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Determination of trace elements and lanthanide (REE) signatures in uranium mine products in South Africa by means of inductively coupled plasma mass spectrometry

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ABSTRACT

The lanthanides are Rare Earth Elements (REE) that exhibit consistent patterns under varying geochemical conditions. Therefore they can be used as signatures to determine the chemical and physical change that has occurred on a uranium ore since it was mined and processed. The objective of this work was to determine the trace elements and REE (Lanthanides patterns) in uranium ore samples using a quadrupole inductively coupled plasma mass spectrometer. The REE fingerprint results presented here suggests that uranium is embedded in uraninite, phosphorite deposit in Apatite & fluorapatite minerals. The uranium is recovered from phosphoric acid, while lime used for precipitation of impurities and magnesia is used for precipitation of uranium. The REE patterns normalized to the mean of CI-Chondrites from this study, show LREE uniformity and HREE fractionation with strong positive Tb anomaly. The ΣLREE/ΣHREE, and La/Sc ratios are relatively constant in these samples. The average composition based on this study are(in $\mu g\, g^{-1}$): Sc = 0.000171 ± 0.000029, Y = 0.00256 ± 0.000046, La = 0.00736 ± 0.00206, Ce = 0.00648 ± 0.00213, Pr = 0.00714 ± 0.0058, Nd = 0.00462 ± 0.00163, Sm = 0.0493 ± 0.00328, Eu = ND, Gd = 0.0125 ± 0.00643, Tb = 30 ± 13, Dy = 0.0165 ± 0.00747, Ho = ND, Er = 0.00515 ± 0.00265, Tm = ND, Yb = ND and Lu = ND. The REE pattern in the fissure water from underground typically shows enrichment in light REE (LREE), depletion in heavy REE (HREE). ND = not detected.

Average values for the trace elements were: Al (567.11), Cr (4.42), Cu (0.47), Fe (1781.69) and Zn (0.46) mg/L. Based on this elemental concentration, Al, Cr, Cu and Zn are at trace level specifically for this site. This family of elements is indicative of a carry through from a precursor ore. V (0.25), Ti (1.13) and Fe represent a type of in-situ leach solution. The uranium concentrations in the Carletonville gold fields suggests strongly that gold and uranium, in detrital pyrites and uraninite, were hydrothermally recycled (uranium may have been recycled by hydrocarbon fluids) from the Witwatersrand Reefs. Also the U concentrations in the water samples is much higher than that in the tailing (except for tailing 4 which is 100 years old), and is a signature for uranium processing. Also the results show a Tb-U correlation signature distinguishing between raw mineral ore and tailing (processed) uranium samples. The U concentrations are between 1.40 and 6.24 ppm while that of Tb is between 0.84 and 1.58 ppm in the fissure water.

1. Introduction

1.1. Nuclear terrorism

Nuclear trafficking arose predominantly during the early 90s with the first case reported in 1991 in Italy and Switzerland as well as the Soviet Union. Later more cases were reported in Germany, Czech Republic, Hungary and other central European countries (Mayer et al., 2007). However, in 1992, the IAEA illicit trafficking database revealed that there were about 11 cases of smuggled Highly Enriched Uranium or plutonium specifically in Russia and Europe. Consequently, questions concerning the origin, trafficking route and intended use of the nuclear or radioactive material were raised. When Chondrite-normalized REE are plotted against the Lanthanides in ascending atomic number, the patterns thus obtained do provide very predictive indicators for the source origin of the interdicted uranium sample. This is possible due to the REE's similar chemical properties based on the stable oxidation state of +3 (except Ce and Eu). The REE do not change under different geological or industrial processes (Asai and Limbeck, 2015a). The goal of nuclear forensics analysis is to identify forensic indicators in

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prohibited nuclear and radiological samples or the surrounding environment.

1.2. Role of REE in nuclear forensic signatures

The Witwatersrand Supergroup in South Africa has one of the largest gold and uranium deposits in the world. Although many studies have researched onto the mineralogy, geochemistry and chronology of this Reef (Barton, 1996; Fuchs et al., 2016; Pourmand et al., 2012; Schoene, 2014), few studies have looked at the REE patterns as nuclear forensics signatures. ICP-MS Total Quantity method provides one vital technique which is applied to determine signatures of interdicted radiological nuclear material. These signatures are found in the concentration levels of Lanthanides, also called Rare Earth Elements (REE) in a given nuclear material, where they are residual trace amounts or contaminants of the uranium extraction process (Varga et al., 2010). REE exhibit coherent behavior during different geo-processes and consistent fractionation (Dai et al., 2015) and thus provide a geochemical signature for the mineral deposit (Barton, 1996). Elemental signatures include the detection of major, minor as well as trace elements in the material. REE and Isotopic Signatures of the material can help in the discovery of fission or neutron capture products, which designate that the material has been in a nuclear reactor and are a representative fingerprint for the type and operating conditions of a given reactor (Varga et al., 2010). Molecular isobaric interferences and matrix suppression are the major challenges in low level lanthanide determination (Asai and Limbeck, 2015a).

The objective of this work is resolve the REE nuclear forensic signatures for a uranium mine in the Carletonville goldfield, South Africa (Fuchs et al., 2016), using a quadruple ICP-MS technique (Pourmand et al., 2012). Results from the first stage in the fuel cycle are described here, and the data presented could form a basis for a South Africa's national nuclear forensics library (NNFL).

2. Materials and methods

2.1. Study area

The study area is a gold/uranium mine in the Carletonville goldfields as indicated in Fig. 1 and the authors cannot give further details due to confidentiality agreements.

Fig. 2 shows the tailing dam showing sampling points according to the paddocks.

2.2. Geaology of the mining site

The sampling site falls within the Carletonville goldfields which is part of the so called B-Reef or Witwatersrand Supergroup) of South Africa. The uraninite (UO_{2x}) deposits (Balboni et al., 2016), here are unconformity in nature lying on the sedimentary succession of the Witwatersrand Supergroup, with an estimated age of about 2.59 Ga (Fuchs et al., 2016). Gold (and uranium) mining uses the underground mining techniques as the mines are each estimated to be more than 2 km deep. These mines are now over 132 years old, (SAHO, 2016) and are still operational.

2.3. Sample collection

The tailing dams T1 & T2 in Fig. 1 are located between DSW40/7 & DSW18/3 (T1) and above WV16 (T2). Samples used in this study consisted of a total of 17 water samples (mixture of mine water- also called *fissure* water from underground at the ore deposits- used in cooling the drilling machine, waste water from the processing plant) and 10 soil samples from the mine tailing dam, T1 & T2. It was observed that the slurry from the plant is deposited on the tailing dam in paddocks whose boundary contours are the edges of the different colors of the slurry, although some cross mixing can be seen. Fig. 2 shows an example of a tailing with paddocks at different drying stages. The soil and some water samples were collected from the top of the tailing and the discharge canals respectively to represent uranium that has come from the milling and processing stage of the fuel cycle. Fissure (mine shaft) underground water samples were also collected from the mine shafts outlets to represents uranium from the ore body.

During the manufacturing of uranium fuel, impurities are released from crushing of uranium ore, leaching uranium from the ore, purifying, precipitating and calcination processes (Švedkauskaite-LeGore et al., 2007). The REE impurities indicate production process as well as geo-location (Wallenius et al., 2006).

In this work, soil (2 kg) and water (2 L) were collected from each of the sampling points shown in Figs. 1 & 2 from a Gold mine in

Fig. 1. Water sampling points in the Carletonville goldfields Area of South Africa. From the top of this figure: DSW39/17-Water from DSW36/15 and DSW38/16; DSW36/15-Water from DSW9/14 and DSW42/10); DSW38/16-Discharge water from another mine; DSW42/10-Fissure water straight from underground; DSW9/14-Water from the settling point; DSW7/12-Water coming from the mine shaft and from process plants; DAM3/13-Water after (downstream of) the settling point; DSW43/19-Purified water; DSW40/5 & DSW40/7-Raw water from return water dam; DSW18/3 & DSW112-Sewage water from mine shaft; DSW45/1-water from mine shaft; WV16, WV9, WV13, WV14, WV15 & WV3-Borehole water for public use from West village.