Mineralogy and Geochemistry of Uraniferous Sandstones in Fault Zone, Wadi El Sahu Area, Southwestern Sinai, Egypt: Implications for Provenance, Weathering and Tectonic Setting

Osama R. SALLAM, Hamed I. MIRA, Amira M. El TOHAMY* and Abd Elhadi A. ABBAS

Abstract: Paleozoic rocks in the Wadi El Sahu area are affected by many major faults in different directions. A reverse fault trending NE-SW is exposed for about 300 m of its length as it cuts through the Abu Hamata and Adedia formations on the south side of Wadi El Sahu. A secondary ascending hydrothermal solution carrying heavy metals and radioactive minerals passed through the fault plain and the surrounding fractures, forming mineralized and radioactive zone. The mineralized zone thickness ranges from 60 cm to 200 cm along the fault plain. These rocks were analyzed radiometrically using a portable gamma-ray spectrometer, chemically by employing ICP-ES and ICP-MS, as well as mineralogically by both binocular and Environmental Scanning Electron microscope. Gold content was also determined by fire assay. REE and U contents reached up to 2682 and 1216 ppm, respectively. Mineralogical investigations indicated the presence of uraninite, torbernite, autunite, sklodowskite, kasolite as uranium minerals, thorite as a thorium mineral, monazite, allanite and xenotime as REE-bearing minerals, zircon and columbite as accessory minerals, gold and nickel as precious and base metals, in addition to cassiterite, chalcopyrite, chalcocite and chryscolla. High REE and U contents are attributed to the circulation of epigenetic U and REE-bearing hydrothermal solutions along the fault plain and its surrounding fractures. Hydrothermal alteration processes could then be confirmed by the presence of the M-type tetrad effect in the REE-patterns of the ferruginous sandstone. The non-chondritic ratio of Nb/Ta, Zr/Hf and Y/Ho in the studied sandstone may be attributed to the tetrad effect. The Ce and Eu anomaly with unusual REE-patterns was represented by the presence of conjugated M-W tetrad effects, indicating either the dual effect of hydrothermal solutions or groundwater with seawater. The results clarify that the tetrad-effects could be used as evidence for the environment of deposition and as an indication for gold mineralization.

Key words: uranium, gold, REEs, tetrad effect


1 Introduction

The Paleozoic sedimentary rocks in east Abu Zenima, Southwest Sinai, are of great importance, especially from the mineralogical and radioactive points of view, being rich in mineral deposits such as iron oxides, copper, zinc, lead, cobalt, nickel, silver, gold and uranium. In addition, some industrial ore minerals such as manganese, kaolin and glass sand are also being produced.

The Wadi El Sahu area is a part of this promising area, located about 40 km east of the town of Abu Zenima, Southwest Sinai. Delineated by longitudes 33° 23′ 06″ and 33° 22′ 54″ E and latitudes 28° 57′ 36″ and 28° 59′ 24″ N, it is covered with Precambrian basement rocks and the overlying Paleozoic sedimentary succession (Fig. 1). The basement rocks are well-exposed both upstream and downstream of Wadi El Sahu and are represented by younger granites.

El Kammar et al. (1997) emphasized that uraniferous xenotime predominates in the more argillaceous sediments exposed in the Um Hamad area. The REE contents of these sediments bear the signature of xenotime with significant LREE contribution. El Aassy et al. (2006) emphasized that the upper surface of the Adedia Formation is an active one as it is subject to intense weathering processes. They attributed the high radioactivity to the predominant xenotime-bearing sandstones of the Adedia Formation, which were also the main source of HREE in the prospecting area. Moreover, El Aassy et al. (2008) reported that the soil profile formed at the top of the Adedia Formation displayed the xenotime overprint of the REE distribution. They also noted the marked predominance of HREE with heavy metals, compared to other elements.

Shata et al. (2011) also concluded that the radioactivity of the ferruginous lithofacies at the topmost part of the Adedia Formation was controlled by laterization processes which led to the mobilization of U and LREE from the...
lattices of detrital mineral grains and their reprecipitation in the form of secondary mineral phases, as indicated by the presence of the minerals allanite and xenotime. Abu-Zeid et al. (2016) concluded that the radioactive mineral deposits in the Adedia type section were mainly the product of epigenetic processes within which laterization played a major role. Bishr et al. (2018) stated that the mineralized fault zone in the El Rakaiz-El Sahu area occurs in a large fracture system trending in a NE-SW direction.

2 Geological Background

The exposed Paleozoic rocks in the Wadi El Sahu area are represented by a succession which began with the Cambro-Ordovician clastics of the Sarabit El Khadim, Abu Hamata and Adedia formations, which are exposed on the south side of Wadi El Sahu. The Lower Carboniferous rock units, including carbonates of the Um Bogma Formation and clastics of the El Hashash, Magharet El Maiah and Abu Zarab formations are well-exposed in the south and north sides of Wadi El Sahu. The Paleozoic succession is capped by a lateritic soil zone representing an unconformity with the overlying Um Bogma Formation.

2.1 Cambro-Ordovician sediments

These are represented by a clastic sequence underlying the Carboniferous rocks of the Um Bogma Formation. Issawi and Jux (1982) used trace fossils and assigned a Cambro-Ordovician age to these sediments. Soliman and Abu El Fetooh (1969) subdivided these sediments into three formations: Sarabit El Khadim, which comprises fine-grained sandstones alternating with very coarse-grained sandstones. It is conformable with the Abu Hamata Formation, which is represented by three different units, two reddish to brownish sandy shales interbedded with a greenish sandy shale with copper mineralization. It is easily distinguished by its characteristic brownish and greenish colour. The Adedia Formation conformably overlies the Abu Hamata Formation (Fig. 2a). It consists of pink to brown, fine- to coarse-grained ferruginous sandstones containing thin intercalations of shale, siltstones and pebbly cross-bedded sandstones. The upper part of the Adedia Formation consists of two facies forming a fining-upward sequence. The Adedia Formation is capped by a lateritic soil zone representing an unconformity with the overlying Um Bogma Formation.

2.2 Lower Carboniferous sediments

They are dominated by carbonates and conformably overlain by clastic rocks (Weissbrod, 1969). Alshami (2019) reported that the Um Bogma Formation comprises seven facies; these facies are Mn-Fe ore (Fig. 2b), gibbsite-bearing sediments, claystone, marl, dolostone, shale and ferruginous siltstone.

Soliman and Abu El Fetouh (1969) subdivided the clastic sediments into the El Hashash, Magharet El Maiah and Abu Zarab formations (Fig. 2c). The El Hashash Formation is characterized by brownish, cross-laminated sandstones, intercalated with thin beds of shales and siltstones. It overlies the Um Bogma Formation and is characterized by the ripple marks at the surface of the bed. The Magharet El Maiah Formation is characterized by two or three horizons of grey to dark grey sandy shale with sandstone intercalated. The Abu Zarab Formation, which conformably overlies the Magharet El Maiah Formation, is characterized by milky white semi-fiabile sandstones (glass sand), with some intercalated siltstone thin beds.

2.3 Permo-Triassic rocks

These are represented by the basaltic sheet or sill overlying the Abu Zarab Formation, the thickness of the basalt reaching up to 40 m at Gabal Farsh El Azraq (Fig. 2d). Structurally, the study area is affected by many major faults moving in different directions, of which the NS, NE and NW directions are the most common (Fig. 1). A reverse fault trending in a NE-SW direction with exposure of part of its length for about 300 m and dipping at about 80° to the north, cuts through the Abu Hamata and Adedia formations on the S side of Wadi El Sahu (Fig.
passing through the Wadi deposits and then cutting through the El Hashash Formation on the other side. A secondary ascending hydrothermal solution carrying heavy metals and radioactive minerals passing through the fault plain and the surrounding fractures formed the mineralized and radioactive zone. The mineralized zone thickness ranges between 60 cm and 200 cm along the fault plain with a dark brown to black colour. The fractures in the fault zone were filled with Mn-Fe deposits from the ascending hydrothermal solution (Fig. 2f). Also, the fault plain and its surrounding fracture reveals high levels of radioactivity, the sandstones of the Adedia Formation showing the highest.

3 Materials and Methods

The field radiometric survey measurements of eU (ppm), eTh (ppm) and K (%) were obtained using a portable differential gamma ray spectrometer, model Rs-230 BGO Super-Spec, serial No. 4333, manufactured by Radiation Detection Systems AB, Backehagen 35, SE-79191 FALUN, Sweden and the readings were taken...
Eight samples of highly radioactive ferruginous sandstones from the El Adedia Formation were carefully selected from the fault zone for mineralogical and geochemical investigation. The representative samples (each sample weighed approximately 3 kg) were collected from the selected stations depending on variation in composition and field radiometric measurements. The collected samples were crushed, ground and quartered. The sample was sieved into three fractions: <63 µm, 63µm –800 µm and >>800 µm. The size fraction range of 63 µm –800 µm for each sample was subjected to heavy liquid separation using bromoform solution (sp. gr. 2.81 g/cm³) to separate the heavy minerals. The obtained heavy mineral fractions were studied under binocular stereomicroscope. Some of the selected mineral grains were analyzed by an environmental scanning electron microscope (ESEM) (XL30-ESEM, Philips) attached to an EDAX microanalysis unit set at 30 kV (low-vacuum) and using X-ray diffraction (XRD) for mineral identification. These analyses were carried out in the laboratories of the Nuclear Materials Authority (NMA), Cairo, Egypt.

The determination of the gold content required a specific procedure; fire assay analyses were carried out at the EMRA. Fifty gramme samples (crushed and sieved to 200 mesh grade) were fired in the presence of alkali fusion agents. More specifically, the ground sample was added to a mixture of litharge, borax, sodium carbonate, flour, silica and silver in a ceramic crucible. The mixture was melted at 1000°C for 90 min; this step was followed by the cupellation of the lead/gold/silver alloy at 900°C for 60 min. The resulting alloy (Ag/Au) was then dissolved with concentrated nitric acid and aqua regia under heat to dissolve the gold; the solution was further analyzed by atomic absorption spectrometry (using a Savant AA spectrometer, GBC Scientific Instruments, Braeside, Australia).

The chemical concentrations of the major oxides, trace and rare earth elements (REEs) were determined in the Acme Lab, Vancouver, Canada, by inductively coupled plasma emission spectrometry (ICP-ES). Detection limits for trace elements and major oxides were 0.01–0.5 ppm and 0.001 wt%–0.04 wt%, respectively. The analytical precision, as calculated from replicate analyses, was 0.5% for major oxides and varied from 2% to 20% for trace elements.

4 Mineralogical Studies

The mineralogical studies indicated the presence of more than one mineral association, as described below.

4.1 Uranium minerals

4.1.1 Uranium oxide (U₃O₈)

The most common uranium oxides in nature are U₃O₈ and uranium dioxide UO₂ (Lambert et al., 1966). Uranium oxide was detected near to the study area by El Aassy et al. (2008). According to Heinrich (1958), the composition of uraninite ideally is UO₂, U = 46.5% to 88.2%. Normally U⁴⁺ is oxidised to U⁶⁺ to varying degrees. The EDX data indicated that the concentration of U is 60 wt%. Small proportions of K, Fe and Si were present (Fig. 3a).

4.1.2 Torbernite [Cu(UO₂)₂(PO₄)₂·12H₂O]

The chemical formula of torbernite is similar to that of autunite in which a Cu²⁺ cation replaces a Ca²⁺ cation (Locock and Burns, 2003b). EDX analysis of a representative torbernite crystal indicated that the main components ratio of U: Cu: P was 3: 3: 1 (Fig. 3b). There is a transition phase between torbernite and autunite (Fig. 3c).
4.1.3 Autunite \([\text{Ca}(\text{UO}_2\text{)}_2(\text{PO}_4)_2\cdot10\rightarrow12\text{H}_2\text{O}]\)

Autunite is the oxidation product of pitchblende and uraninite and most of the other primary minerals. It may also be derived from some of the other secondary minerals, like gummite and uranophane. EDX analysis of autunite indicated that the main ratio of U: Ca: P was 2: 1.5: 1 (Fig. 3d).

4.1.4 Sklodowskite \([\text{Mg}[\text{UO}_2\text{]}(\text{SiO}_3\text{)}\text{OH}]_2(\text{H}_2\text{O})_6\]

Sklodowskite has been recorded in the Um Bogma Formation (Shata, 2006; Bishr, 2012), occurring as disseminations scattered throughout the oxidation zone as a secondary mineral which contains magnesium. Sklodowskite in the study area gradually turns into cuprosklodowskite, \(\text{Cu}(\text{UO}_2\text{)}_2(\text{HSiO}_4\text{)}_2\cdot6(\text{H}_2\text{O})\). The latter is a secondary uranium mineral formed essentially in place by alteration of earlier uranium minerals, or deposited from solutions in the oxidized zone of uranium deposits (Frondel, 1958). The structure of cuprosklodowskite was determined by Piret-Meunier and Van Meerssche (1963) to be very similar to the structure of sklodowskite, except that the copper atoms that occur between the sheets are bound in a linear arrangement to a uranyl oxygen atom from each of the adjacent sheets, instead of a free oxygen atom of the silicate tetrahedra from each sheet, as in sklodowskite. Sklodowskite and cuprosklodowskite are relatively abundant in the study area, having an acicular crystal habit (50 to 100 µm) and mainly being composed of U (45 to 50%), Mg (4 to 5%) and Cu (3 to 8%) (Fig. 4a, b).

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

The examination of kasolite by ESEM reported its chemical composition as U 59 wt%, Pb 35 wt%, Si 3.5 wt% with traces of Fe (Fig. 4c). El-Balakssy (2006) detected the mineral kasolite in the stream sediments of the Wadi El Shallal area, which is located at the west of the study area.

4.2 Thorium mineral-Thorite \((\text{ThSiO}_4)\)

The EDX analysis showed that the thorite was essentially composed of Th (60%), U (5%) and Si (9%), in addition to subsidiary Fe and Ca (Fig. 4d).

4.3 REE-bearing minerals

4.3.1 Monazite \([\{\text{Ce, La, Th, Nd, Y}\} \text{PO}_4\]

Monazite is a primary source of several light rare earth metals (66 wt%). Monazite is radioactive, sometimes highly so, specimens often being metamict. The EDX analyses show that monazite in the study area has REEs (54.8–60%), Th + U (8–11%) and P (5–10.4%) (Fig. 5a, b).

4.3.2 Allanite \((\text{Ce, Ca, Y})_2(\text{Al, Fe}^{+++})_3(\text{SiO}_4)_3(\text{OH})\)

Allanite is a REE-rich epidote-group mineral with the general formula \(\text{A}_2\text{M}_2\text{Si}_3\text{O}_{12}(\text{OH})\) (Dollase, 1971). The majority of the present allanite analyses have Ce as the most dominant REE cation (30%) (Fig. 5c) and, therefore, are classified as allanite-(Ce) according to the nomenclature of Levinson (1966).

4.4 Accessory minerals

4.4.1 Xenotime \((\text{YPO}_4)\)

Authigenic xenotime in sedimentary rocks has begun to receive significant attention in recent years (Rasmussen, 1996). The apparently widespread occurrence of diagenetic xenotime in sedimentary rocks promises new opportunities to place precise constraints on depositional ages (Rasmussen et al., 2004). Xenotime forms isometric,
short-to-long prismatic crystals, sometimes in radial or rosette-like aggregates. The obtained EDX data showed the chemical composition of xenotime with significant amounts of HREEs (15–19%) (Fig. 6a). Some xenotime grains are also found as a solid solution with thorite (Fig. 6b).

4.4.2 Zircon (ZrSiO₄)
Zircon usually has uranium and thorium contents ranging from 0.01% to 0.19%, 1% to 2%, respectively (Cuney and Friederich, 1987). In the study area, zircon was examined by ESEM and was found to contain considerable amounts of U + Th (20%) and Y (15%), with Zr/Hf equalling 25/1 (Fig. 6c).

4.4.3 Columbite [(Fe, Mn)Nb₂O₆]
The EDX analyses of this mineral showed that Nb (65%), Mn (13%), Fe (12%) and Ta (4%) are the main components present (Fig. 6d).

4.5 Precious metal-gold (Au)
Native gold occurs in the El Sahu sandstone as fine-grained crystals (20 µm), Au (80%) with a minor amount of Cu (5%) (Fig. 7). The gold content was estimated by the fire assay technique, with a preliminary estimate of 1.63 g/t. Alshami (2019) recorded native gold in many facies of the Adedia Formation in the Um Bogma area.

4.6 Base metals
4.6.1 Native nickel (Ni)
This mineral was found in the study area and confirmed by ESEM (Fig. 8a). The analyses showed that Ni forms about 99% with traces of Ca (qualitative).

4.6.2 Cassiterite (SnO₂)
This mineral was reported as broad flakes (~20 µm), having Sn (50–75%), Si (3–9%) and Fe (10–27%) (Fig. 8b).

4.6.3 Copper minerals
Chalcopyrite (CuFeS₂) is the most important copper ore. It is a copper iron sulfide mineral that crystallizes in the tetragonal system and occurs in most sulfide mineral deposits (Fig. 9a). In the study area, chalcopyrite was found to be associated with other copper minerals as chalcocite (Cu₂S) (Fig. 9b) and chrysocolla (Cu, Al)₂H₂Si₂O₅(OH)₄·n(H₂O) (Fig. 9c).

5 Radioactivity
5.1 Radioactivity of the El Sahu sandstones
Thorium is naturally three times as abundant as uranium in rocks (Rogers and Adams, 1969). The study’s sandstone samples have a range of chemically analyzed uranium (200–1216 ppm) and eU (263–1396 ppm) (Table 1).
There is a significant dominance of U over Th in all samples; Th has a range of 15–123 ppm. The Th/U ratio is useful for studying the source characteristics of clastic sedimentary rocks (Roddaz et al., 2006). The Th/U ratio varies from 3.5 to 4.0 for most upper crustal rocks. Enrichment of U is commonly found in anoxic sediments. During weathering and sedimentary recycling under oxidizing conditions, insoluble U\(^{4+}\) ions are converted into soluble U\(^{6+}\) ions. Clastic sedimentary rocks derived from the upper crust are characterized by Th/U ratios equal to or greater than 4, whereas Th/U ratios lower than 4 have been related to a mantle contribution (Roddaz et al., 2006).

Higher Th/U values are indicative of dissolution and loss of U during sedimentation (McLennan et al., 1993). Low Th/U ratios indicate the enrichment of U in the sediments. The El Sahu sandstones have a low Th/U ratio (ave. 0.1), signifying uranium enrichment.

The authigenic uranium content is calculated as \(U_{\text{authigenic}} = U - \frac{Th}{3}\). Values of authigenic uranium below 5 are thought to represent oxic conditions, while values above 5 are indicative of suboxic to anoxic conditions. The El Sahu sandstones have an average value of 388.

The equilibrium/disequilibrium states for the El Sahu sandstones were determined by calculating the D-factor (Hanskink, 1976) and the activity ratio. Table 1 shows that in all samples eU is approximately higher than when measured chemically, which mean that disequilibrium state leaching processes have been active.
5.2 Uranium mobilization

The equation \( \text{eU} - (\text{eTh}/3.5) \) reflects the mobilization of uranium. If the result of this equation equals zero, it indicates that no uranium mobilization took place (i.e. fresh samples). When it is greater than zero, it means that the uranium was enriched (added to the rock). The negative values mean that uranium was leached out. Nearly all samples plot above the zero line, showing that uranium enrichment took place (Fig. 10).

5.2.1 Type and amount of mobilization

The type (immigration or emigration) and amount of mobilized uranium, as well as its mobilization rate, are calculated through the equations of the Benzing Uranium Institute of China (1977) and the Chinese National Nuclear Corporation (CNNC) (1993):

(a) To calculate the paleo-uranium background (i.e., original uranium content \( U_0 \)), it is necessary to multiply the average Th content detected from \( \gamma \)-ray spectrometric survey by the average regional U/Th ratio.

\[
U_0 = \text{eTh} \times \text{U/Th}
\]

where \( \text{eTh} \) = the average Th content; \( \text{U/Th} \) = the average U/Th ratio.

(b) To calculate the amount of mobilized uranium (i.e., the amount of uranium migration \( U_m \)), the following equation is used:

\[
U_m = U_p - U_0
\]

where \( U_p \) means the average uranium content.

5.2.2 El Sahu sandstones

\( U_0 = 185.5 \), amount of uranium migration. \( U_m = 215.5 \), the mobilized uranium migration rate. \( P (\%) = 52.5 \). So \( U_m > 0 \) shows that uranium migrated in and was redistributed with a 52.5% migration rate.

6 Geochemistry

The major oxides (wt%), trace (ppm) and rare earth element (ppm) concentrations of the El Sahu sandstones (located in the fault zone) are reported in Appendix 1.

6.1 Depletion/enrichment of major and trace elements

6.1.1 Major oxides
Si increase could be due to the considerable quantity of free Si-bearing mineral phases (e.g., quartz). The partial depletion of Ca, Na and K (Fig. 11) is mainly related to feldspar alteration. The decrease of Mg may result from the destruction and alteration of ferromagnesian minerals. The high Mn content could be related to the conversion of \( \text{Mn}^{2+} \) to \( \text{Mn}^{4+} \) due to changes in the redox potential condition of the fluids and also to its fixation as insoluble oxides and hydroxides (Koppi et al., 1996), or to the presence of Mn and Fe in the fault zone. P enrichment is mainly related to the presence of minerals such as monazite, autunite and torbernite.

6.1.2 Trace elements
Depletion of Rb, Ba, Sr and Cs is likely due to the decomposition of feldspars during alteration processes (Fig. 11). The loss of Co is mainly controlled by the destruction of ferromagnesian minerals by altering solutions (Kadir and Erkoyun, 2013). Uranium, thorium and lead enrichment is essentially related to the presence of minerals such as uranium oxide, autunite, torbernite.
sklodowskite, kasolite and thorite. Zr, Y, Cu, Zn, Bi, Nb, Sn, Ta and REEs incrimination is commonly controlled by the presence of monazite, xenotime, chalcopyrite, columbite and allanite.

6.2 Geochemistry of isovalents

6.2.1 La/Y ratios

La/Y ratios less than unity are an indication of acidic environments, while the values higher than unity clearly signify an alkalic environment (Abedini et al., 2018). All samples of the El Sahu sandstones have La/Y ratios <1, suggesting prevalent acidic conditions in the relevant depositional environment. The mobility of REEs is mainly controlled by the pH conditions of the medium (Karadag et al., 2009). REEs are highly mobilized under the acidic conditions of weathering products, while they are precipitated under neutral-to-alkaline conditions (Abedini et al., 2018). Though acidic conditions are prevalent in the studied formation, its high REE contents may indicate that acidic conditions in the meteoric percolating waters result from their dissolved CO₂ (Fernandez-Caliani and Cantano, 2010). These acidic solutions were probably neutralized by a rising alkaline underground water table level from the lower (Adedia Formation) to the upper (Um Bogma Formation) that came into contact with carbonate rocks (dolostone) causing changes to alkaline or neutral conditions leading to differentiation and enrichment of HREEs in the lower formation in contrast to the higher formations. Abu Bakr et al. (2016) indicated that the Um Bogma, El Hashash, Magharet El Maiah and Abu Zarab Formations are more enriched in LREEs relative to the lower Adedia Formation, which has high HREE contents. These conditions were clearly confirmed by the high values of HREEs/LREEs in the studied sandstone. The mobilization and precipitation of REEs by the effects of high and low pH are well known in weathered environments (Pantino et al., 2003). The REEs were therefore probably leached from the upper oxidized zone by acidic solutions and concentrated in the lower alkaline zone under reducing conditions. La/Y ratios indicate that all samples suggested an acidic environment. In addition to that, the presence of a Ce-negative anomaly and Eu-negative and positive anomaly values indicate severe changes in the oxidation-reduction conditions that enhanced low-temperature alteration processes (Ebyan et al., 2019).

6.2.2 Nb/Ta and Zr/Hf ratios

Nb and Ta have the same charge and ionic radius, so their behavior in geochemical processes is similar (Ballouard et al., 2016). The mobilization of Nb increases with temperature (Stepanov et al., 2014), so that high Nb/Ta ratios occur in high-temperature deposits. The solubility of Nb in F-bearing solutions increases under reducing and low temperature conditions (Zaraisky et al., 2010). According to Jahn et al. (2001), the chondritic value of Nb/Ta is 17.6 ± 1, only one sample (sample 1) having a subchondritic Nb/Ta value, while the other samples have superchondritic values (Appendix 1). The subchondritic ratios could be related to the M-type tetrachor effect inherited from the surrounding granitic rocks, while the superchondritic values are linked to the solubility of these elements in low temperature F-bearing solutions.

Firdausi et al. (2011) reported that the Zr/Hf and Nb/Ta value range in oceans and seawater is high (45-350 and 14-85, respectively). This may show that low temperature Fe-rich solutions could be marine or oceanic water. Zr, Hf, Nb and Ta are highly soluble in seawater, so Zr/Hf and Nb/Ta ratios could provide indicative parameters to clarify the paleoconditions of marine environments (Schmidt et al., 2014). Zr/Hf ratios are within the range 26–46 (Bau et al., 1996), the studied ferruginous sandstone has superchondritic Zr/Hf ratio values, with the exception of one sample (sample 1) which has a subchondritic value, suggesting that the fractionation of Zr, Hf, Nb and Ta could be related to the effect of marine or oceanic water (Appendix 1). The subchondritic and superchondritic values could be related to M- and W-type tetrachor effects.

6.2.3 Y/Ho ratio

The Y/Ho ratio would deviate from the chondritic value (Y/Ho = 28.8) for samples showing a tetrachor effect (Zhang et al., 1994; Bau et al., 1996). The studied samples have Y/Ho ratios lower than the chondritic value and one sample (sample 5) has a chondritic ratio (Appendix 1). Y/Ho ratio values could result from the M-type tetrachor effect inherited from the surrounding granitic rocks. A slight admixture of terrigenous material with the studied rocks will rapidly reduce the Y/Ho ratio in marine environments, concomitantly increasing the Zr and Th concentrations (Bolhar and Van Kranendonk, 2007).

6.2.4 Sm/Nd

All samples are higher than the Sm/Nd ratio of the Upper Continental Crust at 0.17 (Taylor and McLennan, 1985). The different electronic configuration of REY affects their complexing behavior in a weathering system.

6.2.5 Ce and Eu anomaly

The Ce anomaly is strongly controlled by the fugacity of oxygen during geochemical processes (Dill et al., 2019).
2016). Oxidizing environments cause Ce³⁺ to be converted into Ce⁴⁺ with a smaller ionic radius and higher charge (Kraemer et al., 2017). Ce in a tetravalent oxidation state is generally much less mobile, relative to other REE³⁺ (Constantopoulos, 1988). This means that under oxidative conditions Ce³⁺ increases in sediments and causes a positive anomaly (Mongelli et al., 2014). In contrast, under reducing conditions, the more soluble Ce³⁺ will be dominant, causing a negative Ce anomaly in sediments (Hannigan et al., 2010). Ce anomalies in ferruginous sandstone (<1) suggest its formation under reducing conditions.

Eu is an oxidation-sensitive element. It has two oxidation states (Eu²⁺ and Eu³⁺) during geochemical processes. Eu-bearing mineral (feldspars) solubility during hydrothermal alterations will mobilize Eu into solutions/ fluids, which is strongly mobile, with reduction of Eu³⁺ to Eu²⁺ able to occur at temperatures >200ºC (Schwinn and Markl, 2005). Most ferruginous sandstone samples have negative Eu anomalies, except for two samples. Negative Eu anomalies may be controlled by hypogene hydrothermal fluids, having temperatures >200ºC, low pH and relatively high J'O₂. Organic material can produce positive Eu anomalies under anoxic conditions (Kidder et al., 2003). Recently, studies indicated that reducing conditions can prevail during upwelling of deep anoxic waters rich in organic material and/or mixing with shalloweroxic seawater prior to deposition (Khan et al., 2016).

6.3 Rare earth elements

Abundance of REEs in sedimentary rock is an indicator of the source area. REE patterns reflect the characteristics of source rocks, from which sediments are derived and accumulate in the basin. Sediments derived from a common source do not show any noticeable fluctuation in their REE patterns. On the other hand, REEs show variable patterns in sediments that originated from heterogeneous source rocks (Taylor and McLennan, 1985; Cullers, 1995).

The average REEs concentration is (2156 ppm), LREEs (Ave. 297 ppm) and HREEs (Ave. 1859 ppm). Also, the average values of Ce/Ce* and Eu/Eu* is 0.8 and 0.3, respectively (Appendix 1). In figure 12, the studied sandstones tend to have HREE enrichment and flat LREE patterns. The averaged REE content is higher than 14-fold that for UCC, as quoted by Rudnick and Gao (2003).

6.3.1 The Lanthanide Tetrad Effect in the El Sahu sandstones

The REE pattern kinks are characterized by prominent convex and concave tetrads and negative Eu anomalies. Visual inspection suggests that the third and fourth tetrads in most samples are more prominent than the first. The second tetrad is comparatively difficult to recognize due to the anomalous behavior of Eu and the fact that Pr does not occur in nature.

Masuda et al. (1987) classified the tetrad effect into two different types, M-and W-type (M-type in solid sample as residues and W-type in the interacting fluids as extracts). The values of the tetrad effect were calculated according to the quantification method of Irber (1999):

\[ t_1 = (\text{Ce}/\text{Ce}^* \times \text{Pr}/\text{Pr}^*) \]
\[ t_2 = (\text{ Tb}/\text{Tb}^* \times \text{Dy}/\text{Dy}^*) \]
\[ t_3 = (\text{Tm}/\text{Tm}^* \times \text{Yb}/\text{Yb}^*) \]

Degree of the tetrad effect \( T_{Ei} = (t_1 \times t_3)^{0.5} \)

The calculated values of the tetrad effect range from 0.6 to 1.13 in the studied sandstones. The M-shaped pattern shows \( T_{Ei} > 1.1 \) and the W-shaped \( T_{Ei} < 0.9 \). The use of first, third and fourth tetrads (T1-4) gives a more correct estimate.

It is clear that most of the ferruginous sandstone samples have a pronounced M-type effect in the first, second and third tetrads, whereas W-type tetrad effects are only shown in some samples, such as 3, 4, 6 and 8, primarily in the first and third tetrads (Fig. 12). However, samples 3, 6 and 8 show clear convex (M-type) \( T_2 \) with concave (W-type) \( T_3 \) (Fig. 12 and Appendix 1).

6.3.2 Genesis of tetrad effects

Zhao et al. (2008) suggested that the new MW-type of tetrad effect is likely to be caused primarily by the interaction of aqueous liquids with alkaline rocks. Abedini et al. (2018) indicated that the co-existence of W- and M-shape tetrad-effects in the Kanigorge residual horizon of bauxite deposits in Iran supports the idea that penetration of low-pH surface waters into the upper part caused destruction of REE-bearing minerals, leaching and transportation of REE downwards and their ultimate concentration in the lower part. Conjugate types of this effect (M- and W- shape) have been reported from different environments, such as the Qahr-Abad fluorspar deposit and other deposits worldwide (El Nahas et al., 2011; El Mezayen et al., 2019, Ibrahim et al., 2015; El-Tohamy, 2019). The latter indicates that the existence of both W- and M-type tetrad effects in the same deposit can be related to weathering, leaching by groundwater and/or mixing of fluids and/or waters or combinations of these. Zhao et al. (2010) stated that the peculiar M/W-type tetrad effect might be an indicator for Au-mineralization of reworked plutons and this hypothesis could be applied and tested in the study area, throughout its different nature where there are high Au contents in the ferruginous sandstone. This phenomenon of the conjugate M/W-type tetrad effect could be considered as evidence for the
presence of gold mineralization in different environments.

6.4 Source-area weathering

The intensity of the chemical weathering (CIA) of source rocks is mainly controlled by the composition of the source rock, duration of weathering, climatic conditions and rates of tectonic uplift of the source region (Wronkiewicz and Condle, 1987). Exposed rocks are affected to various degrees by a combination of chemical and physical weathering (Bland and Rolls, 1998).

In order to determine the degree of source rock weathering, a few indices of weathering have been proposed, based on the molecular proportions of mobile and immobile element oxides (Na₂O, CaO, K₂O and Al₂O₃). The indices of weathering/alteration include the chemical index of alteration (CIA) and the chemical index of weathering (CIW). The chemical index of alteration (CIA), proposed by Nesbitt and Young (1982), is the most widely-used chemical index for determining the degree of source area weathering, the formula being as shown in the equation below:

\[
\text{CIA} = \left[ \frac{\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{Ca}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O})} {\text{M}_{\text{Al}}/\text{M}_{\text{Si}}} \right] \times 100
\]

where CaO resides in the silicate fraction (McLennan et al., 1993). The CIA value (55–80) and CIW (59–82) of the sandstones are considerably higher than the upper continental crust value (50). This suggests that the source region was subjected to moderate-to-high intensive chemical weathering, likely under tropical paleo-climatic conditions with abundant rainfall. The CIA and CIW values also signify a dominant felsic source and sediment recycling processes. This indicates that chemical alteration played a major role during weathering, or alternatively during sediment recycling (Nesbitt and Young, 1982; McLennan et al., 1993).

Geochemical data of the El Sahu sandstones were plotted in the ternary diagram of Nesbitt and Young (1982), Al₂O₃–(CaO + Na₂O–K₂O) (represented as A–CN –K) (Fig. 13a). It is useful for identifying compositional changes of sandstones that are related to chemical weathering, diageneis and source rock composition. The samples were parallel to the A–CN edge. This is possibly due to the fact that the removal rate of Na and Ca from plagioclase is generally greater than the removal rates of K from microcline (Nesbitt and Young, 1982). Also, the sandstones plotted mostly in the field of intermediate-to-low weathering conditions (Fig. 13b).

6.5 Climatic Conditions and Sediment Maturity

The original character and maturity of the sediments, as well as the prevailing climatic conditions, can be determined by calculating the index compositional variation (ICV), as proposed by Cox et al. (1995). The ICV tends to be highest in minerals that are high in weathering intensity and decreases in more stable (less weathered) minerals.

\[
\text{ICV} = \left( \frac{\text{Fe}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{MnO} + \text{Al}_2\text{O}_3} {\text{Al}_2\text{O}_3} \right) \times 100
\]

As documented by Cox et al. (1995), sandstones with ICV > 1 are compositionally immature, with the first cycle of sediments deposited in tectonically-active settings. On the other hand, those with ICV < 1 are compositionally mature and were deposited in the tectonically quiescent or cratonic environment, where sediment recycling was active.

The El Sahu sandstones have ICV values ranging from 4.1 to 14.5 (ave. 7.2). Based on the average ICV values, it can be inferred that the sandstones are compositionally immature. The binary plot of CIA against ICV for the studied samples (Fig. 14a) shows that most of the El Sahu sandstone samples are geochemically immature, with a weak weathering trend.

To constrain the climatic conditions during sedimentation of siliciclastic sedimentary rocks, the proposed plot of SiO₂ against (Al₂O₃ + K₂O + Na₂O) after Suttner and Dutta (1986) was used to classify the maturity of the El Sahu sandstones as a function of climate. Figure 14b shows that the sandstone samples plotted in the humid climate field.

6.6 Tectonic setting

Major and trace elements are important indicators for inferring tectonic setting as well as the depositional environment of sedimentary rocks. Roser and Korsch (1986) identified three tectonic settings, namely a passive continental margin (PM), active continental margin (ACM) and oceanic island arc (ARC). On a K₂O/Na₂O–SiO₂ discrimination diagram, the El Sahu sandstones
samples from the Adedia Formation plot mostly in the ACM field (Fig. 15).

Similarly, REE distributions in sandstones have also been used to infer tectonic settings by various authors (Asiedu et al., 2000). According to these studies, the sediments deposited in the continental margin are characterized by LREE enrichment and high total rare earth elements (ΣREE), whereas sediments deposited by young, undifferentiated oceanic arcs have low ratio, ΣREE content and lack a negative Eu anomaly. Passive margin provenance is typically characterized by a uniform REE pattern similar to PAAS (Bhatia, 1985; McLennan, 1989), while sediments from an active continental margin display intermediate ΣREE abundances with a variable negative Eu anomaly (McLennan, 1989).

In this study, the El Sahu sandstones samples have relatively high HREEs (1859 ppm), LREEs (297 ppm) and variable Eu/Eu* ratios (0.2–2.1) suggesting a combination of passive and active margin settings.

6.7 Provenance
Trace elements such as high field strength elements (Zr, Nb, Hf, Ta and Y) and REE are also very useful for provenance studies, because of their relatively low mobility during surface sedimentary processes as well as being enriched in felsic rather than mafic sources. In contrast, Co, Sc and V are more concentrated in mafic than in felsic source rocks (Feng and Kerrich, 1990).

When elemental ratios from the El Sahu sandstones are compared with those described by Armstrong-Altrin et al. (2004) and Osae et al. (2006) in Table 2, the ratios of the study sandstone samples fall within the range of felsic sources and the upper continental crust (UCC).

### Table 2 Range of elemental ratios of the El Sahu sandstones compared to the ratios in similar fractions derived from felsic rocks, mafic rocks and upper continental crust (UCC)

<table>
<thead>
<tr>
<th>Elemental ratio</th>
<th>Range of sandstones from El Sahu (n = 8)</th>
<th>Range of sediment from felsic sources</th>
<th>Range of sediment from mafic sources</th>
<th>Upper continental crust a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu/Eu*</td>
<td>0.2–2.1</td>
<td>0.4–0.94</td>
<td>0.71–0.95</td>
<td>0.63</td>
</tr>
<tr>
<td>La/Sc</td>
<td>0.59–7</td>
<td>2.5–16.3</td>
<td>0.43–0.86</td>
<td>2.2</td>
</tr>
<tr>
<td>Tb/Sc</td>
<td>0.43–9.4</td>
<td>0.84–20.5</td>
<td>0.05–0.22</td>
<td>0.79</td>
</tr>
<tr>
<td>Tc/Cr</td>
<td>0.09–1.6</td>
<td>0.13–2.7</td>
<td>0.018–0.046</td>
<td>0.13</td>
</tr>
<tr>
<td>Cr/Ti</td>
<td>0.63–11</td>
<td>4–15</td>
<td>25–500</td>
<td>7.76</td>
</tr>
<tr>
<td>La/Co</td>
<td>2.4–9.2</td>
<td>1.8–13.8</td>
<td>0.14–0.38</td>
<td>1.76</td>
</tr>
</tbody>
</table>

Reference: This study; Cullers (2000); Cullers and Podkovyrov (2000); McLennan (2001); Taylor and Armstrong-Altrin et al. (2004); McLennan (1985)
Th/Co vs. La/Sc bivariate diagram can provide information regarding the source rock characteristics (Cullers, 2002). The Th/Co vs. La/Sc plot (Fig. 16a) suggests a felsic nature of the source rocks. Floyd et al. (1991) pointed out that the element ratio La/Th plotted versus (Hf) demonstrates the degree of recycling in sandstones, and also implicates information about their provenance. Figure 16b indicates that El Sahu sandstone samples fall in or beside the felsic source field.

The Th/Sc ratio is an index of provenance. Hydraulic sorting and reworking during sedimentation lead to the concentration of resistant phases like zircon. High ratios represent compositional variation and sediment recycling (zircon addition); it also may indicate the increased concentration of heavy minerals, which is possibly a sign of prolonged recycling of the sediments (Rahman and Suzuki, 2007).

In the Th/Sc vs. Zr/Sc plot (Fig. 17), trend 1 reveals a direct contribution from primary source rocks and trend 2 shows the influence of sedimentary processes. The El Sahu sandstone samples are sub-parallel to trend 2, suggesting heavy mineral addition during sediment recycling and sorting.

7 Discussion

All the results and relationships of Eu anomaly, La/Sc, Th/Sc, Th/Cr, Cr/Th and La/Co make clear that the studied ferruginous sandstones may be derived from surrounding granitic rocks as a felsic source. Also, high uranium and rare earth element contents in the studied rocks are mainly related to two sources, the first source from the descending acidic solutions from the upper formations and the other source connected to the ascending hydrothermal solutions as confirmed from field observations and, ratios of isovalents and the M-type tetrad effect. Eu and Ce anomalies with La/Y ratio show that the descending acidic solutions of surficial water move downward leading to uranium and rare earth mobilization and the changes in the pH conditions from acidic to alkaline come from the rising groundwater in contact with dolostones in the lower formation and conversion from oxic to anoxic environment due to the effect of pyrite and microorganisms. In the upper formations, the LREEs mobilize from their bearing minerals as a result of their larger ionic radius in the highly acidic conditions and precipitate with the pH changes in the upper formations, while the HREEs stay in solution and mobilize to the lower formations and precipitate with the changes to alkaline conditions. This was clarified by the higher HREEs/ LREEs ratios in the lower formations relative to the upper. Y/Ho, Zr/Hf, Nb/Ta and Rb/Sr confirm the role of the groundwater and seawater in the depositional environment of the studied rocks. The M-type tetrad effect could be related to the alteration by hydrothermal solutions accommodated with U and REEs mineralization while the W-type tetrad effect signifies the leaching of these elements by groundwater and seawater. Nb/Ta and Y/Ho values of the ferruginous sandstones could be connected to alteration by hydrothermal solutions, where the unusual values of the
Zr/Hf ratio values may result from the effect of seawater, these contrasting values could point to the seawater effect following the effect of hydrothermal solutions, as evidenced by the inherited values of the isovalents. According to Zhang et al. (2020) uranium mineralization changes from surficial infiltration or phreatic oxidation in the upper part to interlayer oxidation in the lower part. It is worth mentioning that the presence of complex M-W type tetrad effects in the gold-mineralized plutons and in many rocks of sedimentary composition may indicate that these conjugate tetrads could be considered as evidence for gold mineralization.

8 Conclusions

Paleozoic rocks in the Wadi El Sahu area are affected by many major faults in different directions. A normal fault trending NE-SW with exposure of part of its length for about 300 m cuts through the Abu Hamata and Adedia formations at the south side of Wadi El Sahu passing through the Wadi deposits and then cuts through the El Hashash Formation on the other side. A secondary ascending hydrothermal solution carrying heavy metals and radioactive minerals passed through the fault plain and the surrounding fractures, forming a mineralized and radioactive zone. The mineralized zone thickness varies between 60 cm and 200 cm along the fault plain. All deduced results indicate that uranium and the REEs were primarily derived from the surrounding felsic rocks during mobilization from the upper formations to the lower ones, or their movement with the later ascending hydrothermal solutions. Eu and Ce anomalies, La/Y, Nb/Ta, Y/Ho and Zr/Hf ratios, in addition to conjugate M-W tetrads, clearly indicate the effect of groundwater and seawater in the environment of deposition and the changes in pH conditions, which could be related to the carbonate rocks (dolostones) and their role in pH changes from acidic to alkaline. Mineralogical investigations indicate the presence of uranium oxide, torbernite, autunite, sklodowskite, kasolite as uranium minerals, thorite as a thorium mineral, monazite, allanite and xenotime asREE-bearing minerals, zircon and columbite as accessory minerals, gold and nickel as precious and base metals, in addition to cassiterite, chalcocite, chalcopyrite and chrysocholla. It can be concluded that tetrad effects could be used as an indicator of U and REEs migration in or out, or the presence of gold mineralization, in the case of complementary M-W tetrads.

Acknowledgements

The authors would like to express appreciation to Prof. Mohammed Galal ElFeky, from Geology, Nuclear Materials Authority, Egypt, for his revision and critical comments. Also, the authors acknowledge the support of the Nuclear Materials Authority, Cairo, Egypt, for their kind access to field and laboratory facilities during the preparation of this work.

Manuscript received Oct. 6, 2019 accepted Dec. 15, 2019


About the first author
Osama SALLAM, Male: born in 1966 in Qalyub City, El Qalyubia, Egypt. Assistant Professor of Geology, Nuclear Materials Authority (NMA), Cairo, Egypt. Interested in rocks and minerals, Email: orsallam@yahoo.com.

About the corresponding author
Amira Mohammed El TOHAMY, Female: born in 1984 in Minufiya, Egypt. Lecture in Geology, Nuclear Materials Authority (NMA), Cairo, Egypt. Interested in the geochemistry and mineralogy of different rock types, Email: amira_elthamy2011@yahoo.com.