

# Advanced Investigations of Unconventional Uranium and Thorium Deposits by *In-Situ* $\mu$ -EDXRF Analysis

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**Abstract.** Exploration and identification of primary and secondary uranium and thorium enrichments can be facilitated by the  $\mu$ -energy dispersive X-ray fluorescence (EDXRF) technique that allows the high resolution, *in-situ*, multi-element determination at the microscopic scale (10 to 100 $\mu$ m). EDXRF analysis is fast and useful for the identification of unconventional uranium and thorium deposits, the localisation of primary uranium and thorium minerals as well as secondary uranium- and thorium-bearing phases. A current project aims at the siting of uranium and thorium mineralisation in ores from the Witwatersrand Au (uraninite), Vergevoeg Fe-F (uraniferous monazite), and Palabora Cu (uranthorite) deposits.

## Resource situation

Uranium deposits associated with unconformities at the base of Proterozoic sedimentary basins represent the most important type of uranium deposits of the world. Other uranium (and thorium) sources include sandstone deposits, hematite breccia complex deposits, quartz-pebble conglomerate deposits, vein-type deposits, intrusive deposits, volcanic and caldera-related deposits, metasomatite deposits, collapse breccia pipe deposits, and phosphorite deposits. Uranium is also produced as a by-product in other deposit-types, and elevated uranium contents in country rocks may be regarded prospective in the near future. At present, primary uranium production accounts for only about 50% of the annual consumption in the nuclear fuel cycle. Uranium prices have more than doubled since 2004, and worldwide demand and exploration activities are strongly growing. It has been estimated that 2004 uranium exploration expenditures in the Athabasca basin, which hosts world's most important uranium reserves, will be total more than 25 M\$, almost double the year 2003 spending. Other countries renewed the interest in the

use of thorium in the nuclear fuel cycle. As a consequence, the increasing demand for uranium results in new exploration activities also on alternative uranium and thorium resources in many countries (e.g., China, India, Brazil). There is large potential for unconventional low grade but moderate to large scale uranium deposits. Low grade uranium deposits are quite often dominated by uraniferous thorianite that was regarded largely uneconomic in the past. Highly elevated uranium and thorium concentrations are associated with alkaline magmatic systems and hosted by uraniferous rare earth phosphates. The unaltered basement country rocks underneath the largest uranium deposits and elsewhere account for up to 60% of the uranium in these systems and uranium might be developed as a significant by-product from deposits of other commodities.

## Methodology

The acquisition of solid phase geochemical data is time-consuming, requires challenging sample preparation techniques and results in loss of sample material. The development of non-destructive energy differentiated  $\mu$ -X-ray fluorescence analysis ( $\mu$ -EDXRF) provides the capability of acquiring high-resolution geochemical analyses from different types of geological materials. The sample preparation is minimized since no coating is necessary. Depending on the application, the effect of surface roughness can be neglected. The  $\mu$ -EDXRF instruments allow relatively fast, continuous, and reliable spot analysis, line or area scans (mapping) of samples such as thin sections, flat hand specimens, as well as split cores, providing records of variations in the geochemical composition. The latter can be used in order to study element distributions even over wider structures and core length. The  $\mu$ -EDXRF technique provides non-destructive, multi-element,  $\mu$ -scale analysis of elements down to the trace concentration level.

## Facilities

Two  $\mu$ -EDXRF facilities by COX Analytical Instruments / Sweden based on X-ray fluorescence are in use at the BGR, the ITRAX<sup>TM</sup> X-ray microscope and the ITRAX<sup>TM</sup> geoscaner (Rammlmair et al. in press and therein). Both systems operate under normal air conditions using a 3 kW long fine focus Mo side-window tube. This allows for optimized analyses of different element groups.

- The ITRAX<sup>TM</sup> X-ray microscope using X-rays for element analysis, using an energy-dispersive Roentec<sup>TM</sup> UHV Dewar Si(Li)-detector. The element range includes all elements from Mg and heavier ( $Z > 12$ ), with detection limits at the  $\mu\text{g/g}$  level. For most applications the tube runs with 45 kV and 30 mA having the capacity for the simultaneous detection of light and heavy elements. High sensitivity is obtained by the mounted Cox<sup>TM</sup> mono capillary X-ray optical unit of 100 $\mu\text{m}$  beam size. Typically, the step size equals the spot size of the capillary and a counting time of 500 or 1000  $\mu\text{s/spot}$  are used. The data can be per-

formed as point, line or accumulated spectra of an area. The measuring spot, and thereby the lateral analytical resolution, can be varied in the 10 – 100  $\mu\text{m}$  range. The sample stage is designed to enable precise movement of the sample at steps of 10  $\mu\text{m}$ . Based on analytical parameters, these spectra will be processed to present information on the semi-quantitative concentrations of the achieved elements at a single spot or resulting in element maps. The pixel size of the resulting map equals the spot size of the measurement. Almost any type of sample can be mounted on an x-y-z-stage allowing weight of several kilograms and an element mapping of sample sizes up to 250 x 300 mm.

- The ITRAX™ geoscanner allows for the characterization of the chemical composition along samples up to 750 mm in length. The X-ray beam focuses through a Cox™ flat-beam capillary optic of a rectangular cross-section of 250  $\mu\text{m}$  x 22 mm. Because of the relative large beam size and high counting times (up to 120 seconds) and step sizes of 10 to 250  $\mu\text{m}$ , the geoscanner is more sensitive than the ITRAX™ microscope. The X-ray fluorescence signal is detected by a Roentec XFlash® 2001 Detector. An X-ray line-scanning camera provides optical images of X-ray absorption by the sample at a defined thickness at a microscopic scale. The transmitted X-rays are recorded with an array of 1024 diodes, each 25  $\mu\text{m}$  wide. The optical line camera system consists of a CCD color camera operating in line mode, synchronized with the stepper motor movement. The camera has 640 pixels/line and is equipped with a Schneider CM 120 BK COMPACT XENOPLAN lens system giving a field view of about 8 mm (depending on the chosen spacing) perpendicular to the scanning direction corresponding to 0.0125 mm/pixel (Cox Analytical Systems, pers. com).

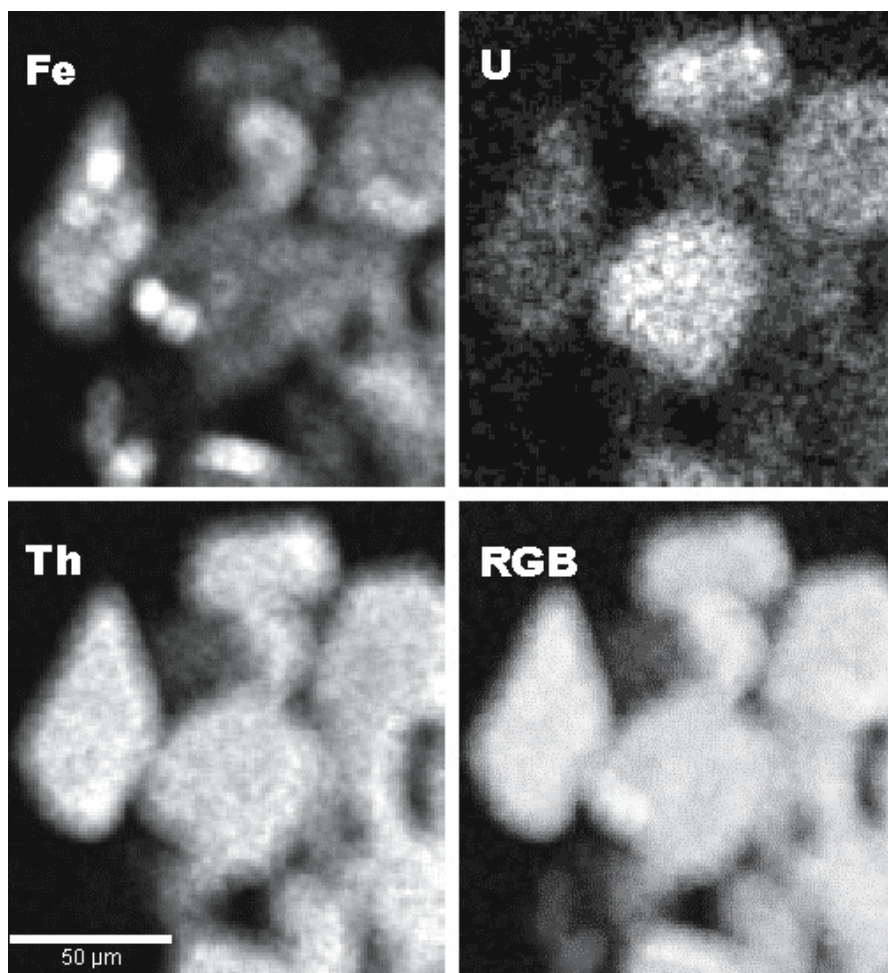
## Measurements

Exploration and identification of primary and secondary uranium and thorium enrichments is greatly facilitated by the  $\mu$ -EDXRF technique that allows the high resolution in-situ and simultaneous determination of a number of elements, combined with minimal sample preparation efforts (i.e., plain surface). Thus, ordinary thin or thick sections, as well as flat hand specimens can be used. This method is fast and optimized for the localization of primary and secondary uranium and thorium minerals and uraniferous mineral phases at concentrations of about 500 $\mu\text{g/g}$  to several weight percent of uranium and thorium.

A current project aims at the localization of uranium mineralization and the mineralogical siting in ores from the Witwatersrand Au (uraninite), Vergenoeg Fe-F (uraniferous monazite), and Palabora Cu (uranothorite) deposits.

## Results

In order to optimize the technique for current research activities, electron microprobe mineral standards as well as a sample collection, studied in greater detail by electron microprobe (EMP) measurements, were used. The X-ray microscope measurements were performed at 45 kV and 30 mA with 500, 1000 and 2000 ms/spot and step sizes of 10, 50 and 100  $\mu\text{m}$ . A thorite EMP-standard shows dis-



**Fig. 1.** Element maps of an EMP thorite standard (standard # 215-15 by Micro-Analysis Consultans™). Measurement was performed with a step size of 10  $\mu\text{m}$ . The intensity corresponds to the amount of the studied element at that particular point. The RGB color model was used in order to combine the single element maps. Color key: Fe – red; Th – green; U – blue; Fe + Th – yellow; Fe + U – violet; Th + U – turquoise; Fe + Th + U white.

tinct inhomogeneous chemical distributions of uranium and thorium (Fig. 1), which are not specified within the recommended values. However, since the recommended values are specified only by EMP analysis, the observed mineralogical heterogeneity is very unlikely to be recorded. Additional measurements with a step size of 10  $\mu\text{m}$  resulted in very detailed image resolution and allows for the study of the mineralogical distribution and siting.

Besides uranium and thorium mineral samples, a collection of samples from different ore deposits which hosts elevated to significant uranium and thorium concentrations of unknown distribution was investigated (Fig. 2). As an example, the distribution and compositional variability of uranothorianite from the Palabora carbonatite, South Africa, was studied (Neff 2003). The distribution of thorianite and its close association with the world-class copper and significant gold mineralization was clearly established. The distribution of uranium within the thorianite is heterogeneous and rather confined to distinct zones of secondary remobilization.

## Concluding remarks

The *in situ*  $\mu$ -EDXRF analysis is a suitable, fast and valid technique that can be used to localize uranium and thorium mineralization and low-grade uranium- and thorium-bearing phases over a large sample volume. The significant advantage of this technique is the avoidance of any contamination due to sample preparation like grinding. Instead, measurements already on plain surfaces result in good-quality data that allows the definition of uranium- and thorium-bearing, mineralized zones. In cases of strong uranium and thorium enrichments and the formation of uraninite and thorianite as ore-forming minerals, high quality and reproducible measurements can be performed at simple analytical conditions (100  $\mu\text{m}$  step size by 500  $\mu\text{s}$  counting time). In contrast a higher resolution is needed (down to 10  $\mu\text{m}$ ) in cases of uranium and thorium concentrations at the trace element level and very finely dispersed distributions of uranium- and thorium-bearing minerals. The higher resolution, however, leads to precise and reliable detection limits.

In contrast to already existing techniques to identify uranium this method allows the fast localization of uranium simultaneously to the recording of other elements. Due to the intensity of a signal (count rate) the relative distribution of the detected elements corresponding to its concentration can be visualized. Hence, besides the localization the measurements allow a quick identification of the mineralogical composition of the host.

## References

- Neff J (2003) Mineralogical and geological characterisation of carbonatite with focus on fault zone samples, Palabora copper orebody, South Africa. Diplomkartierung und Diplomarbeit TU Freiberg, pp. 92