Mineralogical characterisation of gem zircon from Ratanakiri, Cambodia

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Heat treatment is commonly done to improve the colour of gemstones. In the case of gem zircon, the highly priced blue-coloured material is produced from reddish brown raw stones by heat treatment under reducing conditions at ca. 1000 °C for several hours. Especially zircon from the Ban Lung area, Ratanakiri province, Cambodia, is susceptible to this colour change (Fig. 1; see also Balmer et al. 2009; Smith and Balmer 2009). The cause of the blue colour, and the reason for the particularly rich colouration of the Ratanakiri material, are still controversial; these problems are currently addressed in a joint research conducted at Universität Wien and Burapha University, Chanthaburi. Here we report results of a preliminary study done to characterise the raw material and especially its structural state (i.e. degree of radiation damage).

The Ratanakiri gem zircon is extracted from sediments or gravels in numerous small mines, mostly from layers at ca. 2–15 metres below the Earth's surface. The zircon originates from young volcanic rocks (tholeiitic basalts or pyroclastic rocks) with ages in the range 0.8–4.3 Ma (Hoang et al. 1998; Rangin et al. 1995).

We have studied a series of large, gem-quality specimens that were first crystallographically oriented on a four-circle X-ray diffractometer. Specimens were cut in half along the crystallographic c-axis. One half was then subjected to heat treatment whereas the second half was left in its original state. Both halves were then prepared as doubly polished sections. This enabled us to analyse chemically and texturally equivalent specimens with matching faces, hence providing direct comparability of untreated (brown) and treated (blue) material.

Fig. 1. *Image of a gem-quality zircon specimen (longest dimension 17 mm) from Bo Keo that was cut in two halves. The right half was subjected to heat treatment whereas the left half is in its initial state.*

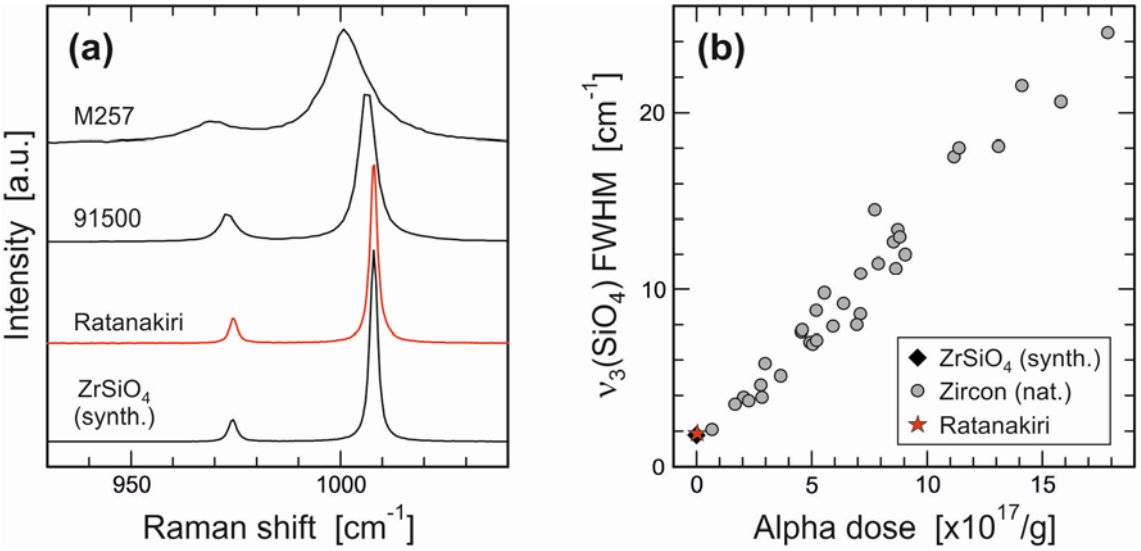

Fig. 2. *(**a**) Raman spectrum of the Ratanakiri zircon in comparison with reference samples, including synthetic $ZrSiO_4$, zircon 91500 (Wiedenbeck et al. 2004; mildly radiation-damaged) and M257 (Nasdala et al. 2008; moderately radiation-damaged). (**b**) Plot of the width of the main Raman band versus alpha dose for a range of zircon samples (from Nasdala et al. 2004, modified). Note that spectral parameters of the Ratanakiri zircon are indistinguishable from those of synthetic $ZrSiO_4$, indicating that the Ratanakiri zircon has accumulated extremely low amounts of radiation damage.*

The Ratanakiri zircon was found to be relatively uniform in chemical composition, with generally low contents of non-formula elements. The HfO_2 content averages ca. 0.7 wt%, and the actinides U and Th have low concentrations of 40–240 ppm and 10–270 ppm, respectively. This results in a remarkably low time-integrated self-irradiation dose on the order of 10^{16} alpha-decay events per gram. Note that readily detectable radiation damage is observed after accumulation of $0.1–0.2 \times 10^{18}$ α/g, and complete metamictisation requires ca. $5–10 \times 10^{18}$ α/g (Nasdala et al. 2004, and references therein). The amount of radiation damage in the Ratanakiri zircon was correspondingly found to be negligible.

As a consequence, the heat treatment does not result in measurable structural reconstitution. Unit-cell constants, Raman spectral parameters, and widths of Nd^{3+} emissions obtained from untreated and treated samples are indistinguishable and do not vary notably from data for synthetic $ZrSiO_4$ (Fig. 2). Reliable detection of colour enhancement appears hence difficult in case of the nearly non-radiation-damaged Ratanakiri material.

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