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Thermal-induced matrix effects in LA-ICP-MS analysis of accessory minerals with implications for U-Pb geochronology

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Matrix effects hinder the accuracy of U-Pb dating by LA-ICP-MS. They have largely been attributed to differences in downhole fractionation between the external calibrant and the unknown: the change in Pb/U ratios with the deepening of laser ablation craters, whose trends vary considerably from matrix to matrix. However, moderately inaccurate ages may still be obtained when performing non-matrix matched U-Pb dating by rastering instead of drilling spots. This implies the existence of a matrix-dependent Pb/U bias/offset beyond mass discrimination in the ICP-MS. The aim of this investigation was to explore the dependencies of Pb/U and ablation behaviour on the physical and thermal properties of dated minerals.

A series of well-characterised reference materials (apatite, monazite, titanite, zircon, baddeleyite, rutile) were systematically analysed over one LA-ICP-MS session using a 193 nm Ar-F excimer laser coupled to an Agilent 8900 triple quadrupole ICP-MS, over a range of fluences (2-6 J/cm^2) with a pulse width of 7 ns. Pb/U offset was calculated by dividing the background-corrected measured $^{206}Pb/^{238}U$ ratios by the accepted values from the literature (with apatite and titanite first being corrected for common Pb). From the beginning of each analysis, the experiment revealed significant differences in the Pb/U offset of each mineral with ablation time (see figure where data was collected at a fluence of 4 J/cm^2). Minerals of the same class (phosphate, silicate and oxide) yielded the most similar Pb/U offset evolutions, but there was still divergence as ablation progressed, including at higher fluences. An important finding is that the average Pb/U offset for each mineral species correlates strongly with thermal properties (e.g., thermal conductivity), being greatest for oxides, followed by silicates and phosphates.

We assessed thermal effects during ablation by studying the morphology of ablation craters using scanning electron microscopy (SEM) and optical profilometry, and crater and ejecta blanket chemistry using Raman spectroscopy, SEM-energy dispersive spectroscopy (EDS) and LA-ICP-MS elemental mapping. Our analyses revealed considerable differences in melting between the mineral classes, which led to incongruent ablation as volatile elements (such as Pb) were preferentially released. The results reinforce the importance of matrix-matched calibration.