Effects of chemical abrasion on zircon crystal structure, chemistry and ID-CA-TIMS U-Pb ages

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Recognition and mitigation of post crystallisation loss of radiogenic lead is a still an unresolved problem in high-precision U-Pb dating. The loss of radiogenic Pb preferentially occurs along altered zones of the crystal lattice as a consequence of the structural damage produced by U decay (Nasdala et al., 2005) and results in biased ages that are too young. Reliable and meaningful U-Pb ages require a control on factors that cause Pb loss and create age dispersion. Despite state of the art procedures using chemical abrasion (CA) on single zircon grains (Mattinson, 2005) there is no guarantee to completely mitigate the loss of radiogenic Pb. Furthermore, this technique is entirely empirical and is often modified by different laboratories in terms of duration and temperature of the annealing and the partial dissolution steps. Without a proper understanding of how (1) the applied annealing temperature and (2) the temperature and duration of partial dissolution affect metamict and non- metamict zones. Therefore, data from different U-Pb geochronology laboratories following different procedures are problematic to compare quantitatively. In consequence the rejection of respectively too young zircon grains with suspected loss of radiogenic lead, while reviewing a complex data set, is often difficult to justify without a robust analytical proof. Previous studies have investigated the effect of annealing on radiation damaged zones at different time and temperature conditions (e.g. Nasadala et al., 2002), or the effect of temperature at a fixed duration during the partial dissolution step (Huyskens et al., 2016) on the reproducibility of U-Pb dates. However, no study has investigated the effect of the chemical abrasion procedure on the zircon trace element chemistry and compared this to the state of the crystal structure and the U-Pb date.

Our study intends to develop improved protocols for the chemical pre-treatment of zircon based on the state of the crystal structure and chemistry. We will present an experimental approach to quantify the effects of chemical abrasion on the zircon chemistry and crystal structure. For this purpose we have chosen the natural standard zircon Plešovice, due to its variations in trace element concentrations and domains rich in actinides (Sláma et al., 2008). Plešovice grain fragments were annealed for 48h at 900°C. Eight aliquots were separated and attacked in concentrated hydrofluoric acid at 180 °C and 210°C for 6h, 12h, 18h and 24h. We performed Raman spectroscopy, EMPA, CL imaging and LA-ICP-MS trace element analysis on each of the fractions. The zircon treated by CA are then compared to untreated and solely annealed zircons. We will show first results from the Raman and trace element analysis corresponding U-Pb dates.

Our primarily results indicate that most unannealed zircon fragments follow the radiation damage trend, exceptions are most likely the result of previous natural annealing. Successive increase in CA duration at 180°C results in more crystalline zircon fragments, indicating removal of metamict parts of zircon. However, even at 24h CA duration metamict parts are present. In contrast, Raman data from the CA at 210°C show less scatter and are more consistent. The remaining increased short range distortion of the crystal lattice (increased FWHM) is most likely the result of the trace element content.

CA does not affect the overall trace element pattern, but reduces the overall scatter, due to the removal of metamict zones. Therefore, we suspect that CA cannot fully restore the crystallinity of a pristine zircon. Based on our primarily results, we conclude that more effective removal of metamict zones at CA temperatures of 210°C already at 12h.

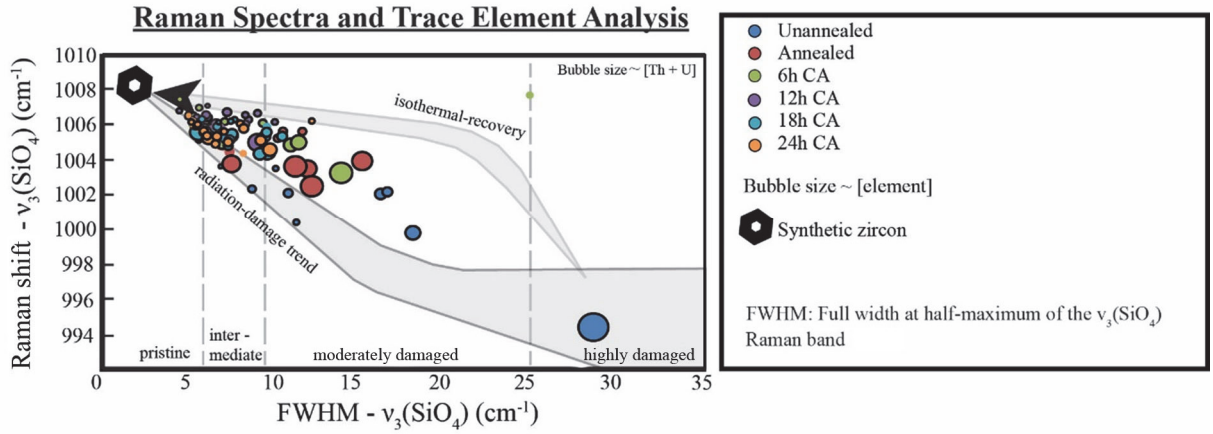

Fig. 1. *Plot of Raman shift vs. FWHM of the $\nu_3(SiO_4)$ Raman band, showing a general increase in Raman shift and decrease in FWHM with increasing time of chemical abrasion*

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