



Study of rare metal mineralization of granitoids at South Um Ara-Wadi Murrah area, Southeastern Desert, Egypt: implications for a characterization of mineral paragenesis

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Abstract

The region of Um Ara-Wadi Murrah is situated in Egypt's arid Southeastern Desert. The region contains a variety of tectono-stratigraphic units, with the earliest being ultramafic rocks, serpentinite, metavolcanics, metasediments, monzogranite, and syenogranite. Strong shearing, fracturing, and jointing control the high radioactivity in the anomalous areas. Uranophane, kasolite, and autunite make up the majority of visible secondary uranium mineralization. A variety of rare earth minerals, including monazite, bastnäsite, allanite, chernovite and xenotime were recorded in the study area. Betafite, ishikawaite, columbite, fergusonite and samarskite were recorded as radioactive bearing-minerals (Nb–Ta minerals). Finally; base metals represented by gold, bismite, cassiterite and wolframite. Secondary processes primarily influenced the post-magmatic addition of uranium to these granitic sites, known as uranium enrichment. We can identify the three types of ore minerals (magmatic, hydrothermal, and supergene) using a suggested paragenetic sequence. The latter comprises secondary uranium minerals and altered uranotorite. There are several ways that rare metal enrichment can happen, such as ascending hydrothermal solutions (alkaline solutions first, then acidic hydrothermal solutions) and descending acidic meteoric water during supergene enrichment processes. Changes in physicochemical conditions and the fugacity of oxygen and sulfur led to the initial precipitation of gold in mesothermal and epithermal solutions. Mineralogical and geochemical evidence confirms the different stages of mineralization. The study area has been enriched in uranium and rare earth elements (av. 3451.4, 273 ppm, respectively). The calculated values of the tetrad effect are 1.12. The chondrite-normalized REE patterns for syenogranite are M-type tetrad. The Th–U variation diagram reveals that all samples fall within the supergene enrichment field, with all Th/U ratio values being less than 0.1. Regarding the correlations between U and trace elements, we observe positive correlations with Zr, Y, and very weak to ill-defined correlations with LREEs, Nb, and F, indicating partially magmatic processes followed by post-magmatic processes.

Keywords Um Ara-Wadi Murrah syenogranite · Radioactive minerals · Rare metals · Gold · Egypt

1 Introduction

Commonly referred to as rare metals, felsic to alkaline magmatic rocks are abundant in zirconium, tantalum, niobium, lithium, beryllium, hafnium, and rare-earth elements (REE) [1]. Subsequent processes, such as the supergene enriching process (descending acidic meteoric water) and the ascending hydrothermal solutions (acidic and alkaline solutions),

contribute to the formation of the rare metal enrichment. The alkaline hydrothermal solution had a pH of more than 7 and a temperature range of 300–350 °C. The acidic solution had a pH range of 2–3, and its temperature ranged from 200 to 250 °C [2]. The hydrothermal metal-bearing solutions traversed faults and micro fractures, precipitating metals and inducing modifications in the wall rock. The abrupt alteration in pH and temperature of the fluids will result in the instability of rare metal complexes, promoting their deposition [3–5]. The rare metals mineralization accumulates in the rest of the late fractionated melt, particularly in the upper regions of the magmatic system. Uranium seems to form a soluble uranyl ion (UO_2)²⁺ depending on the oxygen fugacity ($f\text{O}_2$) during the final magmatic fractionation;

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thus, hydrothermal processes in the concluding stages of granitic magma crystallization are crucial for regulating the late redistribution of uranium within the rocks [6].

The Arabian-Nubian Shield (ANS) development constitutes four significant tectono-magmatic events happened from 550 to 800 Ma. They are: (1) the breaking apart of the supercontinent Rodinia (around 800 Ma, [7], (2) the seafloor spreading, the formation of the arc basins, back-arc, and the creation of young crust (690–870 Ma), (3) the collision of two continental plates (650–750 Ma), and (4) the shortening of the east–west crust (550–640 Ma) when West and East Gondwana hit each other. According to [8–10], the ANS is the biggest exposed region of Neoproterozoic juvenile continental crust and the finest preserved.

In Egypt, pegmatites and granitic rocks are the primary hosts of U and Th mineralization [11–18]. The mineralization exhibits significant enrichment in high-field-strength elements such as Nb, Zr, Y, Th, U, and Ta, in addition to the REEs (rare earth elements) accompanied with an alkaline A-type granite. These granites are primarily formulated during the post-collisional phase at Late Neoproterozoic approximately (580–630 Ma), as hydrothermally altered granites inside the shear zones or as disseminations in host granite [19–21]. Radioactive and rare metal minerals change in different ways during similar global events because of the circulation and the deformation of hydrothermal fluids [22, 23]. This can result in a number of secondary minerals hosting Th-U-Ta-Nb-REEs.

Calcium uranyl silicate minerals predominate in secondary uranium mineralization in the research area, according to [24–26]. These minerals are primarily the result of a two-stage process that alters the primary U minerals. The first step is the creation of uranyl oxide hydrates, which happens when hydrothermal fluids corrode fundamental minerals. Later, oxic groundwater disintegrates the uranyl oxide hydrates at a different phase. Uranophane and β -uranophane were created when the freed U reacted with silica and calcium after being moved as a uranyl ion.

Additionally, uranyl silicates are ideal examples of the oxidized contents of the U-bearing deposits around the world, according to [27]. They occur when uraninite, UO_2 or coffinite, typically $\text{U}(\text{SiO}_4)$, is weathered oxidizing. The Eastern Desert of Egypt had a period of uranium migration and secondary mineral development ($\approx 100,000$ years ago), according to [28]. Surface water inundated the Eastern Desert during Egypt's pluvial episodes, which correspond to this era.

The main target of this research is to study and delineate, in more detail, the mineralogy and petrography of the southern part of the Um Ara-Wadi Murrah granitic pluton. The study used in situ spot studies, including EDS (energy-dispersive spectral) analysis, to acquire the chemical characteristics of secondary minerals and their

regulated behavior resulting from alteration events. The study also seeks to provide a paragenetic sequence for the different phases of ore mineral crystallization. It also presents a comprehensive scenario on the origin of rare metals, emphasizing structural instability and the transformation of mineral phases via alteration and deformation.

2 Geological setting

The Google Earth image encompasses a significant portion of the Um Ara-Wadi Murrah region (Fig. 1a) and was utilized for the identification and classification of rock types. The region under examination is situated in the SED, bounded by longitudes $33^\circ 48'$ & $33^\circ 54'$ E and latitudes $22^\circ 31'$ & $22^\circ 35'$ N (Fig. 1b). It has an area of around 230 km^2 . The basement rocks in the southern Um Ara-Wadi Murrah region are considered part of the Arabian Nubian Shield. The Um Ara area is situated in the southern region of the Eastern Desert, approximately 250 km southeast of Aswan. The study region includes various metamorphic and igneous rocks from the Precambrian-Early Paleozoic era. The differences in lithology, structures, and erosional processes primarily control the topographic features. The prominent peaks are Gebel Um Ara granites (490 m) above sea level [29]. The geology of the Um Ara-Wadi Murrah area comprises a tectono-stratigraphic sequence that begins with the oldest as follows: ultramafic rocks (serpentinite), metavolcanics, metasediments, monzogranite, syenogranite, and post-granitic dykes and veins (acidic dykes, pegmatite veins).

The following paragraphs provide a concise field description of the various rock units based on the previously established classification [29]:

2.1 Serpentinite rocks

Serpentinites occupy an area of about 35 km^2 distributed in the mapped area trending mainly NE-SW. The serpentinite rocks are considered one of the diagnostic rock units in the Late Precambrian of Egypt. They occur as isolated masses, blocks, sills, and sheets of varying dimensions. Strong shearing and cataclasis, along with the development of chlorite, mark the contact between massive serpentinites and talc carbonate rocks. They have a light brown color, are soft, compact, and soapy, and have developed foliation in certain areas. Alteration in the Um Ara-Wadi Murrah area has increased the compositional and textural complexities of these rocks.

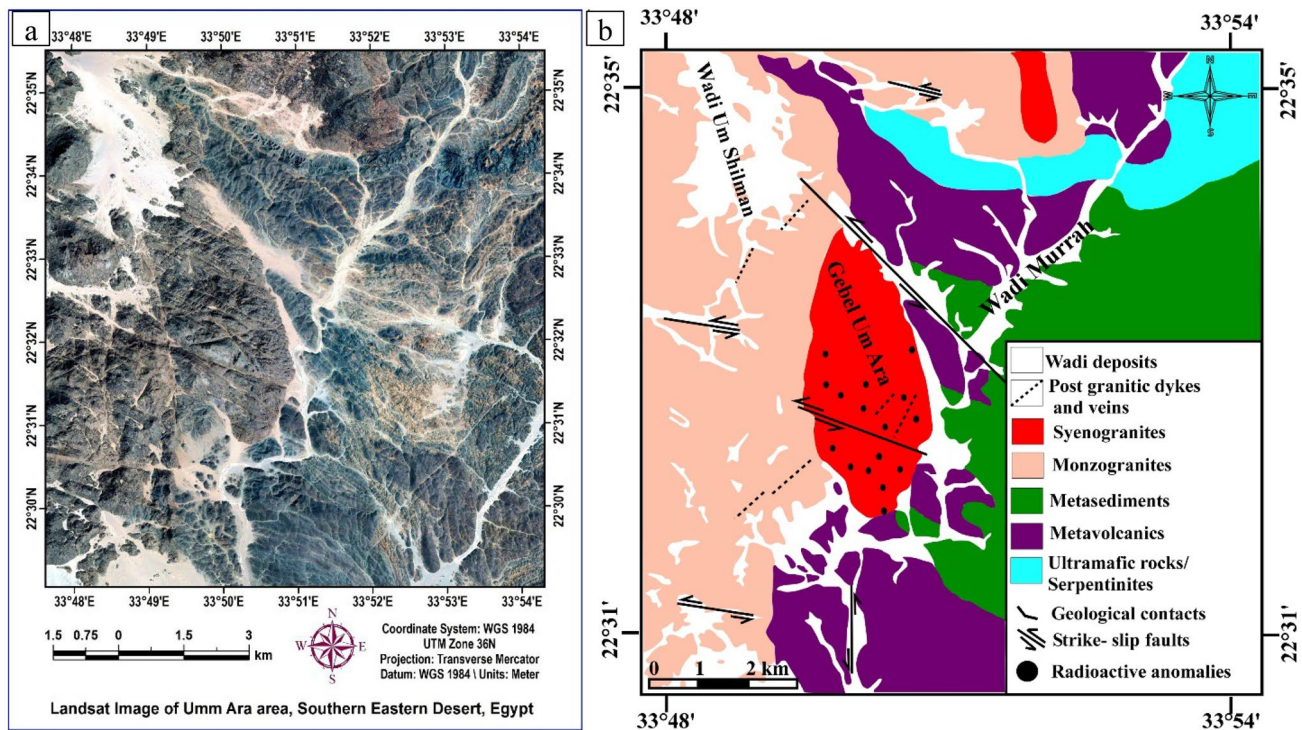


Fig. 1 a Landsat-image and b geological map of G. Um Ara-Wadi Murrah area, South Eastern Desert, Egypt (Mapping by Saleh [29])

2.2 Metavolcanic (basic and acidic) rocks

The central part of the studied area features metavolcanics, which have a more or less elongated shape and trend S–N direction, with moderate to low relief in the Um Ara-Wadi Murrah area. They are hard, massive, dark green to grey in color, and intruded by the younger granites (monzogranites and syenogranites). Originally, metavolcanics were formed by repeatedly alternating and interfingering dacite lava flows, their corresponding metatuffs, and highly foliated serpentinite thrusts. The majority of this metavolcanic association is composed of basaltic metavolcanics.

2.3 Metasediments

The metasediments (quartzo-feldspathic schist and garnetiferous-biotite schist) have relics of primary foliations, bedding, laminations, and macro and minor folding and are highly tectonized (Fig. 2a) and crop out in the southwestern part of the studied area as isolated masses. Metavolcanics intrude these rocks, forming sharp contacts in the Um Ara-Wadi Murrah area. Frequent presence of boudinaged quartz veins (of 10.0 m long) trending parallel to the foliation surfaces marks the well-exposed, strongly deformed mesoscopic structure of the rocks. These rocks are intruded by metavolcanics with sharp contacts overlying the downstream of Wadi Murrah on the two sides.

2.4 Younger granitoids

The southeastern part of the mapped area, Gabal Um Ara-Wadi Murrah area (Fig. 2b), hosts monzogranite, which forms the primary granitic masses of the Um Ara-Wadi Um Shilman area, which extends in NW–SE, NE–SW, and NNE–SSW directions. Monzogranite is described as coarse to medium-grained, massive, exfoliated and jointed, and pinkish grey foliated leucocratic. The direction of the foliation is mainly concordant with the direction of the elongation of the whole pluton (NNW–SSE). The monzogranite, is dissected by a set of faults, particularly on the western sides of the pluton, trending in the NNW–SSE direction, with NE–SW trending acidic dykes and pegmatite veins.

Syenogranites are exposed at the northwestern sides of the regional mapped area [29]. This exposure spans a large area (> 50.0 km²) and is positioned along NE–SW and N–S trends, measuring approximately 4.0–15.0 km length and 1.5–4.0 km width. The metavolcanics and monzogranites are being intruded upon. Intensive tectonism has severely deformed the syenogranites in certain locations, revealing the presence of metasediment xenoliths. The syenogranites featured fine to medium grains and ranged in color from pinkish gray to dark pink. Alkali feldspars, quartz, and plagioclase make up their composition. Some acidic dikes (NE–SW) are cutting through the younger granites. The syenogranites with NE–SW trends are associated with quartz

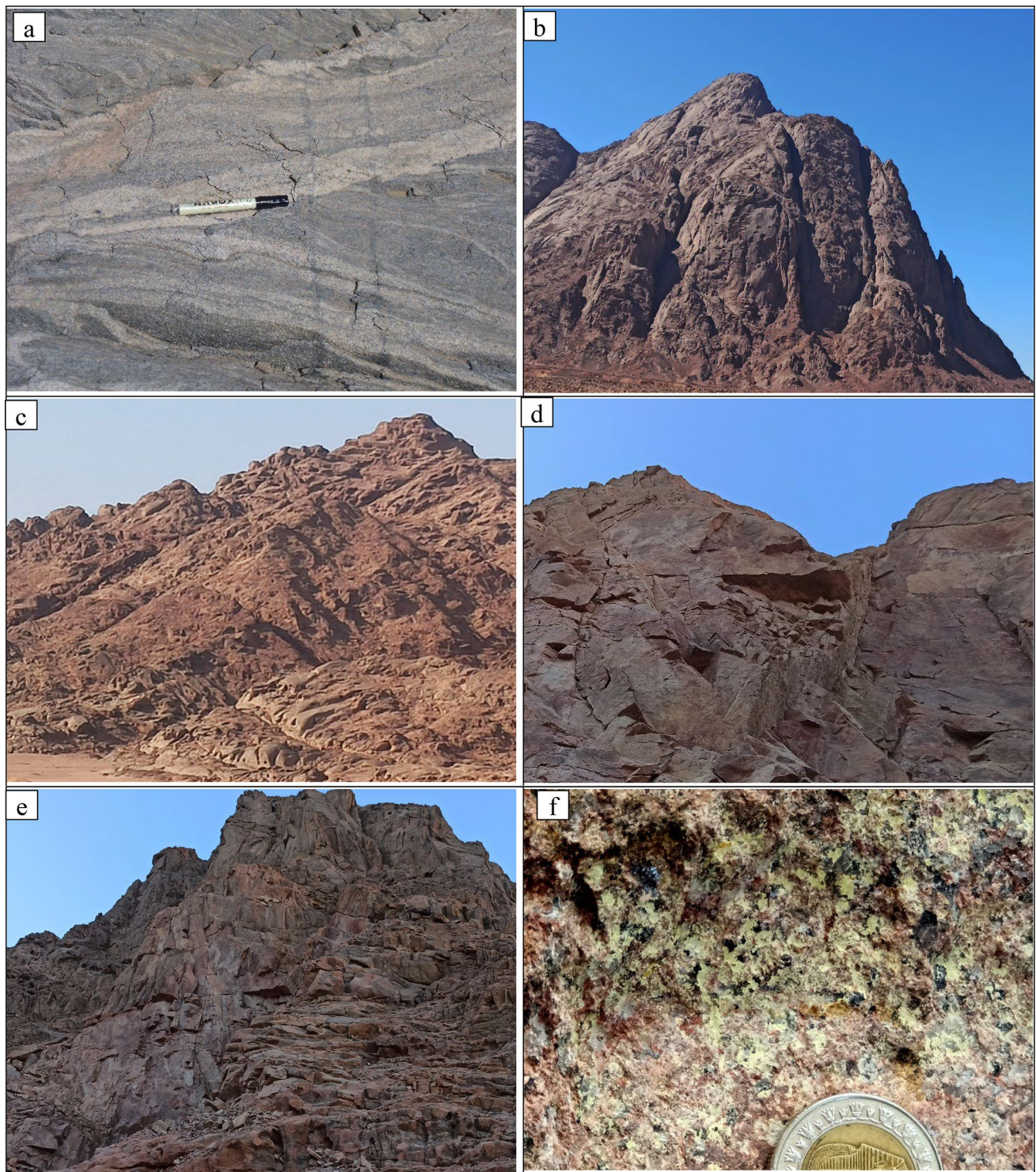


Fig. 2 Field photographs and hand specimen of syenogranite, Um Ara-Wadi Murrah area, SED, Egypt showing: **a** photograph showing the metasediments are highly tectonized, looking NE. **b** Photograph showing panorama of the Um Ara-Wadi Murrah younger granites which characterized by relatively low to medium topography, looking to the NW. **c** Photograph showing exfoliated and cavernous due to

highly weathered, looking NE. **d** Photograph showing highly sheared granites and dissected by numerous of faults of the younger granites, looking to the NE. **e** Photograph showing highly sheared granites and dissected by numerous of a nearly vertical joint pattern, looking NW. **f** visible uranium (uranophane) in syenogranite, Um Ara Area, SED, Egypt

veins that are cutting through the country rocks. Syenogranites, with an N 55° E trend, are associated with reddish and highly deformed quartz veins that cut through the country rocks. Some outer contacts of younger granites are highly reddish in color due to hematitization caused by hydrothermal solutions, or whitish due to kaolinization (high radioactive anomaly). As a result, the rocks are highly weathered (Fig. 2c), exfoliated, and fractured due to deformation. These altered rocks are referred to as either hematitized or kaolinized granites. Numerous faults severely shear and dissect them (Fig. 2d). The pluton's periphery experiences slight exfoliation, while the center of the pluton didn't experience deformation. For instance, there are two dextral faults in the NW part of the Um Ara-Wadi Murrah area; one of them trends N 40° E, and the other is the latest one, as it cuts the first dextral fault and trends N 130° W. In the wadis, the granite possesses a nearly subhorizontal and vertical joint pattern, which sometimes becomes closed space, approaching the appearance of columnar jointing (Fig. 2e).

The silicification and partial kaolinization of syenogranite, along with the common presence of violet and green fluorite, Mn oxides, and U mineralization (uraninite, coffinite, uranophane, autunite, and kasolite), are indicative of hydrothermal activity. Hand specimens of the syenogranite identify visible secondary uranium crystals (Fig. 2f). They appear as acicular crystals filling voids and as stains along the fracture surfaces.

2.5 Post granitic veins and dykes

Various veins and dykes cut across the basement rocks of the Um Ara-Wadi Murrah area. They comprise the following rock types: (1) Acidic dykes, ranging in trends from NE-SW, are more in width and cut through the monzogranites and syenogranites, and (2) Pegmatite veins.

3 Methodology

Sixteen granitic samples were selected from the southern Um Ara-Wadi Murrah region based on the mineral portion separation method. The samples were firstly concentrated using heavy liquids such as the bromoform (specific gravity 2.85 g/cm³), then crushed, split, granulated, and separated them to a size fraction of + 120 to – 60 meshes. An environmental scanning electron microscope (ESEM type Prisma E) supported with an EDX device was then used to identify the heavy fractions. XRF and ICP-MS analyses are carried out at the GeoAnalytical Lab, Washington State University (WSU), USA. The concentration of the principal and some trace elements was ascertained using X-ray fluorescence (ThermoARL XRF Spectrometer). Each powdered sample was weighed, combined with two parts di-lithium tetraborate

flux, fused at 1000 °C in a muffle furnace, and subsequently cooled. The resultant bead was re-grinded, refashioned, and polished on a diamond lap to yield a smooth, flat surface for examination. The calibration standard utilized was the reference material 650CC from the USGS standard rock powder GSP2. The loss on ignition (LOI) was ascertained by the weight differential upon combustion at 1000°C. Concentrations of rare earth elements and certain trace elements were quantified using ICP-MS (Agilent 7700 ICP-MS) spectrometry. It takes at least 8 h of refluxing in hot (250°C) 3:1 nitric and hydrofluoric acid to dissolve about 50 mg of each sample in acid-washed Teflon containers. With the help of USGS standards AGV-2 and RGM-2 and a blank fused bead from the same batch of flux used to prepare the unknowns, a working curve for instrument sensitivity was set up. To ensure quality control, supplementary USGS standards (DTS-2, BCR-1, G-2) were incorporated as unknowns.

4 Results

4.1 Petrography

The modal composition of eight samples from the syenogranite were plotted on the QAP diagram [30] (Fig. 3a). The primary constituents of the syenogranite are plagioclase, quartz, and K-feldspar. Uranophane, fluorite, zircon, and opaques are accessory minerals. Iron oxide solutions have a strong staining effect on the rock, giving it a red appearance on its surface. Perthite-displaying flame and coarse-grained patch-like formations (phenocrysts) are instances of K-feldspar (Fig. 3b). Quartz can be found in the form of anhedral to subhedral grains up to 1.5 mm across, and fine crystals that occur as interstitial grains between the other constituents. The crystals exhibit wavy-to-undulose extinction (Fig. 3c). Subhedral crystals of Plagioclase range in composition from albite to oligoclase (An₄₋₁₄) (Fig. 3d, e). Some plagioclase crystals wedge into another crystal, forming an association with perthite (Fig. 3f). Fluorite encloses euhedral, minute, short, prismatic zircon crystals up to 0.05 mm length (Fig. 3g, h). Fluorite crystals are a late-stage mineral in granite and usually crystallize at low temperatures (around 500 °C). The euhedral fluorite crystal (F), which exhibits high relief, typically forms as coarse, massive aggregates with a violet color. The individual crystals (Fig. 3d) are subhedral to euhedral, characterized by cracking, high relief, and isotropy. Furthermore, the hydrothermal alteration of the granites typically reveals fluorite crystals as filling microfractures and cavities, indicating their late origin. They also exist as interstitial grains between opaques, quartz, and perthite. Uranophane is a secondary uranium mineral that can be found as anhedral crystals or as fan-shaped (Fig. 3i, j) groups of plagioclase and fluorite. These

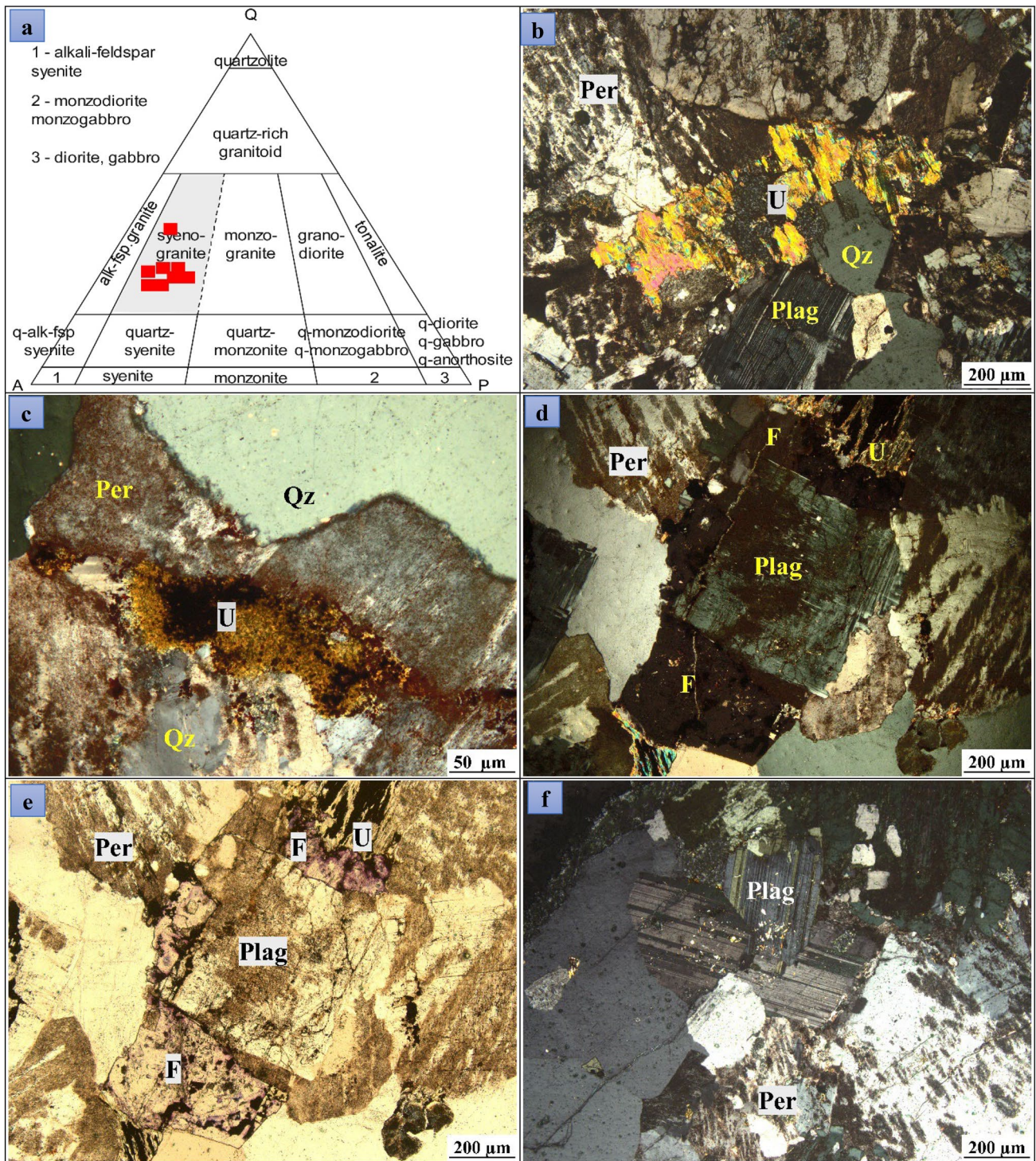


Fig. 3 Photomicrographs for the syenogranite, south Um Ara-Wadi Mura area, South Eastern desert, Egypt, showing: **a** Q-A-P ternary diagram [30] for the studied syenogranite. **b** Euhedral crystal of perthite associated with uranophane and plagioclase. CN. **c** Euhedral crystal of Qz associating with amorphous radioactive mineral and perthite. **d** Cubic crystal of plagioclase surrounded by fluorite and uranophane. CN. **e** Cubic crystal of plagioclase surrounded by fluo-

rite and uranophane. PPI. **f** Plagioclase wedged in another crystal of plagioclase associating with perthite. CN. **g** Violet fluorite associated with uranophane and zircon. CN. **h** Violet fluorite and uranophane. CN. **i** Radiated crystal of uranophane associated with perthite (flame-string-rod). CN. **j** Unhedral crystal of uranophane associated with potash feldspar. CN

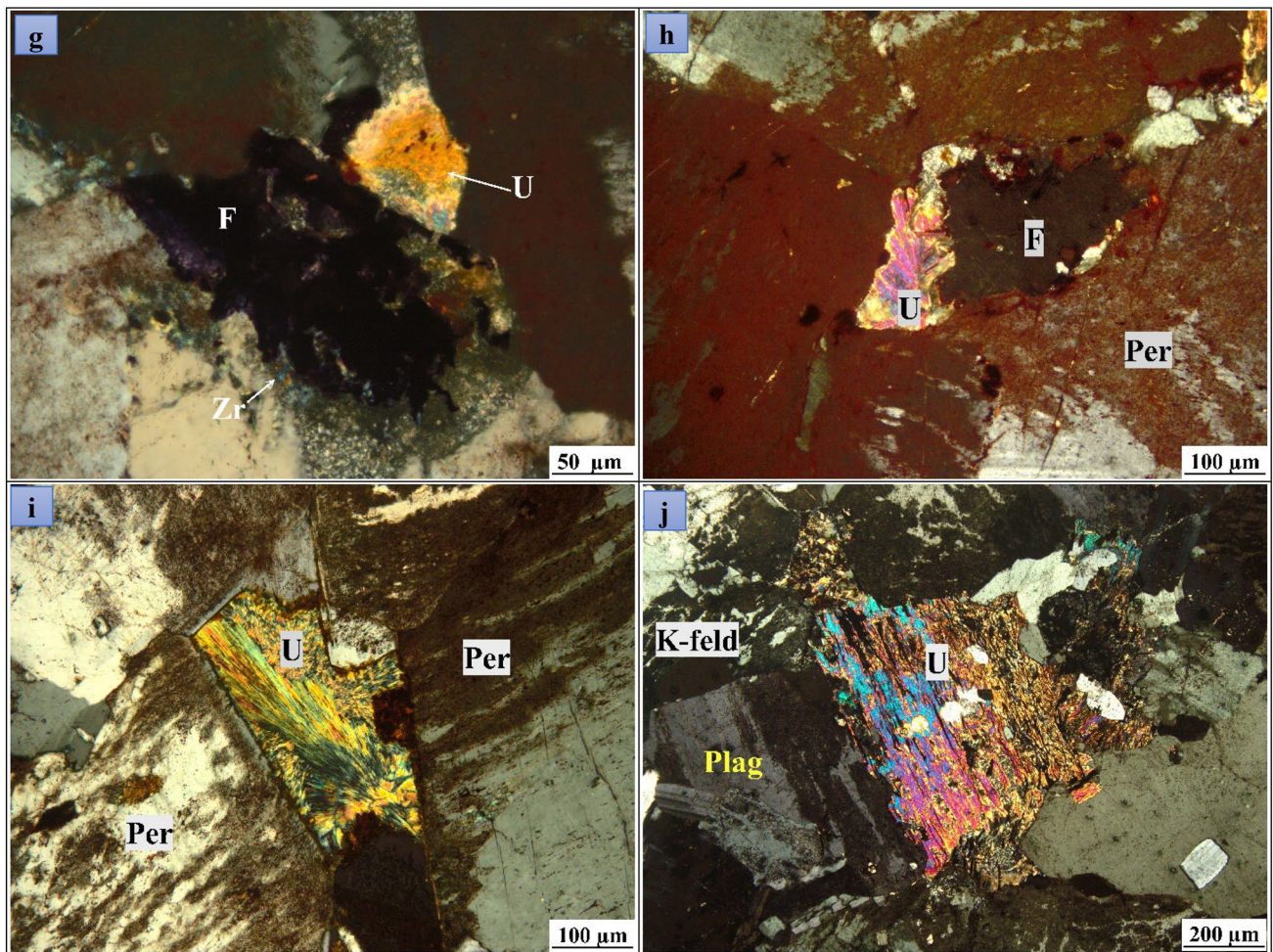


Fig. 3 (continued)

opaque minerals are represented as iron oxides and are found as abundant grains scattered throughout the rocks.

4.2 Mineralogy

4.2.1 Radioactive minerals

Studying the south Um Ara syenogranite is crucial in terms of mineralogy.

(1) Uranium minerals

Uraninite [UO₂]

The primary uranium mineral exists in euhedral to subhedral crystal forms. Coffinite and uranophane gradually replaced the uraninite grains (Fig. 4a). Due to the varied composition of U-mineral phases, some of these U-minerals exhibit areas of varying brightness (Fig. 4a, b). The gradual conversion

manifested itself in the appearance of the coffinitized U-phase. According to EDX analysis (Fig. 5a), uraninite primarily consists of U (89.5 weight percent), with traces of Ca and Si. The ESEM data of the uranyl minerals from the south Um Ara-Wadi Murrah syenogranite indicated the presence of uranyl silicate minerals (coffinite, uranophane, and kasolite) and uranyl phosphate mineral (autunite).

Coffinite [USiO₄]

It is a known alteration product of uraninite in a Si-rich reducing environment [31]. The pseudo morphs of uraninite are the most common form of this product. The coffinite-rich areas of these crystals are usually not as bright in backscattered electron images as the uraninite-filled core (Fig. 4a). This is because U has a higher atomic mass than Si. Moreover, it appeared as a vein-type U-phase or replacement (Fig. 4b, c).

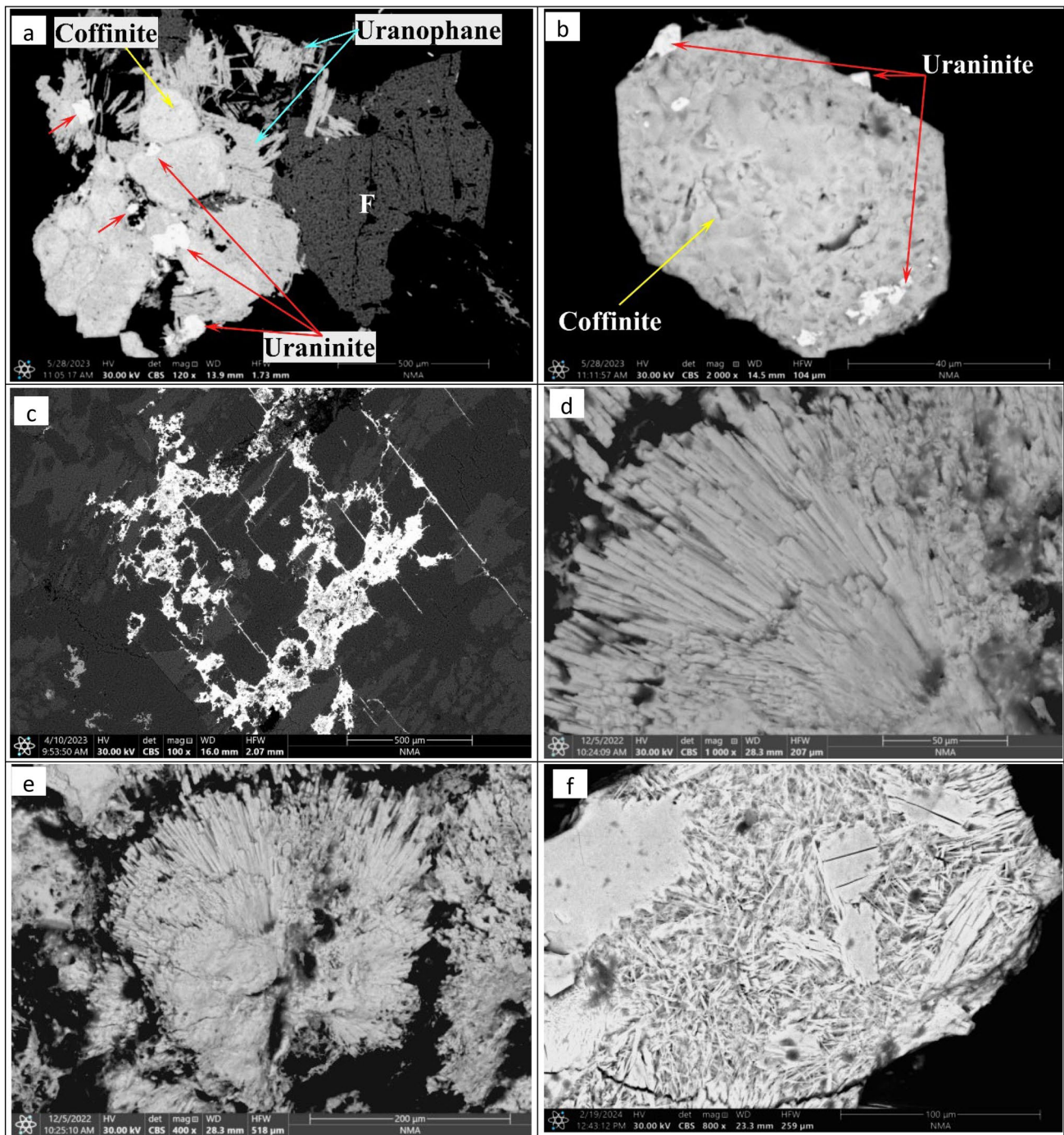


Fig. 4 Back-scattered Electron images (BSE) represent the mineralization in south Um Ara-Wadi Murrah syenogranite **a** uraninite, **b** coffinite, **c–g** uranophane, the dominant crystal forms acicular and fan-shaped, **h** radial shape of uranophane intercalated together with

The concentrations of Si and U in coffinite from the present samples are 79.3 wt% and 13.9 wt%, respectively, with traces of Ca (Fig. 5b). There is an incompatibility between U and Si, as evidenced by the fact that both elements show a negative interrelationship in these U-bearing phases.

fluorite, **i, j** uranophane-xenotime-zircon association, **k, l** kasolite, **m** autunite and **n** uranothorite, south Um Ara-Wadi Mura area, South Eastern desert, Egypt

Uranophane $[\text{Ca}(\text{UO}_2)(\text{SiO}_2)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}]$

It appears under a binocular microscope as small, large fiber aggregates, as yellow radial fibers in the spaces, and as a coating along banding planes. According to [32] uranophane can appear as a complete pseudo morph following uraninite

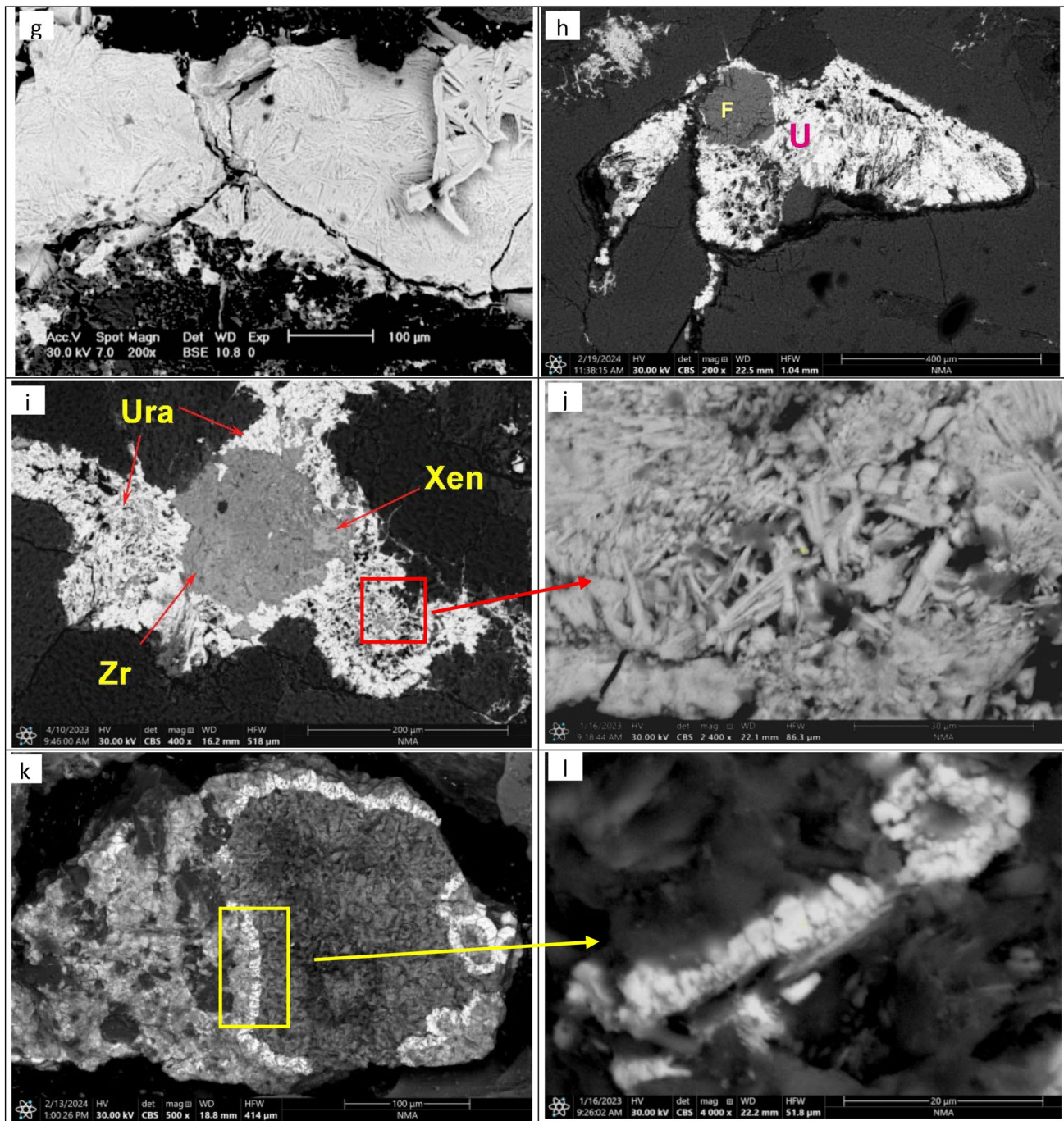


Fig. 4 (continued)

crystals. If the alteration is zonal, it makes up the outermost aureole. The BSE images revealed uranophane crystals exhibiting a matted intergrowth of fine threads arranged in a fan configuration (Fig. 4c–h). The XRD pattern of uranophane shows that the d-spacing of its characteristic peaks (7.88, 3.9, and 2.9 Å) at 2theta (11.22, 22.5, and 29.8), respectively, matches PDF-2 Card No. (83-1847) (Fig. 10b) (Fig. 10a). The EDX analysis confirmed the composition of

the material to be U (75.3–71.9 wt%), Ca (10.8–7.9 wt%), and Si (13.9–17 wt%), as shown in (Fig. 5c, d).

Kasolite [$\text{Pb}(\text{UO}_2)\text{SiO}_4 \cdot \text{H}_2\text{O}$]

It is a hydrated silicate composed of hexavalent uranium and lead; it is the sole uranyl silicate with lead as a predominant cation. The BSE images made it clear that kasolite is

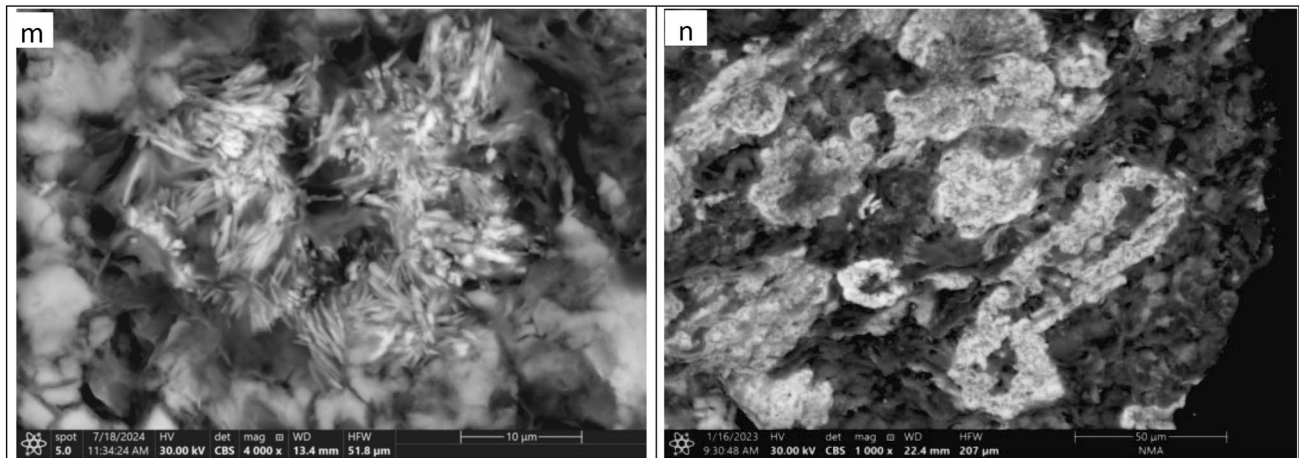


Fig. 4 (continued)

connected to uranothorite (Fig. 4k, l), and the spectrograph confirmed its make-up, showing that uranium, lead, and silica are the main ingredient. The XRD pattern of kasolite shows that the d-spacing of its characteristic peaks (3.07, 2.92, and 3.2 Å) at 2theta (29.07, 30.6, and 27.4), respectively, matches PDF-2 Card No. (08-297) (Fig. 10b). The ESEM data (Fig. 5e) reveals the main elements in kasolite: U (67.4 wt%), Pb (10.6 wt%), and Si (6.7 wt%).

Autunite [$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{--}12\text{H}_2\text{O}$]

The ore comes into contact with oxygen from water and air in the oxidation zone of uranium deposits. Autunite can be found in small aggregates on the surface of quartz at the syenogranite. An XRD investigation analysis was carried out. The XRD pattern shows that the d-spacing of its characteristic peaks (8.62, 3.48, and 3.66 Å) at 2theta (15.27, 38.39, and 36.37), respectively, matches PDF-2 Card No. (28–247) (Fig. 10c). The BSE (Fig. 4m) analysis yielded values of Ca (10.9 wt%), U (66.1 wt%), Si (15.5 wt%), and P (7.4 wt%) (Fig. 5f).

(2) Thorium mineral

Uraniothorite [$(\text{Th}, \text{U})\text{SiO}_4$]

It manifests as elongate, anhedral to subhedral crystals, with individual grains varying in size up to 50 μm (Fig. 4n). Thorite is consistently found in association with xenotime and zircon. The EDX microanalyses data show that uranothorite consists primarily of Th (56.5 wt%), Si (27 wt%), and

U (15.7 wt%) (Fig. 5g). The kasolite cores exhibit minute crystals arranged in a radiated form, indicating their possible exsolution from the $(\text{PbSiO}_4\text{--ThSiO}_4)$ solid solution. XRD pattern shows its characteristic peaks d-spacing (3.56, 4.71, and 2.65 Å) matches PDF-2 Card No. (8-395) (Fig. 10d). The EDX analysis and XRD revealed that the system consisted of U (66.5 wt%), Th (5.7 wt%), Si (10.8 wt%), and Pb (17 wt%) (Fig. 5h).

4.2.2 Radioactive bearing-minerals (Ta–Nb minerals)

Betafite [$(\text{U}, \text{Ca})_2(\text{Ta}, \text{Nb}, \text{Ti})_2\text{O}_6(\text{OH})$]

It is a uranyl titanate mineral that belongs to the primary U minerals. It has a black appearance and is found in sub-angular to subrounded grains. The EDX identifies the composition of betafite U (57.6 wt%), Nb (12.8 wt%), and Si (15.2 wt%). In some samples, betafite has a composition of U (51.5 wt%), Nb (15.4 wt%), and Y (7.7 wt%) (Fig. 6a, b).

Ishikawaite [$(\text{U}, \text{Fe}, \text{Y}, \text{Ca})(\text{Nb}, \text{Ta})\text{O}_4$]

It is considered a member of the samarskite group due to its significant uranium content. The particles are either angular or subangular in shape. The relative semi-quantitative ESEM-EDX microanalysis also showed that up to 45.5–17.4 weight percent of U was linked to 25–30 weight percent of Nb, which is within the normal range in Ishikawaite (Fig. 6c, d).

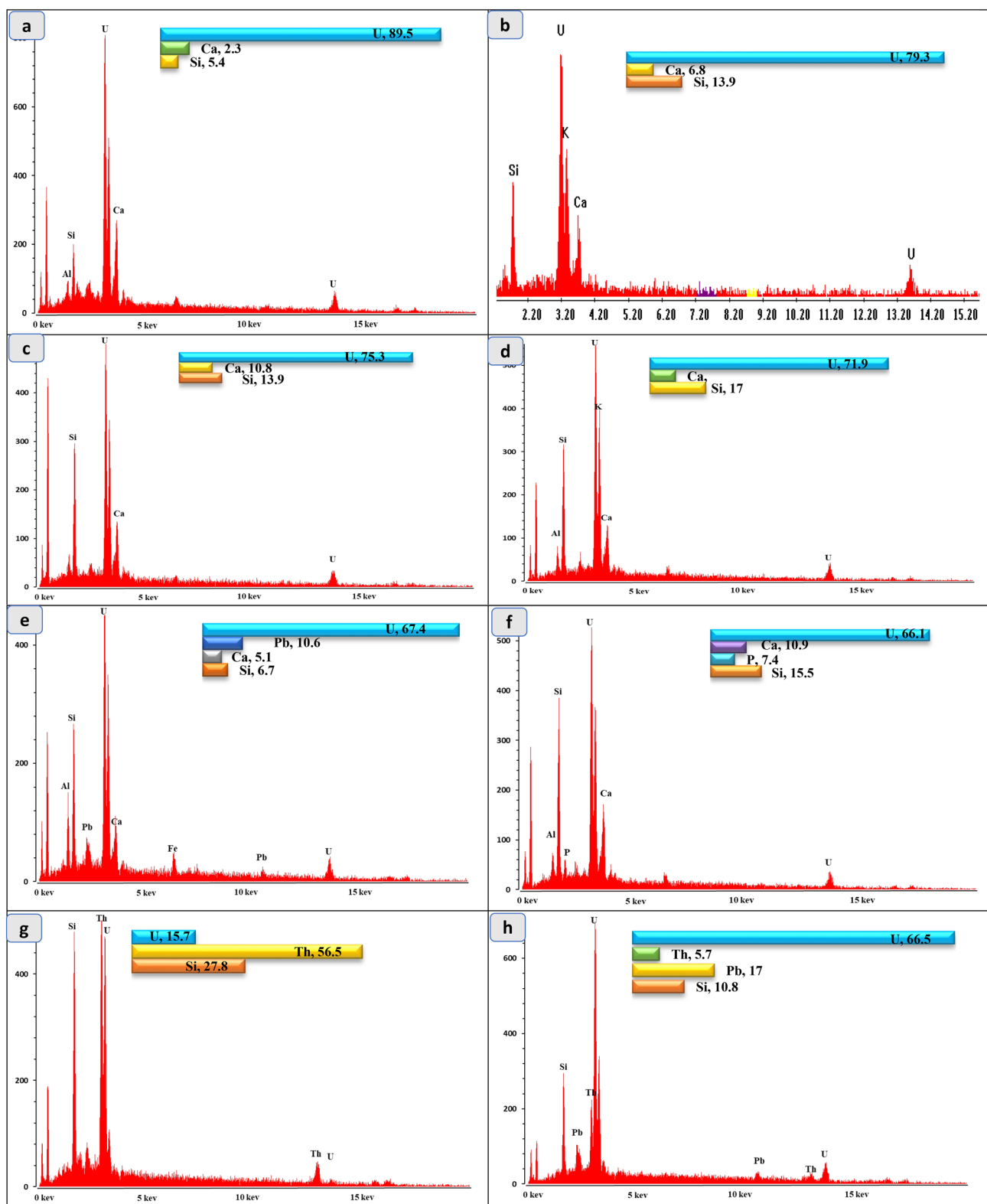


Fig. 5 Spectral analyses of: **a** uraninite, **b** coffinite, **c**, **d** uranophane, **e** kasolite, **f** autunite and **g**, **h** uranothorite, south Um Ara-Wadi Murrah syenogranite, SED, Egypt

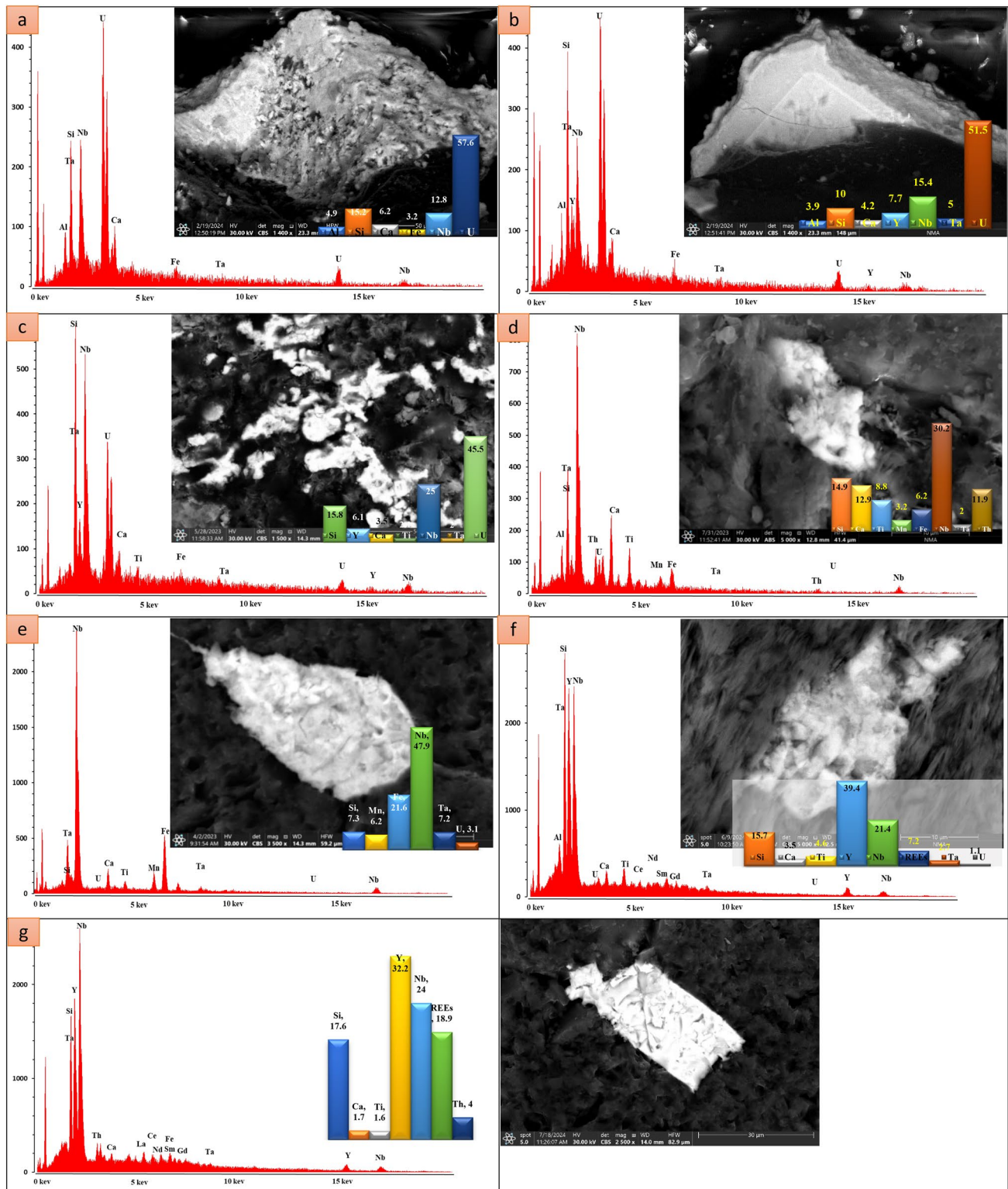


Fig. 6 Spectral analyses, and BSE images of **a, b** betafite, **c, d** ishkawaite, **e** columbite, **f** fergusonite and **g** samarskite, south Um Ara-Wadi Murrah syenogranite, SED, Egypt

Columbite [(Fe,Mn)Nb₂O₆]

AB₂O₆ is the general formula for the orthorhombic columbite-tantalite group minerals (CGM). Fe²⁺ or Mn²⁺ occupy the A-site, and Nb⁵⁺ or Ta⁵⁺ occupy the B-site [33, 34]. Heinrich [35] attributed the lack of U in the columbite structure to a reduction in crystallization temperature, indicating the influence of hydrothermal solutions on the mineral's precipitation. The XRD pattern of columbite shows that the d-spacing of its characteristic peaks (2.98, 3.6, and 7.15

Å) at 2theta (29.9, 24.2 and 12.36), respectively, matches PDF-2 Card No. (16-0337) (Fig. 10e). The analysis indicates that Fe (21.6 wt%), Ta (7.2 wt%), and Nb (47.9 wt%) constitute the predominant components of ferro-columbite, with minor amounts of Ca and U present (Fig. 6e).

Fergusonite [YNbO₄]

It appears in corroded and severely deformed forms, with fine to coarse grains up to 50 µm, subhedral to anhedral, and

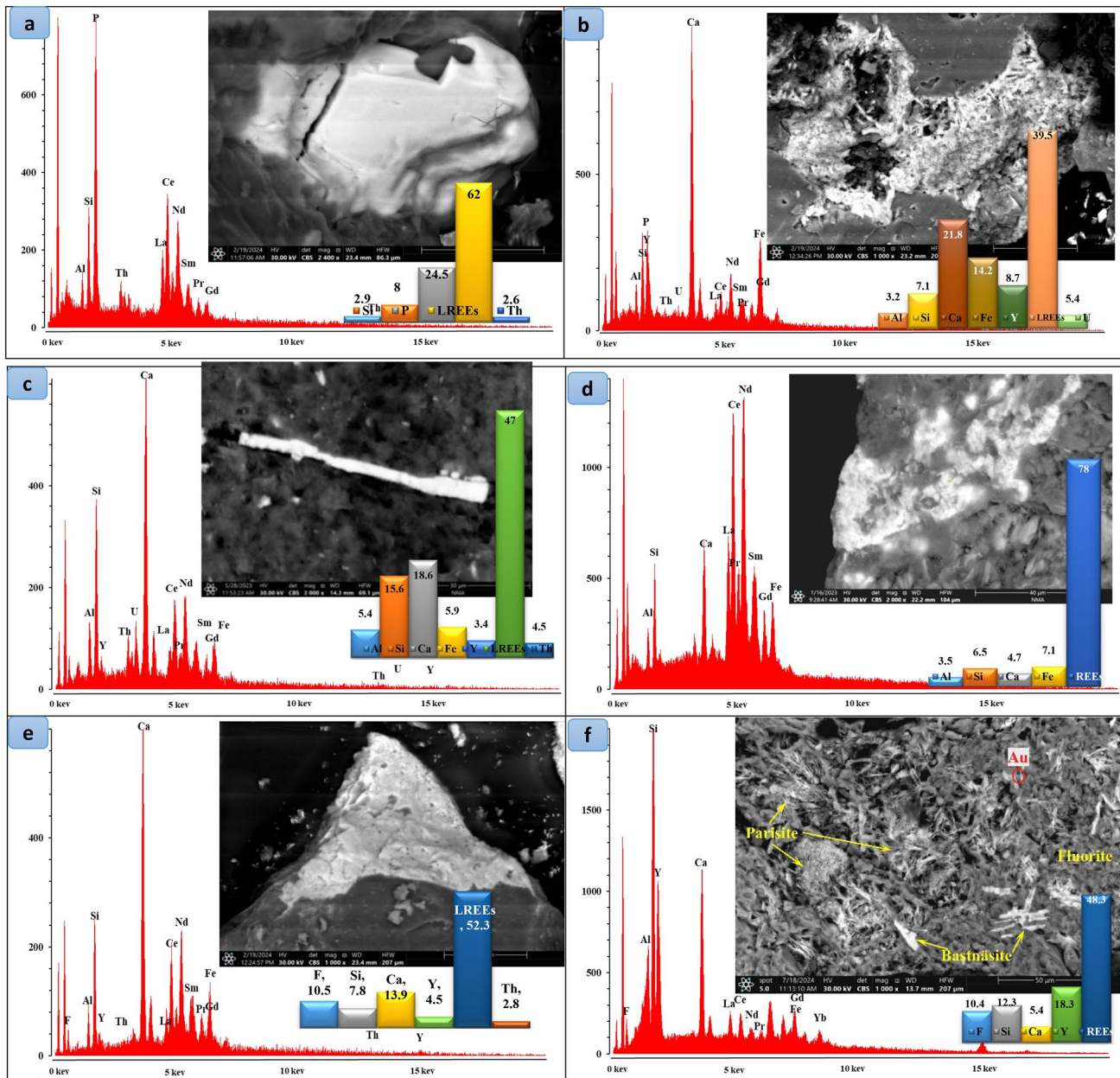


Fig. 7 Back-scattered Electron images (BSE), EDX patterns and XRD of **a** monazite, **b–d** allanite, **e** parisite, **f, g** bastnäsite, **h** xenotime, **i** uraniferous xenotime and **j** chernovite, south Um Ara-Wadi Murrah syenogranite, SED, Egypt

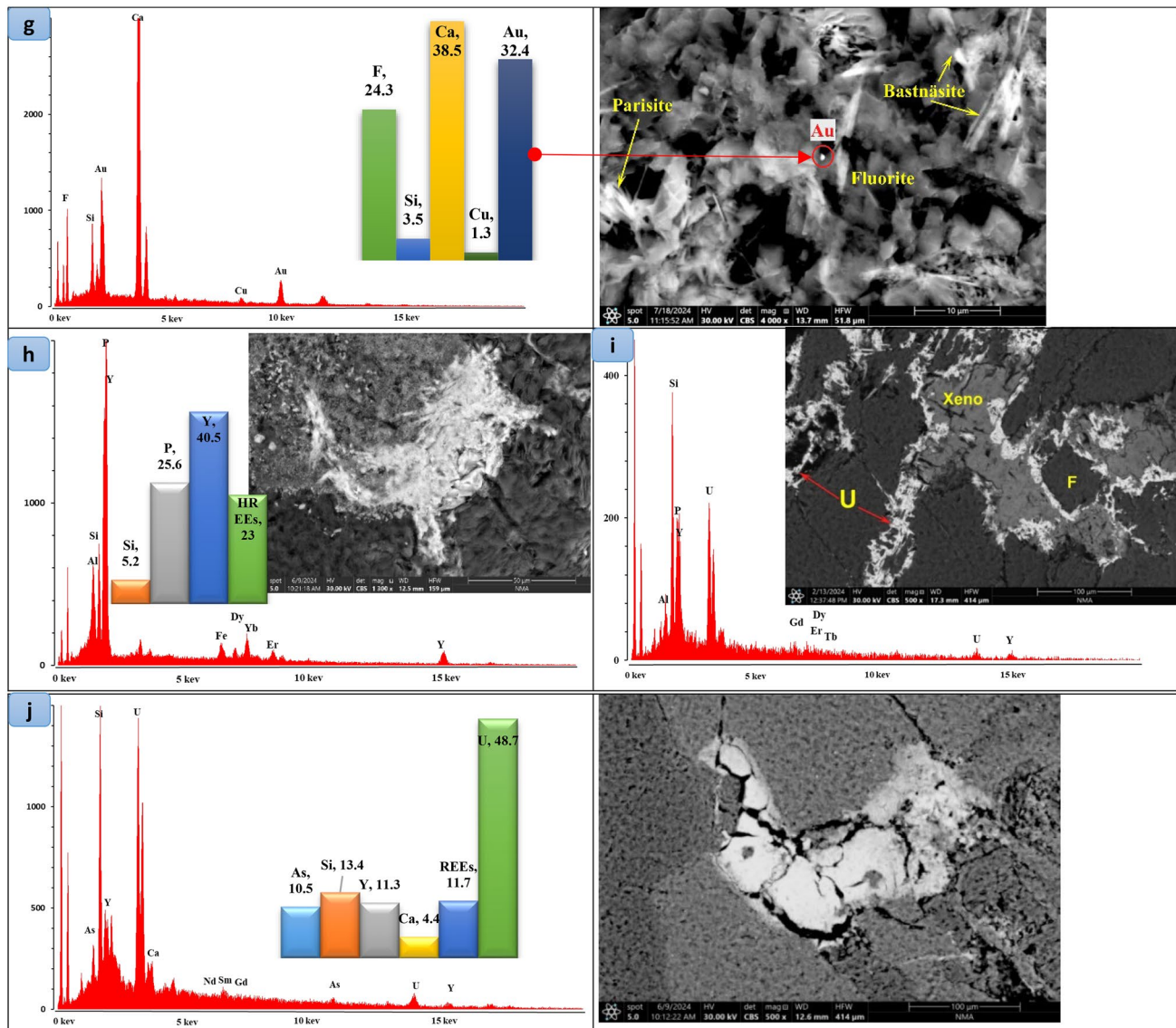


Fig. 7 (continued)

tabular to prismatic shapes. Columbite's peripheries display fine-grained fergusonite. Using SEM, the semi-quantitative chemical composition of the fergusonite grains revealed an enrichment in niobium (21 wt%), tantalum (2.7 wt%), yttrium (39.4 wt%), and REE (7.2 wt%) (Fig. 6f).

Samarskite [(Ca, U, Y, Th)(Ti, Ta, Nb)O₆]

The grains can range from angular to subangular in shape. The EDX data revealed that the recorded samarskite grains (Fig. 6g) consist of Y (32 wt%), Th (4 wt%), Nb (24 wt%), and REEs (18.9 wt%).

4.2.3 REEs minerals

Monazite-(Ce) [(Ce, Y, Nd, Th, La) PO₄]

It is stable at either intermediate pressure or low temperature, or both [36]. XRD pattern shows its characteristic peaks d-spacing (3.09, 2.87, and 3.3 Å) matches PDF-2 Card No. (11-556) (Fig. 10f).

An EDX test showed that it has a lot of light REEs (62% of the total weight), especially Ce. It also has a lot of P (24.5 wt%) and Th (2.6 wt%) (Fig. 7a).

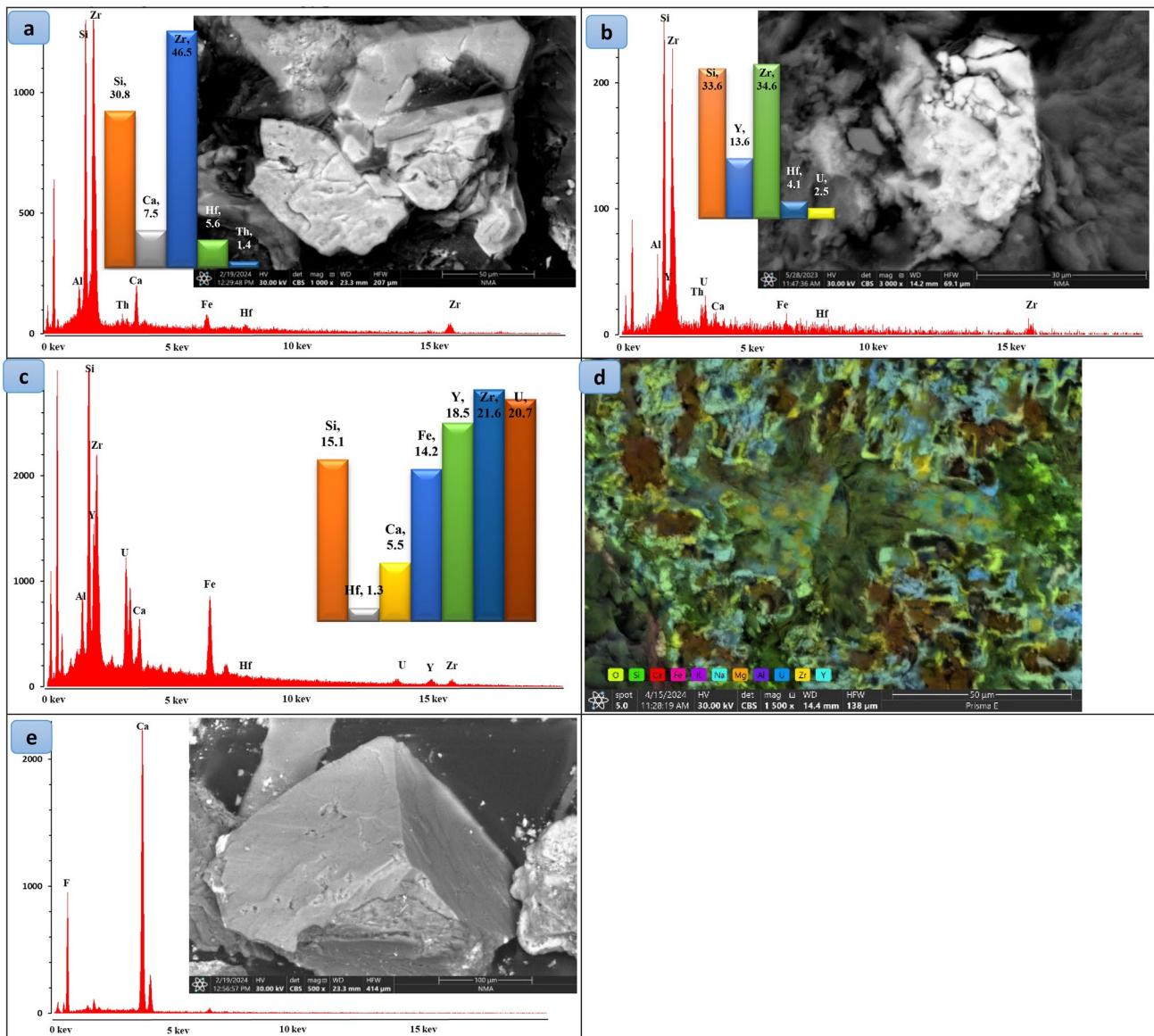


Fig. 8 SEM images with EDX spectrum analyses of of **a–d** zircon and **e** fluorite, south Um Ara-Wadi Murrah syenogranite, SED, Egypt

Allanite [$\text{Ca}(\text{Ce}, \text{La}, \text{Y}, \text{Ca})\text{Al}_2(\text{Fe}^{2+}, \text{Fe}^{3+})(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$]

The EDX analyses give Ca from 21.8 to 4.7 wt%, LREEs from 39.5 to 78 wt% with traces of Y and Th (Fig. 7b–d).

Parisite [$\text{Ca}(\text{Nd}, \text{La}, \text{Ce})_2(\text{CO}_3)_3\text{F}_2$]

It belongs to the REE fluorocarbonates group, also known as the bastnäsite series [37]. ESEM (Fig. 8e) confirmed the presence of Parisite, and analyses revealed a total LREE of approximately 52.3 wt%.

Bastnaesite [$(\text{La}, \text{Ce}, \text{Nd})(\text{CO}_3)\text{F}$]

It is an uncommon REE-bearing carbonate mineral, which occurs in a mineral series with hydroxyl-bastnaesite. It is related to parisite [$\text{Ca}(\text{Ce}, \text{La})_2(\text{CO}_3)_3\text{F}_2$] and may form replacement crystals after allanite [38]. LREE dominates bastnaesite, which is one of the world's primary sources of REEs [39]. Granitic rocks contain bastnaesite in a solid solution with other minerals like fluorite, parisite, and gold (Fig. 7g). The XRD pattern of bastnaesite shows that the d-spacing of its characteristic peaks (2.87, 3.55, and 4.87 Å) at 2theta (29.8, 25 and 18.18), respectively, matches PDF-2 Card No. (81–1537) (Fig. 10g). The ESEM

technique confirmed displaying the total Y (18.3 wt%), LREEs (48.3 wt%), and F (10.4 wt%) (Fig. 7f).

Xenotime [YPO₄]

It is a rare earth phosphate mineral containing mostly yttrium orthophosphate. Xenotime has different crystal structures, such as prismatic (stubby or thin and long) with dipyramidal ends, radial or granular aggregates, and rosettes [40]. The EDEX analysis shows P (25.6 wt%), Y (40.5 wt%), and HREEs (23 wt%) (Fig. 7h). The XRD pattern of xenotime shows that the d-spacing of its characteristic peaks (3.44, 4.53 and 2.56 Å) at 2theta (25.88, 19.5 and 35), respectively, matches PDF-2 Card No. (5-454) (Fig. 10h).

The studied granitic rocks occasionally contained other morphological types of xenotime known as uraniferous xenotime, including large leaf-shaped crystals associated with uranophane and fluorite (Fig. 7i). Due to uranium partially replacing yttrium in xenotime, some crystals of xenotime specimens may be strongly radioactive. According to [41], it's possible that xenotime originated from coffinite when Y and P replaced U and Si, respectively.

Chernovite-(Y) [YAsO₄]

It is a rare mineral; it is a member of the xenotime group. Fluids containing As influence felsic rocks, leading to hydrothermal alteration and the creation of this rare mineral. Chernovite and xenotime have the same structure and are part of an almost continuous series that is isomorphic to AXO₄. In this series, A stands for Sc, U, Th, REE (Sm–Lu), Y, and Ca, and X stands for V, Si, P, As, and Nb [41–43]. Scanning electron microscopy showed that the bright spots have different amounts of Y (11.3 wt.%), As (10.5 wt.%), U (48.7 wt.%), and LREEs (11.7 wt%) (Fig. 7j).

4.2.4 Accessory minerals

Zircon [ZrSiO₄]

They are presented by prismatic, anhedral to subhedral crystals, and subrounded to oval-shaped crystals that reached up to 200 µm (Fig. 8a, b). Usually zoned, the radioactive zircon also exhibits metamictization. Zircon sometimes occurs as a solid solution with Y (18.5 wt%) and U (20.7 wt%) (Fig. 8c,

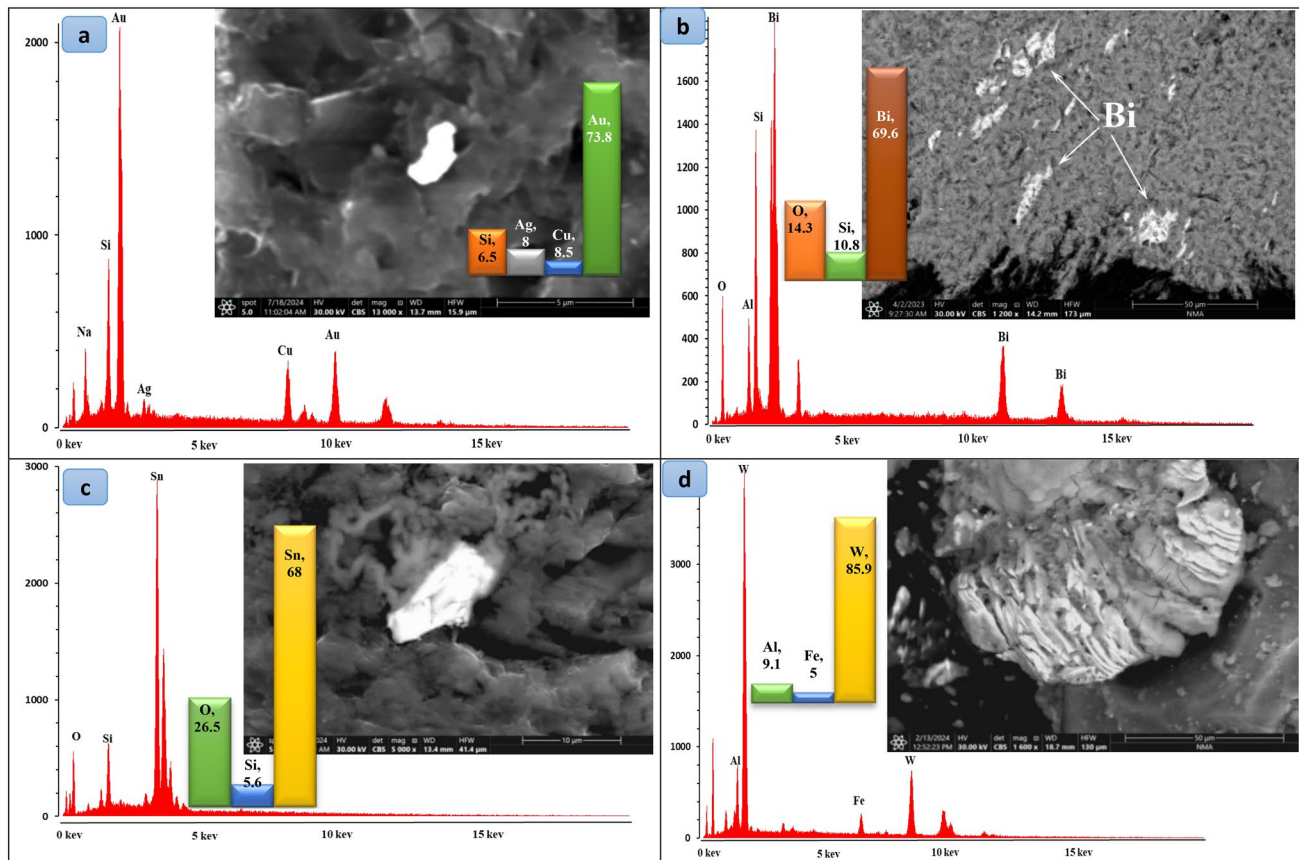


Fig. 9 Back-scattered Electron images (BSE) and EDX patterns of **a** gold, **b** bismite, **c** cassiterite and **d** wolframite, south Um Ara-Wadi Murrah syenogranite, SED, Egypt

d). The XRD pattern shows that the d-spacing of its characteristic peaks (3.30, 2.52 and 4.4 Å) at 2theta (26.99, 35.5 and 20), respectively, matches PDF-2 Card No. (6-6266) (Fig. 10i).

Fluorite [CaF₂]

It has a violet color, mainly attributed to the radiation effect [44, 45]. Consequently, the deep violet fluorite has a higher content of fluorine relative to calcium. Fluorite, a common mineral in hydrothermal veins, frequently coexists with uranium minerals. Additionally, it can be found as tiny crystals (25 µm) that might have been created by hydrothermal solutions and associate with uranophane. Fluorite is confirmed by ESEM techniques and XRD having a Ca:F ratio equals to 2:1 (Fig. 8e). The XRD pattern of fluorite shows that the d-spacing of its characteristic peaks (3.15, 1.9 and 1.6 Å) at 2theta (28.2, 47 and 55.8), respectively, matches PDF-2 Card No. (89-4794) (Fig. 10j).

4.2.5 Base metals

Gold [Au]

In the chemical progression of the Periodic Table, Au normally between Pt and Hg. Gold typically manifests as native minute crescent shapes, with sizes averaging around 50 µm (Fig. 9a). It is the first time that the native gold is assigned in the study area; it is confirmed by ESEM, containing Au (73.8 wt%), with traces of Ag (8 wt.%), and Cu (8.5 wt.%).

Bismite [Bi₂O₃]

It is an oxidation product of bismuth minerals. It was recorded as a veinlet (~50 µm). Additionally, it can be found in magmatic-hydrothermal deposits of W, Mo, Cu, Sn, and Au that are genetically related to granites [46, 47]. According to SEM analysis, bismite contains 69.6% Bi, with trace levels of Si and Al (Fig. 9b).

Cassiterite [SnO₂]

It belongs to the rutile group and appears as coarse to medium-grained crystals, either angular to subangular or anhedral to subhedral. Hydrothermal veins with medium to high temperatures contain it. EDX found Sn (68 weight percent) with traces of Al and Si (Fig. 9c).

Wolframite [(Mn, Fe) WO₄]

It is detected by the ESEM technique, having W (85 wt%) and Fe (5 wt%) (Fig. 9d).

4.3 Geochemistry

4.3.1 Geochemical characteristics

Major oxides, total REEs, and some trace elements were estimated in sixteen samples of south Um Ara-Wadi Murrah syenogranite (Table 1). The samples have an average of SiO₂ (av. 76 wt%) and Al₂O₃ (av. 11.47 wt%) with total alkalis (K₂O + Na₂O) content of (av. 7.4 wt%). The Um Ara-Wadi Murrah syenogranites exhibit a high uranium content, ranging from 264.8 to 6349.7 ppm, with av. = 3451 ppm. The presence of radioactive minerals (uraninite, coffinite, autunite, kasolite, and uranophane) and the presence of xenotime, monazite, and allanite, contribute to the enrichment of uranium.

Plotting the studied granites in the classification diagram of [48] (Fig. 11), they fall consistently within the syenogranite in a complete harmony with petrographic studies. Plotting the studied granites on the Chondrite-normalized REE patterns [49] indicates higher values for most elements than the primitive mantle values (Fig. 12). The REEs content varies from 159.72 to 884.66 ppm with av. = 273 ppm (Table 1) and indicate fractionated REE patterns presented by the LREE enrichment and HREE depletion. They show significant negative Eu anomalies with average Eu/Eu* = 0.02 (Table 1). Europium (Eu) anomalies are mainly controlled by plagioclase fractionation especially in felsic magmas. Thus, removal of feldspars from a felsic melt by crystal fractionation or by partial melting of a rock in which feldspars are retained in the source will give rise to negative Eu anomaly in REE patterns. The -ve Eu anomaly could be due to low pressure fractionation of plagioclase that led to depletion in Sr and Eu. The perceptible negative Eu anomaly is either due to the partitioning of Eu into feldspar during fractionation, which is an important process in developing peralkalinity, or the presence of residual feldspar in the source [50].

Ce/Ce* in nearly all samples are positive Ce anomaly (Av. 1.04), revealing the oxidizing condition, in which the REEs were enriched, where Ce is oxidized into its immobile Ce⁴⁺ state.

The tetrad impact has been progressively increased, in particular for the granitic rocks, which suffered from a high degree of fractional hydrothermal alteration, crystalization, and mineralization [50, 51].

Values of tetrad implication were estimated using the quantification method [50]: $t_4 = (Tm/Tm^* \times Yb/Yb^*)$, $t_3 = (Tb/Tb^* \times Dy/Dy^*)$, $t_1 = (Ce/Ce^* \times Pr/Pr^*)$, where degree of the tetrad effect $T_{1,3} = (t_1 \times t_3)^{1/2}$. The REE tetrad effect is primarily observed in late magmatic differentiation due to strong deuteric alteration or hydrothermal interactions [51]. The calculated values of the tetrad effect are 1.12. The chondrite-normalized REE patterns for syenogranite

Table 1 Chemical composition of major oxides (Wt. %), some trace elements and REEs (ppm) analyses of syenogranite of the Um Ara- Wadi Murrah area, SED, Egypt

	UR1	UR2	UR3	UR4	UR5	UR6	UR7	UR8	UR9	UR10	UR11	UR12	UR13	UR14	UR15	UR16	Av
<i>XRF analyses</i>																	
SiO ₂	69	78.2	76.02	77.7	77.02	76.7	73.43	77.16	74.47	76.44	77.08	73.43	77.01	76.46	77.9	79.36	76.09
TiO ₂	0.07	0.04	0.04	0.03	0.04	0.04	0.05	0.04	0.05	0.03	0.04	0.06	0.05	0.04	0.02	0.02	0.04
Al ₂ O ₃	12.83	10.5	11.45	12.04	11.26	11.59	11.35	11.28	11.21	11.88	11.65	11.35	10.94	12.06	11.4	10.65	11.47
Fe ₂ O ₃	5.5	1.85	2.69	0.95	1.94	1.88	4.86	1.76	3.84	1.74	1.69	4.66	1.78	1.52	1.56	1.08	2.46
MnO	0.04	0.01	0.01	0.01	0.01	0.01	0.04	0.01	0.01	0.01	0.01	0.04	0.01	0.01	0.01	0.01	0.02
MgO	0.21	0.11	0.15	0.06	0.12	0.1	0.2	0.09	0.17	0.11	0.13	0.19	0.11	0.12	0.08	0.05	0.13
CaO	1.95	0.31	0.58	0.29	0.39	0.43	0.86	0.31	0.69	0.35	0.33	0.76	0.46	0.33	0.36	0.32	0.55
Na ₂ O	3.61	3.45	3.64	3.93	3.62	3.79	2.96	3.68	3.7	3.86	3.8	2.96	3.51	3.8	3.75	3.46	3.60
K ₂ O	3.01	3.93	3.96	4.21	3.74	3.97	3.35	4.09	3.8	3.99	3.99	3.34	3.87	3.76	4.15	3.62	3.80
P ₂ O ₅	0.03	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.01
LOI	3.05	0.81	0.97	0.81	0.93	0.89	1.89	1.03	1.11	0.93	0.89	1.89	0.96	1.2	0.63	0.74	1.17
Total	99.31	99.21	99.52	100.0	99.09	99.39	99.1	99.45	99.04	99.36	99.62	98.7	98.71	99.3	99.86	99.31	99.31
ClA	59.95	57.72	58.33	58.82	59.23	58.59	61.29	58.26	57.78	59.16	58.93	61.65	58.25	60.45	57.99	59	59.09
Ba	92.22	45.36	39.54	61.63	34.56	47.94	52.06	58.1	42.1	41.34	47.5	23.45	26.1	33.5	36.41	46.74	45.53
Rb	217.7	264.59	258.6	314.8	261.46	267.6	217.84	281	256.79	280.45	281.1	238.87	272.09	270.9	304.5	341.6	270.62
Sr	72.63	16.37	21.43	14.36	19.77	17.85	26.57	17.66	21.52	18.33	17.38	23.29	17.42	16.61	14.89	13.81	21.87
Y	350.2	135.93	182.81	141.89	121.86	148.54	897.36	111.46	158.19	118.81	93.89	157.87	185.5	120.86	116.21	112.15	197.08
Zr	698.7	136.06	224.8	301.4	119.28	113.84	920.93	135.2	224.41	166.04	440.13	111.09	225.79	117.6	161.4	107.3	262.67
Nb	192.9	133.12	82.13	294.2	125.37	106.6	565.65	171.4	73.94	101.22	113.86	66.52	144.07	143.7	193.8	206.7	169.67
Cr	102.8	69.35	84.89	65.22	92.9	80.52	91.34	69.63	84.89	82.22	84.77	92.13	78.14	73.56	65.05	65.81	80.20
Ni	29.27	5.48	11.54	4.48	7.69	8.1	19.5	5.71	12.63	7.65	5.29	8.66	6.51	4.39	3.66	1.89	8.90
Cu	4.34	3.18	4.2	2.71	20.4	6.3	10.17	3.54	8.19	4.64	6.03	10.17	3.55	33.24	2.46	2.12	7.83
Zn	88.14	23.44	55.91	18.52	49.03	54.29	243.27	19.56	84.85	55.42	47.18	273.39	34.27	28.12	20.88	20.88	69.82
V	5.4	5.53	8.82	5.13	7.4	7.01	12.25	6.25	7.4	6.65	6.31	7.2	6.71	6.67	5.36	3.11	6.70
Co	2.23	1.02	Ud	Ud	1.25	Ud	1.01	0.75	Ud	1.08	1.76	2.83	1.12	Ud	Ud	0.96	1.40
F	2301	2386.9	2495	2742	2577.1	2483.5	3214.9	1990	3232.3	2410.4	2857.6	3460.5	4848.4	2305	2639	2713	2791.2
<i>ICP-MS analyses</i>																	
Li	42.3	10.12	Ud	Ud	Ud	Ud	44.28	6.11	Ud	Ud	Ud	4.44	Ud	Ud	2.17	Ud	18.24
Be	11.2	6.26	7.75	5.26	8.13	5.85	19.32	7.3	8.57	5.52	9.45	10.83	6.91	11.58	5.46	5.38	8.41
B	15.9	12.41	12.36	Ud	Ud	Ud	14.46	Ud	Ud	2.07	Ud	Ud	Ud	Ud	Ud	Ud	11.38
Sc	Ud	Ud	3.41	Ud	Ud	Ud	3.51	Ud	Ud	1.01	Ud	Ud	Ud	Ud	Ud	Ud	2.22
Ga	40.7	39.83	34.33	41.49	30.42	34.21	50.25	38.08	30.87	35.26	34.64	34.76	40	37.26	39.45	44.02	37.83
As	60.5	177.56	66.54	65.29	110.92	251.36	251.15	48.44	78.9	317.8	69.45	60.47	39.95	94.39	22.71	168.6	117.75
Sn	18.8	15.31	20.65	18.49	13.38	14.14	23.18	14.89	17.93	14.32	17.54	11.23	10.69	16.55	10.66	12.51	15.64
Hf	31.7	18.96	10.83	21.18	6.56	6.49	45.21	8.31	10.24	3.5	19.72	4.72	9.58	6.86	5.88	4.47	13.37

Table 1 (continued)

	UR1	UR2	UR3	UR4	UR5	UR6	UR7	UR8	UR9	UR10	UR11	UR12	UR13	UR14	UR15	UR16	Av
Ta	8.97	6.49	5.64	7.39	4.4	5.82	8.2	7.41	16.38	5.69	5.79	6.66	6.72	5.8	7.51	7.42	7.27
Pb	784	72.02	218.5	50.93	156.36	92.97	569.13	70.78	121.87	79.33	114.83	97.27	76.28	224.2	106.9	61.01	181
Th	42.9	23.74	28.47	31.54	17.61	23.29	36.62	29.67	24.51	33.63	25.55	18.34	23.44	22.92	22.18	38.87	27.71
U	6286	1655.95	307.26	600.59	4382.24	4858.78	6349.77	1305.1	4855.31	4359.72	3695.25	2338.55	4394.21	4668.7	264.83	4900.9	3451.4
Cs	7.61	2.29	3.3	2.47	2.5	2.51	3.07	2.68	7.04	2.06	9.86	2.79	2.55	3.16	1.8	1.97	3.60
La	35.62	11.24	25.19	14.98	11.75	14.78	51.94	21.36	18.51	10.29	21.62	18.25	17.45	10.37	20.68	22.72	20.42
Ce	112.94	40.75	81.68	53.09	44.45	43.88	148.49	62.05	53.08	35.34	64.42	58.04	59.11	38.17	57.03	64.91	63.59
Pr	17.12	6.59	13.1	8.96	7.06	7.15	25.52	9.47	7.58	6.01	12.53	9.39	9.46	5.6	8.94	12.21	10.42
Nd	84.89	28.74	58.74	43.13	31.67	33.23	119.53	53.48	38.68	23.84	51.12	46.18	44.05	25.19	41.06	52.71	48.52
Sm	27.01	11.54	20.03	16.88	12.16	14.41	55.75	14.04	14.38	9.59	16.16	16.9	18.25	10.17	15.34	19.77	18.27
Eu	0.22	0.14	0.12	0.1	0.02	0.03	0.39	0.11	0.15	<dl	0.11	0.17	0.01	0.03	0.04	0.03	0.11
Gd	29.59	13.71	23.69	16.03	14.45	16.72	83.29	16.41	17.07	15.24	12.01	20.9	21.29	15.69	19.17	19.93	22.20
Tb	6.64	3	4.14	3.21	2.96	3.96	20.13	2.82	3.62	3.59	2.26	4.1	4.73	3.24	3.65	3.48	4.72
Dy	45.93	21.47	30.98	23.17	19.68	29.45	154.17	18.21	26.25	25.2	15.99	29.13	33.14	22.2	23.28	24.2	33.90
Ho	10.36	4.43	6.56	4.77	4.14	6.01	32.43	3.89	5.6	5.13	3.72	6.38	6.99	4.69	4.97	4.63	7.17
Er	32.61	13.23	20.53	15.44	11.33	16.89	97.09	11.38	16.29	13.41	10.36	18.49	20.58	13.2	13.86	12.54	21.08
Tm	4.78	1.73	2.87	2.29	1.5	2.16	12.69	1.57	2.34	1.81	1.25	2.53	3.06	1.86	2.04	1.62	2.88
Yb	31.95	11.2	19.39	14.88	9.43	13.12	74.03	9.08	14.25	9.21	8.27	16.44	17.57	11.1	12.69	10.5	17.69
Lu	4.38	1.53	2.21	1.65	1.14	1.51	9.21	1.23	1.91	1.06	0.95	2.16	2.22	1.4	1.45	1.17	2.20
REEs	444.0	169.3	309.2	218.6	171.7	203.3	884.7	225.1	219.7	159.7	220.8	249.1	257.9	162.9	224.2	250.4	273.2
LREEs	277.8	99.0	198.9	137.1	107.1	113.5	401.6	160.5	132.4	85.1	166.0	148.9	148.3	89.5	143.1	172.4	161.3
HREEs	166.2	70.3	110.4	81.4	64.6	89.8	483.0	64.6	87.3	74.7	54.8	100.1	109.6	73.4	81.1	78.1	111.8
Eu/Eu*	0.02	0.03	0.02	0.02	0.00	0.01	0.02	0.02	0.03	0.03	0.02	0.03	0.002	0.007	0.007	0.005	0.02
Ce/Ce*	1.07	1.11	1.05	1.074	1.14	1.00	0.96	1.02	1.05	1.05	0.92	1.039	1.08	1.17	0.98	0.91	1.04
t1	1.13	1.29	1.20	1.21	1.30	1.13	1.10	1.01	1.06	1.31	1.21	1.13	1.20	1.28	1.09	1.15	1.17
t3	1.08	1.12	0.99	1.07	1.07	1.17	1.17	0.98	1.08	1.17	0.98	1.03	1.12	1.08	1.03	1.04	1.07
t4	1.07	1.01	1.15	1.20	1.08	1.09	1.06	1.05	1.07	1.12	1.06	1.06	1.12	1.10	1.18	1.12	1.10
t1,3	1.11	1.20	1.09	1.14	1.18	1.15	1.13	0.99	1.07	1.24	1.09	1.08	1.16	1.17	1.06	1.09	1.12

CIA is defined as $\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}) * 100$

Ud: Under detection limit

Eu anomaly is calculated by: $\text{Eu}/\text{Eu}^* = [(\text{Eu}_N)/(\text{SQR}(\text{Sm}_N, \text{Gd}_N))];$ value of Ce anomaly is calculated by: $\text{Ce}/\text{Ce}^* = [(\text{Ce}_N)/(\text{SQR}(\text{La}_N, \text{Pr}_N))]$

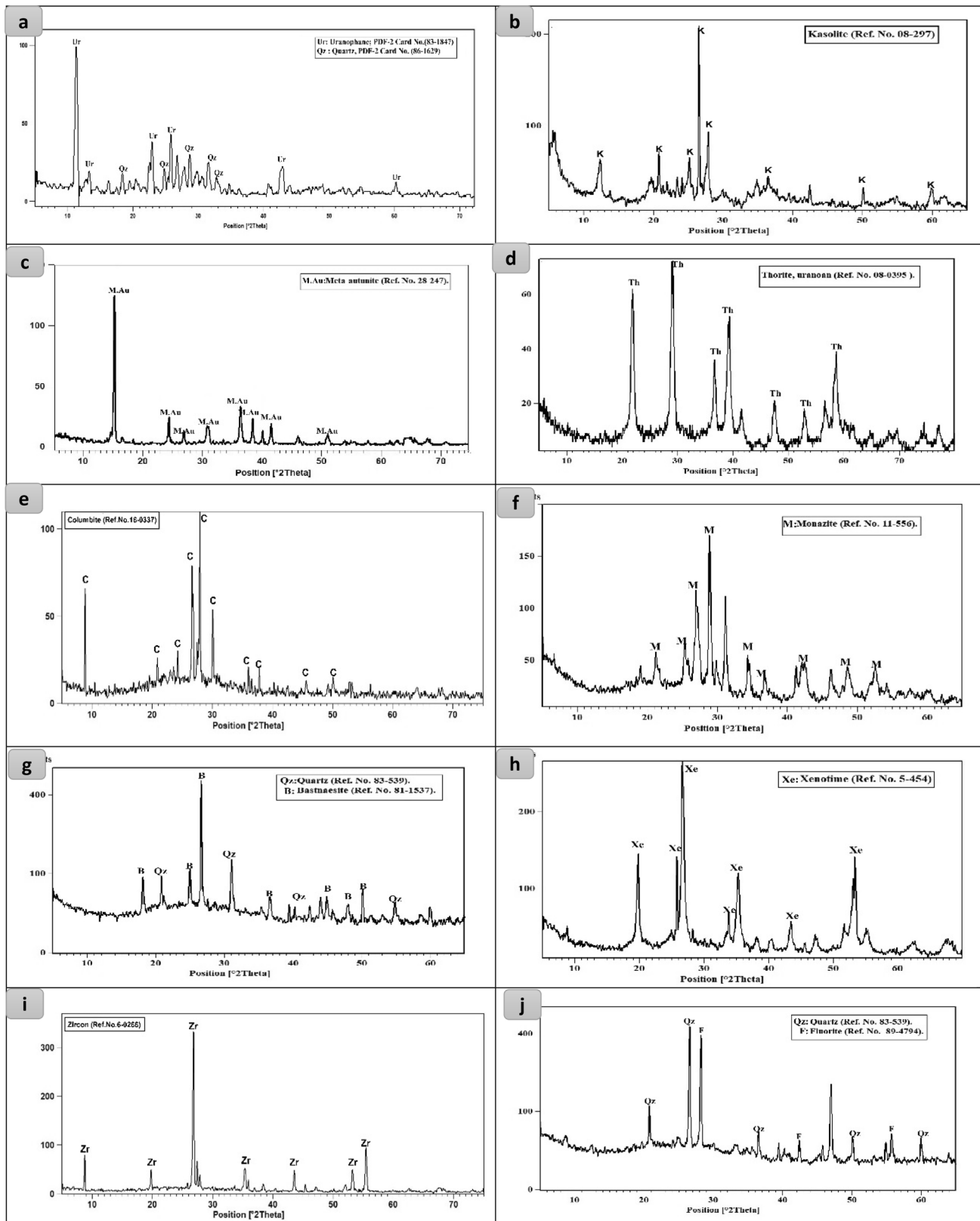


Fig. 10 XRD pattern for some recorded minerals in the south Um Ara-Wadi Murrah syenogranite, SED, Egypt

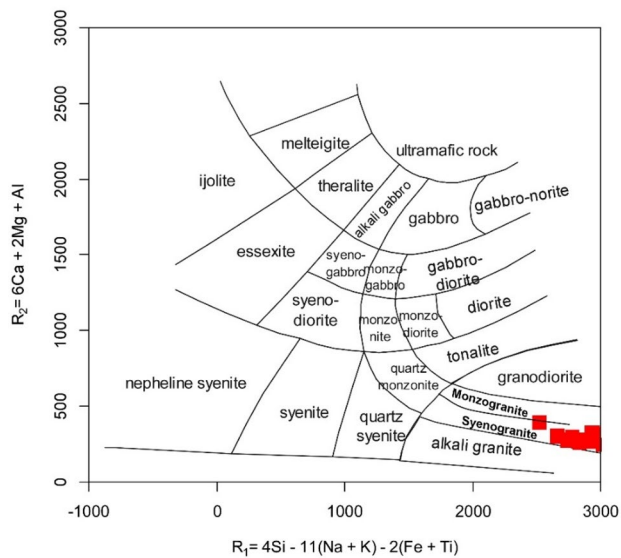


Fig. 11 Plots of the studied granites on R1 vs R2 classification diagram [48]

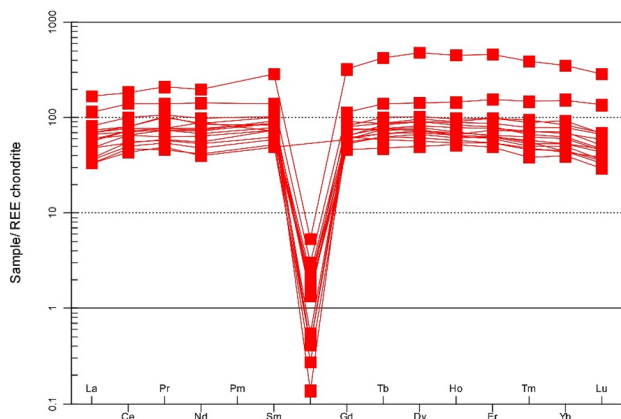


Fig. 12 Chondrite normalized REE patterns for the studied granites. Normalization values after [49]

are M-type tetrad implication similar to that quoted by [52] (Fig. 12).

The standard deviation (SD) reflects the variability in the geochemical dataset and denotes that certain values of elemental concentrations are further away from the mean it marks the frequency of extreme values (Table 2). The standard deviation (SD) values are higher for Ce (29.4), Nd (24.2), La (10.6), and relative higher for Pr (5), Tm (2.7) indicating an asymmetric distribution of these elements in the investigated samples.

Table 2 Descriptive statistics of REEs

	SD	CV	MAX	MIN
La	10.63	0.52	51.94	10.29
Ce	29.45	0.46	148.4	35.34
Pr	5.04	0.48	25.5	5.60
Nd	24.2	0.49	119.5	23.84
Sm	10.8	0.59	55.75	9.59
Eu	0.09	0.89	0.39	0.01
Gd	16.8	0.75	83.2	12.01
Tb	4.2	0.89	20.130	2.26
Dy	32.8	0.96	154.17	15.99
Ho	6.92	0.96	32.430	3.72
Er	20.97	0.99	97	10.36
Tm	2.74	0.95	12.6	1.25
Yb	16.09	0.9	74	8.27
Lu	2.0395	0.92	9.21	0.95

(SD) Standard deviation, (CV) coefficient of variation

Th/U variation diagram

The Th–U intercept doesn't show a clear relationship, which suggests that uranium was added later on instead of magmatic and hydrothermal processes controlling uranium mineralization in the altered granites that were studied. Th/U ratio could be used to differentiate between various uranium mineralization stages. For the granite-hosted U mineralization, magmatic and post-magmatic origins are assumed when the Th/U ratios drop below 2.5 and beyond the usual range. Supergene or hydrothermal solutions can be used as the post-magmatic source. Using the Th/U ratio, which is attributed to the hydrothermal uranium mineralization range " $0.1 < \text{Th/U} < 2.5$ " the former can be distinguished from the latter [53, 54]. The supergene enrichment is linked to values ≤ 0.1 [55–58]. The Th–U variation diagram (Fig. 13a) reveals that all samples fall within the supergene enrichment field, where all Th/U ratio values are less than 0.1.

U-(Th/3.5) variation diagram

The U-(Th/3.5) crosscut shows a positive correlation (Fig. 13b) that shows how the uranium in the studied granites changed after the magma erupted. This can be considered a good economic indicator in the granites of the Um Ara area [53, 58, 59].

U and U/Th with some major oxides

The weak negative relationship between U and SiO_2 (-0.5) shows that uranium levels rise when silica levels drop, which

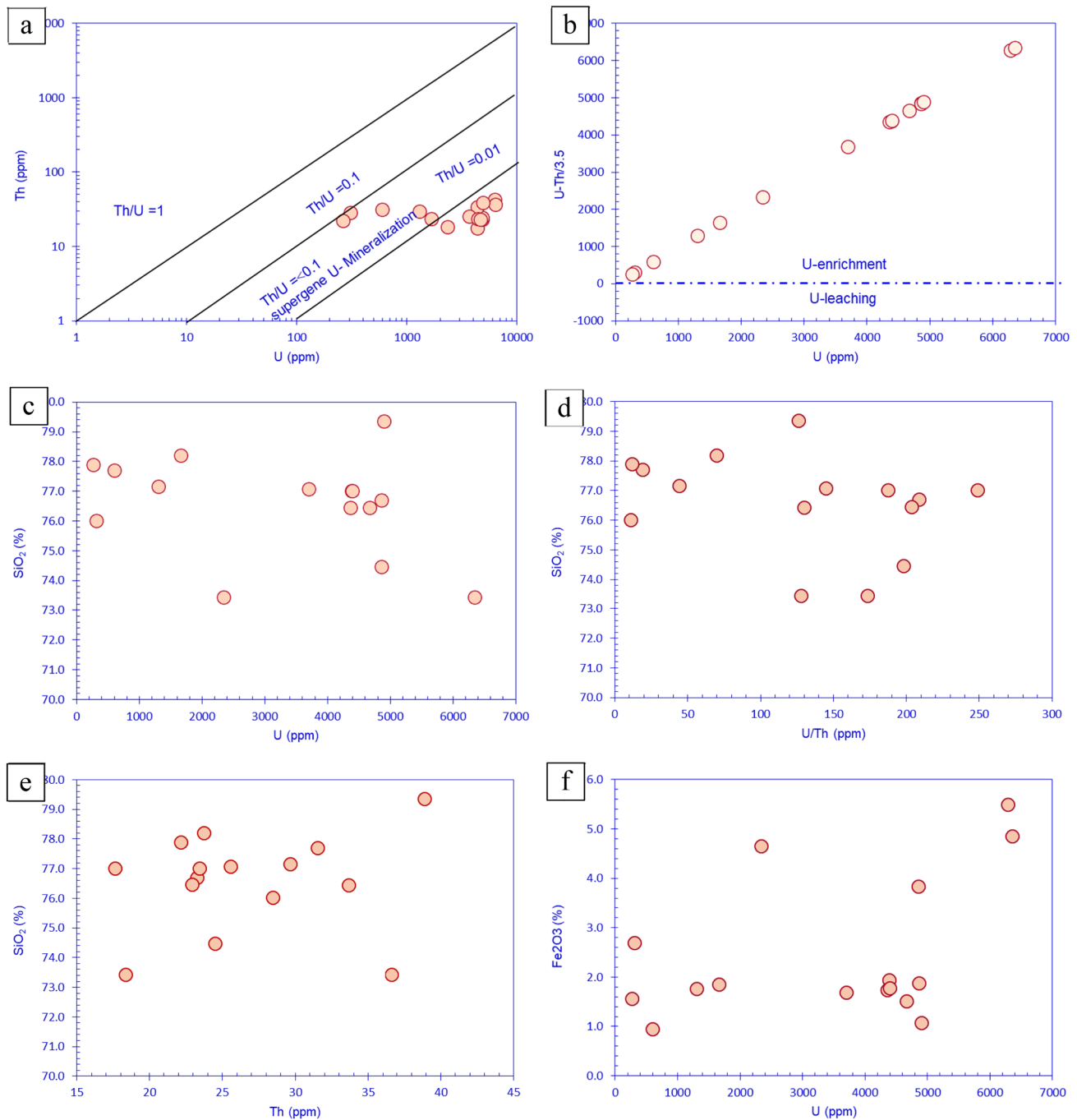


Fig. 13 Binary diagram between uranium and some major oxides, south Um Ara-Wadi-Murrah syenogranite, SED, Egypt

suggests that it comes from a secondary source (Fig. 13c). U/Th ratio is generally constant during magmatic differentiation (nearly 0.33). The productive uraniferous rocks have a U/Th ratio > 1 [60–63]; this ratio reaches up to 250, indicating the uranium redistribution. The relationship between U/Th ratios and SiO_2 (-0.06) (Fig. 13d) shows ill-defined

trends illustrating the redistribution of uranium by post magmatic processes.

Th with SiO_2

It's clear that post-magmatic processes played a part in breaking down the accessory minerals and moving U, Th,

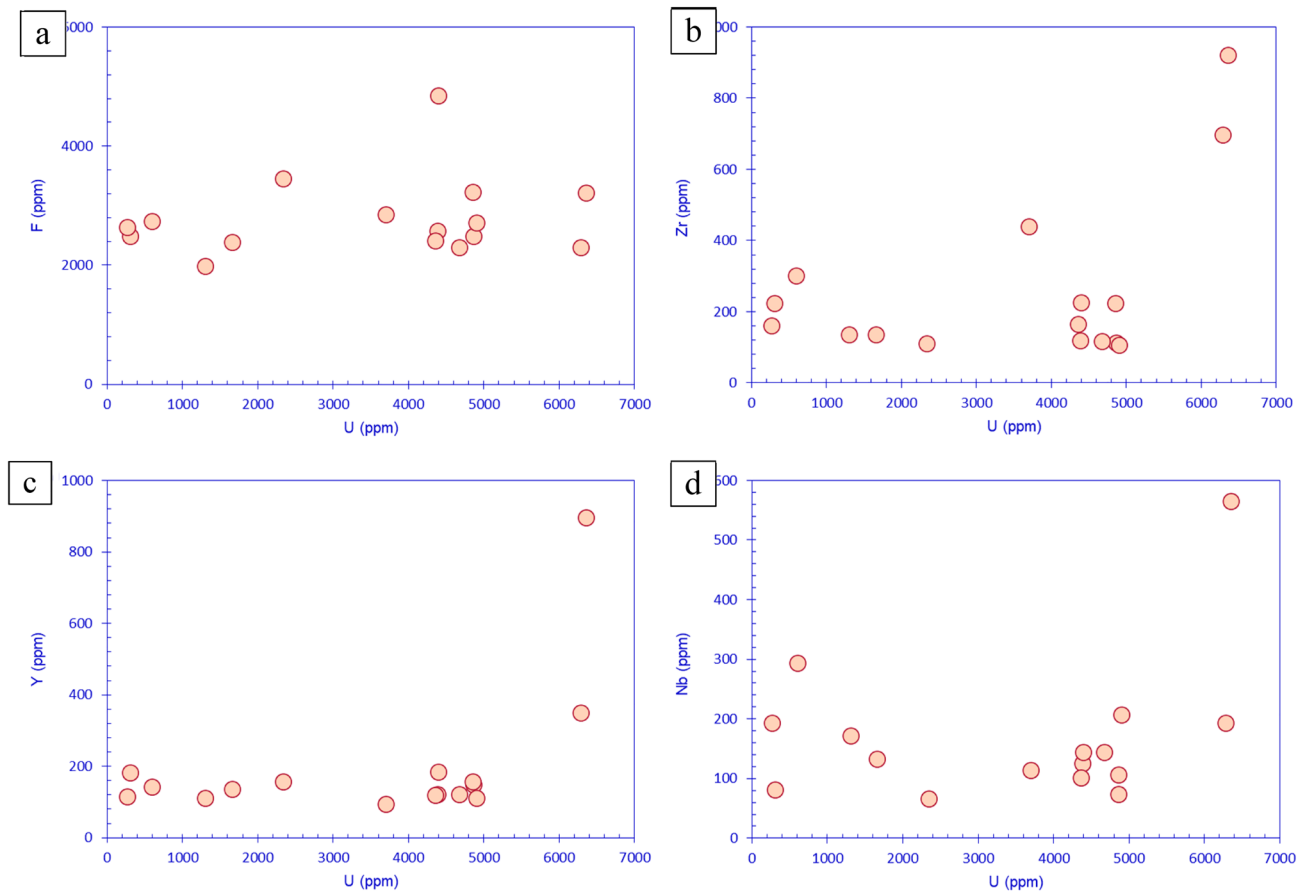


Fig. 14 Binary diagram between uranium and some trace elements, south Um Ara-Wadi-Murrah syenogranite, SED, Egypt

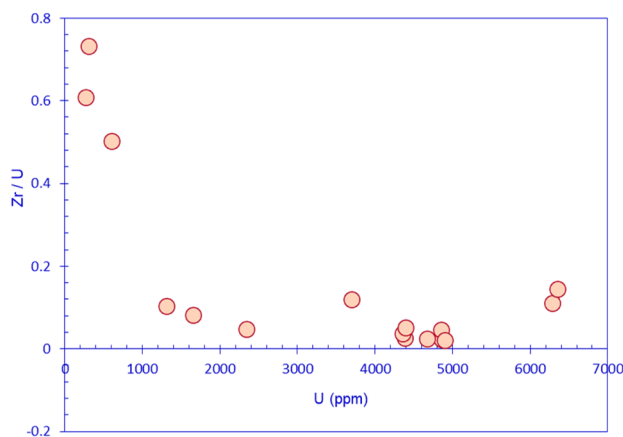


Fig. 15 Binary diagram between **a** U-Zr/U, south Um Ara-Wadi-Murrah syenogranite, SED, Egypt

U with Fe_2O_3

There is a weak positive relationship between U and Fe_2O_3 (0.4) (Fig. 13f), which indicates that U is attached to the surface of secondary iron oxides and has something to do with processes that happen after magma has cooled down [56, 64].

U with trace elements

The correlations of some trace elements with U (Fig. 14) show positive correlations with Zr, Y, while the correlations with Nb and F, are very weak to ill-defined, indicating partially magmatic processes followed by post-magmatic processes. Conversely, Fig. 15 records a negative correlation between Zr/U and U. This is because the size of the U ion is similar to the Zr ion; thus, U will replace Zr, and crystallize in zircon [65].

and other elements around. This is shown by the weak inter-relationship between Th and SiO_2 (−0.3) (Fig. 13e).

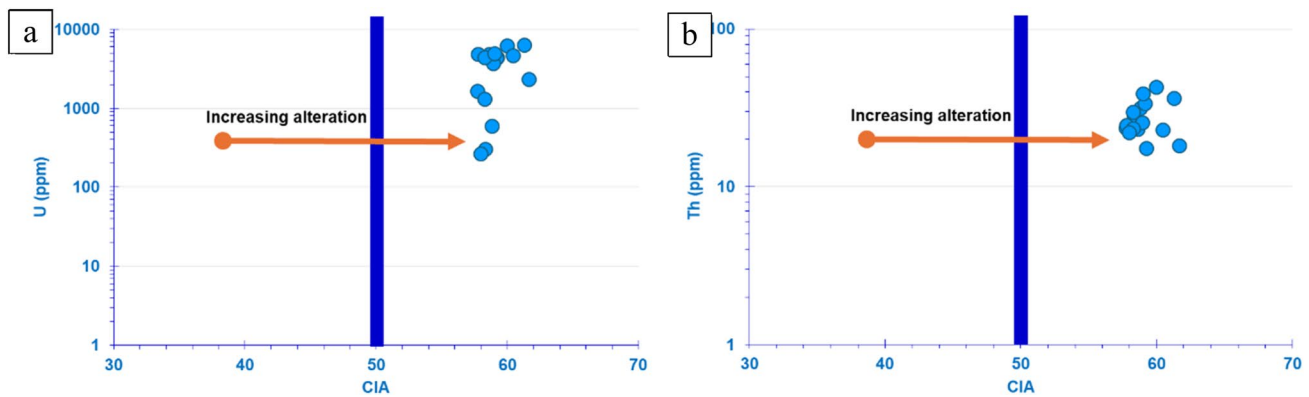


Fig. 16 Binary diagram between **a** U-CIA and **b** Th-CIA, south Um Ara-Wadi Murrah syenogranite, SED, Egypt

4.3.2 Chemical index of alteration with Th and U

The CIA may serve as a helpful index for categorizing various rock types based on variable source terrains. The global av. CIA values for shale are in the range 70–75, although new granites provide approximately 50 [66], and excessive weathering may result in values nearing 100 [67]. The initial CIA values for the various intact igneous rock types and their forming minerals vary from sample to another; e.g., basalts range from 30 to 45, whereas granite and granodiorite range from 45 to 55 [68]. The CIA values of the analyzed rocks ranged from 20.55 to 67.38, with an average in the syenogranite, indicating a slightly to moderately sourced landscape. Uranium accumulation in the syenogranite is noticeable as the chemical index of alteration increases (Fig. 16). As the index of alteration in the syenogranite increases, thorium also exhibits slight changes, potentially due to its adsorption on clay minerals, a result of alteration processes.

5 Discussion

5.1 Paragenesis of uranium minerals

The oxidation of uraninite can readily release uranium into the environment [69, 70]. In aerobic conditions, this process starts with the oxidation of unstable phases like ferric sulfides. This breaks down the primary mineralization in polymetallic deposits [71]. A variety of secondary minerals can crystallize in these areas. Uraninite becomes unstable, and uranium readily leaches at low pH levels. During the oxidation process, uranium transitions from the 4^+ to the 6^+ oxidation state and is primarily found in water as the uranyl cation (UO_2^{2+}). Uranium can move over a significant distance in this way. When various anions and

cations are present, it can precipitate rapidly as secondary U-bearing minerals. Weathering zones may include a wide range of secondary U minerals [72].

Uraninite and coffinite are the two most common minerals found in U-ore. They both have impurities like Ti, S, Fe, Si, Ca, Zr, Pb, Th, and REEs that can change the thermodynamic characteristics of uraninite and the rate at which it changes. These impurities and chemical composition of the fluids involved in uraninite alteration dictate the type of alteration products. As a result, uraninite frequently changes into uranophane or autunite.

The most significant ore mineral for U is coffinite, which comes after uraninite. Typically, it includes water, and the right recipe is $\text{USiO}_4 \cdot n\text{H}_2\text{O}$ [73]. The most common impurities in coffinite are REE and P, which points to a solid solution with xenotime (YPO_4) that has the same structure as coffinite [22].

Most likely, uranophane is a precipitate of groundwater that contains dissolved Si and Ca and is near neutral to alkaline. When diluted meteoric water (low CO_3 ; $\text{pH} > 7$) is exposed, soddyite may replace uranophane [74].

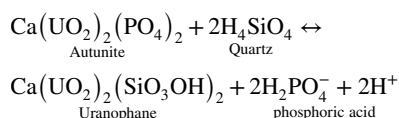
The syenogranite of the south Um Ara-Wadi Murrah area hosts both secondary and primary U-mineralization. Zircon, thorite, and U-rich thorite manifest the primary Th and U mineralization, while uranophane, kasolite, and autunite primarily represent the secondary U-mineralization. Based on EDS data, some thorite grains show U enrichment (Fig. 5h), which means that U moves from the core to the rim through diffusion.

Two types of uranophane were described: the main type represents the ideal composition of uranophane with low Fe and Al content (Fig. 5c), whereas the second type has high Al concentration (Fig. 5d).

Both low and high-temperature alteration have affected the syenogranite. High-temperature changes are caused by

hydrothermal processes that also cause corrosion of primary U-bearing minerals, albitization, K-feldspathization, and fluoritization. Changing the normally made thorite, xenotime, and zircon can simultaneously make the fluid richer in Th, Zr, and Y (Figs. 4i, 8c). This results in the emergence of solid-solution ranges between these two phases, along with intermediate phases. The near-surface profile changed because of low temperatures, and moving meteoric water was a key part of moving the early changed primary uranium minerals around (Fig. 4a, b). It is likely that uranyl carbonate complexes transported uranium. Upon losing stability through calcite precipitation, these complexes disintegrated in the presence of silicon and calcium, resulting in the formation of uranophane (Fig. 4c–g).

An assemblage of needle-like crystals was discovered to be uranophane. The secondary uranyl silicate mineral is the last mineral in the uranium mineral series. It is made when autunite and silica get confused with heat. [75] Equation suggests that the association of uranophane with the reworked silica may strengthen the presumption of misunderstanding.



Autunite is a representation of uranyl phosphates, which aid in regulating the levels of U in numerous natural waterways. Often, their solubilities are lower than those of uranyl silicates, and they are accompanied with a variety of weathered U deposits. One can find uranyl phosphates far from any U source [76].

The fluid that forms the ore always moves from a relatively deep and tight environment to a somewhat shallow and open one during granite-related uranium mineralization. A wealth of geochemical data links uranium mineralization associated with granite to mantle-derived fluids [77, 78]. It's not clear if the theory of hydrothermal uranium mineralization "uranium oxidizing migration and reducing precipitation-mineralization" can explain how fluids that form ore change over time and fluids that come from the mantle lose some of their properties.

Supergene uranium mineralization systems widely accept and demonstrate the aforementioned theory. Additionally,

the presence of fluorite in Um Ara syenogranite confirms its origin from high-volatile magma [79], which is ideal for the crystallization of hydrous uranyl minerals like autunite.

5.2 Paragenesis of REEs

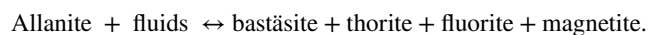
Late- to post-magmatic, volatile-rich water fluids moving up through the solidified granite cupolas may have caused the metasomatic change and the rare metal mineralization processes that accompanied it [80]. In order for these fluids to reach a state of equilibrium with the host rock, subsolidus reworking will happen. This will create zonal alteration assemblages.

According to [81], alkaline solutions likely transformed most of the lanthanides in hydrothermal deposits into carbonate, fluorine, or sulfate complexes. In fact, the Ce-group REEs are more "basic" than the Y-group REEs, which is why certain minerals like allanite, bastnaesite, and monazite are Ce-selective and prefer the LREEs, while others like xenotime and fergusonite are Y-selective and prefer the HREEs. Thus, highly fractionated acid rocks, such as alkaline granite, tend to concentrate the Ce-group, or LREEs.

Allanite

Anderson [82] reported that allanite may have been replaced by calcite that usually occurs together with fluorocarbonates, mainly parisite: $\text{Ca}(\text{Y, Nd, La, Ce})_2(\text{CO}_3)_3\text{F}_2$. Progressive weathering considers the parisite mineral as preliminary evidence of allanite dissolution, leading to the dissolution of the carbonate [83]. Higher degrees of alteration may liberate thorium from allanite and concentrate it in secondary phases. During weathering, thorite may replace allanite, causing thorium to remain immobile and depleting the REE, particularly the LREE [84].

Wood et al. [84] provide a schematic illustration of the reaction that results in to partial replacement and widespread corrosion of allanite, most likely fluorite and thorite, respectively.



Another case of alteration is allanite (Ce), which most likely happens under hydrothermal conditions. Consequently, for simplicity, it is assumed that the Th-bearing phosphate, which is a REE, is monazite-(Ce). This initial process is schematically represented by the following reaction:

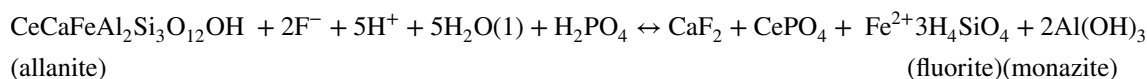
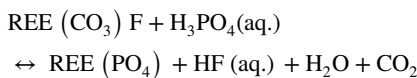


Table 3 A proposed paragenetic sequence of ore minerals (radioactive and rare metal) in south Um Ara-Wadi Murrah syenogranite, SED, Egypt

Mineral	Stage	Or tho- magmatic	Hypogene Hydrothermal	Supergene
<u>Base metals</u>				
Native Au				
Bismite, Wolframite				
<u>Radionuclides</u>				
Uraninite				
Coffinite				
Uranophane				
Kasolite				
Autunite				
Uranothorite				
<u>Rare Earth minerals</u>				
Monazite				
Allanite				
Bastnaesite				
Parasite				
Xenotime				
Chernovite				
<u>Radioactive bearing minerals</u>				
Betafite				
Ishikawaite				
Columbite				
Fergusonite				
Samarskite				
zircon				
fluorite				

Bastnaesite

Mariano [85] described the transformation of hydrothermal bastnaesite into monazite, an alteration that the ascribed to interaction with phosphate-bearing solutions. The following reaction schematically represents these observations:



REEs are redistributed as a result of the hydrothermal variation in magmatic fluorite; physicochemical conditions and the proportions of light components, such as P, Ca, Y, OH, Cl F, and F, serve as recorders of hydrothermal fluid chemistry [86].

Hydrothermal fluids high in Ta and Nb may have caused the production of columbite. Xenotime (Y), associated with zircon, can take on a variety of shapes, ranging from euhedral, igneous-like grains to irregular secondary grains that have been formed when zircon dissolves in phosphorus-containing fluids [87]. Anhydrous zircon, columbite, and xenotime may be linked to fluorine's effect on high-field strength elements, which makes them more soluble. The presence of

xenotime, zircon, and thorite may indicate an intermediate solid solution reaction.

5.3 Paragenesis of gold

When the water cools down to precipitate the gold (epithermal gold deposits), it moves through faults in the form of Au–Cl and Au–S complexes in solution, depositing at temperatures in the range of 300–400 °C and pressures of 1–2 kbars [88]. Hydrothermal solutions may transport the recorded gold specks from the surrounding ultramafic rocks to the Um Ara-Wadi Murrah syenogranite.

It is possible to attribute the enriched rare metal mineralization to crystallization from late magmatic melts. The higher amounts of high-field strength elements (HFSEs) in the Um Ara-Wadi Murrah syenogranite are also thought to be very good signs of late-stage differentiation.

Using textural relationships, microanalytical data, and ore mineral identification, the paragenetic sequence, and the different stages of ore mineral crystallization can be figured out.

Table 3 displays the proposed paragenetic sequence. Additionally, it differentiates between minerals in the two

main stages: hydrothermal and magmatic, in addition to the supergene stage.

5.4 Regional applications

In summary, the uncommon metal granites in the ANS have attracted considerable attention from scientists due to their substantial potential as sources of REEs, U, Zr, Au, W, Nb, Sn, Ta, Mo, and Th. The Central and Southern Eastern Desert of Egypt are the primary distribution of these sources. The structural patterns, primarily SE-NW of the Najd fault, together with the magma composition in granitic plutons, may have affected the high concentration of rare metals [89].

The presence of the rare metal-bearing granites in the SED of Egypt is not incidental, as evidenced by the previously analyzed data. The rare metal mineralization in the Um Ara-Wadi Murrah syenogranites can be attributed to: (1) primary content of magmatic fluids that enhances the concentration of rare metals in mineralized granites during rock-fluid interactions, (2) the existence of altered rocks and rare metal-bearing alteration zones linked to granites, including kaolinitization, sericitization, chloritization, and silicification, and (3) increased concentrations of REE and rare metals in highly fractionated I-type granites and more fractionated or evolved A-type, and (4) the dominant SE-NW structural trend (Najd trend) alongside conjugate NE-SW and N-S faults that influence the distribution of rare metal-bearing granites, with these faults acting as conduits for the rare metal accumulation and fluid circulation.

6 Conclusions

- Um Ara area is situated in the southern parts of the Eastern Desert of Egypt. The syenogranites are exposed at the northwestern sides of the regional studied area.
- The syenogranite is affected by low and high-temperature alteration. The origin of the high-temperature alteration is due to the implication of hydrothermal solutions accompanied with K-feldspathization, fluoritization, albitization, and corrosion of the primary U-bearing minerals.
- Petrographically; the primary constituents of the syenogranite are plagioclase, quartz, and K-feldspar. Uranophane, fluorite, zircon and opaques, are accessory minerals.
- The syenogranite in the Um Ara-Wadi Murrah region contains both primary and secondary uranium mineralization. U-rich thorite, thorite, and zircon exhibit the principal Th and U mineralization, whereas kasolite, uranophane, and autunite predominantly signify the secondary

U-mineralization, and Ta-Nb minerals together with the base metals as gold, bismite, cassiterite, and wolframite.

- There are three types of ore minerals (magmatic, hydrothermal, and supergene) can be identified. The latter comprises secondary uranium minerals, and uranophane.
- Gold is originally deposited from epithermal and mesothermal solutions due to the changes in the fugacity of sulfur and oxygen and the physicochemical conditions.
- The study area characterized by enrichment in uranium and rare earth elements (av. 3451.4, 273 ppm respectively). The calculated values of the tetrad effect are 1.12. The chondrite-normalized REE patterns for syenogranite are M-type tetrad effect.
- The presence of radioactive minerals (kasolite, autunite, uraninite, coffinite, and uranophane) and the presence of monazite, allanite, and xenotime contribute to the uranium enrichment.
- Uranium accumulation in the syenogranite is noticeable as the chemical index of alteration increases. As the index of alteration in the syenogranite increases, thorium also exhibits slight changes, potentially due to its adsorption on the clay surfaces, a result of alteration processes.
- The enrichment of the high-field strength elements (HFSEs) in the Um Ara-Wadi Murrah syenogranite are also thought to be very good signs of late-stage differentiation.
- This study is applicable to the analogue granite and syenogranite plutons in the Eastern Desert of Egypt and may be extended to similar analogues in the Arabian Shield. However, cautions should be considered with applying this study to other types of granites. Also, cautions should be considered when the relationships of the different elements are weak and when some anomalies are present.

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Declarations

Conflict of interest The author hereby declares that there is no conflict of interest.

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