U-Pb geochronology at high spatial resolution using LA-SF-ICP-MS: Addressing variable downhole fractionation in zircon

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Different zircon grains exhibit different laser ablation rates leading to unequal degrees of DownHole Fractionation (DHF) of Pb/U ratios between unknowns and reference standards, depending on their chemical and physical character. This results in a non-matrix matched condition for LA-ICP-MS measurements of U-Pb age. For larger spot sizes (≥20µm) and lower fluences (≤3J/cm^2), the DHF of Pb/U are sufficiently similar in different zircon to allow age measurements to be accurate to 2% on a routine basis when corrected for DHF using a single reference standard. However, for spot sizes less than <20µm and laser fluences >3J/cm^2, the matrix-dependent DHF of Pb/U ratios is much more pronounced. This represents a limiting factor for precise and accurate U-Pb geochronology of zircons with <20µm spots, because it is difficult to predict and match the DHF patterns of unknown zircons with those of appropriate reference standards *a priori* in an analytical session.

We analysed U/Pb ages for a common set of reference zircons (91500, Plešovice, Temora-2, R33, FC-1, Fish Canyon) using a NWR193 ArF excimer laser ablation (LA) system coupled to a Nu AttoM sector field (SF)-ICP-MS to address data handling of DHF for small laser spots. Analyses of 10 - 15µm spots at fluences between 3.5-4.5 J/cm^2 revealed that precision greatly exceded accuracy, as calculated using a smoothed cubic spline DHF correction in Iolite over a 30 second ablation interval. DHF of zircons varied as much as 2-3 times that of the reference standard (91500) resulting in age offsets in excess of >5-14%, even while precision was maintained at <2%. Application of other DHF correction models available in Iolite (linear, exponential, running median) did not improve the age offsets.

We found, however, that accuracy was improved on reprocessing the time series data by gradually masking the ablation time from the end of the ablation signal. For each of the reference zircon, irrespective of the size and shape of the DHF pattern, accuracy within 2% of TIMS age could be achieved by processing only the first 5-10 seconds of the analyte signals, which were the least fractionated.