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Sri Lankan Gem Zircon as Reference Material in Analysis and Research

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1.0 Sri Lankan Zircon

Since the 1950s, a major fraction of the research addressing the accumulation and retention of radiogenic isotopes and structural radiation damage in zircon, $ZrSiO_4$, has been done using sample material from Sri Lanka (e.g. Holland and Gottfried, 1955; Hurley *et al*., 1956; for a review see Nasdala *et al*., 2004). This material was derived from gem gravels in the Ratnapura district (Dahanayake and Ranasinghe, 1985).

2.0 Suitability as Reference Material

The excellent suitability of Sri Lanka zircon for such investigations is explained first by the fact that this material mostly has not undergone notable chemical alteration such as loss of radiogenic Pb. Second, large stones of gem quality (i.e. characterised by compositional homogeneity and absence of fractions and notable inclusions) are found quite frequently, which cover the entire range from mildly radiation-damaged to fully metamict.

Its extraordinary properties have favoured the use of Sri Lankan zircon as international intra-laboratory standards. To name two examples, gem-quality zircon samples CZ3 (Pidgeon *et al*., 1994) and M257 (Nasdala *et al.*, 2008b) are important standards, on an international scale, for U–Pb isotopic analyses used in zircon geochronology.

Gem quality is certainly advantageous, but of course not necessarily required, for U–Pb references: For instance, several standards, including 91500 (Wiedenbeck *et al*., 2004) and Plešovice (Sláma *et al*., 2008), are known to be notably zoned, though with uniform isotopic ratios. Problems in the performance of standards, however, may occur potentially if there are extensive variations in the chemical composition. If for instance, the standard material contains interior regions or zones with particularly high uranium concentrations (which then typically correlate with elevated degrees of radiation damage), unwanted effects such as non-uniform ablation or sputter rates and matrix/charge effects need to be considered (Sláma *et al*., 2008).

Such analytical artefacts are excluded if homogeneous gems (whose chemical and structural compositions should be close to that of unknowns to be analysed) are used as analytical standards. On the contrary, a clear disadvantage of using gems as references is their limited quantity. This hampers their general use in analytical techniques with comparably high consumption of standard material (such as laser ablation-inductively coupled plasma-mass spectrometry, LA–ICP–MS). Gem zircon is therefore used as standard material mostly for micro-techniques with particularly low demand of material, such as SIMS (secondary ion mass spectrometry).

Except from the use as analytical reference material, Sri Lankan zircon specimens have been, and still are, important objects in investigating the metamictisation process, that is, the study of direct and accompanying effects of the accumulation of structural damage as caused by corpuscular irradiation. An excellent example is the zoned Sri Lanka zircon no. 4601 (Figure 1), whose image was published in 1987 on the cover of *Science* (issue 4808). Chakoumakos *et al.* (1987) observed a clear correlation between actinide concentration (and hence the self-irradiation dose) and optical properties, and they discussed consequences of the variable volume expansion among variably damaged growth zones. Such studies contribute to a more quantitative understanding of irradiation effects, that is, the impact of which amount of radioactivity causes which property changes in the zircon irradiated.

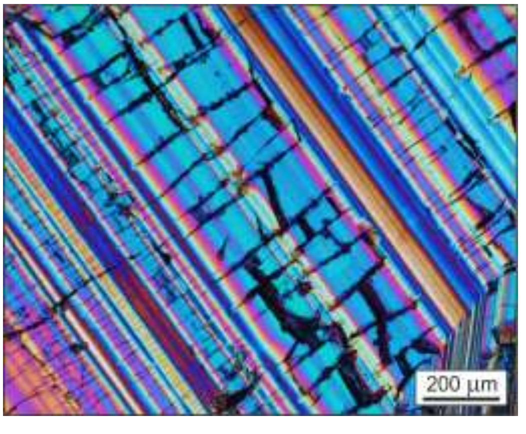

Figure 1 - Photomicrograph (obtained in cross-polarised transmitted light) of a thin section of the strongly zoned Sri Lanka zircon sample 4601 (for details see Chakoumakos *et al.*, 1987). Elevated volume expansion of more radiation-damaged growth zones (recognised from lowered interference colours) has caused intense fracturing of their neighbouring, less damaged and hence less expanded growth zones.

It was only shown much later (Nasdala *et al*., 2004) that, in contrast to previous assumptions, the Sri Lanka zircon has a thermal annealing history: The Ratnapura material is (uniformly) just about half as metamict as would correspond to complete damage accumulation since the time of its primary formation. The incomplete storage of the radiation damage does not affect the suitability of the Sri Lankan zircon for research addressing irradiation effects; however, it needs to be considered carefully to avoid biased quantitative conclusions (Nasdala *et al*., 2004).

It has turned out that for systematic studies on radiation-damaged zircon, the use of gems is of substantial benefit. Only in the case of a widely homogeneous object, small chips or fractions represent well the entire sample, which is a presumption for the application of a complex of micro- and bulk techniques. Also, gems (of sufficiently large size) are excellent candidates for studies that involve series of experiments to be done on the same material, for instance multiple anneals to investigate the recovery of solid-state properties (Nasdala *et al*., 2004). A number of further examples are given below.

It is well known that the impact of the electron beam during EPMA (electron probe micro-analyser) measurements does not create damage in natural zircon but contributes to local, partial recovery of the initial radiation damage. This was studied recently by Váczi and Nasdala (2013) who found in multiple electron irradiations that the amount of structural reconstitution depends both on irradiation time and beam current, though the correlations are not linear (Figure 2). In multi-technique studies it therefore needs to be considered that micro-analyses of the radiation damage may yield biased results if measurements are placed in, or close to, EPMA analysis spots.

Irradiation of zircon with light (i.e. low-mass) ions with energies in the MeV range was found to cause opposite changes. Nasdala *et al.* (2011) performed multiple helium and oxygen irradiation experiments on a suite of Sri Lankan gem zircon with different degrees of radiation damage. These authors observed the creation of additional, irradiation-induced damage (except for amorphous $ZrSiO_4$ in which ion-irradiation

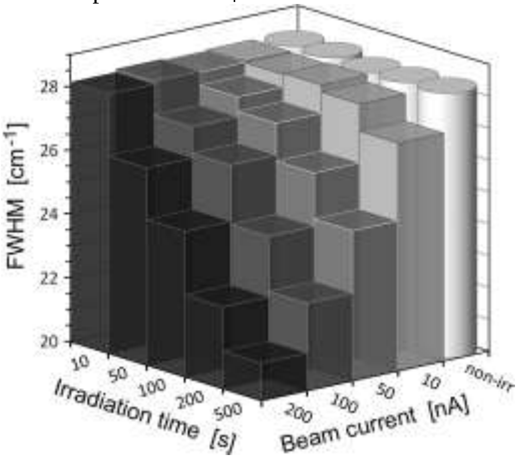

Figure 2 - Partial recovery of the radiation damage in zircon upon electron irradiation of the (strongly damaged) gem zircon G4. Column chart showing the width of the $\nu_3(SiO_4)$ Raman band, which decreases with increasing beam current and irradiation time. From Váczi and Nasdala (2013), modified.

did not cause detectable changes). No indication of notable structural recovery in pre-damaged natural zircon as induced by the light-ion irradiation was found. This observation questions the relevance of the so-called alpha-assisted annealing of fission-track or other radiation damage in natural zircon.

Another excellent example for the use of gem-quality zircon in basic research is a recent helium-diffusion study by Guenthner *et al.* (2013). These authors used pairs of oriented slabs produced from Sri Lanka gems, to investigate quantitatively the directional dependence of the diffusion of radiogenic helium. It is clear that such kind of research can only be done using high-quality, homogeneous samples (whereas for instance the sample shown in Figure 1, due to its zoning and fractures, would be decidedly unsuitable here).

Spectral changes of zircon affected by elevated pressure or compressive strain were investigated by Nasdala *et al.* (2008a) who subjected small chips of well-characterised gems to DAC (diamond anvil cell) experiments. These authors found that, almost independent from the sample's radiation-damage, widths of Raman bands show only minor changes with pressure. For zircon inclusions in other gem materials, notably broadened Raman bands hence cannot be assigned to compressive strain acting on the inclusions, but are a reliable indicator of self-irradiation damage. This in turn allows one to exclude any high-temperature treatment of the gem specimen (because otherwise the damage in the included zircon would have been annealed).

With the examples above, we attempt to underline that, among the Sri Lanka zircon, the most useful material for research purposes are homogeneous, un-altered stones of gem quality. The primary origin of such samples is still somewhat controversial. The Ratnapura zircon, due to its common primary zoning (Figure 1), is generally assigned to an igneous growth milieu (Chakoumakos *et al.*, 1987; Kröner *et al.*, 1987). Unzoned gems such as CZ3 and M257, in contrast, yield $\delta^{18}O$ values well above 13 ‰ VSMOW (Vienna Standard Mean Ocean Water); clearly higher than what is typical of igneous zircon (Figure 3). Cavosie *et al.* (2011) suggested that such gems must have a metamorphic genesis, presumably originating from a marble or Ca-silicate skarn. This rock, if still existing, remains undiscovered thus far.

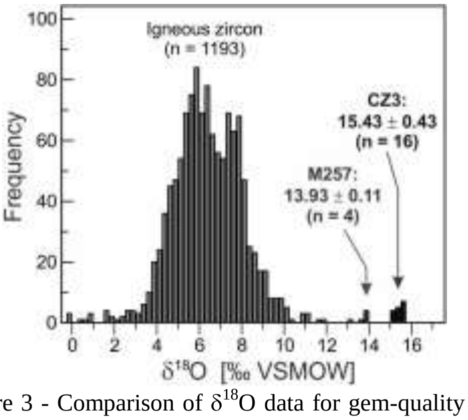

Figure 3 - Comparison of $\delta^{18}O$ data for gem-quality references CZ3 (Cavosie *et al.* 2011) and M257 (Nasdala *et al.* 2008b) with those for igneous zircon from localities worldwide (Valley *et al.* 2005).

Acknowledgments

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