In situ U-Pb dating of carbonate by LA-ICP-(MC)-MS and ID-TIMS

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An easily applicable method to provide absolute age constraints in carbonate has proved elusive except in unusually favourable materials. U-Pb dating of carbonate has so far been restricted to ID-TIMS methods that involve analysis of larger volumes. Unfortunately there is currently no a priori way to know if a sample has a viable U/Pb ratio, and many carbonates are not datable. The challenge is to find a rapid method to date materials in situ by identifying suitable materials (low common Pb, >0.3ppm U), finding the higher-U and highly radiogenic subzones zones that are key to precise ages, so that a substantial robust age on material can be put in a sedimentary or other geological context. Materials of interest include calcite veins in structurally relevant fractures, cements, diagenetic calcite, primary biogenic carbonate, speleothems, lake sediments, tufas and paleosols, etc.

We have successfully adapted LA-ICP-(MC)-MS zircon methods by using a well characterized 254±6 Ma (95% confidence) calcite standard (dated by ID-TIMS at NIGL and Stony Brook) to correct the measured U/Pb ratio for matrix effects. This approach allows in situ U-Pb dating with uncertainties as little as ±4% at 95% confidence with minimal sample consumption, supplemented by ID-TIMS data as appropriate. We have dated samples with average uranium concentrations (0.4-5 ppm) such as speleothems, paleosols, tufa, marine cements (in ammonite chambers), calcite veins from fractures etc. The age of dated materials is as young as 250ky, the latter U-Pb dates agreeing with U-series dating after correcting for U activity. For Quaternary materials beyond the range of U-series, we measure residual disequilibrium of U to make corrections for initial U activity ≠ 1. We have found that our LA-ICP-MS in situ method has distinct advantages over ID-TIMS in its sub-sampling power. Examples of these applications will be presented. This new area of geochronology is likely to grow rapidly in the future.

Long-term residual alteration rates of synthetic basaltic glass

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Laboratory measured residual rates

Basaltic glasses are considered as good analogues to nuclear glasses [1]. However, if forward alteration rates and mechanisms are well-known [2], long-term alteration rates need to be determined in order to deepen this analogy.

We performed batch experiments at high surface-to-volume ratio (high reaction progress) on a Li- or B-doped synthetic tholeiitic basaltic glass at 90°C and 30°C during 1000 days. After 182 days, the rates did not evolve significantly. When considered constant with respect to time, the mean residual rates were 1.2×10^{-5} $g.m^{-2}.d^{-1}$ and 3.9×10^{-6} $g.m^{-2}.d^{-1}$ at 90°C and 30°C, respectively.

The alteration layer was a dense amorphous gel in which some crystalline clayey sheets may be found. Its porosity was sufficient to allow water and Si to pass through. At the alteration layer/solution interface, low density poorly crystalline clays had precipitated.

Comparison to naturally altered samples

The measured alteration rates indicate a drop of 4 to 5 orders of magnitude when compared to forward alteration rate and 1 order of magnitude inferior to the rates at higher progress of reaction reported by Técher et al [3]. This is 10 times higher than the drop between initial and residual rates observed on the SON68 nuclear glass [4].

These values were extrapolated both in temperature (to 5°C with an Arrhenius law) and in time resulting in a value comprised between 0.1 and 0.6 $\mu m/10^3$ y. This result is comparable to naturally altered samples showing a similar alteration layer (i.e. non-zeolitized samples) whose alteration rate is comprised between 0.1 and 10 $\mu m/10^3$ y [3].

[1] Ewing (1979) *Scientific Basis for Nuclear Waste Management I*, 57-68. [2] Crovisier *et al* (2003) *J. Nucl. Mater.* **321**, 91-109. [3] Techer *et al* (2001) *Chem. Geol.* **176**, 235-263. [4] Gin *et al* (2012) *J. Non Cryst. Sol.* **358**, 2559-2570.