The matrix effect as alpha dose: improving LA-ICP-MS Pb/U ages

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The Matrix Effect, New Experiments, and Results

Matrix effects are purported to be the cause of offsets of ages from spot (*in situ*) dating techniques relative to TIMS work in which zircons are dissolved and U and Pb are isolated and concentrated through column chemistry. Moreover they are thought to contribute to Pb/U differences in zircon spot dating. Age offset is the measured age minus the accepted age all divided by the accepted age. Black et al. (2004) showed that there are age offsets among TIMS, SHRIMP and LA-ICP-MS $^{206}Pb/^{238}U$ ages for well characterized zircons and suggested that Nd was a monitor for degree of offset [1]. Klötzi et al. (2009) showed in a LA-ICP-MS experiment using each of 4 standard zircons to deduce the age of a fifth produced a minimum precision of 3-4%, prescision worse than that generally ascribed to the technique [2]. Klötzi's work (rastering not drilling) shows that understanding, minimizing and/or eradicating the matrix effect is vital for truly accurate and precise LA-ICP-MS $^{206}Pb/^{238}U$ ages.

We have shown by 2 different LA-ICP-MS round robin experiments on 6 well characterized zircon standards with TIMS ages (OG1, FC1, 91500, Temora, R33 Plesovice, and LP521) that the matrix effect is not chemical but physical in nature. We have expanded our database to include Miocene zircons with high precision $^{40}Ar/^{39}Ar$ ages (Cougar Point Tuff) as well as some other zircons [3]. Briefly our system consiststs of an Agilent ICP-MS and Excimer 193 nm wavelength laser with in-house ablation chamber. In a He atmosphere we drill 30 μm spots to 20 μm depths while measuring 18 masses. Of these only one variable showed a strong correlation with age offset, radiogenic Pb. The cause of the matrix effect is not the presence of the Pb itself, but what the Pb represents – the accumulated decay of U and Th since zircon crystallization. Our results show that if a zircon is substantially older and/or more radiogenic than the standard (Temora in this study) then the measured ICP-MS age is too old by up to 3%. More startlingly, if the unknown is substantially younger and/or less radiogenic than the standard then the age obtained is too young by up to 8%. We surmise that in grains that have had higher alpha particle doses, Pb escapes the ablation site with greater ease relative to U. The exponential fit of percent age offset vs alpha dose$*10^{-15}$ for 14 populations given below can be used to correct our existing work.

$$y=382.68e^{0.8331x} \quad r^2=0.96.$$

In experiment 2 we have demonstrated that annealing the same 6 standards to the same conditions (850°C for 48 hours) obliterates the matrix effect. Age offsets are then about the uncertainty expected from counting statistics (<1%). We highly recommend annealing standards and unknowns before LA-ICP-MS dating.

[1] Black *et al.* (2004) *Chem. Geol.* **205**, 115-140. [2] Klötzi *et al.* (2009) *Geostd. And Geoanal. Res.* **5,** 5-15. [3] Bonnichsen, *et al.* (2008) *Bull. Volcanol.* **70**, 315-342.

Influence of seawater carbonate chemistry on B/Ca in cultured planktic foraminifera

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The ratio of boron to calcium (B/Ca) in fossil calcite tests of planktic foraminifers has recently been used to investigate the carbonate chemistry of ancient oceans. The theoretical basis for this proxy is rooted in the pH-dependent concentration of dissolved borate ($B(OH)_4^-$) and its subsequent incorporation into foraminiferal calcite (Hemming and Hanson, 1992). Here, we present new insights into B incorporation from laboratory culture experiments with live specimens of *Globigerinoides ruber* (pink) and *G. sacculifer*. We find that in *G. sacculifer*, B/Ca increases with pH (higher $[CO_3^{2-}]$ and $[B(OH)_4^-]$, lower $[HCO_3^-]$), but decreases with total dissolved inorganic carbon (DIC) (higher $[CO_3^{2-}]$ and $[HCO_3^-]$, constant $[B(OH)_4^-]$). This suggests competition between aqueous boron and carbon species for inclusion into the calcite lattice. Similar to previous experiments with cultured *Orbulina universa*, B/Ca increases with salinity, but not with temperature. We evaluate possible control parameters, including $[B(OH)_4^-]/[HCO_3^-]$ and $[B(OH)_4^-]$/DIC. Our culture calibrations are broadly consistent with field data, including new core-tops from the Gulf of Mexico. Some discrepancies may indicate the presence of unidentified controls, and more work is needed to probe specific controls on B/Ca and to test culture calibrations in the open ocean.

[1] Hemming and Hansen (1992) *Geochim. et Cosmochim. Acta* **56**, 537-543.