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# Understanding elemental fractionation by laser-induced phase transformations during analysis of accessory minerals: minimising matrix effects in U-Pb dating by LA-ICP-MS

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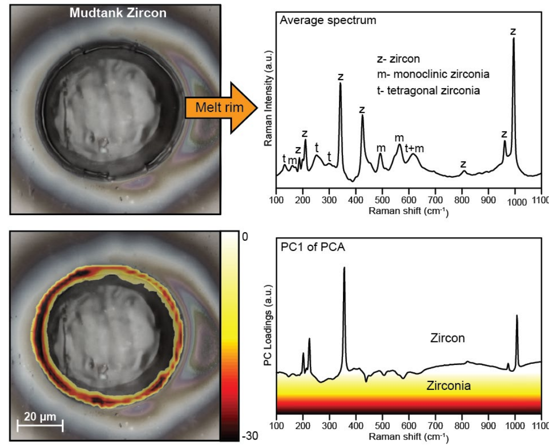


U-Pb geochronology by laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) analysis suffers from significant elemental fractionation due to the highly different chemical properties of U and Pb. This divergent behaviour downhole limits age accuracy and precision. One key cause of fractionation is the decomposition of the target into new phases, which differentially partition elements and masses during ablation. Zircon, for instance, thermally decomposes to its oxide components, $SiO_2$ and $ZrO_2$. This has been proposed as a major source of Pb/U fractionation[1], with refractory $ZrO_2$ preferentially incorporating U and being left behind at the ablation site. Even when correcting for this fractionation of zircon during ablation with matrix-matched standards, differences in radiation damage between the reference materials and unknowns can result in different downhole patterns and, therefore, inaccurate U-Pb ages[2]. The phase transformation and fractionation processes are even less well known for most other accessory minerals used in U-Pb dating. This study sought to characterise the behaviour and phases formed during laser ablation of a range of accessory minerals to find analytical conditions that reduce elemental fractionation.

We will report new combined transient LA-ICP-MS signals and post-analysis crater characterizations on a series of mineral reference materials (zircon, titanite, apatite, rutile, baddeleyite and monazite) over a range of ablation parameters (fluence, focus distance, spot diameter). Craters were analysed with optical profilometry, Raman spectroscopy and scanning electron microscopy (SEM). Raman volumetric mapping and principal component analysis (PCA) of the spectra were found to be effective at determining the identity, relationships, and spatial distribution of phases around the craters. Several newly formed minerals, compounds, polymorphs, and amorphous phases were identified, concentrating in and around the crater melt rim. They form by several mechanisms, including redeposition of ablated material and in-situ decomposition. We will provide insight into the complex and varied behaviour of primary mineral decomposition and the analytical LA-ICP-MS conditions that promote or minimize Pb/U fractionation.

[1] J. Košler, M. Wiedenbeck, R. Wirth, J. Hovorka, P. Sylvester and J. Míková, *Journal of Analytical Atomic Spectrometry* **2005**, *20*, 402-409.

[2] C. M. Allen and I. Campbell, *Chemical Geology* **2012**, *s 332–333*, 157–165.