

A summary of LA-ICP-MS for mineral deposit research at the US Geological Survey

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Methods development and research utilizing laser ablation ICP-MS has been ongoing at the United States Geological Survey since the early 1990's. This paper presents a summary of developments and contributions for mineral deposit related LA-ICP-MS research conducted at the USGS. From geochemical reference materials development such as sulfide calibration materials [1] and a large suite of geologic related reference materials to large scale studies of deposit related materials, the USGS has been well situated for LA-ICP-MS research. Recent work on trace element fingerprinting of deposits including work on magnetite [2], pyrite [3], bitumen [4, 5] and quartz as well as developments of rapid screening of ore related materials, trace element mapping of minerals and rocks and new directions in USGS reference materials development [6] are contributing to our work on mineral deposit research and resource assessments on national and global scales.

Through a combination of fundamental studies and imperical work our work has progressed from the microanalytical applications utilizing high spatial resolution (<100 micron) trace element mapping of mineral targets to new directions utilizing LA-ICP-MS as a rapid analytical tool for bulk powders. Utilizing the full array of LA systems in operation in the lab, full wavelength (193 nm, 213 nm and 266 nm) comparisons have been conducted for many minerals. New developments using complimentary analytical techniques such as electron microprobe, micro-XRF and Raman provide useful supporting and complimentary information that is especially useful prior to trace element LA mapping. A discussion of advantages and disadvantages of the complimentary techniques provides a useful guide for mineral deposit researchers interested in elemental analyses.

[1] Wilson S.A. *et al.* 2002 *JAAS* **17**, 406–409. [2] Nadoll P. *et al.* 2009 *Geoanalysis 2009. Abstracts Volume*. [3] Graham G.E. *et al.* 2009 *GEEA* **9**, 19–37 [4] Koenig, A.E. & Emsbo, P. 2005 *GCA*, **69** [5] Emsbo, P. & Koenig, A.E. 2007 9th Biennial SGA Meeting Proceedings. [6] Wilson, S.A. 2010 *GCA*, this volume.

Pb-incorporation into synthetic Pb-doped zircon

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Zircon ($ZrSiO_4$, $I4_1/amd$, $Z=4$) is an important mineral for U-Pb chronology, and the mechanism for the incorporation of Pb is crucial to understanding the cause of U-Pb discordance. We have investigated Pb-doped zircon that were synthesized under a range of conditions [1]: (i.) wet at 900 °C at 1.5 GPa in the presence of P_2O_5 ; (ii.) dry at 1430 °C w/o P_2O_5 ; (iii.) wet at 800 °C at 1.0 GPa w/o P_2O_5 , utilizing a high-resolution TEM (HRTEM) and a high-angle annular dark-field scanning TEM (HAADF-STEM).

TEM results reveal four different mechanisms for incorporation. Type I: Pb-rich particles, 50 ~ 200 nm, embedded in zircon. Most of the particles are associated with a single vesicle at the size of ~50 nm in diameters. These nanocrystallites are a Pb-oxide hydrate identified by selected area electron diffraction pattern (SAED). Some are present at the grain boundaries of polycrystalline zircon. Type II: Pb-rich phase concentrated at cleavage planes or grain boundaries but lacking euhedral form. Type III: amorphous Pb phase present as small spheres in 20 ~ 100 nm of diameters Type IV: Pb is homogeneously distributed in the lattice of zircon in <1 wt. % that can be detected by energy dispersive X-ray analysis (EDS).

The amount of P_2O_5 present during synthesis affects the form of Pb in zircon. In the P-free system, Pb occurs as type I without detectable Pb in the matrix zircon. Under P-rich conditions (~1.3 wt. % in bulk [1]), Pb is present not only as type I but also as various forms from type II to type IV. Type IV only occurs when P is present, and this suggests that the charge balance mechanism is maintained by the coupled substitution $[2P^{5+} + Pb^{2+}] \leftrightarrow [2Si^{4+} + Zr^{4+}]$.

Our results indicate that the process of Pb incorporation in zircon depends on a unique combination of several experimental parameters: temperature, P_2O_5 and H_2O contents. However it appears that the generation of type I particle is independent of temperature or the presence of H_2O .

[1] Watson *et al.* (1997) *Chem. Geol.* **141**, 19–31