Laser ablation of zircon and implications for U-Pb geochronology

* N.J. PEARSON[1], W. J. POWELL[1], J.L. PAYNE[2], R.C. MURPHY[1], E. BELOUSOVA[1], W.L. GRIFFIN[1] AND SUZANNE Y. O'REILLY[1]

[1]ARC CCFS Centre of Excellence and GEMOC, Macquarie University, Sydney, Australia
[2]TRAX, University of Adelaide, Adelaide, Australia
(*correspondence: norman.pearson@mq.edu.au)

Non-stoichiometric sampling and down-hole fractionation contribute significantly to the uncertainty budget of LA-ICP-MS measurements of trace elements and isotope ratios. An investigation of the ablation characteristics of zircon has explored the optimum set of hardware parameters and operating conditions to maximise spatial resolution, and minimize ablation rate and U-Pb fractionation. This study has assessed the effects of laser wavelength, pulse-width, spot size and fluence, in conjunction with laser cell design (New Wave, HelEx) and gas composition and flow.

Distinctive down-hole fractionation of U and Pb is observed in ablation of zircon using 213 nm (Nd:YAG) and 193 nm (Excimer) wavelength lasers. The change in $^{206}Pb/^{238}U$ from both systems is greatest in the first 150-200 laser pulses (20 to 30 seconds of ablation at 5 Hz) but for a range of operating parameters $^{206}Pb/^{238}U$ shows little further change with time during ablation with the 193 nm laser, whereas the ratios produced by the 213 nm laser steadily increase. Laser fluence and spot size have significant effects on ablation rate and fractionation. Ablation rate increases with fluence but is slower for larger spot sizes. For small spot sizes, or more specifically pits with aspect ratios (depth:diameter) >1, the rate of fractionation is near-linear with time. A crater wall forms from the initial laser pulse and grows in height above the surface of the sample by the addition of condensate and melt extruded from the pit. Over time the inner pit surface develops a fluted structure and the rim of the crater develops a crown-like apperance. The development of these features is more pronounced with small spot size and low fluence. There is also a significant decay in signal intensity with time, especially with small spot sizes, indicating that progressively less material is being removed from the hole and transported to the ICP. The net effect is a greater fractionation of $^{206}Pb/^{238}U$ with small spot size due to the retention of melt and condensed material in and around the laser pit.

A better understanding of such fundamentals of the ablation process is enabling higher spatial resolution measurements and helping to improve the accuracy of analyses and reduce uncertainties.