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Discussion: “Metamictisation of natural zircon: accumulation versus thermal annealing of radioactivity-induced damage” by Nasdala et al. 2001 (*Contributions to Mineralogy and Petrology* 141:125–144)

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Nasdala and coworkers provide important insight into the relationship between radiation damage, age, and radionuclide content of natural zircons using confocal laser-Raman spectroscopy (Nasdala et al. 2001). They investigated a series of naturally damaged zircons and demonstrated that Raman band widening shows a linear increase with total α damage. The one exception in their suite of unknowns is a zircon sample from Sri Lanka which shows considerably less α damage than would be expected if it had accumulated α damage since crystallization at ~ 570 Ma. Due to this apparent discrepancy, they suggest that these Sri Lankan zircons should not be considered as standards for the quantification of radiation damage. Our fission-track ages from Sri Lankan zircon confirm their findings (Table 1).

Zircons from Sri Lanka have a long history of investigation for radiation damage, and data from these zircons are the basis of a number of models of how amorphization proceeds in zircon (see Holland and Gottfried 1955; Murakami et al. 1986; Chakoumakos et al. 1987; Murakami et al. 1991; Woodhead et al. 1991; Ellsworth et al. 1994; Capitani et al. 2000; Zhang et al. 2000a, 2000b). Most Sri Lankan zircons are from placers in the Ratnapura district and are inferred to have been derived from pegmatites intruded into Al-rich sediments of the Archean Highland Group (Munasinghe and Dissanayake 1981; Murakami et al. 1991). Many of these studies use an age of ~ 570 Ma for these zircons, which is based on the early work of Holland and Gottfried (1955). A SHRIMP standard from the same area has an age of 564 Ma (Pidgeon et al. 1994). However, the cooling age rather than the crystallization age is

far more relevant in calculating total accumulated α damage.

The authors state: “We conclude that, after closure of their U–Pb systems 560–570 Ma ago, zircons have been kept at elevated temperatures for a considerable period of time, in the course of this undergoing continuous annealing. This is consistent with the long cooling history of the Sri Lankan basement ... Therefore, their time of radiation-damage accumulation was decidedly shorter than 560–570 Ma”.

The relationship between α damage and fission tracks in natural rocks is of interest to fission-track dating because α damage affects the zircon closure temperature and the etching behavior of zircon (see Rahn et al., unpublished data). In a study of a classic suite of Sri Lankan zircons, Murakami et al. (1991) inferred that α damage alone caused the metamictization of zircon, in part because they report that fission tracks were not present in the samples! Although the inference that α damage is the primary factor which causes metamictization is probably correct because the integrated decay energy is 10^7 times larger, the lack of fission tracks was perplexing because in natural systems they have a similar thermal stability as α damage. Our investigation into these zircons has shown that fission tracks are present. Note that both α damage and fission-damage accumulate in zircon provided the crystal stays below the respective annealing temperatures which fall between 200 and 300 °C (Fleischer et al. 1975; Tagami et al. 1996; Rahn et al., unpublished data). Therefore, a fission-track age is an excellent proxy for the time since α damage started accumulating in a zircon crystal.

Fission-track ages of two Sri Lankan zircon samples collected from gem gravels in the Ratnapura district have nearly identical cooling ages of ~ 43 and 40 Ma (samples are from Murakami et al. 1991; samples 4403 and 4407 were dated as provided by R.C. Ewing; see Table 1). These new fission track data indicate that the source rocks cooled below 240 ± 50 °C in the Late Eocene, and thus have presumably accumulated α damage for no longer than ~ 40 Ma. The implications of these

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Table 1. Fission-track ages of Sri Lankan zircons from gem gravels, Ratnapura district, Sri Lanka

Sample ^a	<i>n</i>	ρ_s	N_s	ρ_i	N_i	$P(\chi^2)$	ρ_d	N_d	Age (± 1 SD)
4403	10	4.932	468	1.021	969	76%	1.341	6,361	43.1 \pm 2.5 Ma
4407	10	6.703	617	1.486	1,368	81%	1.341	6,361	40.3 \pm 2.0 Ma

^aSamples and sample numbers are from Murakami et al. (1991). Grain ages were determined using the standard techniques for the external detector method of zircon. Zircons from single crystals, supplied by R.C. Ewing, were crushed and the fragments were imbedded into PFA Teflon mounts which were polished and etched for 35 h at 230 \pm 2 °C. Samples were irradiated at the Oregon State nuclear reactor with a nominal fluence of 2×10^{15} neutrons/cm². Uranium-doped glass standards (CN-1) were placed at either end of the sample stack to monitor fluence during irradiation. Samples

were counted using an automated stage fitted to a Leitz Ortholux at a magnification of 1,250 \times . Ages were calculated with a zeta factor of 133.58 ± 1.1 . *n*, Number of crystal fragments dated; ρ_s , spontaneous track density ($\times 10^5$ t/cm²); N_s , number of spontaneous tracks counted; ρ_i , induced track density ($\times 10^6$ t/cm²); N_i , number of induced tracks counted; $P(\chi^2)$, chi-squared value; ρ_d , track density on the dosimeter ($\times 10^6$ t/cm²); N_d , number of tracks counted on the dosimeter

data are profound because they mean that some, if not all, of the Sri Lankan zircons have an actual internal α dose well below that calculated in a number of publications. In all previous work on these widely studied zircons (including Nasdala et al. 2001), it is assumed that α damage accumulated in these zircons since ~ 570 Ma. In the light of these FT data, the calculated α dose for typical zircons in these papers was at least an order of magnitude higher than actual damage, given that only 40 Myr have passed since cooling.

It is important to note that the Raman band width of zircon from Sri Lanka reported in Nasdala et al. (2001) indicates that the observed damage is much less than would be predicted if the age since cooling was ~ 560 Ma. Therefore, these FT data support one of their conclusions that the time of α -damage accumulation was “decidedly shorter than ~ 560 – 570 Ma”. Indeed, it was probably about 520 to 530 Ma shorter. Other workers should take note of this result, because it may affect virtually all published α -damage calculations from Sri Lankan zircons.

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References

- Capitani GC, Leroux H, Doukhan JC, Rios S, Zhang M, Salje EKH (2000) A TEM investigation of natural metamict zircons: structure and recovery of amorphous domains. *Phys Chem Miner* 27:545–556
- Chakoumakos BC, Murakami T, Lumpkin GR, Ewing RC (1987) Alpha-decay-induced fracturing in zircon: the transition from the crystalline to the metamict state. *Science* 236:1556–1559
- Ellsworth S, Navrotsky A, Ewing RC (1994) Energetics of radiation damage in natural zircon (ZrSiO₄). *Phys Chem Miner* 21:140–149
- Fleischer RL, Price PB, Walker RM (1975) Nuclear tracks in solids. University of California Press, Berkeley, CA
- Holland HD, Gottfried D (1955) The effect of nuclear radiation on the structure of zircon. *Acta Crystallogr* 8:291–300
- Munasinghe T, Dissanayake CB (1981) The origin of gemstones in Sri Lanka. *Econ Geol* 76:1216–1225
- Murakami T, Chakoumakos BC, Ewing RC (1986) X-ray powder diffraction analysis of alpha-event radiation damage in zircon (ZrSiO₄). In: Clark DE, White WB, Machiels AJ (eds) Nuclear waste management II. *Adv Ceram* 20:745–753
- Murakami T, Chakoumakos BC, Ewing RC, Lumpkin GR, Weber WJ (1991) Alpha-decay damage in zircon. *Am Mineral* 76:1510–1532
- Nasdala L, Wenzel M, Vavra G, Irmer G, Wenzel T, Kober B (2001) Metamictisation of natural zircon: accumulation versus thermal annealing of radioactivity-induced damage. *Contrib Mineral Petrol* 141:125–144
- Pidgeon RT, Furfaro D, Kennedy AK, Nemchin AA, van Bronswijk W (1994) Calibration of zircon standards for the Curtin SHRIMP II. In: *Abstr Vol 8th Int Conf Geochronology and Cosmochronology Isotope Geology, Berkeley*. *US Geol Surv Circ* 1107:251
- Tagami T, Carter A, Hurford AJ (1996) Natural long term annealing of the zircon fission-track system in Vienna Basin deep borehole samples: Constraints upon the partial annealing zone and closure temperature. *Chem Geol* 130:147–157
- Woodhead JA, Rossman GR, Silver LT (1991) The metamictization of zircon: radiation dose-dependent structural characteristics. *Am Mineral* 76:74–82
- Zhang M, Salje EKH, Capitani GC, Leroux H, Clark AM, Schlüter J, Ewing RC (2000a) Annealing of α -decay damage in zircon: a Raman spectroscopic study. *J Phys: Condens Matter* 12:3131–3148
- Zhang M, Salje EKH, Farnan I, Graeme-Barber A, Daniel P, Ewing RC, Clark AM, Lennox H (2000b) Metamictization of zircon: Raman spectroscopic study. *J Phys: Condens Matter* 12:1915–1925