Sources of sulfur and sulfur preservation in subducted rocks: An *in situ* sulfur isotope study

K.A. EVANS*[1] A.G. TOMKINS[2] AND J. CLIFF[3]

[1]Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845, Australia. (*correspondence: k.evans@curtin.edu.au)
[2]School of Geosciences, Monash University, Melbourne, VIC3800, Australia
[3]Centre for Microscopy Characterisation and Analysis, University of Western Australia, WA6009, Australia

A number of lines of evidence suggest that the sub-arc mantle is 1-2 log units more oxidised than mantle elsewhere, though this conclusion is controversial, and the processes that may contribute to sub-arc mantle oxidation are poorly understood. Sulfur has been proposed as a vector for transfer of redox budget from subducting slab to sub-arc mantle. Sulfate may be present in altered ocean crust in significant quantities, and the transfer of 8 electrons as S(+6) in sulfate is transformed to S(-2) in sulfides means that the addition of sulfate to sub-arc mantle could significantly alter mantle redox budget and oxygen fugacity on geologically reasonable timescales. However, little is known of the relative stability or solubility of sulfur-bearing phases under subduction conditions so this possibility is hard to evaluate.

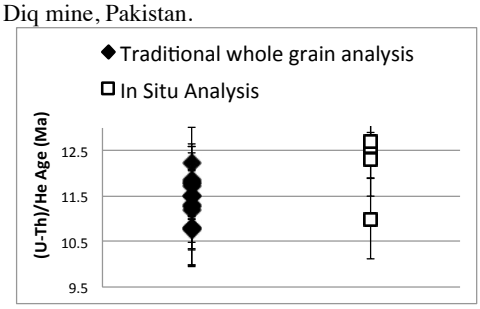
Sulfur isotopes provide one way to investigate sources of sulfur, and the processes that affect sulfur content during subduction. $\delta^{34}S$ of seawater-derived sulfate is around 20‰ while $\delta^{34}S$ of magma-derived sulfides is around 0‰. Calculated fractionation of sulfur isotopes at subduction temperatures for all but the most extreme open system conditions suggest that this difference between sources should be recognisable even after significant devolatilisation. *in situ* sulfur isotope measurements of pyrite associated with high pressure mineral parageneses in high pressure mafic rocks from the Eastern Alps and from New Caledonia were performed. The New Caledonia samples contain pyrite with $\delta^{34}S$ in excess of 5‰, while samples from Pfulwe pass in the Eastern Alps contain pyrite with $\delta^{34}S$ up to 15‰. These elevated $\delta^{34}S$ values suggest that sulfur ultimately derived from seawater is preserved in these rocks to depths greater than 60km.

In situ RESOchron helium dating: Progress, pitfalls and prospects

[1]NOREEN EVANS[1], BRENT MCINNES[1], BRAD MCDONALD[2], PIETER VERMEESCH[3], MIKE SHELLEY[4] AND ESTEPHANY MARILLO SIALER

[1]AuScope GeoHistory Facilty, John de Laeter Centre for Isotope Research, Curtin University, Australia, (noreen.evans@curtin.edu.au);
[2]Department of Earth Sciences, University College London, UK;
[3]Laurin Technic Pty Ltd., Canberra, ACT;
[4]School of Earth Sciences, University of Melbourne, Australia

Recent advances in *in situ* double dating[1-3] prompted us to develop the *RESOchron*, a purpose-built laser ablation U-Th-Pb-He system (see McInnes *et al*., this meeting). Polished zircon grains, mounted in indium, were loaded into an UHV cell where helium was extracted via 193 nm laser ablation for 30 seconds using a 33-75 μm beam at 7Hz. U and Th were subsequently analysed in an adjacent pit using traditional ELAICP-MS methods. Pit volumes were measured on a Zeiss LSM700 confocal laser microscope and (U-Th)/He ages calculated using published methods[1,3]. The mean zircon helium age from the *in-situ* ablation experiment fell within 10% of helium ages obtained using traditional single crystal methods for an 11.4 ± 0.5 Ma subvolcanic stock from the Reko Diq mine, Pakistan.



Improvements in analytical precision require refinement of sample preparation for UHV conditions. Indium, despite being inert under high vacuum conditions, is non-ideal for zircon mounting because its high surface reflectance makes navigating around the mount and focusing the laser difficult. Due to its extreme softness, grains cannot be polished *in situ* and even slight contact can damage the surface and cause grains to shift position. Zonation of U and Th also impacts the accuracy of results, as does the accuracy of pit volume measurements as suggested previously [1-3]. Other mounting media are being explored (eg. FEP teflon) and optimization of laser protocols is underway.

[1] Boyce J.W. *et al*., 2006, *GCA* **70**, 3031–3039; [2] Boyce J.W. *et al*., 2009 *G-cubed* 10. doi:10.1029/2009GC002497; van Soest M.C. *et al*., 2012, AGU Fall Meeting Abstracts, pp. B2161+. [3] Vermeesch, P. *et al*., 2012, *GCA* **79**, 140-147.

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