Geochemical Examination of Surficial Soil Overlying Uranium Deposit in Manyoni, Central Tanzania

Miguta Faustine Ngulimi¹ & Hiroaki Ishiga¹

¹Department of Geoscience, Graduate School of Science and Engineering, Shimane University, Japan

Correspondence: Miguta Faustine Ngulimi, Department of Geoscience, Graduate School of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue,690-8504, Japan. E-mail: mgtfaustine@yahoo.com

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Abstract

Geochemical compositions of surface to shallow soil samples of Manyoni uranium deposit in Tanzania were determined by X-ray fluorescence analysis (XRF). Uranium, calcium and chlorine are abundant at the depth of 40 cm to 140 cm. Strong correlations between U, CaO and chlorine suggest uranium and carbonates deposition in a Salt Lake system. Strontium content is higher (370 to 480 ppm) than the average upper continental crust UCC (320 ppm) at the depth of 60 cm to 120 cm suggesting Sr accumulation in carbonates. TiO₂ and Fe₂O₃ abundances appear along the profile but have normal concentrations below the average UCC content. Vanadium is positively correlated to Fe₂O₃ and Ni (mafic sources) concentrations and negatively correlated to U. Uranium precipitation is suggestive of abrupt evaporation during dry season at Manyoni depositional basin. Chlorine (Cl) with high concentration in the vertical profile may be yielded in the sediments after evaporation of the lake water.

Keywords: calcrete, geochemistry, Manyoni, surficial, uranium deposit

1. Introduction

1.1 Background and Objective

Uranium deposits are widely distributed in central, western and southern parts of Tanzania mainland, East Africa. Deposits were discovered in 1977-78 using systematic airborne survey which was conducted by the Geosurvey International Ltd on behalf of the Tanzania Government. Further ground followed up research carried out by Uranersbergbau-GmbH Company of Germany in 1978-1982. Seventy radiometric airborne anomalies were reported in central Tanzania (Bianconi & Borshoff, 1984).

Manyoni uranium deposits (part of Manyoni Bahi in Block B, Figure 1) are characterized as a surficial type uranium deposits (Bianconi and Borshoff, 1984). The source of uranium mineralization is related to the surrounding granites which are enriched in uranium concentrations (Bianconi & Borshoff, 1984). This type of uranium deposits is known as the largest deposits of the world (International Atomic Energy Agency [IAEA], 2009). Surficial uranium deposits are normally defined as young mineralization (Tertiary to Recent) occurring in surface sediments or soils (IAEA, 2009). Secondary precipitates are calcite, gypsum and dolomite occurred in these deposits (Bowell, Barnes, Grogan, & Dey, 2009; Carlisle, 1984). This study is aimed at analyzing the geochemical compositions of major and trace elements of the surface to shallow depth (0 - 2.5 m) soils overlying the supposed Manyoni uranium deposit. The result can be useful for preventing the effects of hazardous chemical elements to the surrounding environments. Also, the study could be useful in testing exposure of the hazardous higher U content bed near the ground surface as well as outline some environmental precautions for uranium ore extractions by reference to the geochemical compositions.

1.2 Outline of Uranium deposits in Tanzania

The uranium anomalies in Tanzania are discriminated in several blocks (Figure 1) with their geologic setting. In block A, uranium anomalies were found in the upper Carboniferous to lower Jurassic Karoo sandstones and the
granites and gneisses of the Usagarani belt. Potential uranium mineralization similar to that of block A has been identified in Mkju and Madaba areas (Figure 1) of southern Tanzania (Kilimanjaro Mining Company, 2008). In block B, calcrete hosted uranium mineralization was identified which include Manyoni deposit (present study) and other deposit areas such as Bahi Mbuga, Makutopora and Lake Hombolo areas (Figure 1) of Central Tanzania (Kilimanjaro Mining Company, 2008). In block C, uranium anomalies are related to unconformity between upper Proterozoic Bukoban system and the Middle Proterozoic Karagwe Ankolean system, but no uranium potential was identified (Kilimanjaro Mining Company, 2008). In block D uranium anomalies were found in phosphates of Minjingu and the Galapo carbonatite. In block E, uranium anomalies were recorded in the trachytic extrusive rocks of the Tarosero Volcano (Kilimanjaro Mining Company, 2008). Moreover, in block F, uranium anomalies were recorded in sedimentary rocks of Chimala area associated with copper mineralization, and Panda carbonatite. Their uranium anomalies were not potential (Kilimanjaro Mining Company, 2008). In block G, the uranium anomalies dominated at the contact of the two mobile belts, Bukoban system and the Karagwe Ankolean system, and intrusive rocks (granite) along the contact. At present exploration and development projects are ongoing at Manyoni and Bahi districts in block B and Namtumbo district in block A.
1.3 Geology of the Study Area

The Late Archean rocks of the Tanzanian shield (2550 Ma after Bell and Dodson, 1981) consist of predominantly biotite granites, with metasediments (migmatites, gneisses, quartzites, amphibolites) and “greenstones” (metavolcanics of the Nyanzian System) which are underlying the uranium deposits (Bianconi & Borshoff, 1984). Faults were formed during movement of Eastern Rift system occurring in Miocene-Pliocene, which resulted in formation of interior sedimentary basin. Lacustrine and valley filled sediments deposited in sedimentary basins, and these sediments are called “Kilimatinde Cements” (Bianconi & Borshoff, 1984). The rift also accompanied with volcanic activity which resulted in the formation of kimberlites and carbonatites with hot springs (Avrom, 2011).

![Figure 2. Geological map of Manyoni in Central Tanzania showing the study area. Map modified from (Semkiwa and Msechu, 2005)](image)

The rifting ceased in Pliocene-Pleistocene time where the original drainage system was disrupted and modified (Bianconi & Borshoff, 1984). The rifting that resulted in weathering and erosion of granitic rocks in the wider ground surface (Figure 2) (Bianconi & Borshoff, 1984), which are supposed to be source matter of uranium mineralization. The apparent geochemical compositions of the granite in Manyoni area have not been reported. Our present analysis indicates uranium content to be 16 ppm (Table 1) for coarse biotite granite collected at Manyoni Town.

The general stratigraphy was partly obtained from dug pits in Manyoni town (and partly informed by local engineer). It consists of black top soil layer from 0 to 30 cm, followed by a mostly grey to green silty sands at the depth of 30 cm to 270 cm. Green sand layer presumably bearing uranium mineralization lies between 270 cm to 360 cm depth. A thin layer of basal conglomerate occurred between the green sand layer and the underlying granite (Figure 3b). Bianconi and Borshoff (1984) reported the idealized stratigraphy (Figure 3a) of the ‘‘Mbuga’’
heavy dark clays obtained from excavation pits, which is similar to present research with minor differences shown in Figure 3a.

![Diagram of stratigraphy](image)

Figure 3. (a) Idealized stratigraphy of the mineralized Mbuga sediments at Manyoni, central Tanzania. Map modified from Bianconi and Borshoff (1984). Figure 3(b) Stratigraphy of granite and covering sediments at Manyoni, central Tanzania as observed and obtained from personal communication with local engineer. Three sampling columns (MYN 1, MYN 2 and MYN 3) are indicated for correlation to this representative sequence.

1.4 Study Area

The Manyoni deposit is located in the districts of Manyoni about 125 km to the east of Dodoma, the Tanzania capital city. Climate of the area present is characterized by semi arid to arid with lower rainfall averaging 624 mm/year. Mean annual temperature is about 22°C. Study area is located 1 km northeast of Manyoni town (Figure 2). It is surrounded by human settlement areas. The land is used for growing food crops mainly maize (corns), groundnuts and sweet potatoes. Three dug pits existed in the area and are used for the present examination (Figure 4).

Background radiation level measured by Personal Radiation Detector (RADEYEPRD) within Manyoni Town was 3 counts per second (cps; radiation detection per second), and was found to be increasing up to a range of 10 to 15 cps around the study area. Detection increased further to a range of 40 to 60 cps closer to the dug pits. Seasonal water stream channels run trending northwest to south east direction at 500 m north east of the study area.
2. Materials and Methods

2.1 Sampling Methods

Three sections were named as MYN 1 (0 - 50 cm depth), MYN 2 (0 - 140 cm depth) and MYN 3 (140 - 250 cm depth). Correlation of these columns with representative sequence from granite to topsoil is indicated in Figure 3(b). At MYN 1, three samples were taken at horizons of 10 cm, 20 cm and 50 cm depth. Seven samples at MYN 2 were taken with an interval of 20 cm (Figure 5). Five samples were taken at MYN 3 with an interval of 20 cm, starting at the depth of 140 cm to 240 cm (Figure 5). Composite sequence of 240 cm depth joining MYN 2 and MYN 3 sections was made for stratigraphic analysis (Figure 6 and 7). Therefore, a total of 15 soil samples were collected in the sedimentary profile. Basement samples were collected at the bottom of the pits (MYN-2 and MYN-3) for comparison to sediment soil samples.

Approximately 100 g each was collected in plastic bag. Samples were imported with permission of Soil Plant Protection, the Ministry of Agriculture, Forestry and Fisheries, Japan on 20th August, 2015.

2.2 Stratigraphy of the Examined Sequence

Examined stratigraphy is indicated in Figure 5. The dark top layer in MYN 2 lies from the top surface to 39 cm depth, followed by the grey yellowish silt from 39 cm to 64 cm. Light grey silt lies between 64 cm to 80 cm, underneath followed by dark yellowish silt in the interval from 80 cm to 99 cm depth. Grey yellowish colored silt dominates the lower part of the MYN 2 from 99 cm to 140 cm depth. MYN 3 section starts at the 140 cm below the ground surface in which grey yellowish silt lies to 180 cm depth. Yellowish silt with green spots lies between 180 cm to 240 cm depth.
2.3 Sampling Preparations and Analysis

Approximately one-third of each sample were transferred to Pyrex beakers, covered with aluminum foil to protect from contamination, and dried in an oven at 160 °C for 48 hours. Once dried, sub-samples of the soil were crushed in an Automatic Agate Mortar and Pestle grinder to produce a powder sample. Then, the pressed powder pellets were prepared by pressing the powdered sample into 40 mm diameter plastic rings, using a force of 200 kN for about 60 s in an automatic pellet press E-30 M Maekawa.

Abundances of selected major elements (TiO₂, Fe₂O₃*, (total iron expressed as Fe₂O₃), P₂O₅, CaO and MnO wt %) and the trace elements As, Pb, Zn, Cu, Ni, Cr, V, Sr, Y, Nb, Zr, Th, Sc, U, TS, F, Br, I, Cl ppm were determined by using X-ray fluorescence analysis (XRF; Rigaku RIX-2000) in the Department of Geoscience, Shimane University. The XRF analyses were performed following the method of Ogasawara (1987). Average errors for all elements are less than ±10% relative. Analytical results for GSJ standard JSI-1 were acceptable compared to the proposed values by Imai, Terashima, Itoh, and Ando (1996). In this paper analytical results of samples are indicated (Table 1).

3. Results

3.1 Stratigraphic Variations of Elements

Stratigraphic variations of some selected elements are indicated in Figure 6 and 7. Uranium, CaO, Sr, total sulfide (TS) and Cl show significant increase from the horizon of 160 cm deep sample (U=418 ppm, CaO=0.48 wt%, Sr=39 ppm, TS=338 ppm, Cl=nd) to 60 cm sample (U=1304 ppm, CaO=11.75 wt%, Sr=491 ppm, TS=3318 ppm, Cl=1039) (Figure 6). Uranium and CaO variations show significantly concordant, and Sr, TS and Cl show similar change in this interval (Figure 6). Uranium concentration of the bottom sample (393 ppm) of MYN 2 shows similar value to that of 1.45 m sample (336 ppm). And the bottom sample of MYN 3 has lower value (398 ppm) than that of 2.4 m sample (691 ppm). The occurrence of chlorine in that horizon suggests that both uranium and calcite have been deposited in a salt lake depositional system as also indicated by Bianconi and Borshoff (1984). Strontium values are higher compared to the upper continental crust (UCC) content (Table 1) (Rudnick & Gao, 2003), at the depth of 60 to 120 cm ranging from 370 to 480 ppm (Figure 6). Strontium shows strong correlation with CaO (R=0.88) (Table 2).
To evaluate the source material and grain size variation, next elements indicated are used. Fe$_2$O$_3$ and Ni contents show higher values at this horizon (160 cm in Figure 7), suggesting enriched mafic rock source material. This is considered to be concentration of iron rich mineral or related matter. Other elements such as Pb and Zr (Figure 6) and Th and Nb (Figure 7) appear relatively steady in the vertical profile. This shows no great change of grain size of samples. Also these elements have similar or lower values compared to those of UCC (Table 1). Concentration of Sc and TiO$_2$ are representative of mafic source material, showing some vertical variation, but both elements mutually have no correlation.

On the other hand, V content shows higher values of 276 ppm at the horizon of 160 cm (Figure 6). Vanadium content is strongly correlated with Fe$_2$O$_3$ (R=0.73) and Ni (R=0.57) (Table 2). This suggests that V is originated from the weathering of mafic minerals such as hornblende, pyroxene and biotite (Boyle, 1984) or iron rich metasediments. This geochemical behavior of V is similar to that suggested in calcrete hosted uranium deposits in Paterson Region, Western Australia (Liu & Jaireth, 2011).

3.2 On the Uranium Concentrations

Mobility and deposition of uranium has been discussed mainly by paleo-redox reaction (Pownceby & Johnson, 2014). This is because that tetravalent uranium (U$^{4+}$) may have converted to hexavalent uranium (U$^{6+}$) under oxic condition which is soluble in groundwater. The formation of uranium deposits involves fluids which facilitate the transportation and deposition of hexavalent and tetravalent uranium, respectively (Skirrow et al., 2009). Uranium (U$^{6+}$) released from weathered granites can be transported in groundwater as uranyl carbonates complexes (Butt, Mann & Horwitz, 1984).

Uranium precipitation in Manyoni uranium deposit may be controlled by many factors but one possibility considered is the reduction of UO$_2^{2-}$ by sulfides which is expressed by equation (i) (Langmuir, 1978). This process is supported by higher concentration of TS ranging between 2000 ppm to 3800 ppm of the present analysis (Table 1, Figure 7). And strong correlation between U and TS (R=0.71 in Table 2) evidences process of accumulation of both chemical species. Evaporation has also been discussed by Boyle (1984) as one of the important processes for uranium precipitation, especially in the semi arid and arid regions of the world. There uranium concentrated as residue and precipitated at the final stage of desiccation in alkaline and salty lakes. Skirrow et al. (2009) concluded that evaporation resulted in the uranium precipitation at or above water table in calcrete which hosted uranium deposit. Considering the higher evaporation rate than rainfall throughout the year in older Manyoni depositional environment (Bianconi & Borshoff, 1984), evaporation is suggested to be the potential contributing factor for the precipitation of uranium.

$$4\text{UO}_2^{2-} + \text{HS}^- + 4\text{H}_2\text{O} = 4\text{UO}_2 + \text{SO}_4^{2-} + 9\text{H}^+ \quad \text{Equation 1 (Langmuir, 1978)}$$

Vanadium and U are negatively correlated (R=-0.18), despite the fact that they compose the common ore minerals of uranium such as carnotite and metatyuyamunite of the Manyoni deposit as reported by Bianconi and Borshoff (1984). The occurrence of uranyl vanadates, carnotite [K$_2$(VO$_4$)$_2$(UO$_2$)$_2$.3H$_2$O] and metatyuyamunite [K$_2$(VO$_4$)$_2$(UO$_2$)$_2$.3H$_2$O] is generally reported as the combination under geochemical process that controls the concentration of uranium, vanadium and potassium in groundwater and playa lakes (Liu & Jaireth, 2011). Langmuir (1978) described that carnotite precipitation may occur when CO$_2$-rich groundwater approaches to the land surface and equilibrate with the atmospheric CO$_2$ levels. Also, the precipitation of uranyl vanadates may be controlled by pH, of which a solution under acid pH ranges 4 – 7 is sufficient for the precipitation of the vanadates (Vivo, 2012; Langmuir, 1978). More evidence for the formation of uranyl vanadates in Manyoni uranium deposits is necessary for consideration of uranium concentration under this process.

Considering U content at the surface sample (53 ppm), it is significantly higher than the UCC value (2.7 ppm after Rudnick and Gao, 2003). Uranium contents show higher range from 800 ppm to 1300 ppm at a depth of 40 cm to 80 cm. Also at the depth from 40 cm to 120 cm, CaO contents show high values ranging from 4.5 wt% to 8.0 wt% (Figure 7). The high CaO contents are suggestive of calcrete (CaCO$_3$) precipitation during evaporation in dry season. Strong correlation (R=0.9) (Table 2) between U and CaO suggests that the surficial ore deposit of uranium is associated with carbonate formation.
indispensable. Prevention and control of leaching solution is necessary (Siedel, 1981) and management of waste is necessary. Ammonia, sodium or potassium bicarbonate (Connelly, 2008; Siedel, 1981). Yellow cake is precipitated when acidified sodium chloride solution is contacted with the loaded resins. However, in all in situ leach operations the salt content (Connelly, 2008). The alkaline leaching of uranium ores is mainly performed by using the solution of alkaline leach solution can be effectively used as a leaching agent in ores containing carbonate and mineral which results to the formation of salt complex. This reaction may reduce the availability of adsorption sites on ion exchange columns or resins, and finally reduce the efficiency of uranium recovery (Venter & Bolet, 2003). And the reaction will reduce the effectiveness of the leachant and may be resulted in possible environmental contamination (Merrit, 1971). Also, the acid fluid can react with halite (salt mineral) on ion exchange columns or resins, and finally reduce the efficiency of uranium recovery (Venter & Bolet, 2009).

In this case alkaline leach solution can be effectively used as a leaching agent in ores containing carbonate and salt content (Connelly, 2008). The alkaline leaching of uranium ores is mainly performed by using the solution of ammonia, sodium or potassium bicarbonate (Connelly, 2008; Siedel, 1981). Yellow cake is precipitated when acidified sodium chloride solution is contacted with the loaded resins. However, in all in situ leach operations the prevention and control of leaching solution is necessary (Siedel, 1981) and management of waste is indispensable.

Table 1. Major and trace element composition for Manyoni sediments samples, central Tanzania. Basement sites on ion exchange columns or resins, and finally reduce the efficiency of uranium recovery (Venter & Bolet, 2009).

For in situ recovery of uranium, acid heap leach method is not recommended, because acid fluid (leaching agent) can be consumed by carbonates. And the reaction will reduce the effectiveness of the leachant and may be resulted in possible environmental contamination (Merrit, 1971). Also, the acid fluid can react with halite (salt mineral) which results to the formation of salt complex. This reaction may reduce the availability of adsorption sites on ion exchange columns or resins, and finally reduce the efficiency of uranium recovery (Venter & Bolet, 2009).

Table 2. Correlation coefficient between elements from geochemical analysis of Manyoni sediments samples in central Tanzania

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<tr>
<th>Trace elements (ppm)</th>
<th>Major element (wt%)</th>
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<td>Trace elements (ppm)</td>
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3.3 On the Environmental Implications on Recovery of Uranium

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Figure 6. Vertical geochemical distribution of CaO, U, TS, Sr, Cl, V, Pb and Zr in a composite section of 240 cm depth in Manyoni, central Tanzania

Figure 7. Vertical geochemical distribution of Th, Nb, Ni, Fe$_2$O$_3$, Sc, TiO$_2$, P$_2$O$_5$ and MnO in a composite section of 240 cm depth in Manyoni, central Tanzania
4. Conclusion

The present geochemical analysis revealed occurrence of uranium in carbonate deposit in Salt Lake system. The average abundance of uranium is significantly higher than that of UCC value. The high U bearing granite in the study area could be a source of uranium deposit. TS and CaO contents concentrate in the shallow depth. And higher value of TS and its strong correlation with U suggest that HS- and evaporation contributed to the deposition of uranium. Vanadium, Fe₂O₃ and Ni are positively correlated which suggests derivation from some mafic minerals or iron rich metasediments. Vanadium and U are negatively correlated despite the fact that they were reported as the common components of the Manyoni uranium ore minerals such as carnotite and metatyuyamunite.

The concentrations of other elements are normal or below UCC values (Table 1). Presence of CaO and salt (chlorine) associated in uranium deposit as gangue minerals suggest that enough care should be taken in uranium extraction. The process may lead to serious soil contamination and affect ground water quality. The result of this research can be used as background data for monitoring uranium mining development and management.

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