

## Incomplete retention of radiation damage in zircon from Sri Lanka

LUTZ NASDALA,<sup>1,\*</sup> PETER W. REINERS,<sup>2</sup> JOHN I. GARVER,<sup>3</sup> ALLEN K. KENNEDY,<sup>4</sup>  
RICHARD A. STERN,<sup>5</sup> ETIENNE BALAN,<sup>6</sup> AND RICHARD WIRTH<sup>7</sup>

<sup>1</sup>Institut für Geowissenschaften–Mineralogie, Johannes Gutenberg-Universität, D-55099 Mainz, Germany

<sup>2</sup>Department of Geology and Geophysics, Yale University, New Haven, Connecticut 06520-8109, U.S.A.

<sup>3</sup>Department of Geology, Union College, Schenectady, New York 12308-2311, U.S.A.

<sup>4</sup>Department of Applied Physics, Curtin University of Technology, GPO Box U1987, Perth, Western Australia 6001, Australia

<sup>5</sup>J.C. Roddick Ion Microprobe Laboratory, Geological Survey of Canada, Natural Resources Canada, Ottawa, Ontario, Canada K1A 0E8

<sup>6</sup>Laboratoire de Minéralogie-Cristallographie, UMR CNRS 7590, Universités Paris VI and VII, IPGP, 75252 Paris Cedex 05, France

<sup>7</sup>GeoForschungsZentrum Potsdam, D-14473 Potsdam, Germany

### ABSTRACT

A suite of 18 zircon gemstones from placers in the Highland/Southwestern Complex, Sri Lanka, were subjected to a comprehensive study of their radiation damages and ages. The investigation included X-ray diffraction, Raman and PL spectroscopy, electron microprobe, PIXE and HRTEM analysis, as well as (U-Th)/He and SHRIMP U-Th-Pb age determinations. Zircon samples described in this study are virtually homogeneous. They cover the range from slightly metamict to nearly amorphous. Generally concordant U-Th-Pb ages averaging  $555 \pm 11$  Ma were obtained. Late Ordovician zircon (U-Th)/He ages scattering around  $443 \pm 9$  Ma correspond reasonably well with previously determined biotite Rb-Sr ages for rocks from the HSWC. Slightly to moderately metamict zircon has retained the radiogenic He whereas only strongly radiation-damaged zircon (calculated total fluences exceeding  $\sim 3.5 \times 10^{18}$   $\alpha$ -events/g) has experienced significant He loss. When compared to unannealed zircon from other localities, Sri Lanka zircon is about half as metamict as would correspond to complete damage accumulation over a  $\sim 555$  m.y. lasting self-irradiation period, suggesting significant annealing of the structural radiation damage. Insufficient consideration of this has often resulted in significant underestimation of radiation effects in zircon. We suggest to estimate “effective  $\alpha$ -doses” for Sri Lanka zircon by multiplying total  $\alpha$ -fluences, which were calculated using the zircon U-Th-Pb age, by a correction factor of 0.55. This conversion may be applied to literature data as well, because all gem-zircon samples from Sri Lanka (this work and previous studies) seem to reveal the same general trends of property changes depending on the radiation damage. The use of “effective  $\alpha$ -doses” for Sri Lanka zircon contributes to more reliable quantitative estimates of radiation effects and makes possible direct comparison between natural and synthetic radiation-damaged zircon.

### INTRODUCTION

The majority of research addressing the metamictization process and its structural and chemical effects in natural zircon has been done on gem-quality samples from the Highland/Southwestern Complex (HSWC), Sri Lanka (e.g., Holland and Gottfried 1955; Hurlley et al. 1956; Pidgeon et al. 1966, 1972; Vance and Anderson 1972a, 1972b; Wasiliewski et al. 1973; Sahama 1981; Murakami et al. 1986, 1991; Aines and Rossman 1986; Chakoumakos et al. 1987; Woodhead et al. 1991; Mursic et al. 1992; Ellsworth et al. 1994; McLaren et al. 1994; Nasdala et al. 1995, 2001; Biagini et al. 1997; Pidgeon et al. 1998; Salje et al. 1999; Ríos and Salje 1999; Ríos et al. 2000a, 2000b; Capitani et al. 2000; Zhang et al. 2000, 2002; Farnan and Salje 2001; Geisler et al. 2001a, 2001b; Zhang and Salje 2001). Probable reasons for the particular suitability and preferred use of Sri Lanka zircon for such studies include the frequent gem quality, the availability of large crystals covering a wide range of radiation damage, and the relative rarity of chemical alteration

such as secondary Pb loss. Due to these extraordinary properties, zircon samples from Sri Lanka are currently being used as international intra-lab standards by several research institutions worldwide.

One of the most important tasks in the investigation of natural zircon was, and is, to quantitatively assign radiation-induced property changes to their causal radiation dose. Most radiation damage in natural zircon is generated in  $\alpha$ -decay events (recoiled daughter nuclei and emitted helium cores) whereas spontaneous fission events are negligible in considering bulk metamictization because of their relative rarity. Effects of external irradiation can also be neglected since natural zircon is mostly much higher in actinides (U and Th) than adjacent minerals in the source rock. It has, therefore, become usual to quantify the amount of natural radioactivity experienced by a zircon by time-integrated  $\alpha$ -fluences, calculated from the present U and Th content and age (see, for example, Murakami et al. 1991). For zircon samples from Sri Lanka,  $\alpha$ -fluences have always been calculated using the Neoproterozoic to Early Cambrian zircon U-Th-Pb age. These  $\sim 570$ – $550$  m.y.  $\alpha$ -doses quantify the total self-irradiation over the entire period between zircon growth and the present time. By contrast, the

\* E-mail: nasdala@uni-mainz.de

~570–550 m.y.  $\alpha$ -doses do not quantify the amount of radiation that has effectively caused the present damage. The latter would only be the case if significant damage reconstitution was excluded, which we claim is not true for the Sri Lanka zircon.

Evidence for post-growth annealing of the Sri Lanka zircon has been repeatedly discussed. Holland and Gottfried (1955) observed that relationships of unit-cell parameters and  $\alpha$ -dose were self-consistent for all zircon samples from Sri Lanka but differed from zircon samples from other localities, and they assigned this to slight thermal annealing of Sri Lanka zircon. Vance and Anderson (1972b) concluded from neutron irradiation experiments that Sri Lanka zircon samples underwent some thermal annealing late in their geological histories. Murakami et al. (1991) reported fission track (FT) annealing in Sri Lanka zircon and explained this as an effect of a young thermal event. Meldrum et al. (1998) calculated that Sri Lanka zircon has experienced partial annealing at temperatures of at least ~150 °C. Most obvious indications for incomplete damage retention in Sri Lanka zircon samples were found by comparing them with unannealed zircon. Weber (1990, 1993) and Weber et al. (1994) reported that synthetic  $^{238}\text{Pu}$ -doped zircon reached certain degrees of structural alteration, such as volume swelling, density decrease, and increase of the amorphous fraction, after having experienced significantly lower  $\alpha$ -doses than natural zircon from Sri Lanka. In a recent microprobe study, Nasdala et al. (2001) found that Raman parameters and  $\alpha$ -fluences of unannealed natural zircon and Sri Lanka zircon showed two internally consistent but different trends, which was explained by thermal annealing of the zircon from Sri Lanka. In spite of these indications for incomplete damage retention, however, radiation effects observed in Sri Lanka zircon have always been assigned to total  $\alpha$ -doses calculated for ~550–570 m.y. time periods. Self-irradiation effects, i.e., the amount of damage that is generated by a certain  $\alpha$ -dose, have thus been systematically underestimated.

The goal of the present paper is to verify partial  $\alpha$ -damage annealing as a general feature of the Sri Lanka zircon, and to attempt to quantify the degree of radiation damage retention and structural recovery. For this, we have studied structural state, chemical composition, and ages of 18 widely homogeneous, gemstone-quality samples from Sri Lanka. The necessity for avoiding heterogeneous zircon is underlined by the consideration that only homogeneous samples facilitate reliable correlation of results obtained by microscopic and bulk techniques. For example, recent Raman studies by Nasdala et al. (in preparation) indicated that  $\alpha$ -radiation damage may have long-term stability and, correspondingly, high-U zircons are in some cases surrounded by haloes of enhanced metamictization (radii of some 10  $\mu\text{m}$  corresponding to  $\alpha$ -penetration depths). The structural state of narrowly zoned and heterogeneously self-irradiated zircon can, therefore, be difficult to interpret. Also, Raman measurements by Zhang et al. (2000) and Palenik et al. (2003) have indicated that at least some of the samples of Murakami et al. (1991) are greatly heterogeneous, with local Raman parameter variations as extensive as 50%. There may be some uncertainty when correlating microprobe data to, for example, bulk unit-cell parameters. Avoidance of heterogeneity such as internal zoning is, therefore, crucial when samples are to be studied with a variety of macro-

and micro-techniques. Even though there exist several suites of zircon crystals from Sri Lanka that were well characterized in previous studies, it seemed, therefore, appropriate to mainly select new samples for this present study while paying particular attention to their internal homogeneity.

## SAMPLES

Samples were pre-selected from a large number of uncut and cut zircon gemstones after thorough inspection in polarized light using immersion liquids. Zircon crystals described in the present study were clear and transparent and exhibited a range of colors including nearly colorless, lemon-like yellow, hyacinth/pink, smoky brown, and bottle-green. Their sizes were 5–12 mm and weights of stones were in the range 1.5–10 ct (0.3–2.0 g). All of the stones were from secondary deposits, i.e., gemstone placers located in the central Sri Lankan granulite belt, preferentially in the Ratnapura district. Source rocks and their original locations are not known. It is generally agreed that the gemstone zircon has been derived from post-tectonic, granitoid pegmatites that have intruded into Al-rich sediments (e.g., Munasinghe and Dis-sanayake 1981; Murakami et al. 1991). The area has been assigned to the Highland Series (Cooray 1984), the Highland Group (Milisenda et al. 1988), and the HSWC (Kröner et al. 1991), respectively. The latter term is used in the present study.

Gemstones were sliced and slices were crushed. Fragments were hand-picked with a high power (160 $\times$ ) stereo-zoom microscope with cross-polarization for screening inclusions. Fragments to be subjected to (U-Th)/He dating were digitally photographed in at least two different orientations and dimensions were measured to get rough volume estimates. For X-ray diffraction analysis, fragments were ground in an agate mortar and pestle and powders were put on Si sample holders. For Sensitive High mass-Resolution Ion MicroProbe (SHRIMP) analysis, fragments were embedded in epoxy and round microprobe mounts with a flat surface were prepared. Prior to SHRIMP analysis, backscattered electron (BSE) and cathodoluminescence (CL) images were taken in an electron microprobe. This was done (1) to check for notable heterogeneity such as growth zoning and (2) to make sure polished surfaces were free of inclusions and fissures which could affect the sputtering behavior in the ion probe. Also, the general chemical composition was checked to avoid samples with an unusual content of minor elements. Similar mounts were used for Raman, photoluminescence (PL), and proton microprobe analysis. For transmission electron microscope (TEM) analysis, thin sections were prepared. After being detached from the glass slide, flakes were ion-beam thinned and subsequently carbon coated.

## EXPERIMENTAL DETAILS

### Ion microprobe analysis

Zircon samples were subjected to multiple ion microprobe analyses to determine precise actinide (U and Th) concentrations and their internal heterogeneity, and to reconfirm the Late Precambrian to Early Cambrian U-Th-Pb zircon ages and their concordance. The majority of these analyses were done with the SHRIMP II instrument at Curtin University of Technology (Perth, Western Australia). Zircon samples were irradiated with a focused  $[\text{O}_2]^-$  beam, resulting in 15–20  $\mu\text{m}$  analysis pits. Single analyses consisted of 5–7 cycles through nine peaks ( $^{196}[\text{Zr}_2\text{O}]^+$ ,  $^{204}\text{Pb}^+$ , background,  $^{206}\text{Pb}^+$ ,  $^{207}\text{Pb}^+$ ,  $^{208}\text{Pb}^+$ ,  $^{238}\text{U}^+$ ,  $^{248}[\text{ThO}]^+$  and  $^{254}[\text{UO}]^+$ ). The mass resolution  $M/\Delta M$  was better than 5000. Data for unknowns were calibrated vs.

the CZ3 standard zircon. The experimental technique has been described in more detail elsewhere (Vavra et al. 1996; Nelson 1997). All analyses were corrected for common Pb using the measured  $^{204}\text{Pb}/^{206}\text{Pb}$  ratio, and a common Pb composition calculated from the age using the common Pb curve of Stacey and Kramers (1975), and the correction procedure of Compston et al. (1984).

Zircon samples RB140, M144, B188, and M146 were analyzed by means of the SHRIMP II hosted by the Geological Survey of Canada (Ottawa, Canada). Samples were sputtered with a focused  $[\text{O}^-]$  beam and zircon BR266 (lab no. 5589) was used as the calibration standard. The other experimental conditions corresponded widely to those given above; for details see Stern (1997). Multiple analyses were done of all samples and weighted means were calculated, to increase the precision of the results.

### Uranium-thorium-helium age dating

We report the experimental procedure for the determination of (U-Th)/He ages in more detail because no appropriate description has been published to date. Zircon fragments were loaded into  $\sim 1$  mm Pt foil tubes, which were then loaded into a stainless steel sample planchet in a laser cell with a sapphire window, connected to the He extraction/measurement line. The cell was pumped to  $<10^{-7}$ – $10^{-8}$  torr, and the crystal-bearing Pt tubes were individually heated by lasing with a Nd-YAG laser operated at about 1–5 W for 5–15 min. Blanks were determined by heating empty foil packets using the same procedure. Crystals were checked for quantitative degassing of He by sequential re-extractions. Liberated gas was processed by (1) spiking with  $\sim 0.4$  pmol of  $^3\text{He}$ , (2) cryogenic concentration at 16 K on a charcoal trap, and purification by release at 37 K, and (3) measurement of  $^4\text{He}/^3\text{He}$  ratios with a quadrupole mass spectrometer. Estimated analytical uncertainty on sample He content determinations, including precision and accuracy from original manometric  $^4\text{He}$  standard calibrations, is 1–2%.

Following degassing, zircon samples were removed from foil tubes, spiked with a calibrated  $^{229}\text{Th}$  and  $^{233}\text{U}$  solution, and dissolved in teflon microvials in Parr vessels with HF and  $\text{HNO}_3$ , followed by  $\text{H}_3\text{BO}_3$  to remove fluoride salts and final dissolution in  $\text{HNO}_3$ . Resulting solutions were analyzed by isotope dilution with a Finnigan Element2 inductively coupled plasma mass spectrometer (ICP-MS). Routine precisions and long-term reproducibilities of standard  $^{232}\text{Th}/^{229}\text{Th}$  and  $^{238}\text{U}/^{233}\text{U}$  are 0.1–0.4%, and estimated uncertainty on sample U-Th contents are estimated to be 1–2%. Because these grains are fragments of much larger crystals, no  $\alpha$ -ejection correction was applied.

Replicate analyses of Durango apatite and Fish Canyon Tuff zircon samples during the period of these analyses yielded mean ages of  $32.5 \pm 1.5$  Ma ( $2\sigma$ ;  $n = 37$ ) and  $27.8 \pm 2.4$  Ma ( $2\sigma$ ;  $n = 30$ ), respectively. Two-sigma reproducibility for (U-Th)/He ages of most typically sized zircon samples is 6–8%. However, the apparent reproducibility of ages among these Sri Lankan zircon samples (with the exception of radiation-damaged samples C27, C28, K6, and N17), is 4.5% ( $2\sigma$ ). This is similar to the reproducibility for Durango apatite, which is also dated as small fragments ( $\sim 50$ – $100$   $\mu\text{m}$ ) of much larger crystals ( $\sim 1$ – $3$  cm). Since neither Durango apatite nor Sri Lanka zircon require  $\alpha$ -ejection corrections, this suggests that a large proportion of imprecision in typical samples arises from application of  $\alpha$ -ejection correction; probably specifically from the conventional assumption of homogeneous parent nuclide distribution.

### Spectroscopic analyses

To obtain Raman and laser-induced PL spectra, multiple point measurements were done for each zircon using a Jobin Yvon LabRAM-HR spectrometer. This confocal, notch filter-based system had a focal length of 800 mm and was equipped with Olympus BX41 microscope (50  $\times$  long working distance objective; numerical aperture 0.55) and an Si-based, Peltier-cooled charge-coupled device (CCD) detector. To avoid analysis of unrecognized laser-induced luminescence bands, all Raman spectra were recorded three times, with  $\text{Ar}^+$  4879.86  $\text{\AA}$ ,  $\text{Ar}^+$  5145.32  $\text{\AA}$ , and He-Ne 6328.16  $\text{\AA}$  emission. The laser power was decreased to 1–3 mW (measured after the objective), which is well below the threshold for any spectral changes due to absorption-induced local upheating. A grating with 1800 grooves per mm was used. The spectral resolution was  $\sim 0.5$   $\text{cm}^{-1}$  (red) and  $\sim 1$   $\text{cm}^{-1}$  (blue excitation) and the wavenumber accuracy was  $0.5$   $\text{cm}^{-1}$ . In addition, photoluminescence spectra induced by the  $\text{Ar}^+$  4879.86  $\text{\AA}$  emission were recorded. Using a grating with 950 grooves per mm, the spectral resolution was  $\sim 1$   $\text{cm}^{-1}$  (red) to  $\sim 2$   $\text{cm}^{-1}$  (blue), which converts to  $<0.05$  nm. Wavenumber calibration was done by measuring the Rayleigh line and Ne lamp emissions.

Raman band parameters for little to moderately metamict zircon were determined by band fits assuming Gaussian-Lorentzian shapes. In the case of more

metamict zircon [full width at half-maximum (FWHM) of the  $\nu_3(\text{SiO}_4)$  Raman band at  $\sim 1000$   $\text{cm}^{-1}$  exceeding  $\sim 20$ – $23$   $\text{cm}^{-1}$ ], the background Raman signal of the amorphous phase becomes significant and background correction was done by subtracting a full spectrum of amorphous  $\text{ZrSiO}_4$ . In view of potential band asymmetries at high radiation damage (see Nasdala et al. 2002b), various fit models were applied for FWHM determination and mean values with appropriately large errors are reported to consider the potential uncertainties. Measured FWHMs were corrected for the apparatus function according to Imer (1985). Reported errors for Raman parameters are estimates that include experimental limitations (e.g., wavenumber accuracy, apparatus function), uncertainties related to the fit procedure (background correction and peak shape; compare Nasdala et al. 2002b), and sample heterogeneity.

### Other techniques

Powder diffraction analysis was done by means of a Philips PW 1710 diffractometer using  $\text{CoK}\alpha$  radiation with a diffracted-beam graphite monochromator. The range  $15$ – $120^\circ 2\theta$  was scanned with a step width of  $0.03^\circ 2\theta$ . The counting time was 15 s per step. Unit-cell parameters were determined using the XND Rietveld refinement code (Berar and Balinozzi 1998).

The general chemical composition of the zircon samples was determined by means of a JEOL 8900 RL electron microprobe. The electron beam was focused to a 2  $\mu\text{m}$  spot. The accelerating voltage was 20 kV and the beam current was 100 nA. The usual metal, oxide, and mineral standards were used. Counting times varied between 150 s for main elements and 1350 s (450 s background) for U and Th; for more details see Nasdala et al. (2001). Large uncertainties are to be expected when analyzing low concentrations of Pb in zircon by wavelength-dispersive X-ray analysis in an electron microprobe. Lead was, therefore, determined by means of proton-induced X-ray emission (PIXE) analysis. Measurements were done using the nuclear microprobe at Laboratoire Pierre Sue (CNRS/CEA-Saclay, France). A 3.0 MeV proton beam with a current of  $\sim 1.2$  nA was focused to a  $50 \times 50$   $\mu\text{m}^2$  spot. X-rays were analyzed using a Si-Li detector oriented at  $45^\circ$  and located 57 mm from the sample. A 81  $\mu\text{m}$  Al filter was used to improve counting statistics for the trace and minor elements. X-ray spectra were analyzed with the Gupix software (Johansson and Campbell 1988).

Lattice fringes images and electron diffraction patterns for samples M144, OR1, G3, and N17 were obtained by means of a Philips CM 200 transmission electron microscope equipped with a Gatan imaging filter. The TEM was operated at a voltage of 200 kV. The beam current was 1 nA. For more experimental details compare Wirth et al. (2001a, 2001b).

## RESULTS

### Characterization of samples

General chemical compositions of zircon crystals from Sri Lanka are listed in Table 1. These data are mainly presented to underline that there are no “unusual” amounts of minor elements, which hypothetically could account for notable structural variations among samples. As mostly found for natural zircon,  $\text{HfO}_2$  is the only non-formula constituent in the wt% range. Note that there is no indication of chemical alteration during hydrothermal overprinting or weathering, such as enhanced Ca, Al, P, or Fe concentrations. Actinide oxides ( $\text{UO}_2 + \text{ThO}_2$ ) reach up to several thousand ppm. Data characterizing the structural state of samples are presented in Table 2. Following Nasdala et al. (1995, 1998a), the broadening (FWHM) of the  $\nu_3(\text{SiO}_4)$  Raman band at  $\sim 1000$   $\text{cm}^{-1}$  ( $B_{1g}$  mode) was used to estimate the degree of radiation damage. Correspondingly, samples are listed in Tables 1–3 according to increasing metamictization. Table 3 presents precise U and Th values determined by SHRIMP analysis and results of age determinations. Following Holland and Gottfried (1955) and Murakami et al. (1991), and assuming present natural abundances of 0.72 %  $^{235}\text{U}$  and 99.28 %  $^{238}\text{U}$ , time-integrated  $\alpha$ -doses were calculated from actinide concentrations ( $c$ , in ppm) and

**TABLE 1.** General chemical characterization of zircon samples from Sri Lanka

Sample	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	FeO	Y <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	HfO <sub>2</sub>	Yb <sub>2</sub> O <sub>3</sub>	PbO	ThO <sub>2</sub>	UO <sub>2</sub>	Total	Remarks
RB140	32.8	0.01	0.01	0.11	65.0	1.14	0.03	0.003	0.02	0.03	99.2	*
M144	32.8	n.d.	0.01	0.02	65.3	0.94	0.01	0.006	0.02	0.05	99.2	*
CZ3	32.3	n.d.	n.d.	0.01	65.9	1.25	0.02	0.01	n.d.	0.06	99.6	
B188	32.7	n.d.	0.01	0.02	65.4	1.05	0.01	0.008	0.01	0.06	99.3	*
BR1	32.8	n.d.	0.01	0.01	65.6	0.88	0.01	0.006	0.01	0.09	99.4	*
BR231	32.6	n.d.	0.01	0.01	65.1	1.22	n.d.	0.010	0.01	0.09	99.1	*
BR266	32.9	n.d.	0.01	0.03	65.9	0.80	0.01	0.010	0.02	0.11	99.8	*
M146	32.9	n.d.	n.d.	0.03	65.4	1.10	0.02	0.014	0.05	0.11	99.6	*
K5	32.2	n.d.	n.d.	0.02	65.8	0.79	0.03	0.01	0.01	0.09	99.0	
OR1	32.9	n.d.	0.01	0.12	65.2	1.18	0.03	0.012	0.03	0.17	99.7	*
K4	32.5	n.d.	n.d.	0.01	65.7	0.99	0.03	0.01	0.04	0.15	99.4	
G168	32.8	n.d.	0.01	0.03	65.2	1.12	0.01	0.015	0.03	0.17	99.4	*
G4	32.8	n.d.	0.01	0.03	64.8	1.34	0.01	0.026	0.04	0.29	99.3	*
C27	32.4	n.d.	0.01	0.05	65.6	0.98	0.03	0.02	0.07	0.21	99.4	
C28	32.3	0.02	n.d.	0.11	64.9	1.07	0.05	0.03	0.08	0.31	98.9	
G3	32.6	0.06	0.01	0.17	64.3	1.82	0.04	0.024	0.06	0.31	99.4	*
K6	32.7	0.02	n.d.	0.13	64.9	1.33	0.06	0.03	0.10	0.38	99.6	
N17	32.8	0.05	n.d.	0.04	65.0	1.95	n.d.	0.06	0.04	0.75	100.7	†
H4 (treated)	32.8	n.d.	0.01	0.02	65.5	0.91	n.d.	0.007	0.01	0.06	99.3	*
N17 annealed	32.8	0.05	n.d.	0.04	64.3	1.94	n.d.	n.d.	0.04	0.72	99.9	†

Notes: Values are given in wt%. Only major and minor oxides with concentrations  $\geq 0.01$  wt% are reported. All values are means of multiple electron microprobe analyses.

n.d. = Not detected or calculated mean  $< 0.01$  wt%.

\* Lead oxide content calculated from Pb concentrations determined by means of PIXE analysis.

† Data from Nasdala et al. (2002a).

**TABLE 2.** Structural parameters of zircon samples from Sri Lanka and synthetic ZrSiO<sub>4</sub>

Sample	X-ray powder diffraction data			Raman data		Remarks
	<i>a</i> <sub>0</sub> (Å)	<i>c</i> <sub>0</sub> (Å)	Cell volume (Å <sup>3</sup> )	FWHM (cm <sup>-1</sup> )	Shift (cm <sup>-1</sup> )	
RB140	6.612(1)	6.000(2)	262.31(16)	6.3 ± 0.5	1004.7 ± 0.5	
M144	6.614(3)	6.007(4)	262.78(42)	7.2 ± 0.5	1003.7 ± 0.5	
CZ3	6.6156(4)	6.0129(6)	263.16(3)	8.2 ± 0.5	1004.0 ± 0.5	
B188	6.617(1)	6.014(2)	263.32(17)	8.5 ± 0.5	1002.9 ± 0.5	
BR1	6.623(2)	6.023(2)	264.19(24)	10.9 ± 0.8	1001.4 ± 0.5	
BR231	6.632(2)	6.030(2)	265.22(25)	11.0 ± 0.8	1000.6 ± 0.5	
BR266	6.631(1)	6.029(1)	265.13(7)	13.3 ± 1.0	1000.0 ± 0.5	*
M146	6.633(2)	6.035(4)	265.52(34)	13.6 ± 1.0	1000.2 ± 0.5	
K5	6.636(2)	6.037(2)	265.85(25)	14.5 ± 1.0	1000.5 ± 0.5	
OR1	6.670(5)	6.065(5)	269.83(62)	20.7 ± 1.5	996.0 ± 0.5	
K4	6.666(3)	6.076(8)	269.99(59)	23.0 ± 2.0	996.8 ± 0.5	
G168	6.705(5)	6.095(5)	274.01(63)	24.5 ± 2.0	995.3 ± 0.5	
G4	n.d.	n.d.	n.d.	28.1 ± 2.0	996.9 ± 0.5	
C27	6.705(5)	6.105(10)	274.46(86)	29.3 ± 3.0	996.5 ± 0.5	
C28	n.d.	n.d.	n.d.	30.3 ± 3.0	998.3 ± 0.5	
G3	n.d.	n.d.	n.d.	30.4 ± 2.5	996.2 ± 0.5	
K6	n.d.	n.d.	n.d.	30.4 ± 3.0	996.9 ± 0.5	
N17	n.d.	n.d.	n.d.	n.d.	n.d.	†
ZrSiO <sub>4</sub>	6.604	5.979	260.76	1.8 ± 0.5	1008.3 ± 0.5	‡
synthetic						
H4	6.603(1)	6.004(1)	261.77(12)	6.8 ± 0.5	1005.1 ± 0.5	
(treated)						
N17	6.6060(2)	5.9826(2)	261.08(1)	2.6 ± 0.5	1007.7 ± 0.5	†
annealed						

Note: Raman parameters are given for the  $\nu_3$ (SiO<sub>4</sub>) vibration ( $B_{1g}$  mode) of crystalline zircon or the remnant crystalline fraction, respectively.

n.d. = Reliable determination impossible due to insufficient signal.

\* Unit-cell parameters from Stern (2001).

† Data from Nasdala et al. (2002a).

‡ Unit-cell parameters were taken from the ICDD-PDF (International Centre for Diffraction Data, Powder Diffraction File) 6-266; Raman data were obtained from a synthetic pure ZrSiO<sub>4</sub> crystal grown by J.M. Hanchar (flux synthesis; see Hanchar et al. 2001).

U-Th-Pb age (*t*) according to

$$D_{\alpha} = \frac{6 \cdot c_{\text{Tl}} \cdot N_{\text{A}}}{10^6 \cdot M_{232}} \cdot (e^{1.232 \cdot t} - 1) + \frac{7 \cdot c_{\text{Y}} \cdot 0.0072 \cdot N_{\text{A}}}{10^6 \cdot M_{235}} \cdot (e^{1.235 \cdot t} - 1) + \frac{8 \cdot c_{\text{Y}} \cdot 0.9928 \cdot N_{\text{A}}}{10^6 \cdot M_{238}} \cdot (e^{1.238 \cdot t} - 1)$$

where  $N_{\text{A}}$  = Avogadro's number ( $6.022 \times 10^{23}$  atoms/mol),  $M$  = molecular weight of the parent isotope, and  $\lambda$  = decay constant. We will refer to these doses as calculated or total, respectively.

It is not a purpose of the present work to describe in detail the metamictization process in zircon and resulting property changes. Instead, we refer to the large number of papers dealing with this problem which have appeared previously (see Ewing et al. 2003). Analytical data were mainly obtained in the present study to characterize comprehensively the discussed samples and to provide comparability with previously published data for zircon from Sri Lanka. Therefore, we will only briefly summarize observations of structural changes in the following. By contrast, accompanying property changes, such as decreasing density (e.g., Holland and Gottfried 1955), changes in elastic moduli (e.g., Özkan 1976), decreasing refraction and birefringence (e.g., Morgan and Auer 1941; Sahama 1981) and the generally decreased chemical resistance of radiation-damaged zircon (e.g., Pidgeon et al. 1966, 1972; Rizvanova et al. 2000), which have been studied in great detail elsewhere, will not be discussed here.

Long-term self-irradiation of Sri Lanka zircon has resulted in marked deviations from the initial crystallinity, which is seen from peculiar microstructural features observed in TEM images as well as disturbed short-range and long-range orders. In the TEM, radiation-induced damage is directly seen in lattice fringe images (Fig. 1). The amorphous volume fraction increases with progressive metamictization and, simultaneously, both short-range and long-range orders of crystalline remnants decrease (compare, for instance, Murakami et al. 1991; Weber et al. 1994). Correspondingly, strongly metamict zircon well above the percolation point (calculated total  $\alpha$ -dose  $> 3.5 \times 10^{18}$   $\alpha/\text{g}$ ; Salje et al. 1999) consists of crystalline remnants embedded in an amorphous matrix (Fig. 1c), whereas highly metamict zircon (calculated total  $\alpha$ -dose  $\sim 11 \times 10^{18}$   $\alpha/\text{g}$ ) is almost fully amorphous as determined by TEM (Fig. 1d). Analogous information is obtained from electron diffraction patterns in which the dif-

**TABLE 3.** Ion microprobe data and ages for zircon samples from Sri Lanka

Sample	U (ppm)	Th (ppm)	$^{206}\text{Pb}/^{238}\text{U}$ age (Ma)	Calculated alpha dose ( $\times 10^{18}/\text{g}$ )	(U-Th)/He age (Ma)	Remarks
RB140	288 $\pm$ 3	122 $\pm$ 1	566 $\pm$ 3	0.61–0.62	437 $\pm$ 20	
M144	436 $\pm$ 7	140 $\pm$ 3	552 $\pm$ 6	0.86–0.91	430 $\pm$ 20	
CZ3	550 $\pm$ 10	30 $\pm$ 2	563.9 $\pm$ 1.3	1.05–1.10	n.d.	*, †
B188	556 $\pm$ 24	59 $\pm$ 4	559 $\pm$ 8	1.03–1.15	438 $\pm$ 20	
BR1	796 $\pm$ 13	39 $\pm$ 1	558 $\pm$ 13	1.47–1.60	n.d.	
BR231	772 $\pm$ 10	109 $\pm$ 2	571 $\pm$ 4	1.53–1.59	n.d.	*
K5	857 $\pm$ 21	107 $\pm$ 8	555 $\pm$ 6	1.61–1.74	460 $\pm$ 21	
BR266	909 $\pm$ 27	201 $\pm$ 7	559.0 $\pm$ 0.3	1.77–1.88	449 $\pm$ 21	†, ‡
M146	923 $\pm$ 17	411 $\pm$ 9	567 $\pm$ 4	1.92–2.03	434 $\pm$ 20	
					457 $\pm$ 21	
					433 $\pm$ 20	
					450 $\pm$ 21	
K4	1325 $\pm$ 30	327 $\pm$ 13	559 $\pm$ 5	2.59–2.77	444 $\pm$ 21	
OR1	1490 $\pm$ 70	279 $\pm$ 18	522 $\pm$ 3	2.62–2.92	n.d.	*
G168	1499 $\pm$ 33	257 $\pm$ 9	547 $\pm$ 3	2.83–3.00	450 $\pm$ 21	*
C27	1945 $\pm$ 43	625 $\pm$ 26	559 $\pm$ 4	3.87–4.12	381 $\pm$ 18	
G4	2355 $\pm$ 84	330 $\pm$ 12	564 $\pm$ 5	4.48–4.91	n.d.	*
G3	2572 $\pm$ 96	585 $\pm$ 34	542 $\pm$ 5	4.77–5.25	441 $\pm$ 21	*
C28	2759 $\pm$ 73	696 $\pm$ 21	552 $\pm$ 4	5.32–5.70	396 $\pm$ 18	
K6	3087 $\pm$ 106	810 $\pm$ 35	548 $\pm$ 5	5.86–6.40	28.3 $\pm$ 1.4	
N17	5568 $\pm$ 114	344 $\pm$ 45	551 $\pm$ 7	10.27–11.02	99.2 $\pm$ 4.6	§,
H4 (treated)	550 $\pm$ 2	107 $\pm$ 1	553 $\pm$ 5	1.08–1.09	437 $\pm$ 20	
					429 $\pm$ 20	
N17 annealed	5753	382	0	0	n.d.	§

Notes: Alpha-fluences were calculated from U and Th content and U-Th-Pb age; the U-Th-Pb ages are weighted means, quoted at the 95 % confidence level; individual (U-Th)/He ages are given with  $2\sigma$  errors; n.d. = not determined.

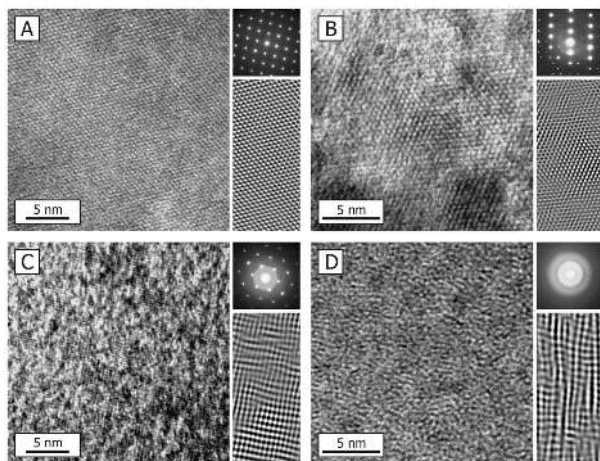
\* U-Th-Pb data from Kennedy (2000).

† reported  $^{206}\text{Pb}/^{238}\text{U}$  ages of the two zircon SHRIMP lab-standards CZ3 (Perth) and BR266 (Ottawa) were determined by isotope dilution TIMS analysis.

‡ U-Th-Pb data from Stern (2001).

§ U-Th-Pb data from Nasdala et al. (2002a).

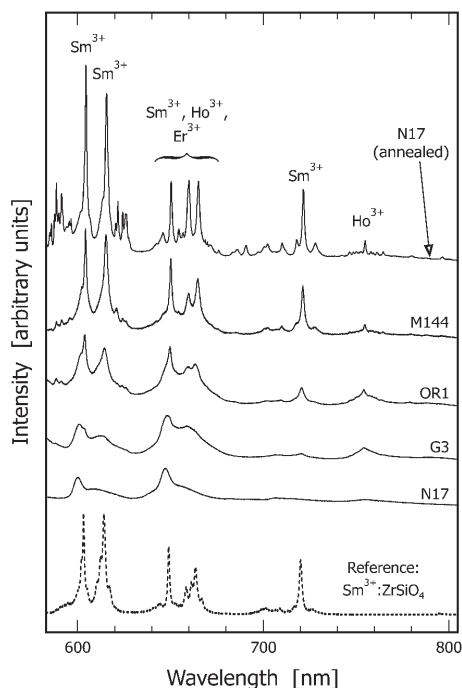
|| The  $^{207}\text{Pb}/^{206}\text{Pb}$  age is given for sample N17.



**FIGURE 1.** Results of HRTEM investigations of four zircon samples. (a) Zircon M144, little radiation-damaged. (b) Zircon OR1, moderately radiation-damaged. (c) Zircon G3, strongly radiation-damaged. (d) Zircon N17, nearly amorphous. Lattice images (main photographs) are shown together with the corresponding electron diffraction patterns (upper right photographs). The lower right photographs are detail enlargements of Fourier-filtered versions of the same lattice images.

fuse “amorphous” halo increases in intensity whereas diffraction maximums of the crystalline phase fade and broaden and finally disappear (Fig. 1).

The short-range order of zircon can be probed by means of various spectroscopic techniques. As an example, we present several laser-induced PL spectra in Figure 2. Spectra are dominated by groups of emission lines related to rare-earth element (REE) centers (for band assignment compare Gaft et al. 2000,



**FIGURE 2.** Laser-induced photoluminescence spectra obtained from Sri Lanka zircon crystals, showing the red and near infrared range of the electromagnetic spectrum. Spectra are stacked for more clarity. Four untreated zircon samples range from highly (N17) to poorly metamict (M144) whereas the fully annealed chip of N17 (spectrum at top) is crystalline. Note the clear broadening of all normally narrow REE emission lines with increasing radiation damage. To support the line assignment, the PL spectrum of a synthetic zircon doped with Sm and P (sample courtesy of J.M. Hanchar) is shown for comparison.

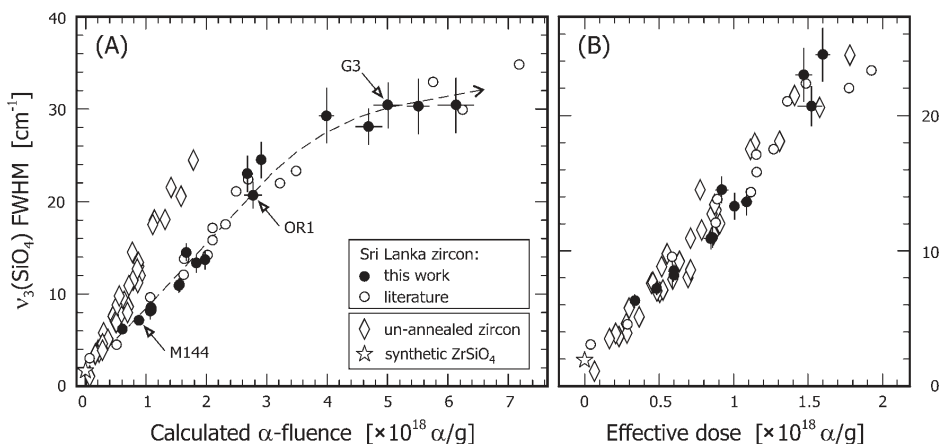
2001; Nasdala et al. 2003). Patterns of relative line intensities are not directly comparable because analyzed samples are likely to have somewhat different REE concentration ratios. All spectra, however, show clear dependence of the widths of emission lines on the degree of radiation damage. In Figure 2, this is particularly striking for the groups of intense  $\text{Sm}^{3+}$  emissions near 604 and 615 nm ( $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$  transitions). The general REE $^{3+}$  band broadening with increasing radiation damage is interpreted to reflect greatly decreased short-range order and crystal-field effects around REE $^{3+}$  sites. Similar observations were made by Panczer (2001) who found that bandwidths of  $\text{Dy}^{3+}$  emissions depended on the metamictization of zircon. Decreased short-range order around the  $\text{Si}^{4+}$  sites in the remnant crystalline phase is revealed by the broadening of internal  $\text{SiO}_4$  vibrations analyzed by Raman spectroscopy. Figure 3 shows that up to calculated doses of about  $3\text{--}4 \times 10^{18} \alpha/\text{g}$ , the FWHM of this Raman band increases almost linearly with the  $\alpha$ -dose, whereas the band broadening is less significant above this damage level, apparently reaching some saturation at very high doses. Note that even though this principal behavior is highly reminiscent of property changes according to the direct impact model for metamictization (e.g., Weber 1990; Rfios et al. 2000a; Ewing et al. 2003), our Raman data support neither the double overlap nor the direct impact amorphization hypothesis. The nearly linear FWHM increase at low to moderate damage levels is mainly due to the nearly linear increase of the point defect density in the crystalline phase (recall that a Raman band of the crystalline phase is discussed here). Therefore, the almost linear  $\nu_3(\text{SiO}_4)$  FWHM increase cannot be used to assess the (linear or sigmoidal) increase of the volume fraction of the amorphous phase. For more details on the Raman spectroscopic estimation of the degree of metamictization see Nasdala et al. (1995, 2001, 2002b). Other spectroscopic studies on effects of decreased short-range order in metamict zircon

include, for example, infrared absorption (Zhang and Salje 2001), X-ray absorption (Farges 1994), and nuclear magnetic resonance (NMR; Farnan 1999; Farnan and Salje 2001; for an overview see Nasdala et al. 2003).

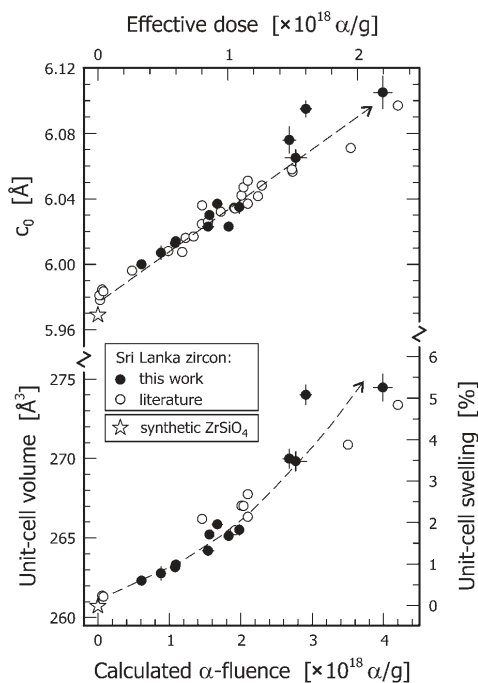
The long-range order and crystallinity, respectively, of Sri Lanka zircon has been studied in most cases using X-ray powder diffraction analysis. With increasing radiation damage, Bragg peaks shift to lower  $2\theta$  values and become broadened, asymmetric, and dramatically less intense (e.g., Holland and Gottfried 1955; Murakami et al. 1986, 1991). The increase of the unit-cell volume as a function of the self-irradiation dose is shown in Figure 4. The apparently sigmoidal swelling behavior of zircon (Holland and Gottfried 1955; Weber 1990; Salje et al. 1999) is mainly due to sigmoidal expansion of  $a_0$  (note that only the lower part of the S-shaped curve is seen in Fig. 4 of the present paper). Weber (1990) has interpreted this as a result of initial structural reconstitution, causing preferential relaxation along the  $a$ -axis. The unit-cell parameter  $c_0$  increases almost linearly or, more exactly, follows an almost straight, exponential curve (Weber 1990, 1993; see again Fig. 4). Note that after reaching an expansion of 6% relative at a total calculated dose of  $\sim 4 \times 10^{18} \alpha/\text{g}$ , the unit-cell volume is not expected to increase any further (Salje et al. 1999; not discernible in Fig. 4 of this work).

#### Age determinations

Ages of the zircon samples were determined by means of SHRIMP analysis (Table 3). Independent of their degrees of radiation damage, all samples gave concordant U-Th-Pb ages. Apart from one measurement on the most radiation-damaged zircon N17, which revealed an initial Pb loss of about 5% (Nasdala et al. 2002a), there was no indication for any notable secondary loss of radiogenic Pb. The zircon U-Th-Pb ages obtained in the present study average  $555 \pm 11$  Ma (Table 3), which is in re-



**FIGURE 3.** Broadening of the  $\nu_3(\text{SiO}_4)$  Raman band ( $B_{1g}$  mode at  $\sim 1000 \text{ cm}^{-1}$ ) plotted vs. self-irradiation dose. Reference data for Sri Lanka zircon from Zhang et al. (2000; original source for  $\alpha$ -doses was Murakami et al. 1991) and Nasdala et al. (2001). Data for unannealed zircon from Nasdala et al. (2001; original sources for a portion of the data were Wopenka et al. 1996 and Nasdala et al. 1998b, 1999). Data pairs for three samples (M144, little damaged; OR1, moderately metamict; G3, strongly metamict) that were subjected to PL and HRTEM analysis (Figs. 1 and 2) are marked with arrows. (a) Total self-irradiation doses calculated from actinide (U and Th) content and U-Th-Pb zircon age. Sri Lanka zircon has accumulated significantly less damage per  $\alpha$ -event than unannealed zircon. (b) When  $\alpha$ -fluences for zircon samples from Sri Lanka are multiplied by 0.55, a uniform damage-dose dependence for both Sri Lanka and unannealed zircon is observed for specimens characterized by  $\nu_3(\text{SiO}_4)$  FWHMs of  $\leq 23 \text{ cm}^{-1}$  (i.e., little to moderately metamict zircon). The thus calculated “effective  $\alpha$ -doses” will also be given on the top abscissa in the following plots (Figs. 4–6).

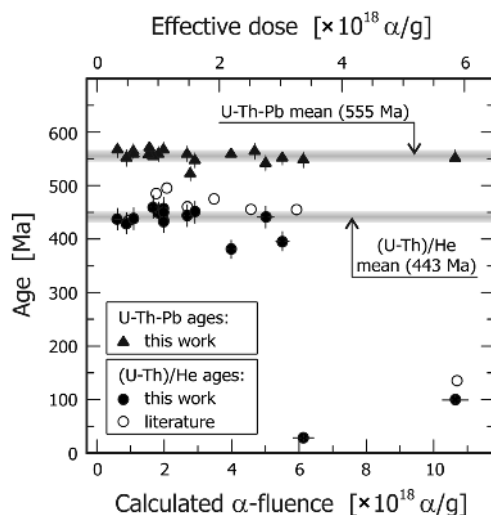


**FIGURE 4.** Unit-cell parameter  $c_0$  and unit-cell volume of the crystalline fraction in Sri Lanka zircon as a function of the self-irradiation dose. Reference data from Holland (1954) and Murakami et al. (1991; “one phase” unit-cell parameters). The relative swelling of the unit-cell volume (right ordinate) refers to the unit-cell parameters of synthetic  $\text{ZrSiO}_4$  (cf. Table 2).

sonable agreement with previous results [570 Ma, Holland and Gottfried (1955); average 564 Ma, Kröner et al. (1987); 580–550 Ma, Hölzl et al. (1991)]. Since zircon U-Th-Pb ages postdate Late Neoproterozoic, high-grade regional metamorphism of the Sri Lankan basement (peak > 600 Ma; Hölzl et al. 1991), they are interpreted as dating post-metamorphic, magmatic zircon growth. The gem-quality crystals under discussion were most probably derived from late- to post-tectonic granites and pegmatites in the HSWC (Rupasinghe and Dissanayake 1987).

Results of (U-Th)/He age determinations are less uniform. Nine slightly to moderately metamict zircon crystals (with calculated total  $\alpha$ -dosages <  $3 \times 10^{18} \alpha/\text{g}$ ; Table 3) gave Late Ordovician ages averaging  $443 \pm 9$  Ma. These ages are interpreted as representing cooling through closure for the (U-Th)/He system of these crystals. Only the strongly radiation-damaged samples with calculated total  $\alpha$ -dosages greater than  $\sim 4 \times 10^{18} \alpha/\text{g}$  (Table 3) have experienced significant secondary (ambient-temperature) loss of radiogenic He (Fig. 5). Note that only these few strongly metamict samples also showed measurable He loss in vacuum while at room temperature; all other samples did not. Assuming all crystals experienced the same thermal history, these observations confirm previous results of Hurley (1954) who found that the ability of zircon to retain radiogenic He is decreased after a zircon has accumulated a significant amount of radiation damage.

The observation that the extent of the secondary loss of radiogenic Pb does not correlate linearly with the degree of radiation



**FIGURE 5.** Results of age determinations for Sri Lanka zircon. Reference data from Hurley et al. (1956). Note that all samples yielded concordant U-Th-Pb ages. Little to moderately radiation-damaged zircon samples gave Late Ordovician (U-Th)/He ages whereas more metamict samples were affected by significant secondary loss of radiogenic He.

damage is of particular interest, especially in view of the fact that the “onset” of secondary He loss seems to correspond reasonably well with the percolation point, which is reached by the Sri Lanka zircon after sustaining a total of  $\sim 3.5 \times 10^{18} \alpha$ -events per gram (Salje et al. 1999; see discussion below). These results suggest that volume diffusion is negligible for the secondary He loss from the Sri Lanka zircon. By contrast, the extensive inter-connection of boundaries between crystalline and amorphous domains at moderate degrees of radiation damage opens up a three-dimensional network of pathways for He migration at low temperatures (i.e., well below nominal closure temperatures). Interestingly, the presence of this pathway network has favored He loss but not yet Pb loss, which reconfirms again that radiation damage enhances the susceptibility for, but does not cause, secondary loss of radiogenic isotopes from zircon (e.g., Nasdala et al. 1998a).

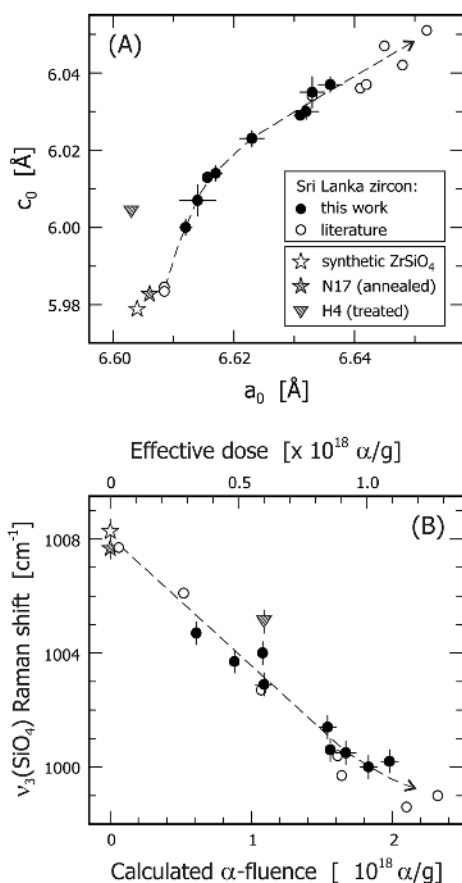
Helium diffusion experiments and calibrations against other thermochronometers indicate a zircon (U-Th)/He closure temperature of about 170–190 °C for typical crystal sizes ( $\sim 60$ – $90 \mu\text{m}$ ) and cooling rates ( $\sim 10^\circ\text{C}/\text{my}$ ) (Reiners et al. 2002; Reiners and Spell 2002). However, several studies have demonstrated that effective closure temperature of the (U-Th)/He systems for apatite and titanite are functions of crystal size (Reiners and Farley 1999; Farley 2000; Reiners and Farley 2001), and preliminary diffusion data suggest that this is probably the case for zircon as well. To estimate zircon (U-Th)/He closure temperatures for the large crystals analyzed in this study, we used He diffusion characteristics measured from several interior fragments of sample M146. These samples yielded Arrhenius plots from cycled step-heating experiments that are very similar to those of typical igneous zircon (Reiners et al. 2002; Reiners and Spell 2002), with  $E_a = 40 \pm 1$  kcal/mol and  $D_0 = 0.1$ – $0.6$   $\text{cm}^2/\text{s}$ . For diffusion domains equivalent to the unusually large original grain dimensions of these crystals (half-widths  $\geq 2.5$ – $5$  mm), and for cooling rates of about 10–50 °C/my, these zircon crystals would

have effective closure temperature of about 250–300 °C.

Two attempts to determine zircon fission-track ages failed. Grains were mounted in FEP Teflon, polished to expose internal grain surfaces, and pre-etched in a KOH-NaOH eutectic melt at 210 °C for 4 h and 228 °C for 1 h. Grains with high degrees of radiation damage tended to be over-etched or dissolved. Grains with lower degree of metamictization were subsequently etched in the same KOH-NaOH melt, but retained sufficient damage to render the grains uncountable for fission track analysis. Note that all zircon crystals discussed in the present study are more  $\alpha$ -damaged than two zircon samples that were successfully FT-dated by Garver (2002). For future FT studies of Sri Lanka zircon, it seems practical to concentrate on crystals showing an exceptionally low degree of radiation damage.

### Degree of damage retention

Comparison of the data set obtained in the present and previous studies reveals that relationships between all structural



**FIGURE 6.** Structural parameters of two laboratory-treated samples compared with untreated Sri Lanka zircon. (a) Trend of anisotropic unit-cell expansion with progressive radiation damage. Reference data from Murakami et al. (1991; “one phase” unit-cell parameters). (b) Raman shift of the main  $\nu_3(\text{SiO}_4)$  band vs. dose. Reference data from Zhang et al. (2000; original source for doses was Murakami et al. 1991). Note that the fully recrystallized sample N17 (heat-treated at 1400 °C for 150 h) plots close to synthetic ZrSiO<sub>4</sub>. Moderate treatment of gemstone H4 is recognized from marked deviations from the progressive trends.

parameters (e.g., unit-cell dimensions, Raman data) and calculated total  $\alpha$ -doses found in the present study are in remarkably close agreement (see Figs. 3–6). This underlines that (1) all Sri Lanka zircon samples are reasonably uniform in terms of their metamictization characteristics and (2) observations and conclusions of the present study can be applied to previously published data as well.

A different observation is made, however, when comparing the Sri Lanka zircon with unannealed zircon (Pu-doped ZrSiO<sub>4</sub>, Weber 1990; natural unannealed zircon, Nasdala et al. 2001). A much higher number of  $\alpha$ -decay events as in unannealed zircon were needed to generate the same amount of structural damage in the Sri Lanka zircon. If zircon crystals from Sri Lanka were also unannealed and had almost completely stored their  $\alpha$ -damage, this difference would imply that other zircon is more and Sri Lanka zircon is less susceptible to the impact of  $\alpha$ -decay events. This, in turn, would point to the improbable existence of different structural types of zircon. Instead, the different trends are explained by radiation-induced parameter changes that are too low for Sri Lanka zircon. Because of significant structural recovery due to thermal annealing, the present structural state does not correspond to the possible total metamictization if  $\alpha$ -damage was accumulated completely over ~550–570 m.y. time periods.

To estimate the degree of  $\alpha$ -damage retention and annealing, respectively, we use data for nearly unannealed natural zircon from four localities, which include a ~4000 Ma old lunar zircon (Wopenka et al. 1996), zircon crystals from a 278 Ma old Saxonian rhyolite (Nasdala et al. 1998b), ~330 Ma old zircon crystals from rapidly uplifted monzonite complex in the Elbe valley (Nasdala et al. 1999), and zircon grains from a ~362 Ma old gabbro from the Odenwald, Germany (Nasdala et al. 2001). These four samples showed a uniform trend of systematic Raman parameter changes in dependence on their  $\alpha$ -fluences (see Fig. 3). Nasdala et al. (2001) have proposed this data set as a first calibration curve for the examination of whether unknown zircon has completely or incompletely retained its radiation damage. Figure 3a underlines that Sri Lanka zircon is clearly not unannealed. By contrast, Sri Lanka zircon is apparently less metamict than expected, considering the total self-irradiation zircon crystallization. It is obvious that the total  $\alpha$ -doses calculated from the U-Th-Pb zircon age overestimate the portion of the self-irradiation that has effectively caused the present level of metamictization. Figure 3b shows that only ~55% of these total  $\alpha$ -doses correspond to the presently observed radiation damage of the Sri Lanka zircon. We suggest, therefore, that one calculates “effective  $\alpha$ -doses” for Sri Lanka zircon by simply multiplying the usually used total doses by 0.55. It is clear that this simple calculation, based on a relatively rough estimate, must result in somewhat uncertain results. Nevertheless, it may help to avoid significant underestimation of radiation effects that need to be considered when quantitatively using total  $\alpha$ -doses for Sri Lanka zircon.

It is generally agreed that the thermal stability of fission tracks (Garver et al. 1999; Rahn 2001) and  $\alpha$ -event damage (Meldrum et al. 1998, 1999) in zircon is lowered with increasing metamictization. By contrast, thermal stabilities of different defect types are still controversial. There are observations indicating preferred



low-*T* annealing of slightly metamict zircon and continuous long-term annealing of point defects (e.g., Murakami et al. 1991; Weber et al. 1994) whereas others have indicated preferred long-term annealing of more metamict zircon and greater stability of point defects (Nasdala et al. 2001). None of these two hypotheses is independently supported by the data obtained in the present study. Conclusions are limited, however, by the fact that the calibration curve in Figure 3a, from which roughly 55% damage retention was estimated for Sri Lanka zircon, spans only low to moderate degrees of radiation damage whereas the degree of damage retention in highly metamict zircon remains more uncertain.

There is, however, an analytical observation that could be relevant for this. We have described above that the Raman band broadening (FWHM increase) of Sri Lanka zircon is accompanied by decreasing Raman band shifts (Table 2). Similar to unannealed zircon, the two parameters correlate almost linearly up to calculated total  $\alpha$ -doses of roughly  $3 \times 10^{18}$   $\alpha/g$  (then reaching Raman shifts of  $-996$   $cm^{-1}$  and FWHMs of  $23 \pm 2$   $cm^{-1}$ ). At higher doses, the  $\nu_3(SiO_4)$  Raman band of Sri Lanka zircon continues to broaden without further Raman shift decrease (Table 2). The same observation was made by Zhang et al. (2000) whereas Geisler et al. (2001b) have even reported re-increased Raman shifts for highly metamict zircon crystals (FWHMs higher than  $25$   $cm^{-1}$ ) from Sri Lanka. This is in apparent contradiction to observations of more extensive Raman shift decrease in the spectra of zircon crystals from other localities. For instance, Nasdala et al. (1998a) have measured a  $\nu_3(SiO_4)$  Raman shift of  $989.5$   $cm^{-1}$  (FWHM  $32$   $cm^{-1}$ ) from a zircon from the Jack Hills, Western Australia, and Balan et al. (2001) reported a Raman shift of  $992.6$   $cm^{-1}$  (FWHM  $26.6$   $cm^{-1}$ ) for a zircon from the Amazon basin, Brazil. The latter observations indicate that Raman spectral changes of highly metamict Sri Lanka zircon do not follow the trend of progressive metamictization. We know that initial structural recovery may lead to significant relaxation (i.e., re-increase) of the Raman shifts whereas the FWHM decrease is much less extensive at this stage (compare Geisler and Pidgeon 2002; Nasdala et al. 2002a). It may, therefore, be suspected that the apparently too low decreases of Raman shifts for strongly radiation-damaged samples from Sri Lanka are also due to some initial recovery. This, if confirmed to be true, would give evidence for a low-grade recovery process that has only affected strongly metamict specimens from Sri Lanka. For more sound evaluation of increasing metamictization on annealing over geological timescales, however, it will be necessary to study additional natural zircon samples, especially with enhanced radiation damage, that have not experienced notable structural recovery. The study of synthetic zircon doped with short-lived  $\alpha$ -emitters [for example, single  $^{238}Pu$ -doped zircon crystals were recently grown by Burakov et al. (2004)] will also prove useful for the understanding of annealing effects in natural zircon.

## DISCUSSION

### Natural or laboratory annealing?

The above observations indicate that Sri Lanka zircon is generally less radiation-damaged than would correspond to continuous and complete  $\alpha$ -damage accumulation since crystallization. This, in turn, suggests that Sri Lanka zircon must have experienced significant structural recovery. Before attempting to

interpret this conclusion, however, we are obliged to check cautiously whether the partial structural reconstitution of Sri Lanka zircon is a natural result of the geological history or alternatively due to some treatment after sampling.

The latter suspicion can be disproved by examining analytical data obtained from zircon samples that were actually treated. It is well known that heat-treatment in the laboratory is unable to directly invert the metamictization process. Heat-treatment does not simply eliminate the  $\alpha$ -event damage step by step, rather progressively damaged and treated samples show different structural features. Zircon samples that have experienced structural recovery through heat-treatment can, therefore, in most cases be distinguished quite easily from naturally annealed but untreated samples. To demonstrate this, we present additional analytical results for two differently treated zircon gemstones in Tables 1–3. Fragments of sample N17 were fully recrystallized through high-*T* annealing at  $1400$   $^{\circ}C$  for  $150$  h. Apart from the polycrystalline microstructure observed in TEM images (Nasdala et al. 2002a), the treatment is most obvious from the escape of radiogenic Pb (complete U-Th-Pb resetting) and the mainly restored short-range order (Raman and PL) and unit-cell parameters (X-ray diffraction). Slight deviations from the structural data of synthetic  $ZrSiO_4$  (compare Fig. 6) are explained by the presence of non-formula elements in sample N17 (Table 1). Sample H4, in contrast, was only moderately heated by a gemstone dealer to improve its yellow color. Here, the treatment was not even intense enough to cause any notable escape of radiogenic Pb and He (Table 3) but partial structural annealing is already observed. If gemstone H4 was untreated, structural parameters similar to those of samples CZ3 and B188 (which have experienced similar  $\alpha$ -doses as H4; cf. Table 1) should have been obtained. By contrast, irradiation-induced parameter changes of H4 are reduced to about  $40$  % (unit-cell swelling) and  $\sim 70$  % (Raman) of the expected deviations from crystalline zircon, respectively. It is interesting to note that the partial reconstitution is more sensitively reflected by X-ray diffraction analysis, which is sensitive to the long-range order, than by Raman spectroscopy. The most obvious indication for the partial structural recovery of sample H4, however, is the miscorrelation of unit-cell parameters  $a_0$  and  $c_0$  (Fig. 6), which is explained by preferential relaxation of the initial expansion along the *a*-axis (e.g., Weber 1990, 1993).

Another argument against treatment is found by the simple consideration that the whole data set for Sri Lanka zircon samples (investigated in the present and all previous studies) is self-consistent. Samples came from different sources and were collected at different times. It would be puzzling if all of them were heat-treated after sampling in the same way, causing identical reconstitution. Note also that in the present and previous studies, some of the samples were collected from gem gravels in central Sri Lanka by the authors themselves. The common practice of professional Sri Lankan gemstone collectors to improve the color and clarity of raw stones before sale by heating them in an open fire, as well as any other heat-treatments, can certainly be excluded at least in these cases.

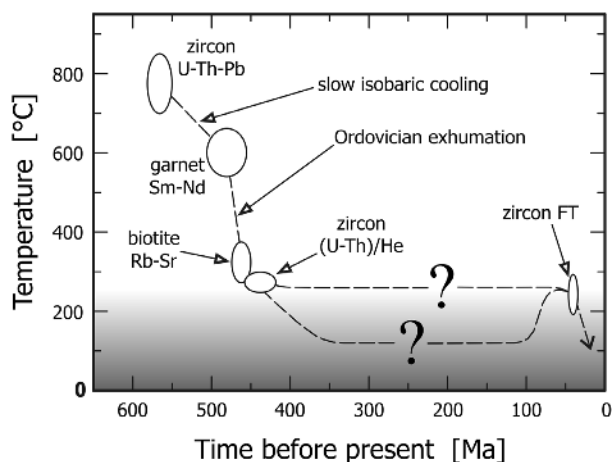
### Post-growth thermal history

As treatment after sampling is excluded, incomplete  $\alpha$ -damage retention must be a natural feature of Sri Lanka zircon. One

possible explanation is that there has been continuous annealing in these crystals, at either enhanced or ambient temperatures (compare Lumpkin and Ewing 1988; Murakami et al. 1991; Weber et al. 1998; Lumpkin 2001). However, if continuous long-term annealing at ambient temperatures was the cause of the relatively low degree of bulk metamictization in Sri Lanka zircon, one would expect to observe even more incomplete damage retention in older zircon samples, which is not the case. There is, for instance, no evidence for continuous annealing in a lunar zircon described by Wopenka et al. (1996), as its radiation damage corresponds very well to the present U and Th content and the estimated age of  $\sim 4.0$  Ga (Nasdala et al. 2001). Similarly, low-U rims in zircon crystals from a  $1,983 \pm 15$  Ma old monzogranitic gneiss from the In Ouzzal Massif, Algeria (Peucat et al. 1996) are as metamict as expected for nearly complete damage accumulation over a  $\sim 2.0$  Ga time period (Nasdala et al. 2001). We do not generally exclude effects of continuous annealing at low, or ambient, temperatures, but it is clear that this process alone is insufficient to explain why only  $\sim 55\%$  of the radiation damage was accumulated by the Sri Lanka zircon.

As long-term recovery of radiation damage is a strong function of temperature (e.g., Meldrum et al. 1998, 1999; Brandon et al. 1998), these observations suggest that the particular thermal history of the Sri Lankan zircon may be responsible for incomplete retention of damage. Annealing includes both the temporarily decreased ability of zircon to store radiation damage that is generated at that particular time, and recovery from previously accumulated damage. Potential causes for this are a prolonged cooling history after closure of the U-Th-Pb system or/and episodic re-heating. In the following, we will attempt to explain the incomplete damage retention in zircon crystals from Sri Lanka by examining their post-growth thermal history. Recall, however, that all zircon samples under discussion came from secondary deposits in the Sri Lankan HSWC. Their source rocks are unknown and, correspondingly, their geological history is uncertain.

Nearly complete storage of  $\alpha$ -event damage in zircon would require that after closure of the zircon U-Th-Pb system, the Sri Lankan basement was rapidly cooled to below  $200^\circ\text{C}$  (below which temperature the recovery rate in zircon is extremely slow; Meldrum et al. 1999). This is in marked contradiction to the fact that Rb-Sr biotite ages for the metamorphic basement in the HSWC (Hözl et al. 1991) and zircon (U-Th)/He ages (Hurley 1954; this work) postdate the magmatic zircon growth by more than 100 m.y. Hözl et al. (1991) concluded that the HSWC underwent prolonged slow cooling in Cambrian time, indicated by correlating garnet ages and equilibrium temperatures, followed by an Ordovician exhumation event (Fig. 7). In view of temperatures above  $300^\circ\text{C}$  during a prolonged cooling history before  $\sim 450$  Ma ago, it is impossible that zircon specimens from the HSWC have accumulated the  $\alpha$ -damage over a period of time of 550–570 m.y. However, when calculating time-integrated  $\alpha$ -doses for Sri Lanka zircon using the Late Ordovician (U-Th)/He age instead of U/Pb ages, and redoing the comparison with unannealed zircon analogous to Figure 1, Sri Lanka zircon is still too crystalline. Therefore, slow cooling through  $\sim 450$  Ma cannot be the only cause of radiation damage annealing in Sri



**FIGURE 7.** Simplified thermal evolution of the Sri Lankan Highland/Southwestern Complex after Neoproterozoic regional metamorphism. The slow cooling of the basement continued until well after magmatic zircon growth (garnet and biotite age data from Hözl et al. 1991). Note that the high (U-Th)/He closure temperature is because of huge sample sizes (see text). Two hypothetically possible paths of the subsequent low- $T$  thermal history, indicated by Tertiary FT ages (Garver 2002), are shown with question marks. Note that the HSWC was at temperatures well above the stability of  $\alpha$ -damage (marked as gray area) for a significant portion of the  $\sim 550$ – $570$  m.y. time period since zircon growth.

Lanka zircon.

These considerations suggest that Sri Lankan zircon may have resided at elevated temperatures for significant portions of time since the Ordovician cooling recorded by the (U-Th)/He ages. Unfortunately, little is known about the post-Ordovician thermal history of the HSWC, and there is no independent petrologic evidence for young low-grade metamorphism. Zircon FT ages would be a valuable constraint on the low- $T$  thermal histories of these samples, as they date cooling through  $240 \pm 50^\circ\text{C}$  (Brandon et al. 1998) or as low as  $220^\circ\text{C}$  (Garver et al. 1999). While we were not able to obtain FT ages on these specific samples due to prohibitively high track densities (described above), other zircon specimens from Sri Lanka have been shown to have FT ages of  $\sim 40$  Ma (Garver 2002). The hypothetical possibility that these FT ages were too young because of FT annealing due to heat-treatment after sampling can be excluded. Firstly, samples 4403 and 4407 studied by Garver (2002) were personally collected by R.C. Ewing to avoid this potential problem (R.C. Ewing, personal communication). Secondly, the samples did not show any evidence for heat-treatment such as unusually short track lengths. The  $\sim 40$  Ma FT ages reported by Garver (2002) clearly postdate Cretaceous uplift and faulting (Cooray 1984) but seem to concur reasonably with the collision of the Indian plate with Asia, after which further exhumation of the central Sri Lankan island may have started. A sound geological interpretation of the temperature path of these rocks cannot be given at present. It is clear, however, that the zircon crystals were either kept at elevated temperatures after the Ordovician exhumation, or they were re-heated in the Tertiary (Fig. 7).

Due to insufficient knowledge on the relation and interaction

of damage accumulation and annealing for  $\alpha$ -decay and spontaneous fission events, detailed conclusions about effects of the Tertiary thermal event on  $\alpha$ -damage are not possible at present. It seems, however, that the intermediate transition range between 10 % annealing and 90 % annealing spans a much wider temperature range for  $\alpha$ -damage than for FT damage. Even though  $\alpha$ -damage may be partially reconstituted over geologic periods of time at temperatures below 200 °C (Meldrum et al. 1998, 1999; Nasdala et al. 2001), it is in general more difficult to fully anneal than FT damage (Murakami et al. 1991). Therefore, zircon FT ages of ~40 Ma (Garver 2002) strongly suggest moderate annealing of the  $\alpha$ -damage in Sri Lankan zircon crystals in Tertiary times.

### Implications

We have shown that zircon samples from gravels in the Sri Lankan HSWC underwent partial structural reconstitution, i.e., they do not represent complete accumulation of  $\alpha$ -event damage. This fact prevents the direct use of the Sri Lanka zircon as a calibration standard for the evaluation of zircon samples from other localities in view of complete or incomplete  $\alpha$ -damage storage, as has been attempted in the past. For example, Pidgeon et al. (1998) suggested it is possible to determine “radiation damage ages” of zircon samples by comparing their radiation damage and total  $\alpha$ -dose with those of standard zircon from Sri Lanka. This concept, however, was based on the assumption that Sri Lanka zircon has stored all  $\alpha$ -event damage since the time of closure of the U-Th-Pb system, which implies rapid cooling after crystallization and no thermal perturbation since. This incorrect assumption would have led to meaningless “radiation damage ages”. Contradictions are most evident when examining the data for a lunar zircon studied by Wopenka et al. (1996). When applying the concept of Pidgeon et al. (1998) to this data set, an impossible “radiation damage age” on the order of ~5,400 Ma is determined for the lunar zircon.

In a recent microprobe study, Balan et al. (2001) found that only poorly to moderately metamict zircon has resisted low- $T$  alteration and weathering in Cretaceous sediments and lateritic soils of the Amazon Basin, Brazil. These authors evaluated the radiation damage of their samples in comparison with Sri Lanka zircon. Because many specimens had experienced much larger self-irradiation doses than zircon crystals from Sri Lanka showing the same Raman band broadening, Balan et al. (2001) concluded their samples must have been annealed. This rather qualitative conclusion is not affected by the incomplete  $\alpha$ -damage retention in Sri Lanka zircon, because the zircon samples of Balan et al. (2001) underwent even more extensive annealing than Sri Lanka zircon. Incorrect results, however, are to be expected when examining zircon samples with low degrees of annealing. Therefore, we emphasize again that any evaluation of the degree of  $\alpha$ -damage retention in zircon samples must refer to unannealed standard materials.

Incomplete damage retention by Sri Lanka zircon has also affected one of the major tasks in radiation damage research, namely, the quantification of the radiation dose necessary to generate certain amounts of structural damage. As previously mentioned, Salje et al. (1999) have postulated that the radiation-induced amorphization of zircon due to random cascade formation and overlap is a percolation transition. This transition

is characterized by the dose  $D$ , at which the macroscopic swelling is identical to the saturation expansion of the crystallographic unit-cell. Salje et al. (1999) have determined  $D_s = 3.5 \times 10^{18} \alpha/g$  from Sri Lanka zircon. Zircon samples from Sri Lanka with calculated  $\alpha$ -fluences close to  $3.5 \times 10^{18} \alpha/g$  are characterized by  $\nu_3(\text{SiO}_4)$  Raman band FWHMs of  $24 \pm 3 \text{ cm}^{-1}$  (Zhang et al. 2000; Nasdala et al. 2001; Fig. 3, this work). Even though all unannealed zircon samples studied thus far are less metamict, which prevents direct comparison with Sri Lanka zircon in the strongly metamict range (compare Fig. 3A), it is clear that unannealed zircon must be expected to show the same Raman band broadening at a clearly lower dose. With the presumption that long- and short-range orders have corresponding trends in Sri Lankan and unannealed zircon, and considering the 55 % damage retention by Sri Lankan zircon, it may be suspected that the unit-cell swelling in unannealed zircon saturates below  $2 \times 10^{18} \alpha$ -events per gram.

Insufficient consideration of annealing effects in zircon from Sri Lanka and other localities may also account for unreasonably low estimates of the stability of radiation-induced defects over geologic timescales. For example, Lumpkin and Ewing (1988) have determined the mean lifetime of  $\alpha$ -recoil tracks in zircon at ~400 my, explained by a simple track fading model. This estimate was based on literature data for natural zircon samples (of which a significant portion were from Sri Lanka). It appears obvious that the above estimate must have been affected by the annealing histories of the samples. An average  $\alpha$ -recoil track lifetime of ~400 m.y. is, therefore, most probably not a general feature of natural zircon. This is supported in a recent study of Archean zircon grains from the Superior province, Canada (Davis and Krogh 2000). These zircon crystals were little affected by thermal annealing and, correspondingly, Davis and Krogh (2000) determined mean lifetimes for  $\alpha$ -recoil tracks of 4947 m.y. and 2717 m.y.

In conclusion, we emphasize that zircon crystals from Sri Lanka may not be generally suitable standards for the investigation of  $\alpha$ -event damage in unknown zircon; at least time-integrated  $\alpha$ -doses calculated for 550–570 m.y. lasting self-irradiation periods should not be used for direct quantitative interpretation. Also, the structural state of zircon crystals from Sri Lanka is not a plain product of natural self-irradiation but overprinted and, thus, potentially complicated by thermal annealing effects. The finding that roughly 55% of the radiation damage has been retained by Sri Lanka zircon may have consequences for previously published results. Insufficient consideration of the annealing history seems to have led to serious underestimation of radiation effects in the past. It appears appropriate to re-check previous quantitative conclusions drawn from studies of Sri Lanka zircon with consideration of their partial structural recovery. We suggest that this can be done by assigning radiation-induced property changes of Sri Lanka zircon to total  $\alpha$ -doses multiplied by a correction factor of 0.55.

Incomplete retention of  $\alpha$ -event damage since the time of zircon growth, however, does not affect the excellent suitability of Sri Lankan zircon crystals as natural standard for isotopic and geochronological analysis. For such purposes, large, homogeneous crystals lacking any significant loss of radiogenic Pb and He are needed, and these qualities remained unaffected.

## ACKNOWLEDGMENTS

We are indebted to W. Hofmeister for providing four cut stones from the collection of the Institute of Gemstone Research, Idar Oberstein and Mainz. J.M. Hanchar made a synthetic zircon crystal doped with Sm and P available for analysis. Sample preparation was done by A. Wagner, D. Dettmar, and K. Paech. Thanks are due to R.A. Donelick, J.-P. Gallien, B. Schulz-Dobrick, N. Groschopf, R. Kleeberg, and A.A. Neuhin for experimental help. Constructive comments by A. Kröner, A. Kronz, and C.L. Lengauer and reviews by two anonymous experts are gratefully acknowledged. We also thank A. Meldrum, R.C. Ewing, and an anonymous reviewer for comments on an earlier version of the manuscript.

## REFERENCES CITED

- Aines, R.D. and Rossman, G.R. (1986) Relationships between radiation damage and trace water in zircon, quartz and topaz. *American Mineralogist*, 71, 1186–1193.
- Balan, E., Neuville, D.R., Trocellier, P., Fritsch, E., Muller, J.-P., and Calas, G. (2001) Metamictization and chemical durability of detrital zircon. *American Mineralogist*, 86, 1025–1033.
- Berar, J.F. and Baldinozzi, G. (1998) XND code: From X-ray laboratory data to incommensurately modulated phases. Rietveld modelling of complex materials. *International Union of Crystallography—Commission for Powder Diffraction, Newsletter*, 20, 3–5.
- Biagini, R., Memmi, I., and Olmi, F. (1997) Radiation damage in zircons. *Neues Jahrbuch für Mineralogie, Monatshefte*, 1997, 257–270.
- Brandon, M.T., Roden-Tice, M.K., and Garver, J.I. (1998) Late Cenozoic exhumation of the Cascadia accretionary wedge in the Olympic Mountains, northwest Washington State. *Geological Society of America Bulletin*, 110, 985–1009.
- Burakov, B.E., Hanchar, J.M., Zamoryanskaya, M.V., Anderson, E.B., Garbuzov, V.M., Kitsay, A.A., and Krivochev, S.V. (2004) Investigation of single crystal zircon, (Zr,Pu)SiO<sub>4</sub>, doped with <sup>238</sup>Pu. *Radiochimica Acta*, 91, in press.
- Capitani, G.C., Leroux, H., Doukhan, J.C., Rios, S., Zhang, M., and Salje, E.K.H. (2000) A TEM investigation of natural metamict zircons: structure and recovery of amorphous domains. *Physics and Chemistry of Minerals*, 27, 545–556.
- Chakoumakos, B.C., Murakami, T., Lumpkin, G.R., and Ewing, R.C. (1987) Alpha-decay-induced fracturing in zircon: The transition from the crystalline to the metamict state. *Science*, 236, 1556–1559.
- Compston, W., Williams, I.S., and Meyer, C. (1984) U-Pb geochronology of zircons from lunar breccia 73217 using a sensitive high mass-resolution ion microprobe. *Journal of Geophysical Research*, 89, B525–534.
- Cooray, P.G. (1984) An introduction to the geology of Sri Lanka (Ceylon) (2nd ed.). National Museums of Sri Lanka Publication, 340 p.
- Davis, D.W. and Krogh, T.E. (2000) Preferential dissolution of <sup>234</sup>U and radiogenic Pb from  $\alpha$ -recoil-damaged lattice sites in zircon: implications for thermal histories and Pb isotopic fractionation in the near surface environment. *Chemical Geology*, 172, 41–58.
- Ellsworth, S., Navrotsky, A., and Ewing, R.C. (1994) Energetics of radiation damage in natural zircon (ZrSiO<sub>4</sub>). *Physics and Chemistry of Minerals*, 21, 140–149.
- Ewing, R.C., Meldrum, A., Wang, L.M., Weber, W.J., and Corrales, L.R. (2003) Radiation effects in zircon. In J.M. Hanchar and P.W.O. Hoskin, Eds., *Zircon*, 53, in press. *Reviews in Mineralogy and Geochemistry*, Mineralogical Society of America, Washington, D.C.
- Farges, F. (1994) The structure of metamict zircon: A temperature-dependent EXAFS study. *Physics and Chemistry of Minerals*, 20, 504–514.
- Farley, K.A. (2000) Helium diffusion from apatite: General behavior as illustrated by Durango fluorapatite. *Journal of Geophysical Research*, 105, 2903–2914.
- Farnan, I. (1999) <sup>29</sup>Si NMR characterisation of the crystalline-amorphous transition in ZrSiO<sub>4</sub>. *Phase Transitions*, 69, 47–60.
- Farnan, I. and Salje, E.K.H. (2001) The degree and nature of radiation damage in zircon observed by <sup>29</sup>Si nuclear magnetic resonance. *Journal of Applied Physics*, 89, 2084–2090.
- Gaft, M., Panczer, G., Reisfeld, R., and Shinno, I. (2000) Laser-induced luminescence of rare-earth elements in natural zircon. *Journal of Alloys and Compounds*, 300–301, 267–274.
- Gaft, M., Panczer, G., Reisfeld, R., and Uspensky, E. (2001) Laser-induced time-resolved luminescence as a tool for rare-earth element identification in minerals. *Physics and Chemistry of Minerals*, 28, 347–363.
- Garver, J.I. (2002) Discussion: “Metamictisation of natural zircon: accumulation vs. thermal annealing of radioactivity-induced damage” by Nasdala et al. 2001 (Contributions to Mineralogy and Petrology, 141, 125–144). *Contributions to Mineralogy and Petrology*, 143, 756–757.
- Garver, J.I., Brandon, M.T., Roden-Tice, M., and Kamp, P.J.J. (1999) Exhumation history of orogenic highlands determined by detrital fission-track thermochronology. In U. Ring, M.T. Brandon, G.S. Lister, and S.D. Willet, Eds., *Exhumation processes: Normal faulting, ductile flow and erosion*. Geological Society, London, Special Publications, 154, 283–304.
- Geisler, T. and Pidgeon, R.T. (2002) Raman scattering from metamict zircon: comments on “Metamictisation of natural zircon: accumulation versus thermal annealing of radioactivity-induced damage” by Nasdala et al. (*Contributions to Mineralogy and Petrology*, 141, 125–144). *Contributions to Mineralogy and Petrology*, 143, 750–755.
- Geisler, T., Ulonska, M., Schleicher, H., Pidgeon, R.T., and van Bronswijk, W. (2001a) Leaching and differential recrystallization of metamict zircon under experimental hydrothermal conditions. *Contributions to Mineralogy and Petrology*, 141, 53–65.
- Geisler, T., Pidgeon, R.T., van Bronswijk, W., and Pleysier, R. (2001b) Kinetics of thermal recovery and recrystallization of partially metamict zircon: a Raman spectroscopic study. *European Journal of Mineralogy*, 13, 1163–1176.
- Hanchar, J.M., Finch, R.J., Hoskin, P.W.O., Watson, E.B., Cherniak, D.J., and Mariano, A.N. (2001) Rare earth elements in synthetic zircon: Part I. Synthesis, and rare earth element and phosphorus doping. *American Mineralogist*, 86, 667–680.
- Holland, H.D. (1954) Radiation damage and its use in age determination. In H. Faul, Ed., *Nuclear geology*, 175–179. Wiley, New York.
- Holland, H.D. and Gottfried, D. (1955) The effect of nuclear radiation on the structure of zircon. *Acta Crystallographica*, 8, 291–300.
- Hözl, S., Köhler, H., Kröner, A., Jäckel, P., and Liew, T.C. (1991) Geochronology of the Sri Lankan basement. In A. Kröner, Ed., *The crystalline crust of Sri Lanka*. Part I. Summary of Research of the German-Sri Lankan Consortium. Geological Survey Department of Sri Lanka, Professional Paper 5, 237–257.
- Hurley, P.M. (1954) The helium age method and the distribution and migration of helium in rocks. In H. Faul, Ed., *Nuclear geology*, 301–329. Wiley, New York.
- Hurley, P.M., Larsen, E.S., Jr., and Gottfried, D. (1956) Comparison of radiogenic helium and lead in zircon. *Geochimica et Cosmochimica Acta*, 9, 98–102.
- Irmer, G. (1985) Zum Einfluß der Apparatefunktion auf die Bestimmung von Streuquerschnitten und Lebensdauern aus optischen Phononenspektren. *Experimentelle Technik der Physik*, 33, 501–506.
- Johansson, S.A.E. and Campbell, J.L. (1988) PIXE: a novel technique for elemental analysis. Wiley, Chichester, U.K.
- Kennedy, A.K. (2000) The search for new zircon standards for SIMS. In J.D. Woodhead, J.M. Hergt, and W.P. Noble, Eds., *Beyond 2000: New Frontiers in Isotope Geoscience*, Lorne, Abstracts and Proceedings, 109–111.
- Kröner, A., Williams, I.S., Compston, W., Baur, N., Vitanage, P.W., and Perera, L.R.L. (1987) Zircon ion microprobe dating of high-grade rocks in Sri Lanka. *Journal of Geology*, 95, 775–791.
- Kröner, A., Cooray, P.G., and Vitanage, P.W. (1991) Lithotectonic subdivision of the Precambrian basement in Sri Lanka. In A. Kröner, Ed., *The crystalline crust of Sri Lanka*. Part I. Summary of Research of the German-Sri Lankan Consortium. Geological Survey Department of Sri Lanka, Professional Paper 5, 5–21.
- Lumpkin, G.R. (2001) Alpha-decay damage and aqueous durability of actinide host phases in natural systems. *Journal of Nuclear Materials*, 189, 136–166.
- Lumpkin, G.R. and Ewing, R.C. (1988) Alpha-decay damage in minerals of the pyrochlore group. *Physics and Chemistry of Minerals*, 16, 2–20.
- McLaren, A.C., Fitz Gerald, J.D., and Williams, I.S. (1994) The microstructure of zircon and its influence on the age determination from Pb/U isotopic ratios measured by ion microprobe. *Geochimica et Cosmochimica Acta*, 58, 993–1005.
- Meldrum, A., Boatner, L.A., Weber, W.J., and Ewing, R.C. (1998) Radiation damage in zircon and monazite. *Geochimica et Cosmochimica Acta*, 62, 2509–2520.
- Meldrum, A., Boatner, L.A., Zinkle, S.J., Wang, S.-X., Wang, L.-M., and Ewing, R.C. (1999) Effects of dose rate and temperature on the crystalline-to-metamict transformation in the ABO<sub>4</sub> orthosilicates. *Canadian Mineralogist*, 37, 207–221.
- Milisen, C., Liew, T.C., Hofmann, A.W., and Kröner, A. (1988) Isotopic mapping of age provinces in Precambrian high-grade terranes: Sri Lanka. *Journal of Geology*, 96, 608–615.
- Morgan, J.H. and Auer, M.L. (1941) Optical, spectrographic, and radioactivity studies of zircon. *American Journal of Science*, 239, 305–311.
- Munasinghe, T. and Dissanayake, C. B. (1981) The origin of gemstones in Sri Lanka. *Economic Geology*, 76, 1216–1225.
- Murakami, T., Chakoumakos, B.C., and Ewing, R.C. (1986) X-ray powder diffraction analysis of alpha-event radiation damage in zircon (ZrSiO<sub>4</sub>). In D.E. Clark, W.B. White, and A.J. Machiels, Eds., *Nuclear waste management II*. *Advances in Ceramics*, 20, 745–753. American Ceramic Society, Columbus, Ohio.
- Murakami, T., Chakoumakos, B.C., Ewing, R.C., Lumpkin, G.R., and Weber, W.J. (1991) Alpha-decay event damage in zircon. *American Mineralogist*, 76, 1510–1532.
- Mursic, Z., Vogt, T., Boysen, H., and Frey, F. (1992) Single-crystal study of metamict zircon up to 2000 K. *Journal of Applied Crystallography*, 25, 519–523.
- Nasdala, L., Wolf, D., and Irmer, G. (1995) The degree of metamictization in zircon: a Raman spectroscopic study. *European Journal of Mineralogy*, 7, 471–478.
- Nasdala, L., Pidgeon, R.T., Wolf, D., and Irmer, G. (1998a) Metamictization and U-Pb isotopic discordance in single zircons: a combined Raman microprobe and SHRIMP ion probe study. *Mineralogy and Petrology*, 62, 1–27.
- Nasdala, L., Götze, J., Pidgeon, R.T., Kempe, U., and Seifert, T. (1998b) Constraining a U-Pb age: micro-scale characterization of zircons from Saxonian Rotliegendes rhyolites. *Contributions to Mineralogy and Petrology*, 132, 300–306.

- Nasdala, L., Wenzel, T., Pidgeon, R.T., and Kronz, A. (1999) Internal structures and dating of complex zircons from Meissen Massif monzonites, Saxony. *Chemical Geology*, 156, 331–341.
- Nasdala, L., Wenzel, M., Vavra, G., Irmner, G., Wenzel, T., and Kober, B. (2001) Metamictisation of natural zircon: accumulation versus thermal annealing of radioactivity-induced damage. *Contributions to Mineralogy and Petrology*, 141, 125–144.
- Nasdala, L., Lengauer, C.L., Hanchar, J.M., Kronz, A., Wirth, R., Blanc, P., Kennedy, A.K., and Seydoux-Guillaume, A.-M. (2002a) Annealing radiation damage and the recovery of cathodoluminescence. *Chemical Geology*, 191, 119–138.
- Nasdala, L., Irmner, G., and Jonckheere, R. (2002b) Radiation damage ages: Practical concept or impractical vision? Reply to two comments on “Metamictisation of natural zircon: Accumulation versus thermal annealing of radioactivity-induced damage”, and further discussion. *Contributions to Mineralogy and Petrology*, 143, 758–765.
- Nasdala, L., Zhang, M., Kempe, U., Panczer, G., Gaft, M., Andrut, M., and Plötze, M. (2003) Spectroscopic methods applied to zircon. In J.M. Hanchar and P.W.O. Hoskin, Eds., *Zircon*, 53, in press. *Reviews in Mineralogy and Geochemistry*, Mineralogical Society of America, Washington, D.C.
- Nelson, D.R. (1997) Compilation of SHRIMP U-Pb zircon geochronology data, 1996. Geological Survey of Western Australia, Record 1997/2, 189p.
- Özkan, H. (1976) Effect of nuclear radiation on the elastic moduli of zircon. *Journal of Applied Physics*, 47, 4772–4779.
- Palenik, C.S., Nasdala, L., and Ewing, R.C. (2003) Radiation damage in zircon. *American Mineralogist*, 88, 770–781.
- Panczer, G. (2001) La photoluminescence résolue en temps, nouvel outil pour la minéralogie. Habilitation thesis, Université Claude Bernard, Lyon, France.
- Peucat, J.-J., Capdevila, R., Drareni, A., Choukroune, P., Fanning, C.M., Bernard-Griffiths, J., and Fourcade, S. (1996) Major and trace element geochemistry and isotope (Sr, Nd, Pb, O) systematics of an Archaean basement involved in a 2.0 Ga very high-temperature (1000 °C) metamorphic event: In Ouzzal Massif, Hoggar, Algeria. *Journal of Metamorphic Geology*, 14, 667–692.
- Pidgeon, R.T., O’Neil, J.R., and Silver, L.T. (1966) Uranium and lead isotopic stability in a metamict zircon under experimental hydrothermal conditions. *Science*, 154, 3756, 1538–1542.
- — — (1972) Observations on the crystallinity and the U-Pb system of a metamict Ceylon zircon under experimental conditions. *Fortschritte der Mineralogie*, 50, Beiheft 3, 118.
- Pidgeon, R.T., Nasdala, L., and Todt, W. (1998) Determination of radiation damage ages on parts of zircon grains by Raman microprobe: implications for annealing history and U-Pb stability. *Mineralogical Magazine*, 62A, 1174–1175.
- Rahn, M.K.W. (2001) The metamorphic and exhumation history of the Helvetic Alps, Switzerland, as revealed by apatite and zircon fission tracks. Habilitation thesis, University of Freiburg, Germany.
- Reiners, P.W. and Farley, K.A. (1999) He diffusion and (U-Th)/He thermochronometry of titanite. *Geochimica et Cosmochimica Acta*, 63, 3845–3859.
- — — (2001) Influence of crystal size on apatite (U-Th)/He thermochronology: An example from the Bighorn Mountains, Wyoming. *Earth and Planetary Science Letters*, 188, 413–420.
- Reiners, P.W. and Spell, T.L. (2002) Intercalibration of (U-Th)/He and K-feldspar <sup>40</sup>Ar/<sup>39</sup>Ar thermochronometry (abstract). *Geochimica et Cosmochimica Acta*, 66, A631.
- Reiners, P.W., Farley, K.A., and Hickey, H.J. (2002) He diffusion and (U-Th)/He thermochronometry of zircon: Initial results from Fish Canyon Tuff (Colorado) and Gold Butte (Nevada). *Tectonophysics*, 349, 247–308.
- Ríos, S. and Salje, E.K.H. (1999) Diffuse x-ray scattering from weakly metamict zircon. *Journal of Physics: Condensed Matter*, 11, 8947–8956.
- Ríos, S., Salje, E.K.H., Zhang, M., and Ewing, R.C. (2000a) Amorphization in zircon: evidence for direct impact damage. *Journal of Physics: Condensed Matter*, 12, 2401–2412.
- Ríos, S., Malcherek, T., Salje, E.K.H., and Domeneghetti, C. (2000b) Localized defects in radiation-damaged zircon. *Acta Crystallographica B*, 56, 947–952.
- Rizvanova, N.G., Levchenkov, O.A., Belous, A.E., Bezmen, N.I., Maslenikov, A.V., Komarov, A.N., Makeev, A.F., and Levskiy, L.K. (2000) Zircon reaction and stability of the U-Pb isotope system during interaction with carbonate fluid: experimental hydrothermal study. *Contributions to Mineralogy and Petrology*, 139, 101–114.
- Rupasinghe, M.S. and Dissanayake, C.B. (1987) The geochemistry and mineralogy of zircons from Sri Lanka. *Bulletin of the Geological Society, Finland*, 59, 3–19.
- Sahama, T.G. (1981) Growth structure in Ceylon zircon. *Bulletin de Minéralogie*, 104, 89–94.
- Salje, E.K.H., Chrosch, J., and Ewing, R.C. (1999) Is “metamictization” of zircon a phase transition? *American Mineralogist*, 84, 1107–1116.
- Stacey, J. S. and Kramers, J. D. (1975) Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth and Planetary Science Letters*, 26, 207–221.
- Stern, R.A. (1997) The GSC Sensitive High Resolution Ion Microprobe (SHRIMP): Analytical techniques of zircon U-Th-Pb age determinations and performance evaluation. In Geological Survey of Canada, *Radiogenic Age and Isotopic Studies: Report 10, 1997-F*, p. 1–31.
- — — (2001) A new isotopic and trace element standard for the ion microprobe: preliminary TIMS and electron microprobe data. In Geological Survey of Canada, *Radiogenic Age and Isotopic Studies: Report 14, 2001-F*, 7 p.
- Vance, E.R. and Anderson, B.W. (1972a) Study of metamict Ceylon zircons. *Mineralogical Magazine*, 38, 605–613.
- — — (1972b) Differences among low Ceylon zircons. *Mineralogical Magazine*, 38, 721–724.
- Vavra, G., Gebauer, D., Schmid, R., and Compston, W. (1996) Multiple zircon growth and recrystallization during polyphase Late Carboniferous to triassic metamorphism in granulites of the Ivrea Zone (Southern Alps): an ion microprobe (SHRIMP) study. *Contributions to Mineralogy and Petrology*, 122, 337–358.
- Wasiliewski, P.J., Senftle, F.E., Vaz, J.E., Thorpe, A.N., and Alexander, C.C. (1973) A study of the natural  $\alpha$ -recoil damage in zircon by infrared spectra. *Radiation Effects*, 17, 191–199.
- Weber, W.J. (1990) Radiation-induced effects and amorphization in zircon. *Journal of Materials Research*, 5, 2687–2697.
- — — (1993) Alpha-decay-induced amorphization in complex silicate structures. *Journal of the American Ceramic Society*, 76, 1729–1738.
- Weber, W.J., Ewing, R.C., and Wang, L.-M. (1994) The radiation-induced crystalline-to-amorphous transition in zircon. *Journal of Materials Research*, 9, 688–698.
- Weber, W.J., Ewing, R.C., Catlow, C.R.A., Diaz de la Rubia, T., Hobbs, L.W., Kinoshita, C., Matzke, H., Motta, A.T., Nastasi, M., Salje, E.K.H., Vance, E.R., and Zinkle, S.J. (1998) Radiation effects in crystalline ceramics for the immobilization of high-level nuclear waste and plutonium. *Journal of Materials Research*, 13, 1434–1484.
- Wirth, R., Dobrzhinetskaya, L.F., and Green II, H.W. (2001a) Electron microscope study of the reaction olivine + H<sub>2</sub>O + TiO<sub>2</sub> → titanite clinohumite + titanian chondrodite synthesized at 8Gpa, 1300K. *American Mineralogist*, 86, 601–610.
- Wirth, R., Langer, K., and Platonov, A.N. (2001b) TEM study of a chromium-bearing kyanite from mantle xenolith: evidence for an alumina-rich exsolution precursor phase. *European Journal of Mineralogy*, 13, 311–318.
- Woodhead, J.A., Rossman, G.R., and Silver, L.T. (1991) The metamictization of zircon: Radiation dose-dependent structural characteristics. *American Mineralogist*, 76, 74–82.
- Wopenka, B., Jolliff, B.L., Zinner, E., and Kremser, D.T. (1996) Trace element zoning and incipient metamictization in a lunar zircon: application of three microprobe techniques. *American Mineralogist*, 81, 902–912.
- Zhang, M. and Salje, E.K.H. (2001) Infrared spectroscopic analysis of zircon: Radiation damage and the metamict state. *Journal of Physics: Condensed Matter*, 13, 3057–3071.
- Zhang, M., Salje, E.K.H., Farnan, I., Graeme-Barber, A., Daniel, P., Ewing, R.C., Clark, A.M., and Lennox, H. (2000) Metamictization of zircon: Raman spectroscopic study. *Journal of Physics: Condensed Matter*, 12, 1915–1925.
- Zhang, M., Salje, E.K.H., and Ewing, R.C. (2002) Infrared spectra of Si-O overtones, hydrous species, and U ions in metamict zircon: radiation damage and recrystallization. *Journal of Physics: Condensed Matter*, 14, 3333–3352.

MANUSCRIPT RECEIVED DECEMBER 19, 2002

MANUSCRIPT ACCEPTED MAY 28, 2003

MANUSCRIPT HANDLED BY PETER BURNS