

## XRF Microscopy and Boron K-edge XANES Analysis of Bulk Rock Samples Associated with Uranium Deposits.

Neil R. Banerjee<sup>1,\*</sup>, Lisa L. Van Loon<sup>1,2</sup>, and David Quirt<sup>3</sup>

<sup>1</sup>. Department of Earth Sciences, Western University, London, Ontario, Canada.

<sup>2</sup>. LISA CAN Analytical Solutions Inc., Saskatoon, Saskatchewan, Canada.

<sup>3</sup>. AREVA Resources Canada, Saskatoon, Saskatchewan, Canada.

\* Corresponding author, [neil.banerjee@uwo.ca](mailto:neil.banerjee@uwo.ca)

Canada is one of the largest producers of uranium and demand for uranium is projected to increase as society shifts from dependence on fossil fuels to alternative energy sources. Current uranium exploration and production has focused on the unconformity-related deposits of the Athabasca Basin in Saskatchewan and the Kiggavik project area situated in the Thelon Basin, Nunavut [1]. But differences exist in mineral chemistry of pathfinder elements at Kiggavik despite geological similarities with the Athabasca basin [2].

Boron is one element commonly cited as a key pathfinder element associated with unconformity-type uranium deposits [1]. However, a genetic relationship has not been rigorously established despite the spatial relationship between boron and uranium mineralization being well established in the literature [1,3,4]. Various theories are proposed which have focused on basement rocks or basin fill as the source of boron [3,5,6]. Boron is a trace element with an abundance of ~15 ppm in the earth's continental crust, but geological events can concentrate boron in accumulations great enough to form minerals in greater than trace amounts [7].

Synchrotron X-ray fluorescence mapping (SR-XRF Mapping) provides rapid and cost-effective micron-scale trace element analysis and mapping of ore samples with ppm detection limits. Drill core was analyzed by SR-XRF Mapping at the IDEAS Beamline at the Canadian Light Source (CLS) to create two-dimensional trace element maps that reveal spatial, textural, and structural associations with uranium mineralization. The incident X-ray energy of 13750 eV was selected using a double-crystal monochromator (DCM) with a Ge (220) crystal. Collimation of the X-rays was achieved by using a 600 mm Rh-coated bent cylindrical white beam mirror with a 4-jaw beam slit to adjust the beam spot size. XRF maps were created with beam spot sizes of 500  $\mu\text{m}$  x 500  $\mu\text{m}$ , 1 mm x 1 mm, and 2 mm x 2 mm by rastering across the sample in steps of 500  $\mu\text{m}$  to 2 mm, respectively, in both directions using a Ketek® AXAS-M single element silicon drift detector was used to measure the XRF signal. The maps created lack structure and do not reveal patterns that might be useful for mineral exploration (Figure. 1).

X-ray absorption near-edge structure (XANES) spectroscopy is an element-specific measurement that is well-established in earth and environmental sciences over the last 25 years [8-9], but it is rarely, if ever, used by the mining industry. The boron K-edge XANES spectrum has unique features permitting the boron mineral chemistry to be identified as being primarily trigonally-coordinated ( $\text{BO}_3$  moieties) or tetrahedrally-coordinated ( $\text{BO}_4$  moieties). Examples of minerals with trigonal boron coordination include tourmaline, such as the alkali-deficient dravite associated with uranium mineralization (Figure. 1). Tetrahedrally-coordinated boron minerals includes borates such as borax (Figure. 1). Differences in spectra are associated with the atomic coordination of boron in each type of mineral. Many minerals contain a mixture of both trigonally- and tetrahedrally-coordinated boron. More important to uranium

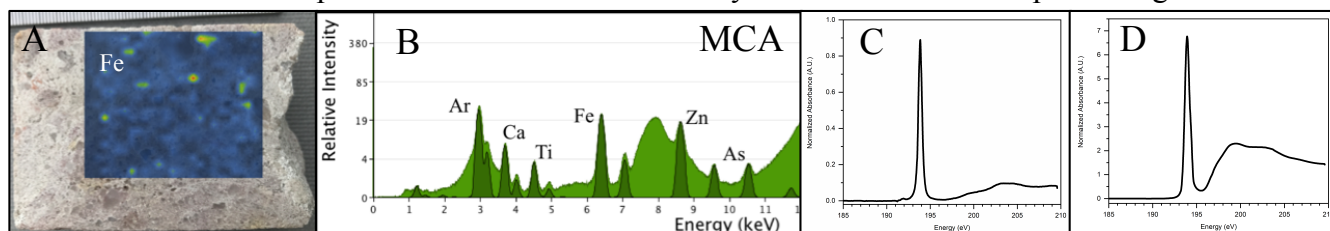
exploration, boron may also be located in tetrahedral sites within clay mineral structures. Because the XANES spectrum is influenced by the local coordination of the element of interest, these different systems result in unique boron K-edge XANES spectra (Figure. 1).

Composite whole-rock powders, provided by AREVA Resources Canada, were spread thinly on double-sided carbon tape attached to a copper sample holder for insertion into the sample chamber. Measurements were conducted at pressures of  $\sim 10^{-8}$  torr. XANES spectra were collected at the VLS-PGM beamline (11ID-2) at the CLS. The source is a 185 mm planar undulator, providing a flux of  $2 \times 10^{10}$  photons/sec over the energy range of 9 - 240 eV and a resolution of 10000 E/ $\Delta$ E. Data was collected over an energy range of 185.0 - 210.0 eV, using entrance and exit slits set at 100  $\mu$ m, and with a resolution of 0.1 eV over the boron K-edge. All sample data were collected in triplicate. Spectra were recorded by fluorescence yield mode using a microchannel plate detector. The spectra were normalized to the intensity of the incident beam, I<sub>0</sub>. A boron nitride standard was measured, and the energy calibration was adjusted to the peak maximum at 192 eV.

Preliminary results demonstrate that boron in tourmaline group minerals and clays and their proportions, are easily distinguished in bulk rock assay powders based on their characteristic K-edge XANES spectra. 2D SR-XRF imaging of core samples is currently underway and will be used to determine correlations between trace element vectors and B speciation. The results provide additional geochemical information that cannot be provided by SR- XRF microscopy or lithochemical analysis [10].

## References:

- [1] Hoeve, J., and Quirt, D.H., Saskatchewan Research Council, Tech. Rep. No. 187, 1984. 187p.
- [2] Riegler, T., *et al.*, Can. Min., 2014 **52**, p. 27-45.
- [3] Kotzer, T.G., and Kyser, T.K., Chem. Geo., 1995 **120**, p.45-89.
- [4] Cloutier, J., *et al.*, Econ. Geo., 2009 **104**, p.815-840.
- [5] Pacquet, A., and Weber, F., Can. J. Earth Sci., 1993 **30**, p. 674-688.
- [6] Kister, P., *et al.*, Clays and Clay Min. 2006 **54**, p. 295-313.
- [7] Fleet, M.E. and Muthupari, S., Amer. Min. 2000 **85**, p. 1009-1021.
- [8] Henderson, G.S., De Groot, F.M. and Moulton, B.J., Rev. Min. Geochem., 2014 **78**, p.75-138.
- [9] McNear Jr, D.H., Tappero, R. and Sparks, D.L., Elements, 2005 **1**, p.211-216.
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**Figure 1.** A.  $\mu$ XRF map of Fe in a sandstone with very little structure visible. B. MCA spectrum of map in A. Boron K-edge XANES spectral pattern of dravite (C; trigonal) and borax (D; tetrahedral).