Can FT ages be derived using LA-ICP-MS?

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A major strength of the fission-track (FT) method is that data are collected from individual apatite grains, essential when analysing sedimentary samples with variable provenance and/or apatite composition. Apatite crystal uranium concentrations are recorded in an external detector as neutron-induced track densities. However, recent political/environmental pressures have led to reactor closures and the number of reactors with suitable thermal/epithermal flux ratios is decreasing, favouring development of alternative approaches to uranium mapping. This study considers the suitability of LA-ICP-MS.

Using the previously analysed apatite FT age standards Durango, Fish Canyon Tuff (FCT) and Mount Dromedary Complex, we measured uranium concentrations by LA-ICP-MS on the same apatite grains used to determine the spontaneous track density. This enabled direct comparison between FT ages based on LA-ICP-MS uranium measurements (NERC facility at Kingston University) and the conventional FT external detector approach. Laser ablation of the crystal surface on which spontaneous tracks had been counted was conducted in scanning-mode using a ~10 µm spot and calibrated against NIST610 and 612 standard glasses. Repeat analyses of standard glasses during analysis provided estimated uncertainties of calculated U content of ~10 %.

For the laser ICP-MS approach FT ages of each grain were calculated using:

\[ t = \frac{1}{\lambda_\alpha} \ln \left( \frac{N_s + \lambda_f M \left( e^{\lambda_\alpha t} - 1 \right) R_k}{\lambda_\alpha} \right) \]

where \( N_s \) is spontaneous FT density, \( \lambda_\alpha \) and \( \lambda_f \) are uranium decay constants, \( C \) is uranium concentration, \( I \) is \(^{238}\)U isotopic abundance, \( d \) is apatite density, \( M \) is \(^{238}\)U mass, \( t \) is age, \( R \) is a half track length and \( k \) is a constant, set at 1 in this study, and but variable depending on experimental factors such as etching and observation conditions. Error of a grain age is given by: \( \delta t = t/\sqrt{(1/N_s + \delta^2)} \), where \( N_s \) is the spontaneous track count and \( \delta \) the uranium measurement uncertainty. Apatite grain uranium concentrations estimated from neutron-induced tracks and from LA-ICP-MS show a linear relationship for FCT and a broader cluster for others. Grain ages calculated by the two methodologies show linear relationships for all samples. Weighted mean ages are concordant with the reference ages for all samples, demonstrating the viability of LA-ICP-MS as an alternative approach to FT geochronology.

Interference reduction by ion-molecule reactions in ICP-MS.

Chemical resolution for the earth sciences.

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The introduction of ion-molecule reactors in ICP-MS instrumentation in the form of the dynamic reaction cell or collision cells has had a significant impact in all areas of elemental analysis. This is also true in geological applications, where some success has been made in finding new solutions for the determination of trace element concentrations. The key features of an ion-molecule reactor for ICP-MS are a) interference reduction by ion molecule reactions with a reactive gas b) reduction of the ions’ energy spread during collisions c) use of controlled condensation reactions to determine an analyte at different m/z. Besides interference reduction by reactive gases, collisions with a chemically inert gas provides the analytical advantage to homogenize the ion beam and improve precision in isotope ratio determinations.

This presentation focuses on “chemical” approaches that can be utilized to resolve spectral interferences, where eventually even high mass resolution is not capable to achieve a separation of the analyte.

Interferences arising from the formation of Ar-based polyatomic ions are numerous and vary especially with the sample matrix. H\textsubscript{2} as reaction gas has been widely applied for this purpose. Ru\textsuperscript{2+} and Pd\textsuperscript{2+} were resolved from NiAr\textsuperscript{+} interferences in NiS assays with laser ablation sampling\textsuperscript{1}. The dominating Ar\textsuperscript{+} ions were successfully reduced at m/z 40 for simultaneous analysis of 30 elements in melt inclusions\textsuperscript{2}, achieving 100 fold improvement for detection of Ca. An improvement for the Nb/Zr geochronometer was achieved by achieving 100 fold improvement for detection of Ca. An improvement for the Nb/Zr geochronometer was achieved by simultaneous analysis of both elements after elimination of the ArCr\textsuperscript{+} interference\textsuperscript{3}. Condensation of Sr with CH\textsubscript{3}F was used for separation from Rb and the precise determination of the \(^{87}\)Sr/\(^{86}\)Sr ratios\textsuperscript{4}.

References