Eliminating U-Pb 'downhole' elemental fractionation and achieving nanometer (nm) depth resolution by low volume single-shot LA-ICP-MS.

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The interaction between incident laser radiation and sample substrate is difficult to predict. Natural zircon is often both structurally and chemically heterogeneous in 3-dimensional space. Encountering growth-related structural microheterogeneities, inclusions and chemical complexities, is almost inevitable during a static ablation of several tens of seconds. A single-shot approach to laser ablation implements a minimal sample exposure time to incident laser radiation for each integration; thus, reducing sample consumption, the probability of thermally induced effects (e.g. substrate melting), and the potential for signal mixing.

Single-shot laser ablation analyses were conducted using a Nu Instruments Attom HR-ICP-MS coupled to a UP213 laser ablation system, a set-up requiring no modification of existing instrumentation or specialised equipment (e.g. low volume sample cell). The acquired data, are processed using NuQuant software, which integrates and collates short-lived signal peaks produced by multiple (x30) individual laser shots, as opposed to the broad signal peak produced by a continuously pulsing laser. This analytical protocol routinely produces age determinations reproducible to <1% (2 $\sigma$ ) on a small sample volume (~1530 um<sup>3</sup>) with a 40um diameter spot. The single-shot laser ablation protocol employed here effectively eliminates 'downhole' fractionation as the resultant pit depths are shallow (average of ~1.2 µm). Pit depths of this magnitude are equivalent if not shallower than those produced during conventional SIMS analysis, and the iterative integration of each laser shot allows for depth resolution on the order of ~40nm pulse<sup>-1</sup>. The single-shot method outlined here is validated with results obtained on zircon standards and samples dated using conventional approaches (e.g. ID-TIMS). Calculated ages are associated with relative uncertainties (for 91500) of 6%, 5%, and 8%  $(2\sigma)$  for the <sup>206</sup>Pb/<sup>238</sup>U, <sup>207</sup>Pb/<sup>235</sup>U, and <sup>207</sup>Pb/<sup>206</sup>Pb ratios, respectively.