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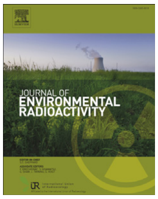

An investigation into heterogeneity in a single vein-type uranium ore deposit: Implications for nuclear forensics

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ABSTRACT

Minor element composition and rare earth element (REE) concentrations in nuclear materials are important as they are used within the field of nuclear forensics as an indicator of sample origin. However recent studies into uranium ores and uranium ore concentrates (UOCs) have shown significant elemental and isotopic heterogeneity from a single mine site such that some sites have shown higher variation within the mine site than that seen between multiple sites.

The elemental composition of both uranium and gangue minerals within ore samples taken along a single mineral vein in South West England have been measured and reported here. The analysis of the samples was undertaken to determine the extent of the localised variation in key elements. Energy Dispersive X-ray spectroscopy (EDS) was used to analyse the gangue mineralogy and measure major element composition. Minor element composition and rare earth element (REE) concentrations were measured by Electron Probe Microanalysis (EPMA).

The results confirm that a number of key elements, REE concentrations and patterns used for origin location do show significant variation within mine. Furthermore significant variation is also visible on a meter scale. In addition three separate uranium phases were identified within the vein which indicates multiple uranium mineralisation events. In light of these localised elemental variations it is recommended that representative sampling for an area is undertaken prior to establishing the REE pattern that may be used to identify the originating mine for an unknown ore sample and prior to investigating impact of ore processing on any arising REE patterns.

1. Introduction

The discipline of nuclear forensics originated some 20 years ago when seizures of illicit nuclear material provoked investigation into their origin and trafficking route. Today, there still exists a genuine public concern about the possible diversion of civil nuclear materials for malicious purposes (Varga et al., 2011). Since the 1990s the IAEA has recorded more than 800 cases of illicit trafficking of nuclear or other radioactive materials. Of the highest importance is the need to trace the origin of these materials so that future trafficking routes can be closed and other illicit material can be seized or intercepted (Mayer et al., 2007).

For intercepted nuclear material, an initial basic characterisation is performed prior to more detailed technical investigations relating to intended use, trafficking route and origin (Mayer et al., 2007). To determine origin, intercepted material is analysed for characteristic signatures or "fingerprints", these may be compared to a set of reference samples of known origin and any matches can quickly provide a potential trafficking route and origin.

The IAEA Illicit Trafficking Database (ITDB) states many incidents of nuclear trafficking have involved low grade material including natural uranium (IAEA, 2006). Therefore natural uranium within early fuel cycle stage materials e.g. ores and ore concentrates is a commonly intercepted material and correspondingly there is an international need to better understand the

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forensic signatures of different ore types such that an origin can be determined for such seized material (IAEA, 2001).

In previous years there have been a number of successful studies which have traced uranium ores and uranium ore concentrates (UOCs) back to specific mining areas via elemental and isotopic fingerprinting (Mayer et al., 2005; Wallenius et al., 2006; Mayer et al., 2007; Keegan et al., 2012; Han et al., 2013). However additional studies have found that heterogeneity within a single deposit can be greater than the variation between different mine sites (Keegan et al., 2008; Badaut et al., 2009 and Varga et al., 2009). This sheds doubt on the reliability of the current UOC fingerprinting process for all the different types of uranium mineralisation.

Characteristic physiochemical fingerprints used in such cross-matching studies includes the concentration of elemental impurities as well as the relative abundance and types of radioisotopes present. For intercepted uranium ore, details of origin and age can be gained by looking at the isotope ratios of uranium, strontium, lead and oxygen. These parameters are measured by a suite of techniques including inductively coupled plasma mass spectrometry (ICP-MS), thermal ionization mass spectrometry (TIMS), secondary ion mass spectrometry (SIMS), gamma spectroscopy, and electron microscopy (Mayer et al., 2005). Keegan et al. (2012), Varga et al. (2010), Keegan et al. (2008) and other authors have identified key attributes within uranium ore concentrate (UOC) which are specific to geographical origin. However only a few studies have looked at unprocessed uranium ore (Švedkauskaitė-LeGore et al., 2008; Richter et al., 1999), which represents the first and most elementally heterogeneous stage in the fuel cycle. Whilst certain forensic fingerprints are thought to be removed along the ore processing route, rare earth element (REE) patterns are suggested by a number of authors to remain representative of the original deposit type post processing (Varga et al., 2010). Wallenius et al. (2006) found a series of impurities including Al, Cr, Cu, Fe and Zn within a fuel pellet; which are unlikely to have been introduced by processing methods and were ascribed to carry-through from the precursor ore. In a complimentary study up to 65 trace element impurities were identified within UOCs, with many of these considered to have originated from the precursor uranium ore (Keegan et al., 2008). Accordingly it is important to understand how REE patterns, which might be important for forensic identification of unknown nuclear materials, can vary between precursor ore deposits and also within them.

This paper provides a nuclear forensic case study for the analysis of uranium ore heterogeneity at the smallest scale. Here the heterogeneity in terms of major and minor element composition in uranium phases across a single uranium mineral vein is measured. Of the different types of geological uranium deposits, vein type mineralisation is often high grade and therefore of economic interest, accounting for 5.9% of the world's uranium resource (IAEA, 2009). It is therefore an important class of uranium mineralisation to test for in-vein heterogeneity and for forensic fingerprinting purposes in general. The samples in the present study were taken from a uranium mineral vein associated with the South West England Cornubian batholith.

2. Geological background

The mining legacy of the South West of England dates back to prehistoric times, the area was the world's main producer of tin in the early-to mid-1800s (Moon, 2010), in addition uranium, radium and many other metals were also mined economically. This wealth of ore deposits can be attributed to hydrothermal mineralisation which is genetically and spatially related to a large intrusive igneous (batholith) complex which runs the length of the South West and was emplaced in stages during the late Carboniferous to early Permian. As the granite crust solidified, fissures opened up along the east-north-east lines of weakness and became filled with quartz porphyry. Later emanations from the magma mixed with fluids originating from meteoric waters, seawater, and formation waters expelled from adjacent sedimentary basins resulted in the deposition of vein minerals (Dines, 1956; Jackson and Willis-richards, 1989). There are in fact two distinct periods of uranium mineralisation evidenced in the region, an older mineralisation occurring with tin and copper mineral veins which trend E–W and a younger set of “crosscourse” veins where the uranium is associated with iron, nickel, cobalt and silver trending N–S (Ball et al., 1984). Erosion and removal of overlying country rocks over millions of years has revealed the string of granite outcrops across the region. Each granite body has since been studied to determine individual mineralogy, age and geochemistry (Moon, 2010; Stone, 1997). Each granite body additionally displays an aureole of metamorphosed killas and associated mineral veins. Up to 2000 tons of uranium is known to have been extracted from the South West, primarily for use in the production on Vaseline glass (Dines, 1956).

The samples in the present study were taken from a uranium mineral vein in King's Wood Mine near Buckfastleigh in South Devon. The mine is situated within upper Devonian slate on the edge of the metamorphic aureole of the Dartmoor granite; the largest and most easterly of the South West granite intrusions. The site selected for the present study was an unviable trial mine for copper excavated in 1918. In 1947 further works were undertaken to determine the extent of the uranium mineralisation discovered in the first trial, however the uranium ore was never mined economically (Darnley et al., 1965). The strike of the vein is fairly constant at NNW however the dip varies between 20 and 90 depending on whether it is following a cleavage or a joint plane. The width of the vein varies between 2 and 20 cm. Previous work denotes that the mineralisation is restricted to those parts of the milky quartz vein that have suffered later brecciation (Darnley et al., 1965).

The specific sampling locality used for this study was picked because samples could be taken *in situ*, in precisely recorded locations such that elemental and mineralogical variation could be determined on a centimetre scale. In addition the vein is within 100 m of the mine entrance, hence it is relatively accessible. Darnley et al. (1965) provided a study on the mineralogy and age of the mineralisation. It was found both macroscopically and microscopically the mineralized zone showed marked variation. Polished sections showed that where the vein quartz was brecciated the minerals pitchblende, galena, chalcopyrite, cobaltiferous rammelsbergite and native bismuth infilled the fractures. They suggested coffinite formed most of the matrix and replaced pitchblende on the margins. Veinlets of pyrite appeared to cut across the earlier formed minerals and there is a later series of micro-veinlets filled with a yellow hydrated uranium mineral which structurally resembles sabugalite. They state galena and chalcopyrite occur as fine disseminations within areas of coffinite and pitchblende. Within pitchblende they are concentrated both in syneresis fractures and in zonal concentrations related to botryoidal textures. Larger areas of galena-chalcopyrite occur outside the pitchblende. In addition to optical examination Darnley et al., 1965 superpanned and separated fragments of sample material by electromagnet. It was found that no secondary minerals were visible in the final concentrate. However the following elements were present: major U; subordinate Bi, Ni, Fe, As; minor Pb, Co, Cu; and very minor Zr (Darnley et al., 1965). $^{206}Pb/^{238}U$ dating placed the mineralisation at 206 ± 5 Ma: this was preferred as the most reliable indicator of age used by the authors as it is least sensitive to mass spectrometer errors and the uncertainty associated with the