Role of geochemical alteration on the formation of secondary Zr- and U-bearing minerals in El Atshan trachyte, central Eastern Desert, Egypt

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El Atshan area, situated in the central Eastern Desert of Egypt, is a good location for studying the influence of high- and low-*T* alterations on the formation of Zr- and U-bearing minerals within a trachyte sill. These minerals are mainly represented by an unidentified secondary Zr-rich silicate mineral, betafite, and liandratite. The unidentified Zr-rich silicate mineral is considered to be an alteration product of the precursor zirconolite during high-*T* alteration. This is indicated by the changes in the composition marked by an increase in the amount of hydration (H₂O), Si, and U and a decrease in the amount of Ca, Ti, Nb, and Fe. The morphology of this unidentified mineral is similar to that of zirconolite. For seven oxygen atoms, the calculated formula of the unidentified Zr-rich silicate mineral is (Si_{1.45}U_{0.18}Ca_{0.32}Pb_{0.01}Nb_{0.06}Zr_{1.18}Hf_{0.01}Fe_{0.06}Al_{0.08}Ti_{0.11}P_{0.09}Y_{0.05}REE_{0.09})_{Σ3.7}O₇. With more extensive alteration, it was found that the unidentified secondary Zr-rich silicate mineral was unstable and it underwent re-equilibration with U-rich fluid, which led to alterations in betafite. The two possible mechanisms responsible for the alteration of the unidentified Zr-rich silicate mineral to betafite are as follows: (1) the dissolution of the unidentified Zr-rich silicate mineral and precipitation of betafite and (2) the ion-exchange between partially to fully amorphized zones and the U-rich fluid. Such alteration is indicated by a marked increase in the amount of U, Ti, and Nb and a decrease in the amount of Zr, Si, Ca, P, Y, and ΣREE. The single substitution of U⁴⁺ ↔ Zr⁴⁺ and the coupled substitution of (U⁴⁺ + Ti⁴⁺ + Nb⁵⁺) ↔ (Zr⁴⁺ + Si⁴⁺ + Ca²⁺ + P⁵⁺ + Y³⁺ + ΣREE³⁺) appear to be the main causes for the formation of betafite. For 2.00 *B*-site cations, the calculated formula of the betafite is ^A(U_{0.44}Ca_{0.25}REE_{0.05}Y_{0.03}Pb_{0.02})_{Σ0.79}^B(Si_{0.79}Zr_{0.69}Ti_{0.23}Nb_{0.12}Al_{0.06}Fe_{0.05}P_{0.03}V_{0.02}Hf_{0.01})_{Σ2.0}O₇. Betafite was altered to liandratite in the late low-*T* alteration stage. For 2.00 *Nb*-site cations, the calculated formula of the liandratite is ^U(U_{1.35}Ca_{0.41}Pb_{0.04}REE_{0.04}Y_{0.01})_{Σ1.86}^{Nb}(Ti_{0.67}Si_{0.46}Nb_{0.40}Zr_{0.26}Fe_{0.09}V_{0.08}Al_{0.03}Ta_{0.01})_{Σ2.0}O₈. Among different uranium complexes, the influence of fluoride on the solubility and mobility of uranium is confirmed.

Keywords: Egypt, Unidentified Zr-rich silicate mineral, Betafite, Liandratite, Alteration

INTRODUCTION

Natural pyrochlores are grouped into three types: pyrochlore (niobium-rich), microlite (tantalum-rich), and betafite (titanium- and uranium-rich). The simplified general formula of the pyrochlore group is A₂B₂X₇Y·nH₂O, where A denotes Ca, Na, actinides, rare earth elements (REEs), Ba, Sr, Bi, Pb, and U; B denotes Nb, Ta, Ti, Zr, Sb, W, and Fe; X denotes O and OH; and Y denotes O, OH, and F (Hogarth, 1977). Some alteration in natural betafite is due to the loss of relatively soluble cations such as Na, K, Ca, and U (Lumpkin and Ewing,

1985, 1996; Lumpkin et al., 1994). The fluids responsible for alteration range from dense, supercritical magmatic fluids to mixed magmatic-meteoric fluids to groundwater of low ionic strength. Studies of natural pyrochlore have provided a considerable amount of information on the aspects of the long-term performance of pyrochlore phases in titanate-based ceramic nuclear wastes, including tailored ceramics (Harker, 1988) and Synroc (Ringwood et al., 1988; Ball et al., 1989).

In contrast, the chemical alteration of natural zirconolite is relatively uncommon and the Th and U contents remain almost constant (Lumpkin et al., 1994). The limited corrosion of zirconolite has been documented in a natural hydrothermal vein system at temperatures of

Figure 1. Geological map of El Atshan area.

500–600 °C by a relatively acidic aqueous fluid with significant concentrations of H_2S , HF , and HCl (Gieré and Williams, 1992). The complete replacement of zirconolite by zircon, sphene, and rutile has been observed in metamorphic systems at very high temperatures of 620–680 °C (Pan, 1997). Several other examples of zirconolite alteration have been presented by Hart et al. (1998), but none of these appear to involve significant losses of actinide elements. Williams et al. (2001) have studied zirconolite from 19 carbonatite occurrences. Zirconolite displays varying degrees of alteration that ranges from incipient minor effects to major corrosion, recrystallization, and complete replacement by an unidentified actinide-rich (ACT), Ba, Ti, Zr, and Nb silicate phases.

El Atshan is a good location for studying the influence of high and low- T alteration on the formation of Zr- and U-bearing minerals within volcanic rocks. These rocks have previously been recognized as bostonite (El Hazek, 1968; Attawiya, 1971; Hussein and El Kassas, 1972). Recently, Dawood et al. (2004) classified these rocks as trachyte on the basis of their geochemical characteristics. However, the term trachyte is used in the present study that refers to the mineralized volcanic rock in El Atshan area. Presence of some primary ore bodies have been reported in this trachyte by many authors (Obrenovic et al., 1966; El Hazek, 1968). This primary uranium mineral is represented by coffinite and pitchblende with some sulfide minerals such as galena, sphalerite, pyrite, and chalcopyrite. The secondary uranium minerals are represented by uranophane, kasolite, soddyite, gummite, schoepite, schroeckingerite, rutherfordine, zippeite, and uranopilite (Attawiya, 1971). However, only soddyite, kasolite,

and uranophane have been confirmed to be present in El Atshan (e.g., Osmond et al., 1999; Dawood et al., 2004).

In this paper, I report the first documented occurrence of an unidentified secondary Zr-rich silicate mineral, betafite, and liandratite in the trachyte of the El Atshan area, central Eastern Desert, Egypt. The main objectives of the present study are to (1) characterize the chemical composition of uranium-bearing minerals in El Atshan area, (2) establish a general chemical framework for the interaction of Zr- and U-bearing minerals with high- and low- T fluids, and (3) present a genetic model for this uranium mineralization.

GEOLOGICAL BACKGROUND

The geology of the El Atshan area has been investigated by Obrenovic et al. (1966), Hussein and El Kassas (1972), Osmond et al. (1999), and Dawood et al. (2004). The main rock units are (from older to younger) metasediments, metavolcanics, Hammamat sediments, granites, and post-tectonic volcanics (Fig. 1). The post-tectonic volcanics are represented by trachyte, felsite, granite porphyry, quartz veins, and less common basic rocks. The alkaline trachyte dikes and sills are the most predominant volcanic rocks. The age of the trachyte is 273 ± 20 m.y. (Late Carboniferous to Early Permian, El Manharawy, 1972). Similar ages were reported for volcanic dikes of the Wadi Kariem area (Sayyah et al., 1978). Trachyte forms sills, dikes, and sometimes plugs and cone-like masses of variable thickness. Uranium mineralization occurring at the El Atshan area is mainly associated with a trachyte sill that intruded the foliated Hammamat sedi-

Figure 2. (a) Image showing the trachyte sill intruded in Hammamat sediments. (b) Image showing fissures and fractures in the trachyte sill.

ments (Fig. 2a). This sill extends for approximately 1.5 km and has a variable thickness (average: 28 m). It strikes N26°E and has a variable dip to the NW, ranging from 20° to 45°. This sill is affected by some faults, joints, and fractures in different directions (Fig. 2b); however, the most predominant ones are striking in the NW-SE and NE-SW directions. The fractured rock is usually altered, and most of the joints and fractures are stained with alteration products, including iron, manganese oxides, and clay minerals. Uranium mineralization is generally controlled by these structures, where they fill some tension fractures that are connected to the contact zone between the trachyte sill and the surrounding foliated Hammamat sediments. The upper contact is generally more mineralized than the lower one. The hydrothermal alteration accompanying the deposition of uranium in the host trachyte consists of hematitization, kaolinitization, and carbonatization. The alteration occurs in narrow zones, 0.1–1.0 cm wide, along the margins of uranium mineralized veinlets and disseminated in the host trachyte. Hematitization is the most distinct style of alteration. The alteration of rock forming minerals is represented by sericite and clay minerals after feldspars, and limonite, goethite, and hematite after magnetite and iron-bearing sulfides. Calcite forms in the altered host rock as disseminations and veins along fractures. Textural evidence shows that the deposition of carbonate minerals was due to syn- and post-mineralization. Similarly, the foliated Hammamat sediment beds are altered along their contacts, faults, and fractures.

The trachyte rock is massive, fine grained, and buff

in color. The weathered parts are creamy yellow and sometimes brown in color. The trachyte rocks of the El Atshan area are fine grained (average grain size of approximately 0.5 mm) and holocrystalline; however, small amounts of secondary chalcedony or cryptocrystalline quartz are also present in the rocks. The rocks consist mainly of alkali feldspars (anorthoclase and orthoclase), which form around 90% of the entire rock. Anorthoclase is generally lath-shaped, highly altered, and sericitized, whereas orthoclase occurs as irregular disseminated grains in the matrix and is relatively less altered. Quartz also exists in small amounts not more than 5% of the rock. It is present in the groundmass filling the interstices. The other constituents are ferromagnesian minerals that are mainly represented by chlorite, which is an alteration product of pyroxenes and amphiboles. Hornblende and aegirine are also present; they are generally obscured due to intense hematitization. The heavy minerals present in the trachyte are non-opaques, opaques, and uranium minerals. The non-opaque minerals are represented by zircon, betafite, apatite, titanite, and fluorite. The opaque minerals are mainly represented by galena, pyrite, chalcocopyrite, and sphalerite. They form thin veinlets, fracture fillings, and disseminated grains around the mineralized fractures. In the highly altered parts, the sulfides show partial alteration to iron oxides, especially hematite and limonite. The trachyte is characterized by subtrachytic texture, where the feldspars laths are arranged in a parallel to subparallel orientation. Sometimes, the rock shows porphyritic texture where feldspars are relatively coarse-grained embedded in a microcrystalline groundmass of feldspars, quartz, and iron oxides. The trachyte is sheared and brecciated in some parts; the resulting fractures are filled with uranium minerals deposited from solutions.

Dawood et al. (2004) studied the geochemistry of the trachyte in the study area. They concluded that this rock was subjected to two phases of alteration. The early stage of hydrothermal alteration included argillization, dissolution of iron-bearing sulphides, formation of iron-oxy hydroxides, and corrosion of primary uranium minerals. The second phase of alteration occurred near the surface when the late-stage hydrothermal fluids cooled to the temperature of meteoric water and possibly mixed with it; the pH of the fluids became more alkaline, and at these conditions, U and Eu were precipitated into the fracture system, mainly being adsorbed on the clay minerals and probably being co-precipitated with iron oxy-hydroxides. The disequilibrium state of the secondary uranium minerals in the El Atshan area is reported by many authors (Hussein et al., 1970; Osmond et al., 1999).

Figure 3. Sketch diagram showing the trench locations and the main levels of the El Atshan mine (after El Hazeq, 1968).

ANALYTICAL METHODS

Eight uranium ore samples were collected from four trenches (T1, T2, T3, and T4) and from an inclined shaft at the El Atshan mine (Fig. 3). The ore samples were scraped from their host rock and their color ranged from pale yellow to brownish yellow, depending on the degree of iron and manganese contamination. After mounting and polishing of the scrapped grains, a JEOL JEE-400 Vacuum Evaporator was used to coat the samples with a carbon layer prior to the analysis. Morphological and textural details of the grains were investigated at a higher magnification, as indicated in the backscattered electron images (BSE) and X-ray compositional mapping presented in this study. The qualitative composition of the grains was initially determined using wavelength-dispersive spectral line scans (WDS) on a JEOL JXA-8900 Electron Probe Microanalyzer (EPMA) available at the Institut für Geowissenschaften – Mineralogie und Geodynamik – der Universität Tübingen, Germany. Quantitative analyses of Zr- and U-bearing minerals were performed on the same machine. The analytical conditions were as follows: the accelerating voltage was 15 kV, the beam current was 10–20 nA, and the beam diameter was 1–2 μm . The standards used were a combination of well-characterized natural minerals, synthetic compounds, and pure metals. Data reduction for the various elements was performed by considering the matrix corrections between the standards and the samples and the analytical parameters. Errors in microprobe analyses due to counting statistics are less than 1% for uranium and thorium but slightly larger for other elements.

MINERAL CHEMISTRY

Unidentified secondary Zr-rich silicate mineral

The unidentified secondary Zr-rich silicate mineral in the trachyte in the El Atshan area is usually accompanied by betafite (CaUTi_2O_7) and liandratite [$\text{U}(\text{Nb,Ta})_2\text{O}_8$]. None of these minerals have been previously reported. They are reported herein as the first documented occurrence of Zr- and U-bearing minerals in the trachyte of the El Atshan area. The morphology, mode of occurrence, and paragenetic association of the unidentified Zr-rich silicate mineral are illustrated in a series of BSE images (Figs. 4–6). At high magnification, most grains appear to have a consistent prismatic shape (Fig. 4). However, some grains were found to have an irregular shape (Fig. 5). Textural observations indicate that Zr-rich betafite replaces the unidentified Zr-rich silicate mineral (Figs. 4 and 5). However, further studies using different techniques [e.g., X-ray diffraction (XRD) and transmission electron microscopy (TEM)] are required for the characterization of this unidentified Zr-rich silicate mineral.

Fifty electron microprobe analyses were performed with the grains of the unidentified secondary Zr-rich silicate mineral (Table 1). ZrO_2 , SiO_2 , UO_2 , and CaO were found to be the essential constituents, whereas Nb_2O_5 , TiO_2 , Y_2O_3 , Ce_2O_3 , Gd_2O_3 , P_2O_5 , FeO , and Al_2O_3 were the minor constituents. Negligible amounts (<1 wt%) of PbO , HfO_2 , and Ta_2O_5 were also measured (Table 1). The concentration of ThO_2 is very low and varies from 0.04 to 0.18 with an average of 0.09 wt%. The formula of the unidentified Zr-rich silicate mineral was calculated on the basis of seven oxygen atoms. The resulting chemical formula is $(\text{Si}_{1.45}\text{U}_{0.18}\text{Ca}_{0.32}\text{Pb}_{0.01}\text{Nb}_{0.06}\text{Zr}_{1.18}\text{Hf}_{0.01}\text{Fe}_{0.06}\text{Al}_{0.08}\text{Ti}_{0.11}\text{P}_{0.09}\text{Y}_{0.05}\text{REE}_{0.09})_{\Sigma 3.7}\text{O}_7$.

A similar unidentified secondary Zr-rich silicate

Figure 4. (a) BSE image of the unidentified secondary Zr-rich silicate mineral in the trachyte of the El Atshan area. The crystal shows the common prismatic form of the precursor zirconolite. It altered to Zr-rich betafite near its margins. (b), (c), and (d) X-ray maps showing the distribution of Zr, U, and Si, respectively, in the crystal of image "a." They reflect an increase in the amount of Zr and Si and a decrease in the amount of U in the unidentified Zr-rich silicate mineral relative to the Zr-rich betafite.

Figure 5. (a) BSE image for the unidentified Zr-rich silicate mineral with a Zr-rich betafite rim. (b), (c), and (d) X-ray maps showing the distribution of U, Zr, and Si, respectively, in the crystal of image "a." They reflect a decrease in the amount of Zr and Si and an increase in the amount of U after the alteration of the unidentified Zr-rich silicate mineral.

Figure 6. (a) BSE image showing the association of the unidentified Zr-rich silicate mineral, Zr-rich betafite, Zr-poor betafite, and liandratite veins. (b) X-ray map showing the distribution of U in the crystal of image (a). Liandratite shows the highest U value, followed by Zr-poor betafite, and Zr-rich betafite, whereas the unidentified Zr-rich silicate mineral shows the lowest U value. (c) X-ray map showing the distribution of Zr in the crystal of image (a). Liandratite shows the lowest Zr value, followed by Zr-poor betafite, and Zr-rich betafite, whereas the unidentified Zr-rich silicate mineral shows the highest Zr value. (d) SEI image for liandratite as veins in betafite. (e), (f) SEI images for some liandratite crystals showing the dominant fibrous structure.

mineral has been identified by Williams et al. (2001). They interpreted it as being an alteration product of zirconolite, which occurs at Cummins Range, Sokli, Phalabora, and Sebl'yavr (Table 1). In these examples, zirconolite grains have been altered to form unidentified secondary Zr-rich silicate minerals of variable composition, but which are all hydrated, enriched in Ba and Si, and depleted in Ca and Fe. These minerals are more abundant in U than in the precursor zirconolite, suggesting that these elements were mobilized and transported by magmatic-derived fluids enriched in CO_2 , P, F, Na, and K, and subsequently deposited with the alteration products (Williams et al., 2001). Figure 7a shows the REE distribution patterns in the unidentified Zr-rich silicate mineral. These patterns are nearly flat with a clear negative Nd anomaly.

Betafite

The chemical composition of betafite strongly varies, and based on the following condition $2 \text{ Ti} > \text{Nb} + \text{Ta}$ and $\text{UO}_2 > 20\%$ (Table 2), the mineral is placed in the betafite subgroup (Hogarth, 1977). The concentration of Ta is very low and is sometimes below the detection limit. It is found as separate grains or as rims around the unidentified Zr-rich silicate mineral (Fig. 5). X-ray maps show that the amount of Zr and Si in betafite is lower than that in the unidentified Zr-rich silicate mineral; however, betafite is enriched in U, Ti, and Nb (Figs. 4 and 5). When compared to other UO_2 wt% in stoichiometric non-metamict betafite reported in the mineralogical literature (average of 31.19 wt%; Cámara et al., 2004), the studied betafite has a similar value (31.23 wt% UO_2 , Table 2). The amount of ZrO_2 ranges between 13.24 and 29.01 wt% with an average of 23.25 wt%. However, some analyses

Table 1. Selected electron microprobe data (in wt%) of the unidentified secondary Zr-rich silicate mineral in the trachyte of the El Atshan area

Sample	1	2	3	4	5	6	7	8	Will.et al.*
SiO ₂	24.54	20.46	23.01	23.03	18.96	23.38	23.63	25.51	22.70
Al ₂ O ₃	1.19	1.13	1.08	1.09	1.15	1.05	1.17	1.15	<0.05
TiO ₂	2.61	3.50	3.25	3.08	2.13	0.72	0.71	2.65	10.00
P ₂ O ₅	1.63	1.15	1.15	0.74	1.19	2.98	4.05	1.24	0.00
Nb ₂ O ₅	2.08	1.90	1.37	1.15	2.77	2.14	2.44	1.73	3.27
Ta ₂ O ₅	0.23	b.d.***	0.23	0.01	0.20	b.d.	0.14	b.d.	0.46
FeO	1.48	0.98	0.94	0.96	1.04	1.29	1.24	1.45	1.20
ZrO ₂	37.76	32.87	32.91	32.99	36.75	47.66	45.44	38.24	43.10
HfO ₂	0.58	0.44	0.70	0.73	0.29	0.53	0.82	0.47	1.05
CaO	5.88	5.79	5.85	5.42	3.69	3.01	2.19	5.43	1.56
UO ₂	11.34	17.64	16.42	16.04	16.70	4.03	4.87	10.04	0.60
ThO ₂	0.04	0.18	0.12	0.10	0.11	0.03	0.01	0.16	1.36
PbO	0.60	0.53	0.64	0.57	0.74	0.35	0.51	0.55	<0.1
Y ₂ O ₃	2.13	1.59	1.14	1.33	1.33	1.42	1.58	1.92	5.8
La ₂ O ₃	0.043	0.052	0.079	0.482	0.427	0.032	0.032	0.126	
Ce ₂ O ₃	1.207	1.984	2.007	1.984	1.931	1.315	1.336	1.043	
Pr ₂ O ₃	0.146	0.231	0.323	0.185	0.163	0.018	0.139	0.119	
Nd ₂ O ₃	0.080	0.044	0.045	0.030	0.030	0.030	0.030	0.030	
Sm ₂ O ₃	0.477	0.410	0.405	0.505	0.396	0.355	0.407	0.475	
Gd ₂ O ₃	0.660	0.455	0.704	0.638	0.338	0.642	0.511	0.708	
Dy ₂ O ₃	1.041	0.428	0.497	0.517	0.479	0.637	0.704	0.824	
Ho ₂ O ₃	0.298	0.159	0.214	0.105	0.286	0.209	0.274	0.334	
Er ₂ O ₃	0.331	0.162	0.266	0.083	0.149	0.389	0.020	0.204	
Tm ₂ O ₃	0.187	0.013	0.015	0.147	0.136	0.079	0.011	0.065	
Yb ₂ O ₃	0.214	0.051	0.422	0.177	0.279	0.186	0.201	0.065	
Lu ₂ O ₃	0.174	0.201	0.051	0.088	0.051	0.053	0.114	0.185	
Total	96.95	92.34	93.84	92.17	91.72	92.53	92.59	94.70	91.10**
ΣRRE + Y	6.99	6.78	6.17	6.27	5.99	5.36	5.36	6.10	5.80
Ce/Y	0.57	1.24	1.76	1.49	1.46	0.93	0.85	0.54	1.50
Structural formula based on O = 7									
Si	1.490	1.380	1.500	1.530	1.310	1.430	1.430	1.560	1.380
Al	0.090	0.090	0.080	0.090	0.090	0.080	0.080	0.080	0.000
Ti	0.120	0.180	0.160	0.150	0.110	0.030	0.030	0.120	0.460
P	0.080	0.070	0.060	0.040	0.070	0.150	0.210	0.060	0.000
Nb	0.060	0.060	0.040	0.030	0.090	0.060	0.070	0.050	0.090
Ta	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.010
Fe	0.080	0.060	0.050	0.050	0.060	0.070	0.060	0.070	0.060
Zr	1.120	1.080	1.040	1.070	1.240	1.420	1.340	1.140	1.270
Hf	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.020
Ca	0.380	0.420	0.410	0.380	0.270	0.200	0.140	0.360	0.100
U	0.150	0.270	0.240	0.240	0.260	0.050	0.070	0.140	0.010
Th	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.020
Pb	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.000
Y	0.070	0.060	0.040	0.050	0.050	0.050	0.050	0.060	0.19
La	0.000	0.000	0.000	0.010	0.010	0.000	0.000	0.000	
Ce	0.030	0.050	0.050	0.050	0.050	0.030	0.030	0.020	
Pr	0.000	0.010	0.010	0.000	0.000	0.000	0.000	0.000	
Sm	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	
Gd	0.010	0.010	0.020	0.010	0.010	0.010	0.010	0.010	
Dy	0.020	0.010	0.010	0.010	0.010	0.010	0.010	0.020	
Ho	0.010	0.000	0.000	0.000	0.010	0.000	0.010	0.010	
Er	0.010	0.000	0.010	0.000	0.000	0.010	0.000	0.000	
Yb	0.000	0.000	0.010	0.000	0.010	0.000	0.000	0.000	
Total	3.75	3.78	3.76	3.74	3.68	3.63	3.57	3.73	3.61

* Microprobe analysis of the unidentified secondary Zr-rich silicate mineral as an alteration product of zirconolite from Cummins Range, Australia (Williams et al., 2001).

** Includes MgO, 0.25; MnO, 0.05 wt%.

*** b.d., below detection limit (ThO₂, 0.01; La₂O₃, 0.02; Pr₂O₃, 0.026; Nd₂O₃, 0.01; Sm₂O₃, 0.028; Gd₂O₃, 0.042; Dy₂O₃, 0.01; Ho₂O₃, 0.01; Er₂O₃, 0.005; Tm₂O₃, 0.006; Yb₂O₃, 0.009; Lu₂O₃, 0.018; Ta₂O₅, 0.01; HfO₂, 0.009 wt%).

Figure 7. Chondrite-normalized REE patterns of (a) the unidentified Zr-rich silicate mineral, (b) betafite, and (c) liandratite. The REE normalization is based on the chondrite data provided by Anders and Grevesse (1989).

show lower values for the Zr content (~ 6 wt%). The incorporation of Zr^{4+} , an ion of intermediate size, is well-known in natural pyrochlore, where Zr^{4+} is assigned to the *B*-site in accordance with the synthetic REE-Zr pyrochlore (Hayakawa and Kamizono, 1993; Subramanian et al., 1983).

The formula of betafite was calculated by assuming 2.00 *B*-site cations per formula unit (Table 2), assuming that Al, P, V, and Zr occupy the *B*-site and all Fe is present as Fe^{3+} at the *B*-site. Si may occupy either the *A*- or the *B*-site because both these sites are octahedrally coordinated. Si was chosen to be placed in the *B*-site because it seems unlikely that small cations such as Si share the same site as large cations such as Pb, Na, and Ca. Placing Si in the *B*-site has been also documented by Subramanian et al. (1983) and Johan and Johan (1994). The obtained chemical formula is ${}^A(U_{0.44}Ca_{0.25}REE_{0.05}Y_{0.03}Pb_{0.02})_{\Sigma 0.79}{}^B(Si_{0.79}Zr_{0.69}Ti_{0.23}Nb_{0.12}Al_{0.06}Fe_{0.05}P_{0.03}V_{0.02}Hf_{0.01})_{\Sigma 2.0}O_7$.

The total amount of REE in betafite is relatively

lower than that measured in the unidentified Zr-rich silicate mineral (average $\Sigma REE = 2.70$ wt%). In general, one can observe that the REE pattern of betafite (Fig. 7b) and the unidentified secondary Zr-rich silicate mineral (Fig. 7a) are quite similar and show negative Nd anomaly. Similarity in the plots of REE data in these minerals suggests that the alteration process did not cause marked fractionation of the REEs during the alteration of the unidentified Zr-rich silicate mineral to betafite.

Liandratite

Liandratite is yellow in color and has a higher BSE intensity than betafite and the unidentified Zr-rich silicate mineral (Fig. 6a). It is found as a vein in betafite (Figs. 6a–6d), as a rim around betafite, or as separate grains (Figs. 6e and 6f). When compared to the unidentified Zr-rich silicate mineral and betafite, liandratite has the highest uranium content and lowest zirconium content. It has REE patterns that are similar to the patterns of the unidentified Zr-rich silicate mineral and betafite with Nd anomaly (Fig. 7c). The formula unit of liandratite is normalized by assuming 2.00 *Nb*-site cations per formula unit (Table 3), with similar assumptions that made for betafite concerning the amount of Zr, Si, Fe, P, and Al in the *Nb*-site. The calculated formula is ${}^U(U_{1.35}Ca_{0.41}Pb_{0.04}REE_{0.04}Y_{0.01})_{\Sigma 1.86}{}^{Nb}(Ti_{0.67}Si_{0.46}Nb_{0.40}Zr_{0.26}Fe_{0.09}V_{0.08}Al_{0.03}Ta_{0.01})_{\Sigma 2.0}O_8$, where U, Ca, Ti, and Nb represent the principle elements with considerable amounts of Si, Zr, and traces of Fe, Pb, V, Al, Ta, P, and REEs.

The composition of liandratite in Madagascar (Lumpkin and Ewing, 1996) is similar to that of the studied liandratite, especially in major constituents such as U and Nb (Table 3). The calculated chemical formula is similar to the theoretical formula of liandratite ($U^{6+}\square Nb_2O_8$) (Mücke and Strunz, 1978; Lumpkin and Ewing, 1996). The average of *U*-site total (1.86 atoms) is in agreement with the normal values (maximum 2). In addition, the ratio of *U*:*Nb*-sites appears closer to 2:2 of liandratite.

DISCUSSION

The formation of the trachyte sill at the El Atshan area is related to the tensional tectonic event that produced big fissures connecting the mantle material with the upper crust. This tectonic event is probably related to the late Pan-African tectono-thermal event that involves Permo-Triassic magmatism, the Late Jurassic–Early Cretaceous hydrothermal phase, Late Cretaceous–Early Tertiary hydrothermal phase, and the Tertiary volcanicity and Oligo-Miocene phase (Dawood et al., 2004). The occurrence of

Table 2. Selected electron microprobe data (in wt%) of betafite in the trachyte of the El Atshan area

Sample	1	2	3	4	5	6	7	8
UO ₂	26.59	27.50	28.02	29.49	24.26	30.17	35.60	31.46
CaO	4.85	3.68	3.97	4.11	4.27	3.40	3.29	3.46
ThO ₂	0.05	0.14	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
PbO	0.77	0.90	0.84	1.10	0.90	1.12	1.21	1.03
Y ₂ O ₃	0.56	0.67	1.35	0.80	1.04	1.05	0.86	0.98
La ₂ O ₃	b.d.	0.24	b.d.	b.d.	b.d.	0.09	0.27	0.02
Ce ₂ O ₃	0.44	0.50	0.61	0.81	1.09	1.37	1.11	1.38
Pr ₂ O ₃	0.15	b.d.	0.08	0.22	0.07	0.22	0.13	0.12
Nd ₂ O ₃	0.08	0.08	0.02	b.d.	b.d.	b.d.	0.04	0.06
Sm ₂ O ₃	0.39	0.34	0.41	0.27	0.40	0.28	0.20	0.15
Gd ₂ O ₃	0.21	0.02	0.50	0.24	0.30	0.29	0.31	0.30
Dy ₂ O ₃	0.45	0.35	0.69	0.50	0.77	0.35	0.26	0.31
Ho ₂ O ₃	0.16	0.22	0.24	0.23	0.07	0.22	0.09	0.04
Er ₂ O ₃	0.13	0.07	0.15	0.07	0.25	0.05	0.09	0.03
Tm ₂ O ₃	0.03	0.03	0.11	0.19	0.04	0.01	0.02	0.02
Yb ₂ O ₃	0.22	b.d.	0.13	0.11	0.18	0.05	b.d.	b.d.
Lu ₂ O ₃	0.02	0.22	0.11	0.10	0.09	0.03	0.05	0.02
SiO ₂	13.45	15.21	15.39	13.21	15.86	13.79	12.46	13.21
Al ₂ O ₃	0.95	0.76	0.84	0.70	1.03	0.95	0.73	0.79
TiO ₂	4.79	4.50	3.60	4.13	3.21	4.24	5.14	4.74
P ₂ O ₅	3.65	0.82	0.71	0.09	0.52	0.46	0.39	0.30
Nb ₂ O ₅	4.39	3.77	3.52	4.36	3.09	4.21	4.82	4.22
Ta ₂ O ₅	0.25	0.25	0.08	0.15	b.d.	0.02	0.27	0.22
FeO	1.41	0.99	1.12	0.94	0.89	0.90	0.91	0.91
ZrO ₂	22.06	29.01	26.19	22.20	29.66	26.41	22.53	25.84
HfO ₂	0.30	0.58	0.32	0.49	0.45	0.34	0.24	0.35
V ₂ O ₃	0.47	0.54	0.51	0.30	0.17	0.39	0.48	0.39
Total	86.804	91.391	89.498	84.781	88.611	90.393	91.488	90.354
Structural formula based on $\Sigma B = 2$								
Ca	0.290	0.210	0.240	0.280	0.250	0.210	0.220	0.220
U	0.330	0.330	0.350	0.420	0.290	0.390	0.500	0.410
Th	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Pb	0.010	0.010	0.010	0.020	0.010	0.020	0.020	0.020
Y	0.020	0.020	0.040	0.030	0.030	0.030	0.030	0.030
La	0.000	0.000	0.000	0.000	0.000	0.000	0.010	0.000
Ce	0.010	0.010	0.010	0.020	0.020	0.030	0.030	0.030
Pr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Nd	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sm	0.010	0.010	0.010	0.010	0.010	0.010	0.000	0.000
Gd	0.000	0.000	0.010	0.010	0.010	0.010	0.010	0.010
Dy	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010
Ho	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Er	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Tm	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Yb	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Lu	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
ΣA	0.680	0.600	0.680	0.800	0.630	0.710	0.830	0.730
Si	0.750	0.810	0.870	0.840	0.860	0.800	0.780	0.780
Al	0.060	0.050	0.060	0.050	0.070	0.060	0.050	0.060
Ti	0.200	0.180	0.150	0.200	0.130	0.180	0.240	0.210
P	0.170	0.040	0.030	0.000	0.020	0.020	0.020	0.020
Nb	0.110	0.090	0.090	0.130	0.080	0.110	0.140	0.110
Ta	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Zr	0.600	0.750	0.720	0.690	0.790	0.750	0.690	0.740
Hf	0.000	0.010	0.010	0.010	0.010	0.010	0.000	0.010
Fe	0.070	0.040	0.050	0.050	0.040	0.040	0.050	0.040
V	0.020	0.020	0.020	0.020	0.010	0.020	0.020	0.020
ΣB	1.980	1.990	2.000	1.990	2.010	1.990	1.990	1.990
$\Sigma A + B$	2.660	2.590	2.680	2.790	2.640	2.700	2.820	2.720

Table 3. Selected electron microprobe data (in wt%) of liandratite in the trachyte of the El Atshan area

Sample	1	2	3	4	5	6	7	L & E*
UO ₃	60.39	56.14	53.24	57.10	56.05	55.20	55.92	54.87
CaO	3.44	3.51	4.04	3.39	3.46	3.79	3.33	0.26
ThO ₂	0.01	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	1.19
PbO	2.00	1.17	1.34	1.43	1.34	1.26	1.00	2.10
Y ₂ O ₃	b.d.	0.16	0.10	0.19	0.20	0.28	0.27	0.18
La ₂ O ₃	0.47	0.09	0.18	b.d.	0.09	0.04	0.16	0.87
Ce ₂ O ₃	0.26	0.87	0.04	0.99	0.84	0.94	0.82	
Pr ₂ O ₃	0.25	b.d.	0.11	0.17	0.10	0.15	0.13	
Nd ₂ O ₃	b.d.	0.02	0.07	0.09	0.04	b.d.	0.01	
Sm ₂ O ₃	0.06	0.11	0.16	b.d.	0.12	0.11	0.07	
Gd ₂ O ₃	b.d.	0.18	0.08	b.d.	b.d.	0.24	0.14	
Dy ₂ O ₃	b.d.	0.11	b.d.	0.16	0.16	0.07	0.21	
Ho ₂ O ₃	b.d.	b.d.	0.01	0.10	0.02	0.09	0.00	
Er ₂ O ₃	0.03	0.10	b.d.	b.d.	0.10	0.07	0.07	
Tm ₂ O ₃	0.03	b.d.	0.10	b.d.	0.09	0.00	0.10	
Yb ₂ O ₃	0.04	b.d.	0.31	0.13	b.d.	b.d.	0.04	
Lu ₂ O ₃	0.08	0.31	b.d.	0.07	0.10	0.07	b.d.	
SiO ₂	3.34	4.07	3.41	3.79	4.80	4.85	6.17	0.00
Al ₂ O ₃	0.12	0.20	0.20	0.24	0.27	0.37	0.55	0.79
TiO ₂	9.45	7.85	9.28	8.28	7.40	8.03	7.21	6.48
Nb ₂ O ₅	10.17	7.82	6.82	8.89	8.28	8.11	6.92	25.20
Ta ₂ O ₅	b.d.	0.20	0.39	0.43	0.20	0.15	0.39	2.37
Fe ₂ O ₃	1.23	0.92	0.89	0.97	0.97	1.04	0.97	1.56
ZrO ₂	1.89	4.25	4.11	4.40	6.72	7.16	6.19	0.10
HfO ₂	b.d.	0.03	0.05	0.13	0.13	b.d.	0.04	
V ₂ O ₃	1.37	0.76	1.07	0.95	0.81	0.86	0.75	
Total	94.62	88.84	85.99	91.88	92.31	92.87	91.45	98.04**
Structural formula based on $\Sigma Nb = 2$								
U	1.480	1.450	1.360	1.400	1.300	1.220	1.250	1.270
Ca	0.410	0.440	0.500	0.400	0.390	0.400	0.360	0.030
Th	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.030
Pb	0.060	0.040	0.040	0.040	0.040	0.030	0.030	0.060
Y	0.000	0.010	0.010	0.010	0.010	0.010	0.010	0.010
La	0.020	0.000	0.010	0.000	0.000	0.000	0.010	0.03
Ce	0.010	0.040	0.000	0.040	0.030	0.030	0.030	
Pr	0.010	0.000	0.000	0.010	0.000	0.010	0.000	
Nd	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Sm	0.000	0.000	0.010	0.000	0.000	0.000	0.000	
Gd	0.000	0.010	0.000	0.000	0.000	0.010	0.000	
Dy	0.000	0.000	0.000	0.010	0.010	0.000	0.010	
Ho	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Er	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Tm	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Yb	0.000	0.000	0.010	0.000	0.000	0.000	0.000	
Lu	0.000	0.010	0.000	0.000	0.000	0.000	0.000	
ΣU	1.990	2.000	1.940	1.910	1.780	1.710	1.700	1.58***
Si	0.370	0.470	0.390	0.420	0.500	0.480	0.620	0.000
Al	0.020	0.030	0.030	0.030	0.030	0.040	0.060	0.100
Ti	0.780	0.690	0.800	0.680	0.580	0.600	0.540	0.510
Nb	0.510	0.410	0.350	0.440	0.390	0.360	0.310	1.190
Ta	0.000	0.010	0.010	0.010	0.010	0.000	0.010	0.070
Fe	0.110	0.090	0.090	0.090	0.080	0.090	0.080	0.140
Zr	0.100	0.240	0.230	0.240	0.340	0.350	0.300	0.010
Hf	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
V	0.120	0.070	0.100	0.080	0.070	0.070	0.060	
ΣNb	2.010	2.010	2.000	1.990	2.000	1.990	1.980	2.020
$\Sigma U + Nb$	4.000	4.010	3.940	3.900	3.780	3.700	3.680	3.600

* Microprobe analysis of liandratite as an alteration product of betafite from Madagascar (Lumpkin and Ewing, 1996)

** Includes MnO, 0.14; BaO, 0.89; K₂O, 0.70; Na₂O, 0.05; MgO, 0.02; F, 0.27 wt%.

*** Includes Mn, 0.01; Ba, 0.04; K, 0.09; Na, 0.01; Mg, 0.00.

Figure 8. Histograms showing a comparison between the chemical composition of the unidentified Zr-rich silicate mineral and betafite.

this event in the Eastern Desert of Egypt is confirmed by paleomagnetic and radiometric data (Ressetar et al., 1981). This is consistent with the 273 ± 20 Ma age of the trachyte found in the El Atshan area (Late Carboniferous to Early Permian, El Manharawy, 1972). El Hazek (1968) studied the mineralogical, geochemical, and physical characteristics of the primary ore at the El Atshan area. He identified two primary uranium minerals—coffinite and pitchblende—and reported the occurrence of carbonates, quartz, and fluorite as gangue minerals. On the other hand, the secondary uranium minerals were found impregnating the fractured trachyte rock at the contact lines, occupying cavities and vugs, and occurred as stains on fracture surfaces. They are usually bright yellow in color, but they may be darker when mixed with reddish-brown iron oxides and black manganese oxides. The most important varieties are soddyite, kasolite, and uranophane (Attawiya, 1971; Osmond et al., 1999; Dawood et al., 2004). In addition, the unidentified secondary Zr-rich silicate mineral, betafite, and liandratite have been identified for the first time in the present study.

Early high-temperature alteration stage

After the formation of the trachyte sill at the El Atshan area, it was subjected to early-stage hydrothermal alteration that included argillization, dissolution of iron-bearing sulphides, formation of iron-oxy hydroxides, and corrosion of primary uranium minerals (Dawood et al., 2004). The hydrothermal solutions follow the main structural lines, including fault lines and the open fractures at both the upper and lower contacts of the trachyte sill with the surrounding Hammamat sediments. While flowing, the hydrothermal solutions may have leached uranium occurring in primary minerals such as coffinite and pitchblende from the host rock, and finally became enriched in U. Changing fluid chemistry, decreasing temperature, and the presence of volatiles (particularly F), played a key role in the transport and distribution of U in the rocks during the hydrothermal alteration. The activity of fluoride in the

present study is significant, as indicated from the occurrence of fluorite in association with U-bearing minerals. The mobility of U and the associated high-field strength elements (HFSE, i.e., Zr, Hf, Nb, and Ti) during fluid/rock interaction has been discussed by many authors (e.g., Chan et al., 1986; Rubin et al., 1993).

The extensive chemical variation in natural zirconolites and their synthetic equivalents has been reported in many publications where thirty or more elements may be accommodated at concentration levels ranging from 0.1 to 1.0 wt% (Williams and Gieré, 1996; Gieré et al., 1998). Zirconolite has the ideal formula $\text{CaZrTi}_2\text{O}_7$, in which the available cationic sites have 8-coordination (*Ca*-site or M8 site) and 7-coordination (*Zr*-site or M7 site) and Ti in three distinct sites have 6-coordination (*Ti*-site or M6 site) and a pair of 5-coordination (M5 sites) (Gieré et al., 1998). When compared to other stoichiometrically ideal zirconolite mineral reported in the mineralogical literature (varies from 2.63 to 16.5 wt% CaO, from 24.3 to 45.4 wt% ZrO_2 , and from 13.6 to 45.9 wt% TiO_2 , Gieré et al., 1998), the identification of the present Zr-rich silicate mineral as zirconolite is excluded. Instead, it appears to be an unidentified secondary Zr-rich silicate mineral that may represent the major alteration and replacement of the precursor zirconolite. This is indicated by the changes in its composition marked by an increase in the amount of hydration (H_2O), Si, and U, and a decrease in the amount of Ca, Ti, Nb, and Fe (Table 1). Some grains of the unidentified Zr-rich silicate mineral show the common prismatic forms of the precursor zirconolite (Fig. 4). Other grains show high degree of metamictization and they are consequently altered to betafite. On the other hand, the zoning commonly observed in zirconolite is absent (Williams and Gieré, 1988, 1996; Bellatreccia et al., 1999). It should be noted that zirconolite has not been observed in the ore and is merely inferred from the secondary mineral assemblage considered to replace it.

It is suggested that the alteration of the unidentified Zr-rich silicate mineral to betafite occurred during a period of time, depending on the hydrothermal solutions ac-

Figure 9. (a) Binary plots (apfu) of Zr versus U. (b) $(U^{4+} + Ti^{4+} + Nb^{5+})$ versus $(Zr^{4+} + Si^{4+} + Ca^{2+} + P^{5+} + Y^{3+} + \Sigma REE^{3+})$. The negative correlation in both plots may reflect the dominant substitution during the alteration of the unidentified Zr-rich silicate mineral to betafite. Cations are calculated on the basis of seven oxygen atoms.

tivity and the amount of available U in these solutions. This results in changes in the stability of the unidentified Zr-rich silicate mineral structure to the extent that it is replaced partly or completely by betafite of variable compositions (Figs. 4–6). The alteration of the unidentified Zr-rich silicate mineral to betafite is indicated by a marked increase in the amount of U, Ti, and Nb, and a decrease in the amount of Zr, Si, Ca, P, Y, and ΣREE (Fig. 8). With more extensive alterations, the unidentified Zr-rich silicate mineral became unstable and underwent re-equilibration with the fluid, leading to the removal of Zr.

The transformation of the unidentified Zr-rich silicate mineral into betafite generally involves at least two different mechanisms: (1) the dissolution of the unidentified Zr-rich silicate mineral and the precipitation of a new phase representing betafite. This can happen by the penetration of hydrothermal fluids containing U, Ti, and Nb into the interior parts of crystals through cracks or zones that act as fluid conduits. These cracks can be produced by metamictization. Amorphous regions are more suscep-

tible to fluid-alteration and dissolution than non-metamict regions. It is probable that such zones with high susceptibility, both within the crystal and at the rim, were fluid-altered to betafite at some time during the geological history of these crystals and (2) the ion exchange where Zr is replaced by uranyl ion (Fig. 9a) as well as other coupled substitution that could be inferred from the negative correlation between $(U^{4+} + Ti^{4+} + Nb^{5+})$ and $(Zr^{4+} + Si^{4+} + Ca^{2+} + P^{5+} + Y^{3+} + \Sigma REE^{3+})$ (Fig. 9b). Which of these reactions take place and to what extent depend mainly on the fluid composition and concurring reactions.

Late low-temperature alteration stage

In this stage, the previously formed betafite was subjected to low-temperature alteration and it was variably altered to liandratite. The effects of alteration are clearly observed in Zr-poor betafite, which was completely broken down to liandratite, whereas Zr-rich betafite was less affected. The presence of significant amounts of Zr considerably increases the radiation damage resistance of the material (Wang et al., 1999; Wang et al., 2000). Thermochemical and radiation damage studies of zirconolite and pyrochlore indicated that their stabilities were improved by the addition of Zr (Helean et al., 2004). This may explain the difficulty of dissolving the Zr-rich betafite, which has a Zr-bonded crystal structure, in low-temperature fluid. The secondary alteration of betafite is influenced by the grain size, prior radiation damage, microfracturing, volume and flow rate of the groundwater, and total exposure time. The geochemical alteration of betafite started with the leaching of Si, Ca, Y, and RREs, followed by the recrystallization of liandratite from fluids rich in U, Nb, Ti, and Pb. The presence of an excess amount of U in liandratite may point to another source of uranium in the solution, apart from betafite. This source could be coffinite and pitchblende, as reported by El Hazek (1968). Therefore, the uranium released from these primary uranium minerals is adsorbed by liandratite, where U is present in the fluid phase as the uranyl group UO_2^{2+} . Many others natural betafite exhibit relatively low temperature, secondary alteration that ended by break down of leached betafite to liandratite + rutile, liandratite + rutile + uranpyrochlore, or rutile + uranpyrochlore (Lumpkin and Ewing, 1996). Uranpyrochlore is not observed in the present study, but rutile is present as separate grains or associated with betafite and liandratite.

Other previously reported secondary uranium minerals such as soddyite, kasolite, and uranophane (Attawiya, 1971; Osmond et al., 1999; Dawood et al., 2004) were also formed during this stage. The uranium series age of 87000 to 140000 years for these secondary uranium min-

Figure 10. Genetic model for the high- and low-T alteration of the Zr- and U-bearing minerals in the trachyte of the El Atshan area. Alteration of previously identified primary uranium minerals (coffinite and pitchblende) to soddyite, kasolite, and uranophane is also presented.

erals has been reported by Osmond et al. (1999).

GENETIC MODEL

Based on field observations, mineralogical and geochemical data, and the previous geochronological data, a two-stage metallogenic model can be proposed for the alteration processes and the origin of uranium minerals in the trachyte of the El Atshan area (Fig. 10). The first stage is dominated by high-temperature fluid-rock interaction that released uranium from primary uranium minerals such as coffinite and pitchblende, as well as other accessory uranium-bearing minerals. The association of uranium-bearing minerals and fluorite in the fracture zones of the El Atshan area may reflect the role of fluoride complexes in the uranium solubility, mobility, and the formation of secondary uranium. The alteration of the unidentified secondary Zr-rich silicate mineral to betafite occurred during this stage. This is indicated by the increase in the amount of U, Ti, and Nb, and a decrease in the amount of Zr, Si, Ca, P, Y, and ΣREE . The single substitution of $\text{U}^{4+} \leftrightarrow \text{Zr}^{4+}$ and the coupled substitution of $(\text{U}^{4+} + \text{Ti}^{4+} + \text{Nb}^{5+}) \leftrightarrow (\text{Zr}^{4+} + \text{Si}^{4+} + \text{Ca}^{2+} + \text{P}^{5+} + \text{Y}^{3+} + \Sigma\text{REE}^{3+})$ are inferred from the EPMA data. The stability of the unidentified Zr-rich silicate mineral during alteration appears to depend on the composition of the associated fluids, especially on their uranium content.

The second alteration stage is dominated by low temperature alteration, as observed from the alteration of betafite to liandratite and the formation of other secondary uranium minerals such as soddyite, kasolite, and uranophane. By decreasing the temperature and increasing the oxygen fugacity (f_{O_2}) of the hydrothermal fluid, U^{4+} -fluoride was converted to uranyl fluoride complexes UO_2F_3 . When the activity of fluorine ions decreased due to a decrease in the temperature and an increase in the pH of the fluids, the uranyl fluoride complexes became unstable and decomposed, forming secondary uranium minerals (soddyite, kasolite, and uranophane) and precipitates of fluorite and calcite.

CONCLUSION

The conclusions of this study are as follows:

1. An unidentified secondary Zr-rich silicate mineral, betafite, and liandratite are identified for the first time in a trachyte of the El Atshan area, central Eastern Desert, Egypt.
2. The unidentified Zr-rich silicate mineral is interpreted to be an alteration product of the precursor zirconolite during high- T alteration. The resulting chemical formula for the Zr-rich betafite is $(\text{Si}_{1.45}\text{U}_{0.18}\text{Ca}_{0.32}\text{Pb}_{0.01}\text{Nb}_{0.06}\text{Zr}_{1.18}\text{Hf}_{0.01}\text{Fe}_{0.06}\text{Al}_{0.08}\text{Ti}_{0.11}\text{P}_{0.09}\text{Y}_{0.05}\text{REE}_{0.09})_{\Sigma 3.7}\text{O}_7$.
3. Betafite is enriched in Zr, and the obtained chemical

formula is ${}^A(U_{0.44}Ca_{0.25}REE_{0.05}Y_{0.03}Pb_{0.02})_{\Sigma 0.79}{}^B(Si_{0.79}Zr_{0.69}Ti_{0.23}Nb_{0.12}Al_{0.06}Fe_{0.05}P_{0.03}V_{0.02}Hf_{0.01})_{\Sigma 2.0}O_7$.

4. The role of high temperature alteration is confirmed from the corrosion of the unidentified Zr-rich silicate mineral and Zr-rich betafite. This alteration is indicated by an increase in the amount of U, Ti, and Nb, and a decrease in the amount of Zr, Si, Ca, P, Y, and ΣREE . Single substitutions of $U^{4+} \leftrightarrow Zr^{4+}$ as well as a coupled substitution of $(U^{4+} + Ti^{4+} + Nb^{5+}) \leftrightarrow (Zr^{4+} + Si^{4+} + Ca^{2+} + P^{5+} + Y^{3+} + \Sigma REE^{3+})$ are inferred from the EPMA data.
5. The calculated formula of liandratite is ${}^U(U_{1.35}Ca_{0.41}Pb_{0.04}REE_{0.04}Y_{0.01})_{\Sigma 1.86}{}^{Nb}(Ti_{0.67}Si_{0.46}Nb_{0.40}Zr_{0.26}Fe_{0.09}V_{0.08}Al_{0.03}Ta_{0.01})_{\Sigma 2.0}O_8$. The average value of the Nb-site total is identical to the stoichiometric value of two atoms per formula, whereas the value of the U-site total is significantly higher than the normal values that could be due to the addition of excess U as well as substantial amounts of Ca.
6. The role of the low temperature alteration in the formation of liandratite at the expense of betafite is also documented in the present study. It is evident that Zr-rich betafite is more durable than Zr-poor betafite and this may be due to the strong Zr bonds with the crystal structure of Zr-rich betafite.

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SUPPLEMENTARY MATERIAL

Color version of Figures 4, 5, and 6 is available online from <http://www.jstage.jst.go.jp/browse/jmps>.

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