Dry annealing of radiation damaged zircon: Which "degree of reconstitution" is probed by which analytical technique?

Chanmuang, C.[1],*, Ende, M.[1], Nasdala, L.[1], Wirth, R.[2]

[1] *Institut für Mineralogie und Kristallographie, Universität Wien, Althanstr. 14, 1090 Wien, Austria*
[2] *Sektion 4.3, Helmholtz-Zentrum Potsdam, Deutsches GeoForschungsZentrum GFZ, Telegrafenberg, 14473 Potsdam, Germany*
* E-Mail: chutimun.chanmuang@univie.ac.at

Radiation damaged zircon recovers upon dry thermal annealing. Several aspects of the structural recovery, however, are still controversial. For several applications, it is crucial to estimate the extent to which the initial radiation damage has been recovered. For instance, CA (chemical abrasion) prior to TIMS analysis (Mattinson 2005) is well known to yield less biased U–Pb geochronology results, however, it is crucial to understand which temperature treatment leads to which degree of structural reconstitution, before the chemical treatment is done (Mattinson et al. 2007). Another example is the gradual change in He-retention performance upon thermal annealing (Guenthner et al. 2013), whose understanding requires quantitative estimation of the structural recovery.

We report here first results of a systematic dry-annealing study that involves zircon samples ranging from mildly to severely radiation damaged. We have observed that "degrees of recovery" estimated from diffraction techniques (e.g. unit-cell dimensions and volumes, sharpness of electron-diffraction spots) tend to be much higher than "degrees of recovery" detected by short-range-order methods (e.g., sharpening of Raman bands and luminescence lines; Fig. 1). For instance, annealing of zircon #GZ8 at 700 °C (96 h) has caused more than 80 % of the total unit-cell reduction. The very same annealing resulted in only ~50 % of the total Raman-bandwidth reduction (Fig. 2a). This apparent mismatch indicates that long-range and short-range methods are not just complementary techniques but detect different types of annealing-induced changes.
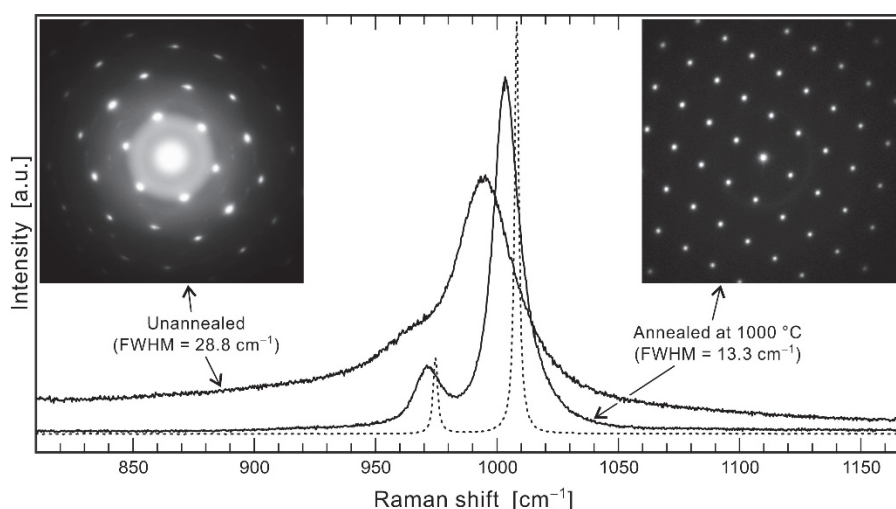

Fig. 1. Apparently incongruent recovery of the long-range and short-range order of the severely radiation damaged zircon #G3 upon dry annealing, visualised by the comparison of Raman spectra and electron diffraction patterns (dotted: reference spectrum of crystalline ZrSiO$_4$). Note that annealing at 1000 °C has resulted in decidedly incomplete relaxation of the Raman band broadening whereas fairly sharp electron diffraction spots imply that the long-range lattice order is widely recovered
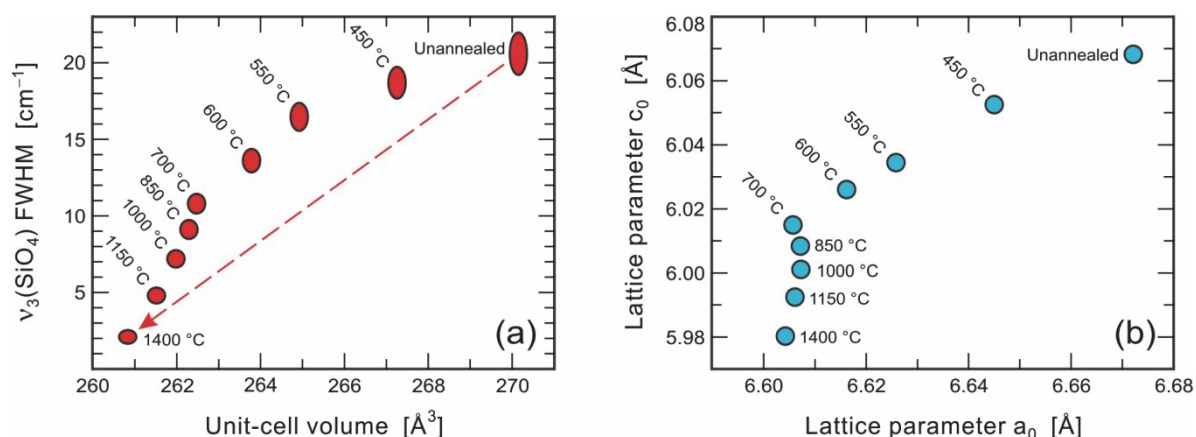
Fig. 2. a *Apparently incongruent degrees of thermal annealing of the moderately radiation-damaged zircon #GZ8, as detected by Raman and X-ray diffraction. Note that the proportionate decrease of the unit-cell volume exceeds appreciably that of the full width at half maximum (FWHM) of the main Raman band near 1000 cm⁻¹.* **b** *Mismatch in the proportionate reduction of the unit-cell dimensions parallel and perpendicular to the c axis upon dry annealing*

The apparently "quick" unit-cell reduction is controlled by extensive changes in lattice parameter a_0 in initial annealing stages. It is well known that upon accumulation of radiation damage, the unit cell expands preferentially along c whereas its a dimension experiences significant increase at more elevated damage-accumulation steps (Holland and Gottfried 1955). Upon dry annealing of radiation damaged zircon, the "mismatch" between a_0 and c_0 is even more striking: Initial annealing is dominated by a_0 decrease (virtually completed at 700 °C) whereas c_0 continues to decrease until nearly complete recovery is achieved at 1400 °C (Fig. 2b). The preferred relaxation of the initial expansion along the a axis (Weber 1990) can be used to distinguish untreated and partially annealed zircon (Nasdala et al. 2004).

Overall, there are vast differences in the "degrees of annealing" as detected by different techniques. Moderately heat-treated zircon (i.e. annealing at moderate temperatures and/or for short durations) may appear widely recovered when studied with diffraction methods but still show significant degrees of disturbance of the short-range order. We present first results of the ongoing, combined Raman and X-ray and electron diffraction study; interpretations and possible implications are discussed.

References:

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