Determination of radiation damage ages on parts of zircon grains by Raman microprobe: implications for annealing history and U-Pb stability

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The advent of ion microprobes has made it possible to determine U-Pb ages on micro-sized (10-30 micron diameter) areas on the polished surface of a U-bearing mineral such as zircon. Previously observed cores and rims can now be dated directly, whereas using conventional techniques, even by measuring single abraded grains, analyses of mixed core-rim phases can rarely be avoided. In making micro-scale analyses geochronologists have become aware that zircons (and other U-bearing minerals) are more complex than previously thought and have a variety of internal structures that reflect geological processes. These structures are studied extensively using back scattered electron and cathodoluminescence imaging. However these techniques do not provide information on the crystallinity of various parts of a complex zircon crystal. It is well known that zircon breaks down to the metamict state through time integrated radiation damage and a measure of the degree of this breakdown on a micro-scale will provide basic information on questions such as the geological significance of recent lead loss observed in many zircon U-Pb analytical results, and together with Th-U concentrations determined by ion microprobe or other techniques, will provide a means for determining radiation damage ages of selected areas of a zircon crystal. The determination of radiation damage ages of zircon on a micro-scale is therefore a new innovation applied to an old idea with scope to provide previously unavailable information for the interpretation of zircon U-Pb ages and the thermal evolution of the host rock.

Radiation damage ages

Holland and Kulp (1950) were the first to propose that the degree of radiation damage of metamict minerals might prove useful as a dating technique. These authors postulated that if the inherent stability of the given mineral structure and the total alpha activity of the mineral were known and if the degree of destruction of the lattice can be quantitatively measured, then the age of the zircon can be uniquely determined. However, it was Hurley and Fairbairn (1963) who first demonstrated the sensitivity of zircon X-ray diffraction (XRD) patterns as a measure of relative degrees of radiation damage in zircons and this technique was refined in a classic paper by Holland and Gottfried (1955) who described systematic relationships between XRD patterns and refractive index, density and total alpha-radiation dosage for a set of gem quality Ceylon zircons of known age and measured alpha activity. Their results showed that unit cell size systematically increased until the total integrated alpha flux reaches about 5×10^{15} α/mg, when characteristic zircon XRD peaks disappeared completely.

With the development of isotope dilution TIMS isotopic measurements of uranium and lead in zircon interest in radiation damage ages declined in the 1950's and were essentially abandoned. Study continued on the nature of the metamict state and early attempts were made to correlate uranium content, and by implication structural damage, with U-Pb age discordance (e.g Silver and Deutsch, 1963). These studies used multigrain aliquots of large zircon samples which could be analysed by XRD and then by isotope dilution to determine the structure, the U and Th contents and the age.

SHRIMP and electron microprobe studies have shown that zircons can be inhomogeneous in uranium and thorium within a single crystal and that within such crystals the total alpha flux would vary such that high-U parts of the grain would be expected to be

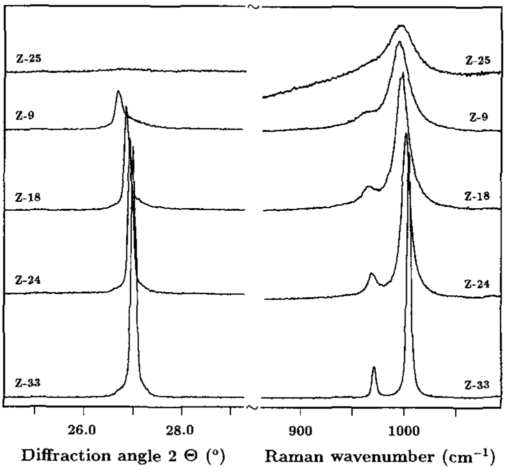

FIG. 1. Comparison of XRD(200) and Raman peaks for Sri Lankan zircons with a range of total alpha flux.

more damaged than low-U parts and to be more susceptible to discordance. Qualitative demonstration of inhomogeneous structural damage in single zircon grains is shown by the pattern of cracks radiating from more expanded high-U metamict parts of grains (Lee and Tromp, 1995) and by variable internal birefringence. However, XRD is not a viable technique for the qualitative determination of the structural damage of zircon on the scale of a 10-30 micron area. Nasdala *et al.* (1995) found that vibrational bands in the Raman spectrum of zircon become increasingly widened with increasing radiation damage and introduced Raman spectroscopy as a method to quantify the degree of metamictisation in zircon. Raman microprobe analysis provides structural information on areas as small as 1 micron in size on single zircon crystals, i.e. within a SHRIMP analytical spot.

The radiation damage information, combined with knowledge of the U and Th concentrations and the U-Pb ages of the same 10–30 micron spot, has the capability to provide a new approach for investigating mechanisms for U-Pb discordance and, depending on the uniformity of radiation damage versus alpha flux in different areas of the same zircon, can also provide an estimate of the annealing history of the host rock.

Calibration of radiation damage ages on a micro scale

To be able to apply this technique it is necessary to calibrate the Raman response to progressive metamictisation produced by a known total radiation flux. We have done this, following the technique of Holland and Gottfried (1955), by measuring the crystallinity of a set of homogeneous, ca 560 Ma old, Sri Lankan zircon crystals with a range of U and Th contents determined by isotope dilution and SHRIMP measurements. Changes in Raman peak widths with time integrated alpha flux correlate very well with the XRD curves of Holland and Gottfried (1955). The effect of increasing total alpha flux in XRD and Raman traces for Sri Lankan zircons with increasing alpha flux (bottom to top) is shown on Fig. 1. As demonstrated previously (Holland and Gottfried, 1955) the zircon XRD peak positions show a systematic increase in unit cell size and decrease in intensity whereas the Raman peaks show systematic broadening and weakening of peaks and a general decrease in wave number with increasing alpha flux (Nasdala *et al.* 1995). The Raman based calibration curve opens up new opportunities for providing structural damage ages within SHRIMP analytical spots, comparing discordance with degree of radiation damage, and providing information on the conditions and timing of annealing of the radiation damaged zircon structure. An important question is whether the Sri Lankan zircons can be taken as generally representative of the radiation damage breakdown behaviour of all zircons or whether other factors, such as trace element contents, significantly effect the rate of radiation damage accumulation.

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