Journal of the Royal Society of Western Australia, 79:119-122, 1996

Zircons: What we need to know

R T Pidgeon

School of Applied Geology, Curtin University of Technology, Perth, WA 6001

Abstract

The SHRIMP ion microprobe provides a new and exciting capability for determining U-Pb ages on parts of complex zircons. This opens up new opportunities for solving some equally complex geological problems, but this will depend on an understanding of the geological significance of the internal structures of the zircons, which is the key to the interpretation of the SHRIMP ages. CL imagery, HF etching, SEM imagery, X-ray and vibrational techniques for resolving zircon internal structures and crystallinity on a micro-scale are discussed.

Introduction

It is said that major advances in technology introduce as many new problems as they solve. Such may yet be the case for the new breed of high-resolution high-sensitivity micro-isotopic analytical instruments of which SHRIMP is the forerunner. SHRIMP has a broad analytical capability but was conceived primarily for the purpose of analysing U-Th-Pb isotopic systems of micro-areas of common uranium-bearing minerals of which zircon is the prime example. SHRIMP was made at a time of rapid improvement in conventional geochronology, particularly in the techniques for measuring zircons on a scale of single crystals or parts of crystals involving high precision mass spectrometric analysis of tens of picograms of Pb with blanks expressed as numbers of atoms. At this time, in the late 1970s, a wealth of knowledge was available for the mineral zircon. For example the breakdown of the zircon structure under radiation, the relationship between isotopic stability and crystallinity, and the ability of crystallised zircon to resist dissolution under magmatic conditions and to retain an isotopic memory of its pre-magmatic age, were well known. It is with this last aspect that the first major advantage of SHRIMP micro-analysis became apparent. This is its ability to measure directly the age and chemical composition of cores of ancient zircon (*e.g.* Williams 1992) encased in a mantle of younger magmatic zircon and then to determine the age of the zircon mantle. Such a feat is impractical using conventional technology and this alone signals that the scale of isotopic analysis and age determinations of zircons and other uranium-bearing minerals has changed forever. From now on, the frontier of zircon geochronology is within individual zircon grains. Where zircons are uniformly the same age, for example in a rapidly crystallising felsic magma, there may be no advantage in making SHRIMP analyses on small areas of zircon crystals. However, it is well known that zircons can have complex structures which are presently incompletely understood, but which are thought to reflect events in their geological history. SHRIMP analytical spots can be located on these structures once they are identified. An example of such a grain is contained in Figure 1. The grain pictured has a complex structure consisting of a crystalline core surrounded by an oscillatory zoned rim. What we need to know now is the geological significance of these structures, so we can interpret SHRIMP U-Pb ages and the U-Th-Zr chemistry of cores and rims of such grains in terms of geological processes. We also need to have further information about the stability of zircon in a variety of geological environments.

de Laeter Symposium on Isotope Science
Curtin University of Technology, Perth, 1995

Zircon microstructures

Chemical and structural inhomogeneities in zircons, such as oscillatory zoning, have been known for many years. What is happening at present is that techniques are being developed and improved for the purpose of highlighting the internal structures of zircons so they can be studied in detail prior to analysis by the SHRIMP. The capabilities of some of the variety of techniques used for this purpose are as follows.

Cathodoluminescence (CL) imagery is possibly the most popular technique for examining the internal structures of zircons. Cathodoluminescence is the light emitted from semi conductor or insulator material when an electron beam creates electron hole pairs which then recombine to emit light in the wavelength range from the ultraviolet to the near infrared (200-2000 nm). Although the controls of the CL spectra are not well known, it has been proposed that concentrations of some trace constituents are the determining factors. In zircons, Dy^{3+} is considered to be the principal spectral factor though other constituents such as Sm^{3+}, Eu^{2+}, Tb^{3+}, and Y^{3+} may also be CL emitters (*e.g* Hanchar & Miller 1993). The application of cathodoluminescence in highlighting micro-structures of magmatic zircons has been demonstrated by Vavra (1994).

Spectral cathodoluminescence (the analysis of the CL light spectrum) also has interesting possibilities for investigating the chemistry and structure of zircons on a micro-scale (e.g. Koschek and Lork, 1992) but up till now has been little used.

Back scattered electron imaging (BSE) reveals contrasts in average atomic number of regions of a phase; the

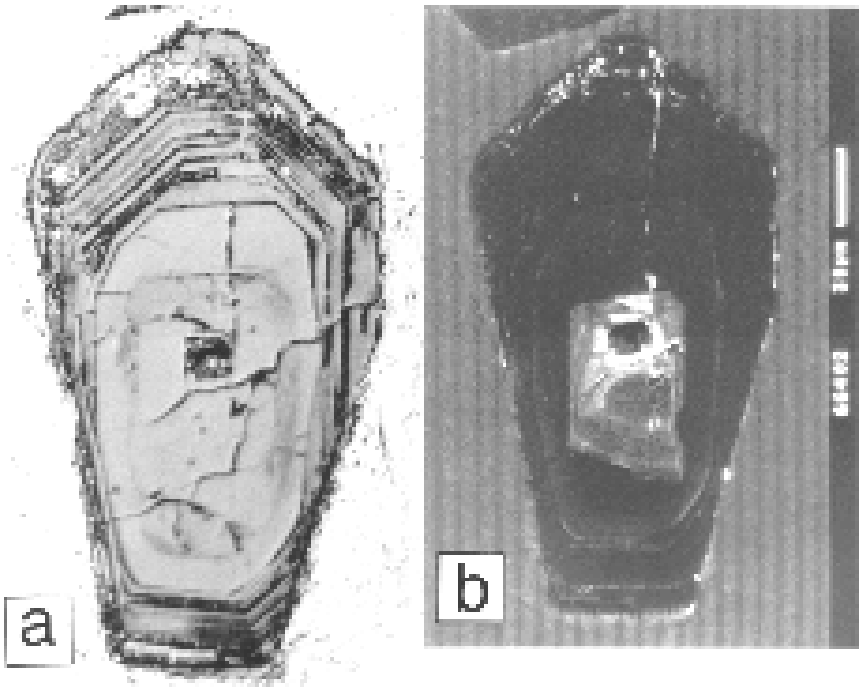

Figure 1. A cathodoluminescence (CL) image and a photomicrograph of the same polished zircon grain that has been subjected to HF etching. **A** CL of this grain is weak, although faint euhedral zoning can be seen in the rim and the rounded outline of a central core can be distinguished. An irregularly-zoned rectangular area defined by relatively strong luminescence is present in the core and may be an earlier zircon fragment. **B** The HF etched zircon also shows the outline of the central zircon core. The core itself is highly crystalline and unetched except for a weakly expressed irregular grey zone within the core at a position approximately marginal to the rectangular centre identified by strong CL. This marginal zone does not appear to be recorded by the CL image. On the other hand the etched zircon shows no sign of the rectangular area in the core clearly defined by CL. HF etching shows the fine euhedral zoning of the zircon margin much more clearly than the CL image.

higher the number, the more electrons an area will " reflect" and the brighter it will appear (Hanchar & Miller 1993). Hence the images can be termed atomic number (Z) contrast images. BSE imaging is now used widely in a variety of geological studies and is recognised as a powerful tool for studying zonation in accessory minerals. (*e.g.* Paterson *et al.* 1992; Miller *et al.* 1992; Wayne *et al.* 1992). Hanchar & Miller (1993) consider that Hf is primarily responsible for the variability in BSE intensity, with U having a secondary effect. Both elements have a much higher atomic number than the principal constituents of zircon (Zr, O, Si), so their substitution results in increased brightness.

BSE and cathodoluminescence appear to be similar except that in general dark areas in CL are bright in BSE, and vice versa. However, in the light of explanations for these effects it is not evident that cathodoluminescence will always provide an identical image to BSE. This has yet to be investigated.

HF etching is another technique used to highlight the internal structures of zircons. This measures the reactivity of the zircon to HF vapour. Radiation damage disordering of the lattice appears to enhance reactivity to HF vapour but high concentrations of contaminant elements may also be a factor in increasing reactivity to HF. There is some suggestion that quartz can form through unmixing in some areas in a zircon lattice (Sommerauer 1976; McLaren *et al.* 1994) and this would certainly enhance reactivity with HF. Highly crystalline zircon is very resistant to HF etching.

We have observed differences in the zircon images determined by CL and HF etching The example in Figure 1 shows HF etching and CL imagery of a single zircon crystal from an Archaean granite from the Darling Range. The HF etching identifies an unetched central area surrounded by an inner rim of oscillatroy zoned zircon and a thin outer rim of granular etched zircon. The CL image shows features in the central part of the zircon not identified by HF etching and also the margin of the central zircon core, but does not resolve the zoned structure in the outer zircon rims. These differences may reflect the sensitivity of the two techniques to differences in zircon crystallinity. So far the possibility that differences in the degree of metamictness of a zircon may influence the CL emission has not been investigated. To investigate this and other questions involving the effects of recrystallisation on SHRIMP results, it is necessary to be able to measure quantitatively the crystallinity of an area on a zircon crystal the size of a SHRIMP analysis spot.

Qualitative determination of the crystallinity of zircon on the scale of a SHRIMP spot

X-ray powder diffractometry is commonly used to measure the crystallinity or the degree of

metamictization in zircons. However, the amount of sample necessary for this method of analysis is much larger than the average mass of a single zircon grain. Thus, in most cases X-ray diffractometry gives only summary information about entire grains or populations of grains.

Important advances in understanding the nature of the metamict state and the relevance of this to the interpretation of zircon U-Pb ages have been made by McLaren *et al.* (1994) using high-resolution transmission electron microscopy (HRTEM) studies of zircon on the scale of the zircon lattice. HRTEM gives local information about the degree of crystallinity, but at present this technique needs specially prepared samples and cannot be used for the routine determination of the crystallinity of micro-areas on the scale of SHRIMP analytical spots.

Vibrational spectral analysis. Vibrational spectra techniques of infrared and Raman spectroscopy appear to have the greatest promise for investigating zircon structure quantitatively on a microscale.

Woodhead *et al.* (1991) report that the **Infrared spectra** of zircon vary as a function of metamictization. This is shown by increasing band widths and decreasing intensities with increasing U-Th content. This technique has also been used to investigate the presence of OH in the zircon lattice (Woodhead *et al.* 1991). These authors have applied the technique to single grains, but although McLaren *et al.* (1994) refer to measurements with this technique on a micro-scale, the author is not aware of applications on the scale of a SHRIMP analytical spot. On the other hand the ability of **Raman spectrometry** to quantitatively measure zircon crystallinity on this scale has been convincingly demonstrated (Nasdala *et al.* 1996; van Bronswijk & Pidgeon 1994). Modern Raman microprobes can determine the crystallinity of zircon with a lateral resolution of about one micron and a volume resolution of less than 5 μm^3. This opens up new opportunities for correlating structural, chemical and isotopic data on the same micro area within a zircon grain. With decreasing crystallinity, the Raman bands become less intense, are increasingly broadened and show lowered frequencies. In particular the increasing width of the internal nu3(SiO_4) vibration (asymmetric stretching of SiO_4 tetrahedra) is sensitive enough to give a precise measure of the increasing degree of metamictization.

Some questions

Numerous question have been raised by studying the complex internal structures of zircons with these techniques combined with SHRIMP measurements. Some of these are as follows.

Radiation damage ages versus SHRIMP ages. An investigation of the relationship between zircon crystallinity and structures revealed by cathodoluminescence has not been made, although Raman spectroscopy has confirmed the relative crystallinity of zircon areas shown by HF etching. With careful calibration, involving standard zircons, crystallinity measurements by Raman spectroscopy can be combined with U-Pb concentrations determined by SHRIMP, to calculate a radiation damage age for a SHRIMP analytical spot. In this way it would be possible to construct a radiation damage age map of the zircon and investigate the recrystallisation history of the zircons and the relationship of recrystallisation to the distribution of U,Th,Hf and U-Pb ages.

Diffusion versus reaction in zircon crystals. Zircon is considered the most refractory of the geochronologically useful uranium bearing minerals and is known to survive anatexis, granitic magma emplacement and magmatic crystallisation without loss of radiogenic Pb. This, together with the sharpness of zonal boundaries in zircons as old as 3000Ma, suggests that diffusion in zircon is extremely slow. However there is now evidence from HF etching studies and Raman spectroscopy that suggests some igneous zircons have undergone recrystallisation, with accompanying loss of Pb and U, soon after crystallisation. This does not appear to be related to radiation damage but is thought to involve expulsion of contaminant elements during lattice recrystallisation.

The significance of low U,Th crystalline cores. The cores of many zircons consist of low U-Th crystalline zircon, very resistant to HF etching, but sometimes show structure revealed by CL (Figure 1). Cores can represent xenocrysts of much older source material and have older SHRIMP ages. In some cases apparent cores have ages close to the magmatic age. These may represent older source material that has been updated or reflect processes affecting early formed zircon in the magma. Cathodoluminescence combined with HF etching and Raman spectroscopy will play an important part in resolving this question.

Structural complexities in other minerals. Cathodoluminescence and etching techniques appear to be limited in investigating minerals other than zircon. However, back scattered electron imagery has successfully revealed complex structures in titanite (Paterson & Stephens 1992) and monazite (De Wolf *et al.* 1993) and it is likely that other minerals will also have complex structures which will be important in interpreting their U-Pb ages.

References

De Wolf C P, Belshaw N & O'Nions R K 1993 A metamorphic history from micro-scale $^{207}Pb/^{206}Pb$ chronometry of Archaean monazite. Earth and Planetary Science Letters 120 : 207-220.

Hancher J M & Miller C F 1993 Zircon zonation patterns as revealed by cathodoluminescence and backscattered electron images: Implications for interpretation of complex crustal histories. Chemical Geology 110:1-13.

Koschek G & Lork A 1992 Material analysis with cathodoluminescence standard spectra. Scanning 14:100-103.

McLaren A C, Fitzgerald J D & 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.

Miller C F, Hanchar J M, Wooden J L, Bennett V C, Harrison T M, Wark D & A Foster D A 1992 Source region of a granite batholith: evidence from lower crustal xenoliths and inherited accessory minerals. Transactions of the Royal Society of Edinburgh Earth Sciences 83:49-62.

Nasdala L, Pidgeon R T & Wolf D 1996 Heterogeneous metamictization of zircon on a micro scale. Geochimica et Cosmochimica Acta 60:1091-1097.

Paterson B A & Stephens W E 1992 Kinetically induced compositional zoning in titanite: implications for accessory-phase/

melt partitioning of trace elements. Contributions to Mineralogy and Petrology 109:373-385.

Paterson B A, Stephens W E, Rogers G, Williams I S, Hinton R W & Herd D A 1992 The nature of zircon inheritance in two granite plutons. Transactions of the Royal Society of Edinburgh Earth Sciences 83:459-471.

Sommerauer J 1976 Die Chemisch-physikalische stabilitat natürlicher zirkone und ihr U-(Th)-Pb system. Ph D Thesis, ETH, Zürich.

van Bronswijk W & Pidgeon R T 1994 The determination of crystallinity in naturally occuring zircons by Raman Spectroscopy. XIVth International Conference on Raman Spectroscopy. Extra Booklet E13-E14.

Vavra G 1994 Systematics of internal zircon morphology in major Variscan granitoid types. Contributions to Mineralogy. and Petrology 117:331-344.

Wayne D M, Sinha A K & Hewitt D A 1992 Differential response of zircon U-Pb isotopic systematics to metamorphism across a lithological boundary: an example from the Hope Valley Shear Zone southeastern Massachusetts. USA Contributions to Mineralogy and Petrology 109:408-420.

Williams I S 1992 Some observations on the use of zircon U-Pb geochronology in the study of granitic rocks. Transactions of the Royal Society of Edinburgh Earth Sciences 83:447-458.

Woodhead J A, Rossman G R & Silver L T 1991 The metamictization of zircon: radiation dose-dependent structural characteristics. American Mineralogist 76:74-82.