High-uranium matrix effect in SHRIMP U/Pb measurements of zircon

Lloyd White[1,2] and Trevor Ireland[1]

1. Research School of Earth Sciences, The Australian National University
2. Current Address: Southeast Asia Research Group, Royal Holloway University of London

Correspondence: lloyd.white@rhul.ac.uk

Introduction

Previous work showed that a correlation existed between highly elevated uranium concentrations (>3000 ppm) and an increase in apparent U/Pb age obtained from ion microprobe analyses (Fig. 1) (Williams and Hergt 2000), though this problem had not been investigated in detail.

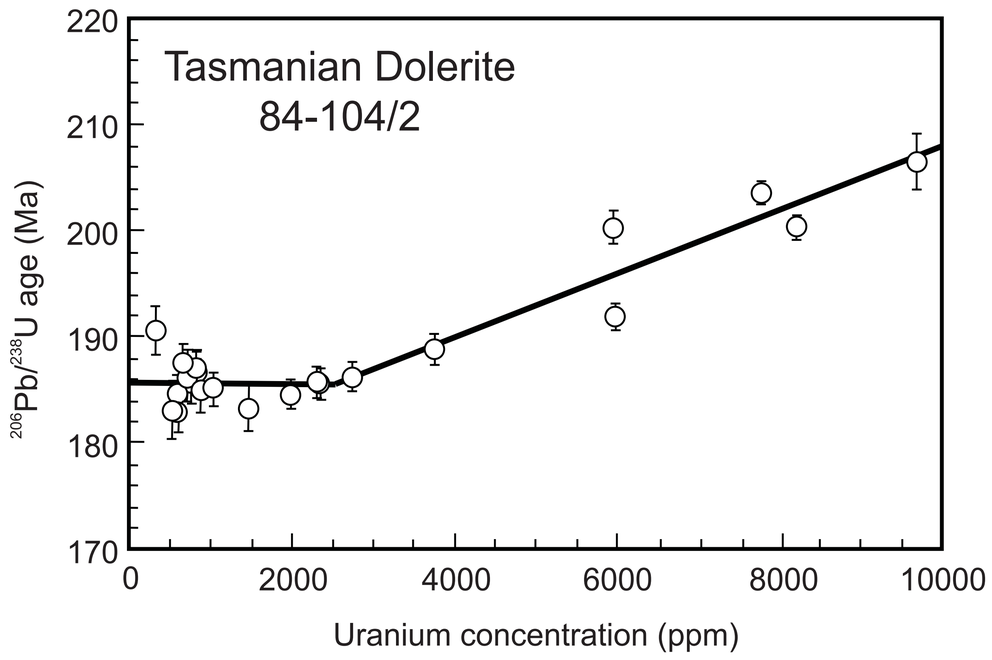

Fig. 1. Williams and Hergt (2000) found that the apparent $^{206}Pb/^{238}U$ ages derived from SHRIMP measurements are mostly similar within analytical uncertainty between 0 and 2500 ug/g U, after which they they increase at a rate of approximately 3% per thousand µg/g U.

Machine Dependence

We used different generations of the SHRIMP (I, II and RG) to analyse samples of varying uranium concentration and age (~180 Ma, ~100 Ma, ~50 Ma and ~20 Ma) to quantify the effects related to the nature of the samples and/or instrumentally induced fractionation (instrument, analytical setup and/or matrix effect).

Of the four samples that were analysed, the high-uranium effect was most pronounced in the ~180 Ma Tasmanian Dolerite (Fig. 2). This typically shows an increase in Pb/U age of around 3% per thousand µg/g of uranium when measured on SHRIMP RG. However, one session on SHRIMP RG obtained a strong correlation of an increase in apparent age with 8% per thousand µg/g of uranium. The effect was not as apparent when the same sample was analysed with SHRIMP I (no correlation) and SHRIMP II (weak correlation) (Fig. 2).

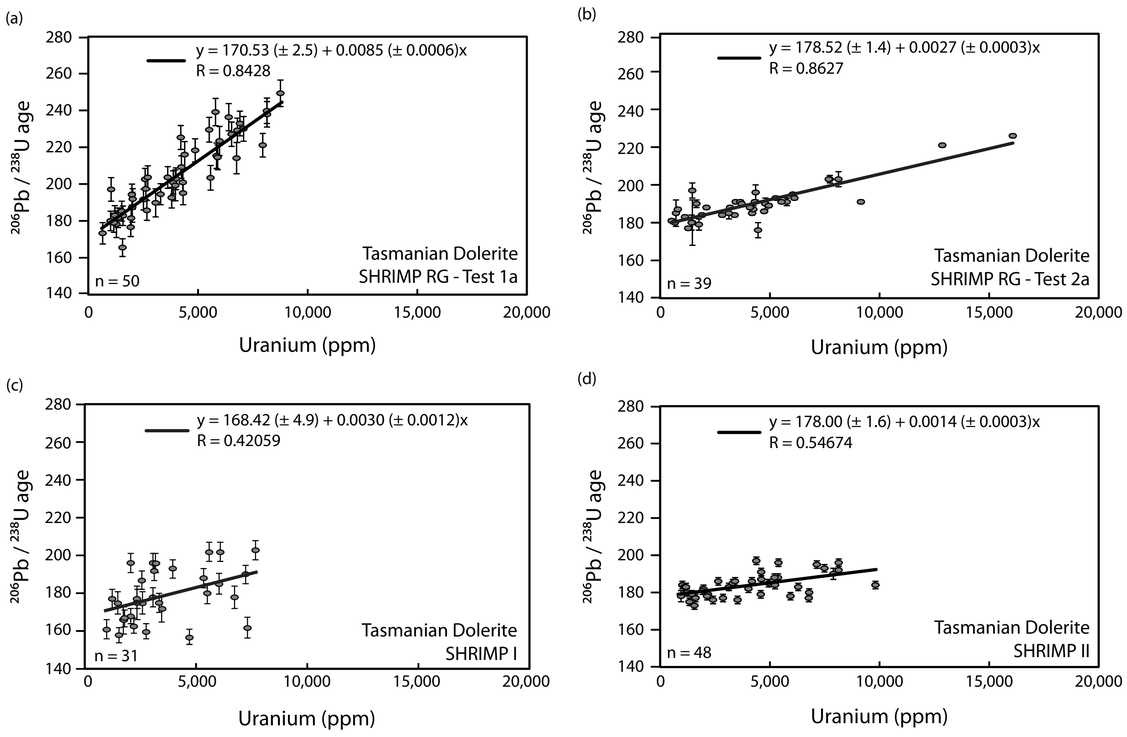

Fig. 2. Age vs uranium concentration plots of (a-b) SHRIMP RG, (c) SHRIMP I and (d) SHRIMP II measurements of zircons from the Tasmanian Dolerite. There is a positive correlation between an increase in apparent age and uranium concentration when measured with SHRIMP RG, but there is considerable different in the slope of the line of best fit for each SHRIMP session (a-b). There is a weak-positive correlation between an increase in apparent age and uranium concentration when measured with SHRIMPs I and II (c-d).

References

- Leech, M.L., 2008. Does the Karakoram fault interrupt mid-crustal channel flow in the western Himalaya? EPSL, 276, 314–322.
- White, L.T., Ahmad, T., Ireland, T.R., Lister, G.S., Forster,M.A., 2011a. Deconvolving episodic age spectra from zircons of the Ladakh Batholith, northwest Indian Himalaya. Chemical Geology 289, 179–196.
- Williams, I.S., Hergt, J.M., 2000. U–Pb dating of Tasmanian dolerites: a cautionary tale of SHRIMP analysis of high-U zircon. In: Woodhead, J.D., Hergt, J.M., Noble, W.P. (Eds.), Beyond 2000: New Frontiers in Isotope Geoscience: Lorne, Abstract Proceedings, pp. 185–188.
- Zhang, M., Salje, E.K.H., Farnan, I., Graeme-Barber, A., Daniel, P., Ewing, R.C., Clark, A.M., Leroux, H., 2000. Metamictisation of zircon: Raman spectroscopic study. Journal of Physics: Condensed Matter 12, 1915–1925.

Age Dependence

High-uranium zircons from the 98 Ma Mt Dromedary monzonite show little to no correlation between uranium concentration and U/Pb age when measured with SHRIMP I, II and RG. Though, a correlation between uranium concentration and an increase in apparent U/Pb age was observed in analyses of younger (~50 - 20 Ma) high-uranium zircons, but these were less pronounced than the results obtained from the older Tasmanian Dolerite (Fig. 3).

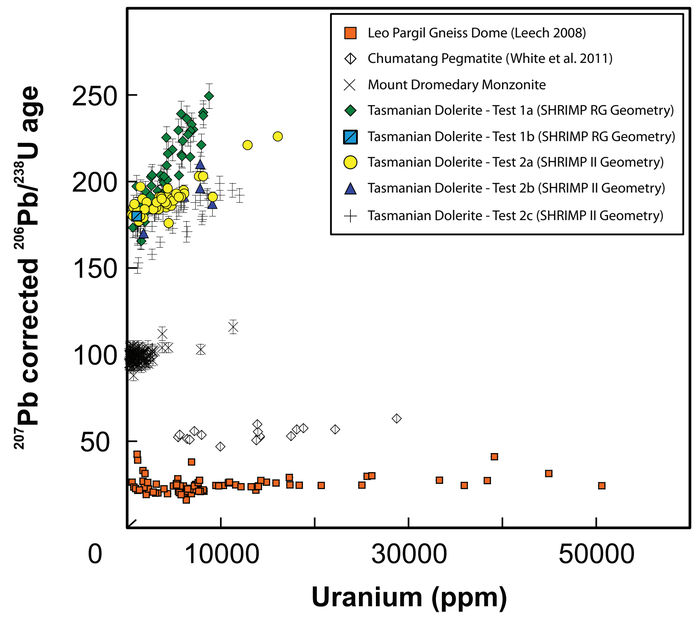

Fig. 3. Apparent $^{206}Pb/^{238}U$ age vs. uranium concentration for SHRIMP RG analyses of several samples of different age. This shows an apparent increase in U-Pb age with uranium concentration, but also shows there is a correlation between an increase in apparent age and an increase in the high-U matrix effect.

The "high uranium effect" is linked to zircon metamictisation

Raman spectroscopy was used to examine the crystal structure of the zircons that had been measured previously with SHRIMP. This was done so that the uranium concentration and U/Pb age was known for each Raman spectrum. The Raman data indicate that the link between uranium concentration and apparent age is related to the degradation of the zircon matrix due to radiation damage (Fig. 4).

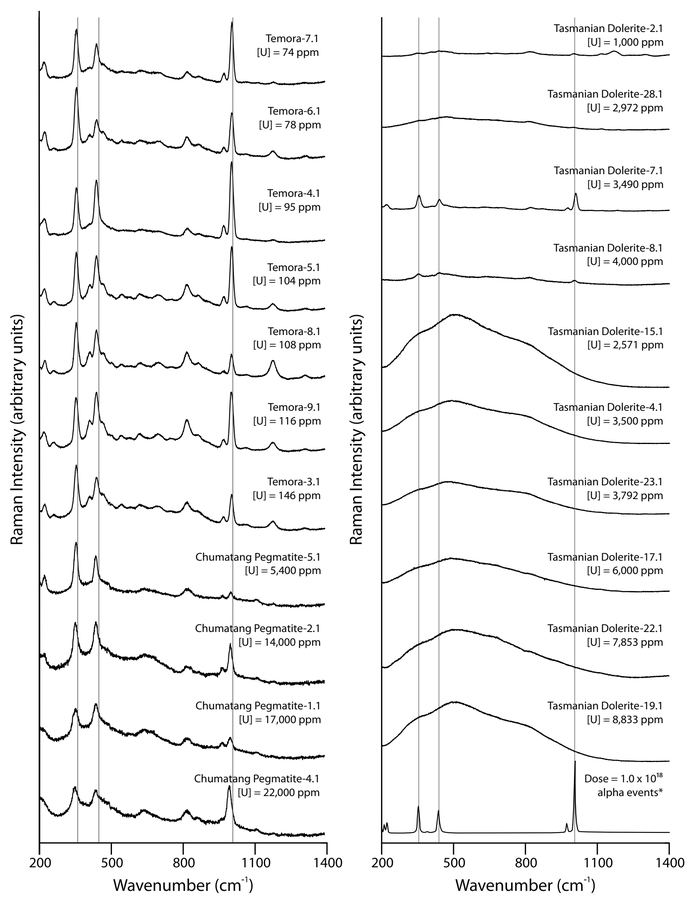

*Fig. 4. Raman spectroscopic analyses of several Temora-2, Tasmanian Dolerite, and Chumatang Pegmatite zircons. Spectra obtained from the Temora-2 and Chumatang Pegmatite zircons all show the distinctive zircon peaks (gray vertical lines). However, zircons from the Tasmanian Dolerite generally show broad patterns with indistinct peaks that indicate that these zircons have an amorphous or semi-amorphous structure, which most likely reflects metamictization (or partial metamictization). *Also shown is a typical Raman spectrum for zircon that has experienced relatively low radiation damage (Zhang et al., 2000).*

Can we correct for the high uranium matrix effect?

- The change in crystallinity of the zircon matrix enhances the emission of Pb+ relative to U and U oxide species analysed with SHRIMP.
- The effect is associated with matrix and machine parameters so an external correction cannot be made assuming a constant correction value.
- It might be possible to quantify the effect with a secondary high-uranium standard, but the matrix of this standard would need to be closely matched in age (radiation damage) and chemistry (U concentration), this is an impractical solution.
- We instead propose that workers be aware of this matrix effect when measuring zircon with SHRIMP, and to use Raman spectroscopy before or after SHRIMP analyses to ensure that the zircon is crystalline.