

LA-ICPMS imaging of micro-inclusions and high compositional gradients in minerals

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Imaging of trace element distribution in a range of geological materials using quadrupole LA-ICPMS is an actively expanding area of geochemical micro-analysis. Determining compositions of diagenetic and hydrothermal sulphide minerals using in-situ analytical techniques presents a significant challenge due to common high compositional gradients (several orders of magnitude over several microns) and wide-spread occurrence of micro-inclusions. Accurate imaging of trace and minor element distribution in such minerals offers significant advantages for genetic interpretations [1], complementing conventional spot analyses. Simultaneously resolving high concentration gradients for a wide range of elements with LA-ICPMS requires fast-response, small-volume ablation cells; minimal mixing within the laser-ICP interface; and short dwell and total sweep times on the ICPMS. The technique developed uses a set of parallel lines with spacing equaling the laser beam size, thus covering the entire sample surface. Pre-ablation of each line is essential for removing surface deposition from previous ablations. Regular measurements of the background and calibration standards are required for controlling memory effects and instrumental drift in sensitivities. Use of square rather than round beam shape is preferred, although not critical for this application. The beam size is determined by size and composition of bands and micro-inclusions of interest. Lines are ablated at 10 Hz and a constant speed covering the size of the beam in 1 sec, resulting in each position on the surface being ablated 10 times. Total sweep times are 0.2-0.3 seconds resulting in 3 to 5 sweeps being recorded each second. The effective pixel size along the lines is dependent on instrumentation design and can be minimised by advanced image processing, to be ~ 1.3-1.5 times the beam sizes. Accurate imaging of gentle compositional gradients (<10 times), especially over short distances (up to several beam diameters) requires a different approach with signal smoothing and slower rastering. Challenges of image quantification will be discussed.

[1] Large *et al.* (2009) *Econ. Geology* **104** 635-668.

Reactivity of U(VI) with H₂, CH₄ and C under hydrothermal conditions

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Giant Unconformity-type U deposits are characterized by massive uraninite often associated with graphite. It has been demonstrated that U was first transported by acidic brines under the form of uranyl chloride complex and further reduced locally into uraninite [1]. However, the reaction mechanism and kinetics of U(VI) reduction into immobile U(IV) remain poorly understood [2]. The objective of our experimental investigations is to measure uranyl chloride reduction rate as a function of the nature of the reducing agent and under hydrothermal conditions relevant for unconformity-type deposits.

We demonstrate that U(VI) reduction occurs readily at temperature above 100°C whatever the reducing agent considered. 10 µm octahedral uraninite crystals precipitated. The initial activation stage probably corresponds to the first uraninite crystals nucleation. Reaction rate measurements allow us to rank the efficiency of electron donors: H₂ > CH₄ > C, and to evaluate the respective activation energies. Furthermore the reaction rate also depends on chlorinity. This suggests that the reaction mechanism is partly controlled by the speciation of uranyl in chloride solutions. This point is highlighted by a Raman spectroscopic study [3].

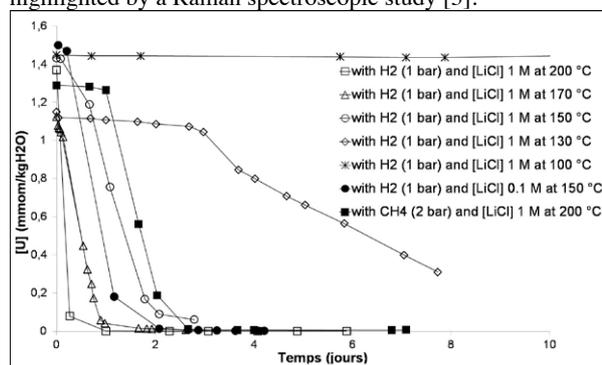


Figure 1: U(VI) concentration (mmol/kgH₂O) vs time (day) for different chlorinity, reductants and temperatures.

[1] Richard *et al.* (2011) *Nature Geosciences* **5**, 142-146. [2] Yeo & Potter (2010) *Summary of Investigations 2010* **2**, 13p. [3] Dargent *et al.* (2013) *Eur. J. Mineral.* (in press)