karoo dolerite. Chem. Geol. 190, 189–194.
- Mbowou, G.I.B., Lagmet, C., Nomade, S., Ngounouno, I., Deruelle, B., Ohnenstetter, D., 2012. Petrology of the Late Cretaceous peralkaline rhyolites (pantelleriteand comendite) from Lake Chad, Central Africa. J. Geosci. 57, 127–141.
- Migdisov, A.A., Williams-Jones, A.E., 2002. A spectrophotometric study of neodymium (III) complexation in chloride solutions. Geochim. Cosmochim. Acta 66, 4311–4323.
- Migdisov, A.A., Williams-Jones, A.E., 2007. An experimental study of the solubility and speciation of neodymium (III) fluoride in F-bearing aqueous solutions. Geochimica et Cosmochimica Acta 71, 3056–3069.
- Migdisov, A.A., Williams-Jones, A.E., 2014. Hydrothermal transport and deposition of the rare earth elements by fluorine bearing aqueous liquids. Miner. Deposita 49, 987–997.
- Mukhopadhyay, S., Ray, J.S., Chattopadhyay, B., Sengupta, S., Ghosh, B., Mukhopadhyay, S., 2011. Significance of mineral chemistry of syenites and associated rocks of Elagiri Complex, Southern Granulite Terrane of the Indian shield. J. Geol. Soc. India 77, 113–129.
- Müller, D., Rock, N.M.S., Groves, D.I., 1992. Geochemical discrimination between shoshonitic and potassic volcanic rocks in different tectonic settings: a pilot study. Mineral. Petrol. 46, 259–289.
- Nagy, R.M., Ghuma, M.A., Rogers, J.J., 1976. A crustal suture and lineaments in North Africa. Tectonophysics 31, 67–72.
- Pearce, J.A., 1983. Trace element characteristics of lavas from destructive plate boundaries. In: Thorpe, R.S. (Ed.), Andesites: Orogenic Andesites and Related Rocks. John Wiley & Sons, Chichester, pp. 525–548.
- Pearce, J.A., 2008. Geochemical fingerprinting of oceanic basalts withapplications to ophiolite classification and the search for Archeanoceanic crust. Lithos 100, 14–48.
- Pirajno, F., 2008. Hydrothermal Processes and Mineral Systems. Springer Science and Business Media B.V., pp. 135.
- Scarrow, J.H., Bea, F., Montero, P., Molina, J.F., 2009. Shoshonites, vaugnerites and potassic lamprophyres: similarities and differences between 'ultra' high-K rocks. Earth Environ. Sci. Trans. R. Soc. Edinburgh 99, 159–175.
- Schandl, E.S., Gorton, M.P., 2002. Application of high field strength elements to discriminate tectonic settings in VMS environments. Econ. Geol. 97, 629–642.
- Serencits, C.M.C., Faul, H., Foland, K.A., El-Ramly, M.C., Hussein, A.A., 1979. Alkaline ring complexes in Egypt: their ages and relationship to tectonic development of the Red sea. Ann. Geol. Surv. Egypt. 9, 102–116.
- Shandelmeier, H., Pudlo, D., 1990. The Central-African fault zone in Sudan-a possible continental transform fault. Berliner Geowiss. Abh. 120-A, 31–44.
- Shaw, D.M., 1968. A review of K-Rb fractionation trends by covariance analysis. Geochimica et Cosmochimica Acta 32, 573–601.
- Sørensen, H., Bailey, J.C., Rose-Hansen, J., 2011. The emplacement and crystallization of the U-Th-REE-rich agaitic and hyperagpaitic lujavrites at Kvanefjeld, Ilimaussaq alkaline complex, South Greenland. Bull. Geol. Soc. Den. 59, 69–92.
- Sørensen, H., Bohse, H., Bailey, J.C., 2006. The origin and mode of emplacement of lujavrites in the Ilimaussaq alkaline complex, South Greenland. Lithos 91, 286–300.
- Sreejith, C., Ravindra Kumar, G.R., 2009. Petrological and geochemical characteristics of Marunthurkota syenites from the Kerala Khondalite Belt, Southern India. J. Geol. Soc. India 73, 386–392.
- Sun, S.S., McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. Geol. Soc. Spec. Pub. 42, 313–345.
- Taylor, S.R., McLennan, S.M., 1985. The Continental Crust: Its Composition and Evolution. Blackwell Scientific Publications, Oxford, UK.
- Taylor, S.R., McLennan, S., 1995. The geochemical composition of the continental crust. Rev. Geophys. 33, 241–265.
- Thomas, J.B., Bodnar, R.J., Shimizu, N., Chesner, C.A., 2003. Melt inclusions in zircon. Rev. Mineral. Geochem. 53 (1), 63–87.

Whalen, J.B., Currie, K.L., Chappell, B.W., 1987. A-type granites: geochemical characteristics, discrimination and petrogenesis. Contrib. Mineral. Petr. 95, 407–419.

- Williams-Jones, A.E., Migdisov, A.A., Samson, I.M., 2012. Hydrothermal mobilisation of the rare earth elements a tale of "Ceria" and "Yttria". Elements 8, 355–360.
- Winchester, J.A., Floyd, P.A., 1977. Geochemical discrimination of different magma series and their differentiation products using immobile elements. Chem. Geol. 20, 325–343.
- Wood, S.A., 1990. The aqueous geochemistry of the rare-earth elements and yttrium. Theoretical predictions of speciation in hydrothermal solutions to 350 °C at saturation water vapor pressure. Chem. Geol. 88, 99–125.
- Zhang, Z., Xiao, X., Wang, J., Wang, Y., Kusky, T.M., 2008. Post-collisional Plio-Pleistocene shoshonitic volcanism in the western Kunlun Mountains, NW China: geochemical constraints on mantle source characteristics and petrogenesis. J. Asian Earth Sci. 31, 379–403.
- Zharikov, V.A., 1976. Grounds of Physico-chemical Petrology. MGU Publ., Moscow, pp. 420 (in Russian).
- Zharikov, F.V.A.F., Pertsev, N.N., Rusinov, V.L., Callegari, E., Fettes, D.J., 2006. Metasotism and metasomatic rocks. Recommendations by the IUGS Subcommission on the Systematics of Metamorphic Rocks. Web version 01.02.07 British Geologic Survey.