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# Using hafnium and oxygen isotopes in zircons to unravel the record of crustal evolution

C.J. Hawkesworth *, A.I.S. Kemp

*Department of Earth Sciences, University of Bristol, Bristol, BS8 1RJ, UK*

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## Abstract

The development of improved techniques for the in situ analysis of U–Pb, Lu–Hf and O isotopes and of trace element contents has revolutionized approaches to modeling the origins and evolution of the continental crust, and the petrogenesis of granite. The key has been to obtain representative samples, and it is increasingly accepted that these are best provided by zircons. In magmatic rocks they may be inherited or have crystallized in the evolution of the host magma, and in sediments they may be detrital from broad areas in the continental crust. In situ Hf isotope ratios are now routinely measured with sub-epsilon unit precision by laser ablation ICP-MS. Trace element contents broadly constrain the tectonic setting of the magmas from which the zircons crystallized, Hf isotopes reflect when new crust was generated from the mantle, and O isotopes are sensitive to low temperature processes, as in erosion and sedimentation. The potential of an integrated approach is explored with new data from the Lachlan Fold Belt in south-east Australia. Inherited (pre-magmatic) zircons in the granites and detrital zircons in the surrounding Ordovician metasedimentary rocks yield very similar information. Their crystallisation age spectra are dominated by peaks at 450–600 Ma and 0.9–1.2 Ga, however the Hf model ages of zircons with broadly mantle-like $\delta^{18}$O values (<6.5‰) fall into two relatively narrow age ranges, c 1.7–1.9 and 2.9–3.1 Ga. Since such crustal formation peaks do not match those registering the predominant zircon crystallisation ages, the 450–600 Ma and 0.9–1.2 Ga periods are essentially times of crustal differentiation, rather than growth, in this region. Furthermore, the Hf model ages of zircons with high $\delta^{18}$O values (greater than 6.5‰) peak at about 1.8–2.0 Ga, close to the Nd model ages of the Ordovician metasedimentary rocks. Variations in Hf, O isotopes and trace elements in zircons from two I-type granite suites from the Lachlan Fold Belt highlight the presence of mantle contributions in the generation of these granites, and when the crustal component is a partial melt of the local metasedimentary rocks. Little of such specific information is available from the whole rock compositions, and yet it is a prerequisite for more physically realistic models for granite petrogenesis, better constrained thermal budgets, and much greater insight into the evolution of particular segments of continental crust.

*Keywords:* Zircons; Hf model ages; Oxygen isotopes; Crustal evolution

## 1. Introduction

Keith O'Nions was one of pioneers in the application of Nd isotopes to exploring the age of the continents and the time scales of their evolution (O'Nions et al., 1983; O'Nions, 1984), in part in the context of the consequences of continent formation on the composition of residual mantle and its integration into

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* Corresponding author. Tel.: +44 117 954 5425; fax: +44 117 925 3385.

*E-mail address:* c.j.hawkesworth@bristol.ac.uk (C.J. Hawkesworth).

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models for the evolution of the Earth (Jacobsen and Wasserburg, 1979; O'Nions et al., 1979). He was heavily involved in case studies for the generation of new crust in recent island arcs (Hawkesworth et al., 1977, 1979) and in the Archaean (Hawkesworth and O'Nions, 1977), he explored models in which the incompatible element content of the continental crust reflected small degrees of partial melting of the upper mantle, and suggested that the residence times of incompatible trace elements and major elements in the crust might be different (O'Nions and McKenzie, 1988).

Nonetheless, the long-standing debate over how the volumes of crust inferred from the distribution of radiogenic isotopes in long lived isotope systems, particularly Sm–Nd, might be linked to the *actual* volumes of total continental crust present at any particular time remains unresolved. Information about the volumes of crust inferred from radiogenic isotopes necessarily derives from crust that has been present for periods of time that are long relative to the rate of change of radiogenic isotopes from radioactive decay, that is, differentiated crust that had stabilized geologically. Clastic sediments such as shales are commonly utilised for this purpose, since sedimentary processes average the exposed continental mass without affecting Sm/Nd ratios, and thus mean crustal residence ages can be inferred from their Nd isotope ratios. However, the average age of the upper crust (2.0 ± 0.3 Ga, Miller et al., 1986) may not be a good proxy for that of the continental crust as a whole, since the residence time of different elements in different parts of the crustal column may be different. For example, the survival rate of Si and K, both major constituents of the buoyant granitic rocks in the upper crust, may far exceed that of Mg, Ca and Sr in the lower crust, where mafic cumulates and dense residues of granite production are more readily recycled back into the mantle (see Kemp and Hawkesworth, 2003). The rates at which the differentiated upper continental crust forms, relative to those at which new crustal material is generated, also remain uncertain.

The challenge in unravelling the age and growth history of the continental crust lies with a better understanding of the timing of the major episodes of crust generation. Although new crust is basaltic and derived from the mantle, crustal growth is most obviously manifest by the emplacement of evolved silicic magmas, given that crust generation and differentiation are intrinsically linked (Tamura and Tatsumi, 2002; Mortazavi and Sparks, 2004; Vogel et al., 2004). For example, the andesite–dacite volcanism witnessed above modern subduction zones testifies to the ongoing generation of new continental crust at convergent plate boundaries. However, studies attempting to chart the growth history of the continental crust through granitic rocks and their volcanic counterparts have encountered two major difficulties:

(1) There is evidence for crust formation as early as 4.4 Ga (Wilde et al., 2001), but the record of early continent generation is fragmentary. It is unclear whether the paucity of felsic rocks older than 3 Ga is a true indication of the amount of crust that was present, or reflects the ready destruction of embryonic continents by asteroid bombardment and/or aggressive tectonic recycling. Uncertainties remain as to how geologically representative the surviving segments of old continental crust actually are, given problems of selective preservation and/or incomplete sampling. This is particularly true of the Archaean, since cratons of this age cover only 7.5% of the Earth's surface, and it is a big issue in assessing the apparent major pulses of crust generation inferred from the frequency distribution of ages of surface rocks (Fig. 1). One way forward is through the study of detrital zircons in terrigenous sedimentary rocks, since they provide the most representative sample of the age distributions in eroded source terranes (see below).

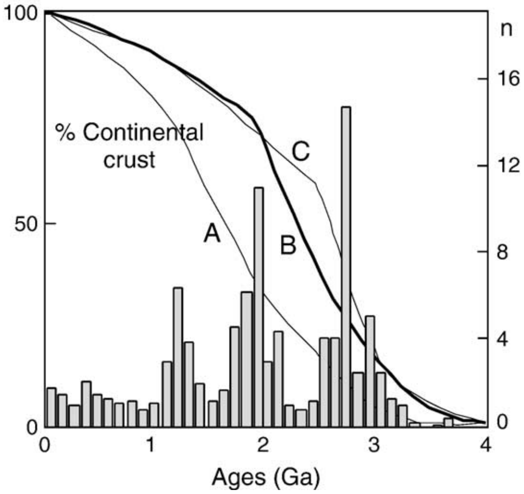

Fig. 1. Histogram of U/Pb ages of juvenile igneous rocks (from Condie, 1998) compared with curves representing different models for changing volumes of stable continental crust through time. Curve A is based on Nd isotopes in shales (Allegre and Rousseau, 1984), B from Pb isotope modelling (Kramers and Tolstikhin, 1997) and C from Taylor and McLennan (1995). A central issue concerns whether the age peaks are truly registering periods of accelerated crustal growth, or are just artefacts of selective preservation.

(2) The precursors of felsic igneous rocks, and thus the proportion and composition of new continental crust generated during given magmatic episodes, are not well understood. The least equivocal case is where the crustal residence age of the rock inferred from Nd isotopes approaches the crystallisation age, as in the Canadian Cordillera (Samson et al., 1989), whereupon silicic magmatism represents the addition of new crust. However, isotope and trace element evidence imply that most granites represent mixtures of material from different sources, and that some have formed entirely by anatexis of older crust (see Kemp and Hawkesworth, 2003). Assessing the balance of recycled versus juvenile components is highly contentious and plagued by ambiguities with interpreting whole-rock data. There is also increasing evidence that the mantle-derived component in many granites itself incorporates some recycled crust, and that the usual assumption of a depleted mantle heritage (e.g. Jahn et al., 2000) is unwarranted. What is required is a mineralogical and hence chemical record of the different components in granitic magmas, and of their source rocks.

The development of greatly improved in situ techniques for determining the isotope and trace element compositions of magmatically zoned minerals has revolutionised approaches in these areas. The robust accessory phase zircon is proving the most valuable, since different growth zones within zircon crystals can be dated by U–Pb isotopes, and it preserves an exceptional record of magmatic, and thus continental crustal evolution in its Lu–Hf and O isotope stratigraphy, and certain trace element ratios. In this contribution, we review recent advances in the in situ measurement of Hf and O isotopes in zircons, and illustrate the unique potential of this approach for unravelling the origins of the continental crust. New Hf and O isotope and trace element data from Palaeozoic granites of southeastern Australia are discussed for this purpose.

## 2. Why zircon?

Zircon has the unique combination of physiochemical resilience and high concentrations of important trace elements that include two radiogenic isotope systems of geochronological importance (viz. U–Pb, Th–Pb) and another (Lu–Hf) that is gaining momentum as a crustal evolutionary tracer. Zircons typically crystallise from high silica melts and at moderate to high grades of metamorphism, and are almost ubiquitous in upper crustal rocks. They retain their isotopic integrity through multiple episodes of sedimentary and magmatic recycling, and, remarkably, even appear to survive transient entrainment into the mantle via lower crustal delamination and sediment subduction (e.g. Gao et al., 2004). Given their low solubility in silicic melts (Watson and Harrison, 1983), zircons persist as refractory relics in some granitic magmas and potentially carry chemical and isotopic information about the deep crust that is otherwise inaccessible. Similarly, because weathering and erosion average large tracts of continental crust, detrital zircons in clastic sediments preserve a more complete temporal record of igneous and (potentially) crustal growth episodes than the exposed basement. For example, the oldest surviving crustal rocks are 4.01 Ga (Bowring and Williams, 1999), but detrital zircons in the Yilgarn Craton of Western Australia extend our coverage of continent-forming processes back to 4.4 Ga (Wilde et al., 2001). Moreover, detailed studies of sediments of known provenance show that the age and Hf isotope populations of detrital zircons mirror that of the rock types from which they were derived (Knudsen et al., 2001). Thus, detrital zircons in young sediments can be used to evaluate the key magmatic and metamorphic events in significant portions of the continental crust, and thus to chart crustal evolution (Amelin et al., 1999; Bodet and Scharer, 2000; Griffin et al., 2004). This approach also has application to studies of the Antarctic continent (which represents ~9% of the volume of continental crust), since even in summer only 2% of it crops out through the ice and snow, but it can be sampled in glacially derived sediments around its margins.

Of enormous benefit is that more of the chemical and isotope information encoded within the complex growth structure of zircon can now be extracted by micro-analytical techniques capable of high precision and spatial resolution. As the ages of discrete growth phases within single grains can be determined by in situ U–Pb isotope analysis (Fig. 2), zircons provide an unparalleled time series of changing magmatic conditions during crystal growth. This record can be deciphered in turn using hafnium and oxygen isotope and trace element compositions.

### 2.1. Hf isotopes

Analysis of Lu–Hf isotopes has been revolutionised by recent advances in plasma-source mass spectrometry and laser-ablation micro-sampling techniques. This has opened up fresh perspectives on crust–mantle differen-

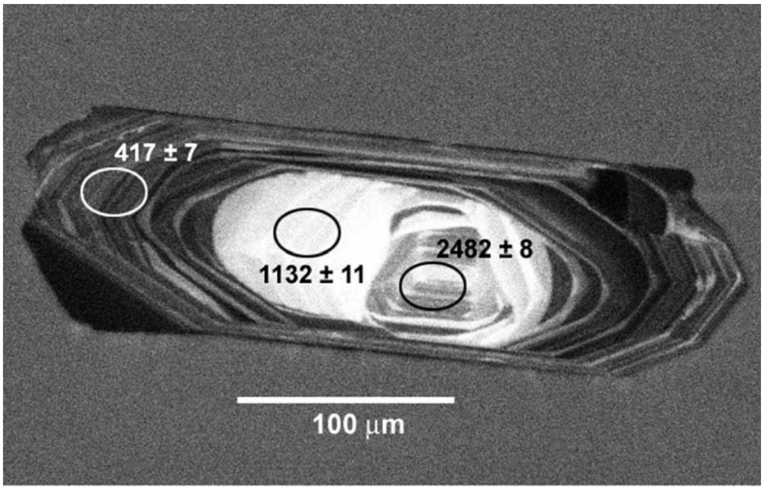

Fig. 2. Cathodoluminescence image of a zircon crystal from a granitic rock, which preserves a complicated and multi-stage growth history. The age of each growth phase (in Ma) has been determined by in situ U–Pb analysis using a Cameca ims1270 ion microprobe at the Swedish Museum of Natural History (see Kemp et al. (2005) for details).

tiation (Vervoort and Blichert-Toft, 1999; Vervoort and Patchett, 1996; Blichert-Toft and Albarede, 1997; Vervoort et al., 1999; Chauvel and Blichert-Toft, 2001). Hf is a lithophile group IVb element whose chemical behaviour resembles that of the much more abundant Zr (Zr/Hf ~35 in crustal rocks). Hf has six naturally occurring isotopes, of which radiogenic $^{176}$Hf is produced by the $\beta^-$ decay of $^{176}$Lu with a half-life of 37.2 Gyr in terrestrial samples. Hf is more incompatible than Lu during melting of spinel and garnet peridotite, and so the long-term enrichment of Hf relative to Lu in the continental crust results in relatively unradiogenic and radiogenic $^{176}$Hf/$^{177}$Hf ratios in crustal and depleted mantle reservoirs respectively (Patchett et al., 1981). In this respect, the Lu–Hf system is analogous to Sm–Nd, and indeed Hf–Nd isotopes form coherent arrays for most mantle-derived rocks (Vervoort and Blichert-Toft, 1999). However, since the fractionation of Lu/Hf during mantle melting is approximately twice that of Sm/Nd, and the half life of $^{176}$Lu is shorter than that of $^{147}$Sm, Hf isotopes may have greater resolution in identifying discrete mantle source domains (Patchett and Tatsumoto, 1980; Patchett, 1983).

The great advantage of Hf isotopes for crustal studies is that they are concentrated and bound in the zircon crystal lattice, whereas the REE are far less compatible. Zircons therefore have very low Lu/Hf ratios (typically <0.001), so that Hf isotope corrections due to in situ radiogenic growth are virtually negligible. In other words, zircons preserve close to the initial $^{176}$Hf/$^{177}$Hf ratio inherited from the magma at the time of formation. Since zircons are highly robust and have high Hf contents (~1%), Hf isotope ratios are largely impervious to deep weathering, deformation and/or alteration, all of which can disturb bulk rock (or other mineral) isotope systems, including Sm–Nd. The intra-crystalline diffusion rate of Hf in zircon is also very low (Cherniak et al., 1999), and so gradients in $^{176}$Hf/$^{177}$Hf within zircon grains, for example as induced by variations in the magmas from which they crystallized (Griffin et al., 2002), or reflecting the presence of components of different age (see below), will be preserved. Such information can contribute greatly towards unravelling the compositional evolution of silicic magmas, to ‘fingerprinting’ the nature of the source rocks, and hence to models of crustal evolution.

The Hf isotope ratios of crustal rocks are a measure of the crustal residence age, or the average time since the sources of the magmas from which the zircons crystallised were extracted from a specified mantle reservoir, usually depleted mantle. This approach requires that the Lu/Hf ratio of the depleted mantle is known as a function of time, which is a reasonable approximation for the purposes of this discussion. Relating these Hf ‘model ages’ and U–Pb crystallisation ages therefore allows investigation of the links between the ages of the major episodes of igneous activity and the formation of new crust. The caveat here is that the Lu/Hf ratio of these protoliths has not been subsequently modified during intra-crustal reworking. The effect of sedimentary processes on Lu/Hf ratios for the global sedimentary system has been investigated by Vervoort et al. (1999). These authors conclude that no significant parent–daughter fractionation occurs in the sedimentary environment, except during the formation of highly mature passive margin sandstones, where accumulation of detrital zircons imparts lower Lu/Hf and $^{176}Hf/^{177}Hf$. Rocks of this nature are infertile with regards to generating granitic melts, and so the 'zircon effect' is unlikely to complicate the interpretation of Hf model ages in granites. As regards magmatic differentiation, Lu/Hf ratios are particularly sensitive to the involvement of garnet ($D_{Lu}/D_{Hf}$ ~25–60), and the Hf and Nd isotope systems are therefore potentially decoupled in the crust by this phase (Vervoort and Patchett, 1996). Indeed, this effect has been observed in some lower crustal xenoliths (Schmitz et al., 2004). However, the Nd–Hf isotope array of crustally derived igneous rocks extends and overlaps the mantle array, implying that reprocessing of garnet-rich residues during later crustal melting is probably rare (Vervoort and Patchett, 1996). Melting in the presence of residual zircon ($D_{Hf}/D_{Lu}$ ~3–10), or fractional crystallisation of this phase, may also drastically shift Lu/Hf ratios. This is only likely to be a concern for low temperature intra-crustal melting of (meta)sedimentary precursors or differentiation of high-silica magmas, whereupon zircon is stabilised. The potential for accessory minerals (chiefly monazite) also to fractionate Sm from Nd during crustal differentiation is well established (e.g. Ayers and Harris, 1997). However, changes in Lu/Hf ratio with increasing silica are minimal in typical igneous suites, as is also the case for Sm/Nd (Fig. 3), and so it is inferred that such magmatic processes do not commonly modify Lu/Hf ratios in ways that would significantly affect their model Hf ages.

A larger pitfall with relying on Hf model ages to infer episodes of crustal growth concerns the possibility that the zircons crystallised from magmas with mixed source rocks that separated from the mantle at different times. A way around this problem is discussed below.

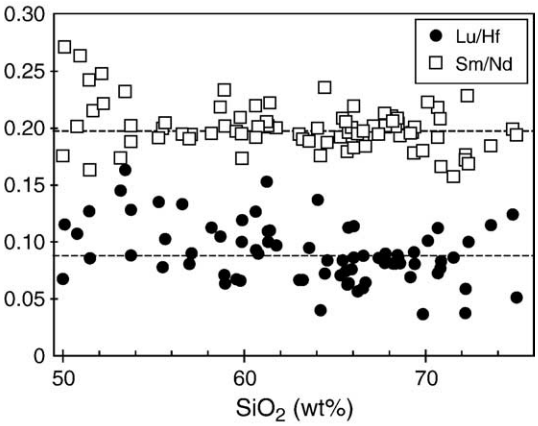

Fig. 3. Plot of Lu/Hf (closed circles) and Sm/Nd (open squares) versus silica for granitic rocks of the Lachlan Fold Belt, SE Australia (data sources as quoted in Kemp and Hawkesworth, 2003). The dashed line shows the mean Lu/Hf and Sm/Nd values estimated for the continental crust (from Rudnick and Gao, 2003).

### 2.2. Oxygen isotopes

Using radiogenic isotopes alone, it is difficult distinguish whether granites with evolved isotope signatures derive from mixed juvenile and recycled (metasedimentary) sources, or from mantle-derived precursors that have simply aged in the deep crust, such as an ancient mafic underplate. The extent to which model ages therefore pinpoint the actual time of crustal addition, as opposed to merely representing the average crustal residence age (Arndt and Goldstein, 1987), remains debatable. The problem is particularly severe for detrital or inherited zircons, since field and whole-rock chemical constraints are not available.

These ambiguities can be greatly reduced by augmenting radiogenic isotope data with stable isotopes, whose fractionation is time-independent. Oxygen isotopes are eminently suitable for this purpose. The $^{18}O/^{16}O$ ratio, expressed as $\delta^{18}O$ relative to SMOW, is only changed by low temperature and surficial processes, and so the $\delta^{18}O$ of mantle-derived magmas ($5.7 \pm 0.3‰$) contrasts with those from rocks that have experienced a sedimentary cycle or hydrothermal alteration on the sea-floor, which have elevated $\delta^{18}O$. This is reflected in the high $\delta^{18}O$ of the crystallising zircons and is a 'fingerprint' for a recycled component in granite genesis. Empirical studies have established that oxygen diffusion in zircon is sufficiently sluggish that the original igneous $\delta^{18}O$ remains intact, even through protracted metamorphism and crustal fusion (King et al., 1998; Peck et al., 2003). Significantly, $\delta^{18}O$ can be measured in situ in zircon with excellent precision ($<0.5‰$) by large radius ion microprobes that have multi-collector capability (Valley, 2003). One potential source of error with this technique is matrix-induced oxygen isotope fractionation resulting from different zircon Hf contents, which can reach 1‰ for every 1 wt.% $HfO_2$ (Peck et al., 2001). This can be negated by applying a correction based on the measured $HfO_2$ content of the 'unknown' relative to that of the standard, and by using standards of the appropriate composition. Fortunately, the two most commonly used zircon standards 91500 (0.66% $HfO_2$) and KIM-5 (1.23% $HfO_2$, Valley, 2003) bracket most of the range of $HfO_2$ values observed within granite-hosted zircons. The variation of instrumental mass fractionation of $^{18}O/^{16}O$ with zircon $HfO_2$ content as measured by multi-collector ion microprobes has yet to be rigorously assessed.

In principle, therefore, the coupling of radiogenic and stable isotopes can uniquely reveal whether zircon crystallised from a juvenile magma during crustal generation, or from magma derived by reworking of pre-existing igneous or (meta)sedimentary rocks. This provides greater insight into crustal evolution than was previously possible.

### 2.3. Trace elements

The complex crystallographic controls on the uptake of trace elements by zircon are being increasingly highlighted by recent studies (see review in Hoskin and Schaltegger, 2003). However, in a broad sense, the trace element inventory of igneous zircons should reflect the composition and crystallisation environment of the magma from which they precipitated (Heaman et al., 1990; Maas et al., 1992; Belousova et al., 2002). Thus, certain trace element data may be used to constrain the nature of the igneous precursor of detrital zircons and inherited zircon cores whose original geological context is lost, as well as the composition of the mantle-derived component in granite mixing systems (Griffin et al., 2002). It follows that in many cases zircon chemistry enables a first order distinction between the major tectonic settings under which the parent magma was generated. In this context, the age distribution data in Fig. 1 may be interpreted in terms of two general forms of crust generation related to (1) deep seated episodic thermal disturbances, as reflected for example in mantle plumes, that produce rapid crustal growth and thus peaks of juvenile igneous activity, and (2) relatively shallow level and continuous subduction-related processes associated with slower rates of crustal growth. The reconnaissance data in Fig. 4 show that zircons that crystallised from intra-plate ‘A-type’ granites have markedly different trace element compositions from those formed from subduction-related or orogenic magmas. Moreover, the shifts in trace element ratios are as predicted from those in basaltic magmas generated in the different settings. The concept of tectonic fingerprinting using zircon chemistry is in its infancy, but it holds considerable promise for establishing the broad geodynamic environment of magma and crustal generation episodes, using ancient detrital zircons with mantle-like isotopic signatures.

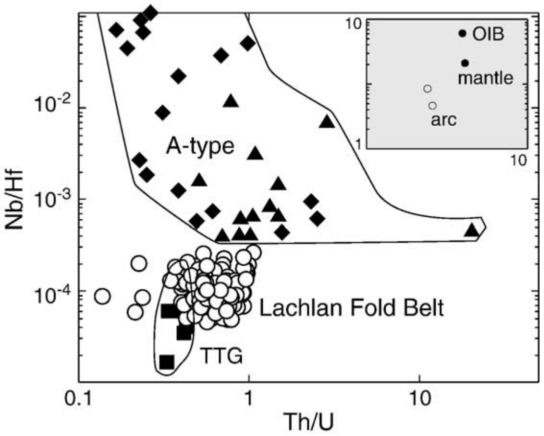

Fig. 4. Plot showing the different trace element signatures of zircons from an Archaean tonalite, granites of the Lachlan Fold Belt (SE Australia) and various intra-plate ‘A-type’ granites, the latter including peralkaline rocks akin to those of Nigeria (CJH and AISK, unpubl. laser ablation ICP-MS data). The inset depicts the same diagram for average arc basalts, primitive mantle and intra-plate basalts (OIB). Note that the Lachlan Fold Belt data include analyses of zircons from the Cobargo and Jindabyne suite granites, the Hf and O isotope compositions of which are shown in Fig. 8B.

## 3. Hf isotope determinations by laser ablation ICP-MS: some observations

### 3.1. Technique

Following pioneering studies by Griffin et al. (2000, 2002), the analysis of Hf isotopes in zircon by laser ablation has become almost routine in the last few years, although the technique is still undergoing refinement (e.g. Woodhead et al., 2004, and see below). The high spatial resolution and efficient ablation afforded by new generation lasers, coupled with rapidity of analysis (between 60 and 90 s) and minimal sample preparation, are obvious attractions of this type of work. However, the single most critical factor in obtaining accurate $^{176}$Hf/$^{177}$Hf ratios by laser ablation concerns the ability to correct for the isobaric interference of the rare earth elements Lu and Yb on $^{176}$Hf. The latter is an order of magnitude more severe, and may exceed 300 000 ppm on mass 176, depending on the REE content of the analysed zircon. Interference from molecular species (oxides, nitrides) is another potential source of uncertainty. This may also affect the non-radiogenic Hf isotopes and instrumental mass fractionation factors calculated therefrom.

To interpret Hf isotope data with confidence it is therefore imperative to establish the veracity of the interference correction over the range of $^{176}$Yb/$^{177}$Hf ratios encountered in zircons, and this requires some explanation. The correction itself is performed by measuring an interference-free Yb isotope during the analysis, such as $^{171}$Yb or $^{173}$Yb, and then calculating the magnitude of the $^{176}$Yb interference using the recommended $^{176}$Yb/$^{171}$Yb or $^{176}$Yb/$^{173}$Yb ratios. The Lu correction is performed in the same fashion by monitoring $^{175}$Lu, and using $^{176}$Lu/$^{175}$Lu=0.02669 (De Bievre and Taylor, 1993). The greatest source of uncertainty in this regard concerns which Yb isotope pairs are used and the precise values of their ratios; the latter becomes particularly critical at high Yb/Hf ratios, where large corrections to the measured 176/177 ratio are necessary. As noted by Griffin et al. (2002), the IUPAC value for $^{176}$Yb/$^{172}$Yb fails to yield the correct value for $^{176}$Hf/$^{177}$Hf in standard materials. The experimental approach to this problem involves spiking a standard solution of known Hf isotope composition with variable amounts of Yb, and iteratively calculating the $^{176}$Yb/$^{x}$Yb ratio required to give the correct $^{176}$Hf/$^{177}$Hf value. This is summarised in Fig. 5A, using corrections based on the $^{176}$Yb/$^{171}$Yb ratio, and using measured $^{173}$Yb/$^{171}$Yb to correct for Yb mass bias, as recommended by Woodhead et al. (2004). Clearly, of the values referred to here, only those of Segal et al. (2003) yield accurate Hf isotope ratios over the full range of Yb/Hf ratios considered using the instrumentation at Bristol. In the other cases, systematic under-correction of the $^{176}$Yb interference generates a positive correlation between $^{176}$Hf/$^{177}$Hf and Yb/Hf. A similar correlation in zircon laser ablation data might also be taken as an artefact of inadequate interference correction. However, this needs to be treated with caution, since such trends might have a geological origin. Such a pattern would arise, for example, during zircon crystallisation from a primitive magma that was assimilating metasedimentary crust with lower $^{176}$Hf/$^{177}$Hf and Yb/Hf ratios. Fig. 5A also shows that the uncertainty on the final $^{176}$Hf/$^{177}$Hf value increases substantially as the magnitude of the Yb overlap correction increases, and this factor limits the precision of Hf isotope measurements in REE-rich zircons.

### 3.2. Ablation effects

Fig. 5B shows data from three zircon standards of different REE content (Temora 2, Mud Tank and 91500), whose $^{176}$Hf/$^{177}$Hf ratios were independently ascertained by analysis of solutions purified for the REE by chemical separation (Woodhead et al., 2004). All laser ablation analyses were conducted in the Department of Earth Sciences, University of Bristol, using a 193 nm ArF laser and Finnigan Neptune multi-collector ICP-MS. The Faraday cup configuration is the same as used by Woodhead et al. (2004). Ablation was conducted in He (flow rate ~1.3 l/min, optimised daily), this being combined with argon (~0.9 l/min) in a small glass mixing chamber prior to transport into the ICP. Initial tests using this set-up revealed that oxide formation in the plasma was significant, with UO/U exceeding 3% depending on the torch ‘z’ position. In view of this, unacceptably high $^{176}$Hf/$^{177}$Hf ratios measured in the most REE-rich zircon standard during this period are consistent with interference of $^{160}$DyO on mass 176. To counteract this, a small (~0.005 l/min) $N_2$ flow was introduced into the Ar carrier gas upstream of the mixing chamber, which suppressed oxide formation and enhanced sensitivity by a factor of two. Subsequent tests on pure REE solutions have established that formation of nitride molecules is negligible.

The Hf isotope data in Fig. 5B were acquired using a 50 μm beam size and 4 Hz laser pulse repetition rate over a sixty second ablation period, producing typical total Hf beams of ~15, 17 and 24 V for zircon standards 91500, Temora 2 and Mud Tank, respectively. The power density at the sample was around 6–7 mJ/cm$^2$, which, for zircon, translated into an estimated drilling rate of between 0.5 and 1 μm/s. Internal precision routinely varies between ±0.000010 and ±0.000030 (at 2 s.e. level), being consistently the best for Mud Tank, reflecting the greater signal intensity and, presumably, higher Hf concentration. External precision was ±0.000018 for 91500 and Mud Tank (62 and 65 ppm, respectively) and ±0.000026 for Temora 2 (93 ppm, all at 2 s.d.). When adjusted slightly to JMC 475 $^{176}$Hf/$^{177}$Hf=0.282160, the laser ablation data on the three zircon standards agree well with the solution-based data of Woodhead et al. (2004). The excellent reproducibility of the data testifies both to the homogeneity of the standards, at least for $^{176}$Hf/$^{177}$Hf, and the robust nature of the interference correction.

It must be borne in mind, however, that Fig. 5B portrays the optimum scenario for laser ablation, in that data are from clear, crack- and inclusion-free grains. The situation for many magmatic and detrital zircons will inevitably be more complicated, given the likelihood of inclusions, radiation damage and pronounced isotopic zoning resulting from magmatic processes and/or the presence of components of different ages. It is therefore desirable to assess the impact of these complexities on Hf isotope compositions, and this is highlighted in Fig. 6. Inclusions, of which apatite and monazite are the most frequently encountered, induce some large excursions in trace element content and increase the Yb/Hf ratios, but have little effect on the corrected $^{176}$Hf/$^{177}$Hf ratio (Fig. 6A, B). This reflects the low concentration of Hf in the included minerals (typically <5 ppm), even though it is potentially highly radiogenic. The situations in Fig. 6A and B pertain to

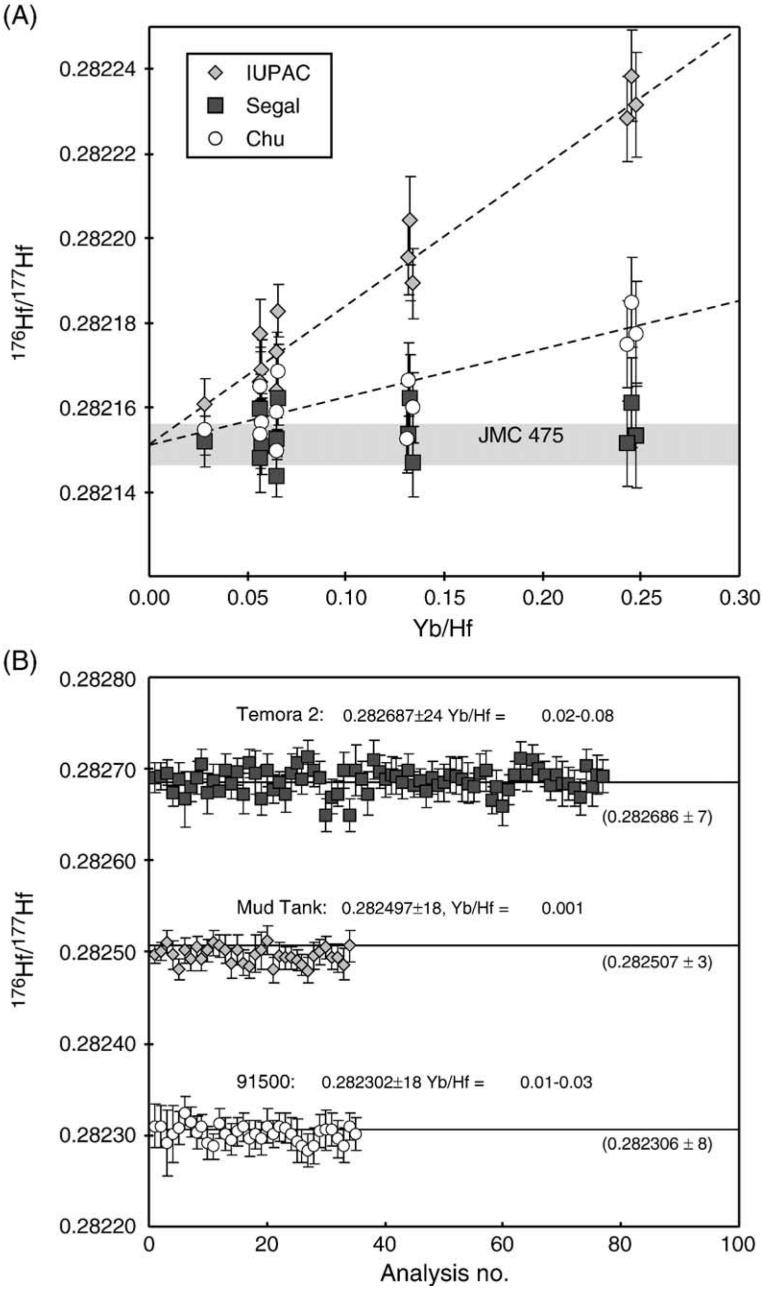

Fig. 5. (A) Analyses of the JMC 475 standard solution ($^{176}$Hf/$^{177}$Hf$=0.282150\pm5$, background corrected $n=16$, shown by the shaded band) spiked with variable amounts of Yb, comparing the interference corrections using the different $^{176}$Yb/$^{171}$Yb and $^{173}$Yb/$^{171}$Yb values quoted in the literature (IUPAC, De Bievre and Taylor, 1993; Chu et al., 2002; Segal et al., 2003). Error bars are at $2\sigma$. (B) Laser ablation Hf isotope data from three zircon standards of different Yb/Hf ratios, as measured at the University of Bristol over a six month period (error bars on individual analyses are shown at $2\sigma$). To facilitate comparison with other literature values, all data are normalised to a JMC 475 value of $^{176}$Hf/$^{177}$Hf$=0.282160$. The mean $^{176}$Hf/$^{177}$Hf values for each standard (quoted at 2 standard deviations) compare favourably with the solution-based data reported by Woodhead et al. (2004), given in parentheses (at $2\sigma$) and shown as the horizontal line. All data were acquired with a 193 nm ArF laser operating at 4 Hz and using a 50 μm spot size. The Yb isotope compositions of Segal et al. (2003) were used for interference corrections.

inclusions that are small relative to the beam size, such that the inclusion and host zircon are ablated simultaneously. Obviously, larger inclusions will produce greater effects, principally by 'diluting' the Hf signal and inducing larger analytical errors; however, such inclusions can be recognised optically and are thus

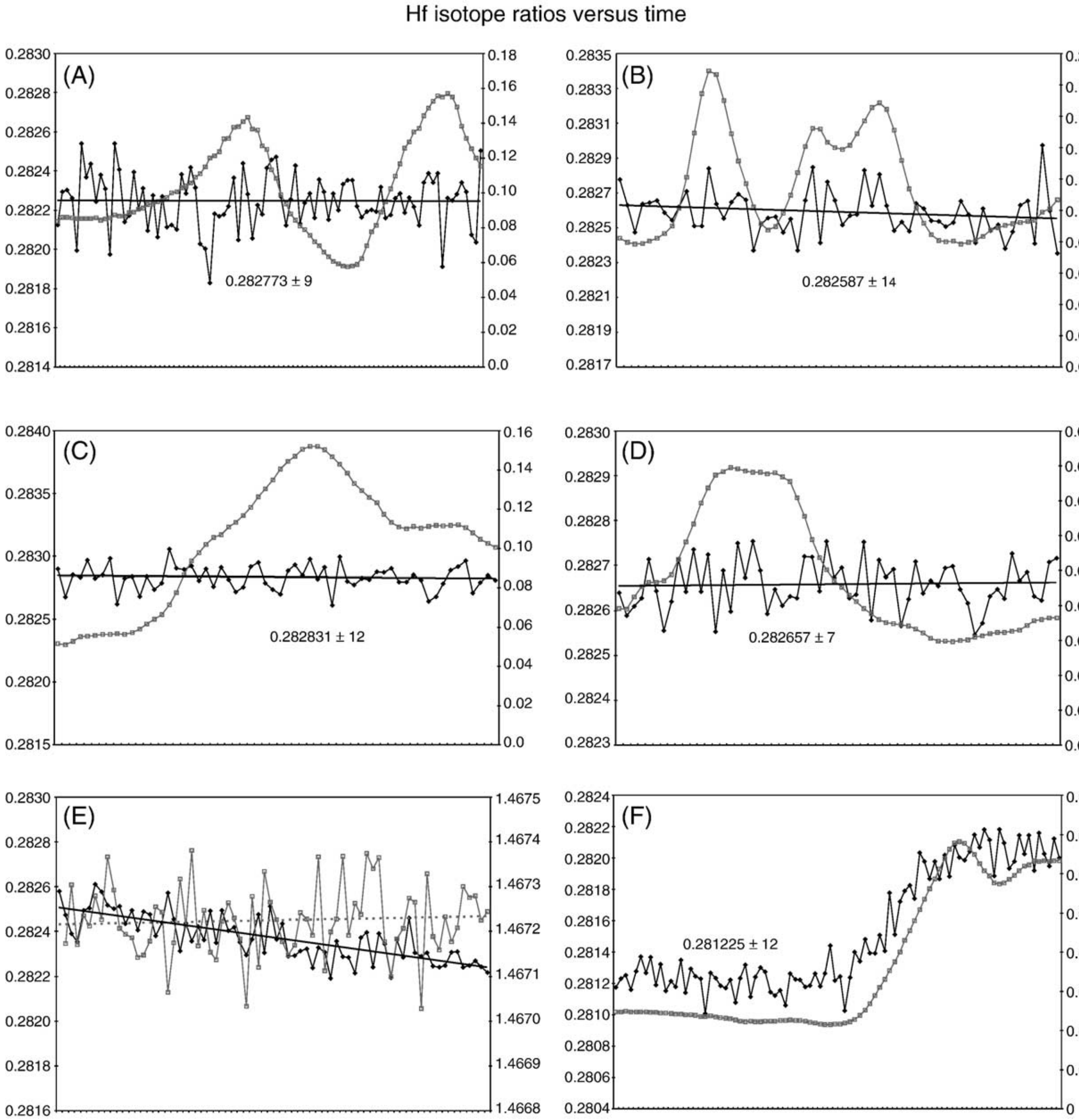

Fig. 6. Time-resolved signals produced by laser ablation depth profiling of zircons, showing the effects of (A) and (B) traversing apatite inclusions, (C) impinging upon a crack related to radiation damage, (D) ablating through a fracture, (E) zoning related to magmatic processes and (F) drilling through an inherited core into a younger magmatic rim. The $^{176}$Hf/$^{177}$Hf ratio is shown on the primary axis (black line and filled diamonds) and the Yb/Hf ratio is indicated on the secondary axis (grey line, open squares), except in (E) where the $^{178}$Hf/$^{177}$Hf ratio is plotted. The solid trend-line is for $^{176}$Hf/$^{177}$Hf, and each data point represents a 1 s integration. Laser operating conditions are as for Fig. 5.

easily avoided. Partially metamict grains (Fig. 6C, D) produce similar effects to minute inclusions. These grains are usually intensely fractured, manifesting expansion related to radiation damage. In the examples studied, traversing such cracks during ablation (as recognised optically during the analysis) produced spikes in Yb and Lu intensities, and Yb/Hf ratios, but again the corrected $^{176}$Hf/$^{177}$Hf shows negligible within-run variation (Fig. 6C, D). The observed enrichment of Yb and Lu probably reflects the localised accumulation of REE (possibly as phosphates, e.g. Price et al., 1991) in fractures related to pervasive hydrothermal alteration and weathering of the host granite. Nevertheless, provided that the isobaric interference on $^{176}$Hf can be adequately compensated, effects such as these should pose few problems.

The effect of magmatic zoning is evident in Fig. 6E, where $^{176}Hf/^{177}Hf$ exhibits continuous decrease with depth in the crystal, i.e., from core to rim. A concomitant change in Lu/Hf and Yb/Hf ratios (not shown) reflect chemical as well as isotopic zoning. An ablation-induced mass fractionation effect can be precluded in this case, since there is no change in the non-radiogenic and interference-free $^{178}Hf/^{177}Hf$ ratio during the analysis. Fig. 6F shows the more dramatic case of intersecting growth phases of different age and $^{176}Hf/^{177}Hf$ and Lu/Hf during depth profiling, in this case drilling from an inherited core (1.2 Ga) into the younger magmatic overgrowth (430 Ma). Given that 193 nm ArF lasers excavate flat-bottomed pits (e.g. Eggins et al., 1998), the mixing effects documented by Griffin et al. (2002) are largely circumvented, as well illustrated by Woodhead et al. (2004). However, because inherited cores are typically rounded by sedimentary abrasion or magmatic resorption, the interface between the two different components may not be orthogonal to the laser beam. A transition period, where the laser samples different proportions of material from each, will therefore result as the overgrowth is approached, as evident on Fig. 6F. Nevertheless, reliable Hf isotope ratios of the two components can be obtained if the signal from each is sufficiently long (Fig. 6F).

A final point concerns whether Hf isotope ratios in zircons are affected by the same processes that cause U–Pb isotopic disturbance. For granite samples showing a single, magmatic zircon age population, we have observed no correlation between Hf isotope composition and the degree of discordance on concordia diagrams, where the latter is probably due to radiogenic Pb loss. In contrast, the situation could be far more complex when discordance relates to zircon overgrowths that form in response to younger metamorphic episodes, since these could have very different Hf isotope ratios. A possible example of this, from the Archaean Watersmeet Gneiss of Wyoming, is documented by Patchett (1983). Similar effects may be partly responsible for the scattered Hf isotope variation shown by Early Archaean detrital zircons from the Narryer Gneiss Complex (Western Australia), as reported by Amelin et al. (1999). As with the Patchett (1983) example, these data were acquired by digestion of whole grains, or fragments thereof. Most of these exhibit some U–Pb discordance, albeit typically <10%, and are known to have complicated internal morphologies and age distributions (Froude et al., 1983; Maas et al., 1992). Such complexities in zircons from rocks with poly-metamorphic histories are only likely to be deconvolved by in situ studies.

## 4. Granites, and zircons, as windows to crustal evolution: an example from the Lachlan Fold Belt, southeastern Australia

The Palaeozoic Lachlan Fold Belt (LFB) has a prominent place in the history of ideas on the origin of granite, as it was here that the global dichotomy between metaluminous and peraluminous granites was first attributed to derivation from disparate crustal protoliths (Chappell and White, 1974). Ironically, however, the exact nature and proportions of the source components, and the role of mantle-derived magmas, have proved almost impossible to resolve from whole rock compositions. The ensuing discussion therefore focuses on how the use of zircons has stimulated new progress on this front, and provides an unparalleled window into the ages of crystallisation events, and periods of new crustal growth, in the source regions of these granites.

The LFB is a 700-km wide segment of a vast orogenic system that formed along the eastern Gondwana margin from the Early Ordovician to Devonian (Fig. 7). The tectonic development of the belt remains contentious, although the complex patterns of deformation, magmatism and metamorphism seem to require multiple subduction zones (Gray, 1997). The LFB has two main components, (1) a monotonous succession of mature (quartz- and clay-rich) Ordovician to Silurian turbidites, variably deformed and mostly metamorphosed in the lower greenschist facies, and (2) abundant granitic and spatially related volcanic rocks, almost entirely emplaced in the 430–350 Ma interval.

Following the seminal suggestion of Chappell and White (1974), the granites and volcanic rocks are subdivided into two lithological categories, each of which crop out in approximately equal proportions. The first group is metaluminous to weakly peraluminous, with high CaO and Ca/Na, and usually contains hornblende, with or without clinopyroxene, titanite and allanite. These rocks are assigned a meta-igneous or *infracrustal* protolith that has not experienced a weathering cycle, such as an accreted mafic underplate, and are termed ‘I-types’ (Chappell and Stephens, 1988). The second group comprises strongly peraluminous, typically cordierite-bearing granodiorites and monzogranites that form composite batholiths along with I-types some distance inboard of the continental margin. These ‘S-type’ rocks have generally lower abundances of seawater soluble elements (Na, Ca and Sr), consistent with derivation by anatexis of sedimentary or supracrustal protoliths formed at the Earth’s surface (Chappell and White, 1974; Clemens, 2003). It is therefore envisioned that granite magmatism in the LFB involved the remelt-

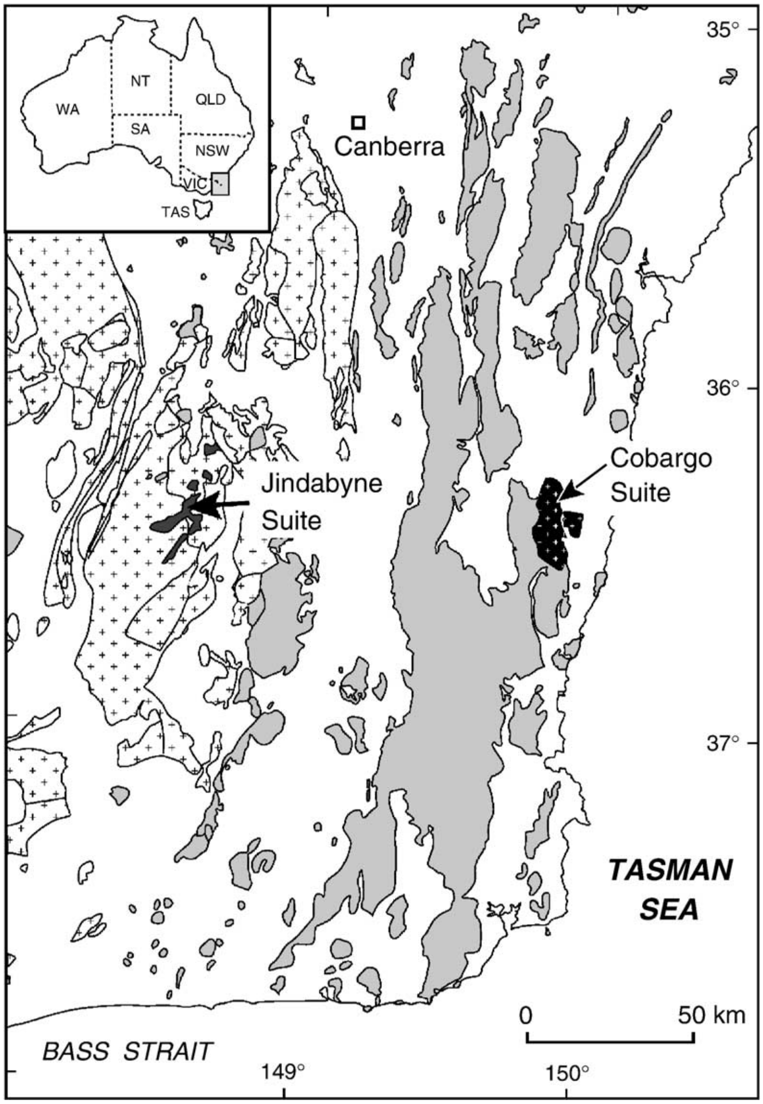

Fig. 7. Simplified geological map of the Lachlan Fold Belt in eastern Australia (after Kemp et al., 2005) showing the major granitic batholiths and the distribution of the 'I-type' (shaded) and 'S-type' (crosses) intrusions. The general locations of the samples from the 390 Ma Cobargo (black with

ing of older protoliths, rather than the addition of juvenile crust. Many of the granites are also thought to be replete with refractory material entrained from the source region (Chappell et al., 1987), thus limiting the amount of crustal differentiation associated with silicic magmatism. Inherited zircons contained by the granites are the best candidates for such residues (Williams, 1992), although these are sparse within many I-type plutons (Kemp et al., 2005).

The S- and I-type scheme has been widely adopted, although the disadvantages of such genetic classifications have been discussed elsewhere (e.g. Kemp and Hawkesworth, 2003). The problem is that despite the envisaged difference in source materials, the whole-rock compositions of the two LFB granite types converge and their trace element patterns are virtually identical. Although lithologically diverse, the granites exhibit a range of bulk rock isotope compositions (O'Neill and Chappell, 1977; McCulloch and Chappell, 1982; McCulloch and Woodhead, 1993) and the I- and S-type granites of the eastern LFB define a single overlapping array on an εNd versus initial $^{87}Sr/^{86}Sr$ diagram. On this basis, alternative models contend that the granite compositional spectrum in the LFB reflects large-scale mixing between primitive, depleted mantle-like magmas and an evolved crustal end-member sourced from the Ordovician metasedimentary basement (e.g. Gray, 1984). This idea receives support from the observed mingling and hybridisation between some granites and coeval basaltic liquids (Keay et al., 1997; Collins et al., 2000). Melts of Cambrian-aged mafic arc crust, which underlies the turbidite sequence, may be an additional granite source component (Collins, 1996; Keay et al., 1997). Nevertheless, simple isotope mixing models fail to reproduce the bulk rock composition of I-type granites (McCulloch and Chappell, 1982; Chappell, 1996). The crux of the problem is that bulk rock data cannot determine whether the evolved isotopic composition of some hornblende granites (which ranges down to εNd = −8) is due to a metasedimentary input or reflects derivation from meta-igneous progenitors of different crustal residence ages (McCulloch and Chappell, 1982).

### 4.1. Magmatic processes

The potential of in situ mineral studies for resolving these issues is highlighted in Fig. 8, with reference to the I-type granites. The zircons from these rocks show variations in Hf isotope ratios within and between melt-precipitated growth phases that are large relative to analytical uncertainty (internal precision is typically 0.5–1.0 εHf units at 2 s.e. level) (Fig. 8A). These variations are masked in the whole rock compositions, and they can only be reconciled by the operation of open-system processes. The original mantle heritage of a mafic enclave is suggested by the high εHf values preserved within the cores of the constituent zircons. More specific information about the processes involved in the evolution of two I-type suites (Cobargo and Jindabyne) is given by Fig. 8B, which summarises, to the best of our knowledge, the first reported Hf and O isotope dataset from zircons in magmatic rocks. The coupled Hf and O isotope variations in zircons of each suite define separate, but near-parallel trends that reflect interaction between isotopically contrasting components during zircon precipitation. Data from the Cobargo sample lie along a curved array that reflects mixing between a component with high εHf and low $\delta^{18}$O, appropriate for a mantle-derived magma, and another with elevated, more ‘crust-like’ $\delta^{18}$O values and relatively low εHf. The identity of the high $\delta^{18}$O source material is less well constrained by Fig. 8B, although the geometry of the mixing curve indicates that this had lower Hf concentrations than the primitive

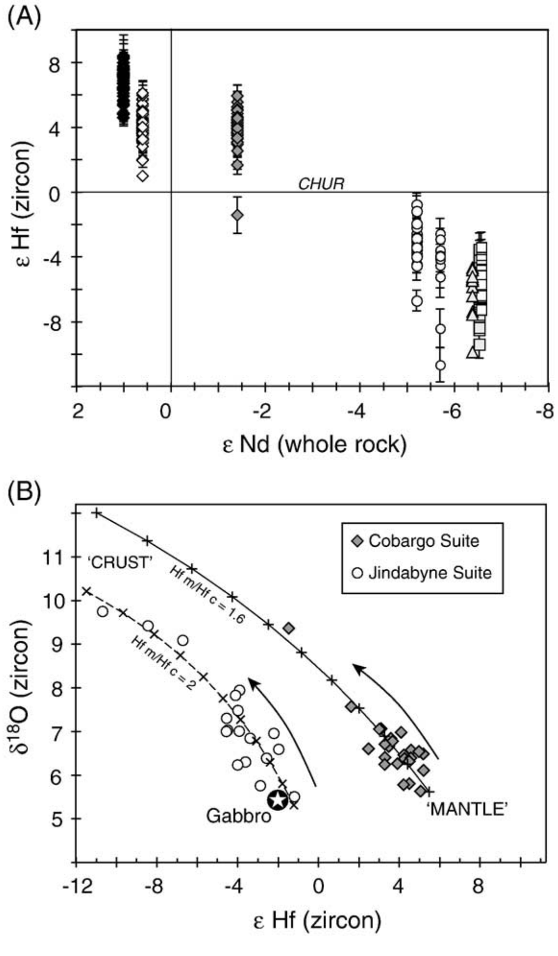

Fig. 8. (A) Comparison of the bulk rock εNd with the $\varepsilon_{\mathrm{Hf}}$ values of magmatically precipitated zircons within selected I-type granite samples of the LFB (Cobargo Suite rocks have diamond symbols, Jindayne Suite samples are shown in circles). Data from a mafic enclave are assigned solid black symbols. The analytical uncertainty in εHf is between 0.5 and 1 epsilon units (2$\sigma$). (B) Plot of εHf versus $\delta^{18}$O for zircons of the I-type Jindabyne (circles, 2 samples) and Cobargo (grey diamonds, one sample) suites, with the direction of crystallisation arrowed, as established by core-rim isotope zonation. The average Hf and O isotope (zircon) composition of a gabbro that is spatially associated with the Jindabyne Suite is shown by the star symbol. Note that changes in $\delta^{18}$O in zircon solely in response to fractional crystallisation are very minor (Valley et al., 1994). The two mixing curves represent the case where the concentration of Hf in the putative mantle end-member is either greater or less than that of the crustal end-member. For convenience the same crustal component is assumed for both suites, although this is obviously less well constrained for the Cobargo sample. Oxygen isotope compositions were obtained using a Cameca 1270 ion microprobe at the University of Edinburgh, and are reported relative to the internal standard zircon 91500 (10.07 ± 0.03‰). Oxygen isotope determinations were either made prior to laser ablation Hf isotope analysis, or adjacent to the laser ablation pit. Repeat analysis of the KIM-5 zircon standard (1.23% $HfO_2$) yielded a mean value of 5.14 ± 0.28‰ (1 s.d., $n = 68$), identical to the accepted value (5.09 ± 0.06‰, Valley, 2003). We therefore conclude that matrix induced fractionation resulting from different Hf contents is negligible for the zircons of this study, which have $HfO_2$ concentrations similar to KIM-5.

component. The high $\delta^{18}$O component in the Cobargo Suite may therefore have been a low temperature crustal melt generated in equilibrium with residual zircon, in which case the Hf–O isotope characteristics of the end-member may be appropriate for a metasedimentary rock (Fig. 8A). Together with the sense of core to rim Hf isotope zonation, it is therefore inferred that the Cobargo Suite sample originated as a mantle-derived magma (or its differentiate) that evolved by assimilation of anatectic melts from the metasedimentary host rocks.

The trend defined by the Jindabyne Suite on Fig. 8B is bracketed between a crustal end-member with high $\delta^{18}$O and low εHf, and a relatively primitive component similar to a spatially associated gabbroic intrusion. The εHf values show a systematic increase from zircon cores to rims. The data are therefore consistent with the Jindabyne suite forming from magmas that were isotopically akin to the local gabbro, which then experienced extensive mixing with crustal, probably metasedimentary material. This accords with the shape of the array, which implies that the Hf concentration of the mantle end-member was about half of that of the crustal component. As with Cobargo, a purely infra-crustal protolith can be precluded for the Jindabyne Suite. However, the 'primitive' end-member in the Jindabyne Suite had markedly lower εHf values, and so could have been derived from pre-existing mafic crust, such as an ancient basaltic underplate that escaped low temperature alteration. Alternatively, this high εHf end-member might originate from enriched, possibly supra-subduction-zone mantle, which itself might have comprised a blend of depleted mantle and crustal components. Given that the Jindabyne Suite extends to low silica values (~55% $SiO_2$) an origin by differentiation of isotopically enriched mantle-derived magma is preferred.

In principle, more details about the compositional evolution of granitic suites, and the broad nature of the mantle-derived end-member involved in mixing, may be deduced by linking Hf isotope variations with changes in zircon trace element composition, as highlighted by Griffin et al. (2002). According to the rationale in Fig. 4, variations in key trace element ratios may also provide general information on the tectonic setting under which the primitive magmatic component in granitic suites was formed. For example, zircons in the Cobargo and Jindabyne suites have low Nb/Hf values relative to zircons of typical A-type granites (see Fig. 4) and these do not correlate with εHf. Thus, an intra-plate setting for these magmas seems unlikely, based on the dataset presented in Fig. 4. This is consistent with models for a destructive plate margin setting for the LFB in the Silurian to Middle Devonian, as proposed by Gray (1997) and Collins (2002).

In summary, the Hf and O isotope stratigraphy of magmatic zircons records processes that are 'invisible' to classical bulk-rock analysis, and not resolvable by radiogenic isotopes alone. Fig. 8 also emphasises the problems with purely genetic classification schemes, since mixed mantle and crustal materials are clearly involved in the generation of both these granite suites.

### *4.2. Evolution of the granitic source region from pre-magmatic zircons*

Further insight into the nature of the sources of the LFB granites, and hence into crustal evolutionary processes in this area, is also provided by pre-magmatic zircons. These occur as inherited cores in the granites and as detrital grains in the surrounding Ordovician metasedimentary rocks, and strikingly both yield very similar information. Their age spectra (Fig. 9A) are dominated by large peaks at 450–600 Ma and 0.9–1.2 Ga, a signature that characterises the clastic sediments deposited along the former Gondwana margin (Ireland et al., 1998; Veevers, 2000). A sedimentary provenance in the Archaean and Early to Middle Proterozoic basement of the Australian cratonic interior is therefore precluded, since it does not contain rocks of those ages. More likely source regions are in the Late Proterozoic terranes of Antarctica and southern Africa (see Veevers, 2000), consistent with the observed southerly palaeo-current directions in the sediments.

The inherited zircons in both S- and I-type granites have the same distinctive crystallisation age patterns as detrital zircons in the Ordovician turbidites (Williams, 1992). In the case of the S-type granites, this is permissible evidence for derivation from the local metasedimentary sequence (e.g. Williams, 2001; Maas et al., 1997; Keay et al., 1999), though an additional, more primitive component is required to explain the chemical and isotopic diversity of these plutons (see Kemp and Hawkesworth, 2003). However, the significance of the older zircons in the I-type granite is less clear; these have been interpreted either as xenocrysts assimilated from the metasedimentary wallrocks (Collins, 1996), and as refractory remnants of the meta-igneous precursors (e.g. Williams, 1992). Given the observed age distributions, Williams (1992) speculates that the I-type granites derive from 500 to 600 Ma meta-igneous precursors, themselves formed by intra-crustal reworking of mafic rocks that separated from the depleted mantle about 0.9–1.2 Ga. The Nd model ages of most

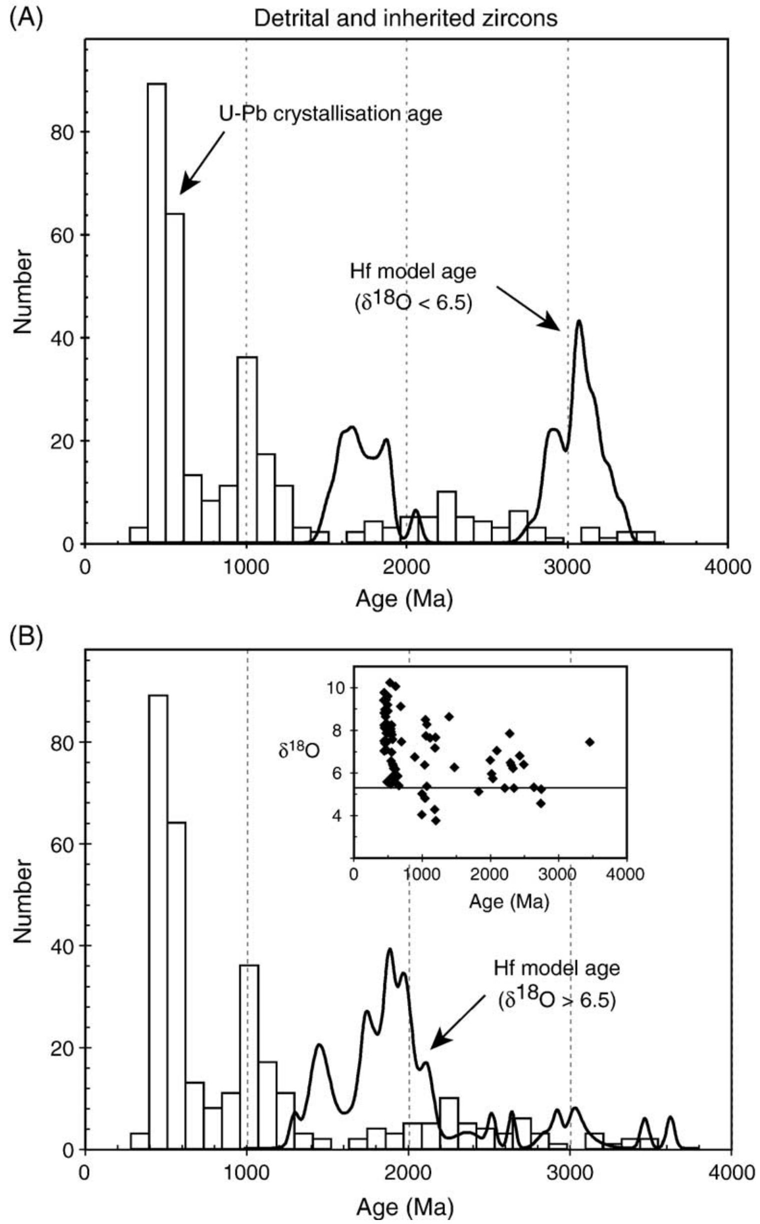

Fig. 9. Comparison of the crystallisation age histogram of detrital zircons from the LFB, as established by ion microprobe U–Pb dating (pooled datasets of Keay et al., 1999; Williams, 2001, and this study), with the distribution of Hf model ages for (A) inherited and detrital zircons with low and approximately mantle-like $\delta^{18}$O values (<6.5‰) and (B) zircons with high $\delta^{18}$O values (>6.5‰). The plot in (A) essentially contrasts episodes of magmatic activity with episodes of new crustal addition. The inset in (B) shows the variation in $\delta^{18}$O for the different age populations, and the $\delta^{18}$O of zircons in equilibrium with mantle oxygen (5.3 ± 0.3‰, horizontal line). Zircons for which Hf and O isotope data are available are from four S-type granites, and two samples of Ordovician metasedimentary rock.

I-type granites also cluster around 0.9–1.2 Ga (McCulloch and Chappell, 1982).

To explore this, the U–Pb crystallisation age and Hf model age distribution for detrital and inherited zircons of the LFB are contrasted in Fig. 9. The Hf model ages were calculated from measured $^{176}$Hf/$^{177}$Hf ratios, assuming that zircons crystallised from magmas with Lu/Hf ratios similar to that of the bulk crust (0.08, Rudnick and Gao, 2003). Such an approach is justified insofar as the average Lu/Hf ratio of common igneous rock suites, including the 32 Precambrian granites analysed by Vervoort and Patchett (1996), approaches the mean crustal value (see Fig. 3). The Hf model ages of zircons that retain mantle-like $\delta^{18}$O values (viz. $\delta^{18}$O < 6.5‰,

Fig. 9A) are the best measure of the time of crust generation, and despite the spectrum of crystallisation ages, these fall into two relatively narrow age ranges, c 1.7–1.9 and 2.9–3.1 Ga (Fig. 9A). These periods overlap the two main peaks of rapid global crustal growth, as reflected by the U–Pb emplacement ages of juvenile igneous rocks worldwide (Fig. 1). They are also typical of igneous episodes in Precambrian terranes of the Australian craton. However, it is striking that the crustal formation peaks on Fig. 9A do not match those registering the predominant zircon crystallisation ages. The implication is that the 450–600 Ma and 0.9–1.2 Ga rocks that dominated the provenance to the LFB sedimentary sequence were themselves formed by the reworking of ancient igneous rocks that were extracted from the mantle up to 2 Ga earlier. The 450–600 Ma and 0.9–1.2 Ga periods are thus essentially times of crustal differentiation, rather than growth, in this region. There was, however, new crustal addition during subsequent Lachlan orogenesis, as shown by the identification of mantle-derived materials in the Siluro–Devonian I-type granites.

The Hf model ages of zircons with high $\delta^{18}$O are shown in Fig. 9B. These have crystallised from magmas that contain a component (probably sedimentary) formed by low temperature processes. The data define a broad Hf model age peak at about 1.8–2.0 Ga, and provide little evidence for the period of new crustal growth in the Late Archaean recorded in the low $\delta^{18}$O zircons (Fig. 9A). The peak at about 1.8–2.0 Ga overlaps with the Nd model age of the Ordovician to Silurian metasedimentary rocks of the LFB (1.7–2.0 Ga, McCulloch and Woodhead, 1993; T. Kemp unpublished data) and also of many S-type granites (calculated from data in McCulloch and Chappell, 1982). The protoliths to the magmas from which the high $\delta^{18}$O zircons precipitated therefore have a similar average crustal residence age as the provenance to the sediments. The inset in Fig. 9B depicts the oxygen isotope composition of all detrital and inherited zircons as a function of their crystallisation age. The progression to higher $\delta^{18}$O with decreasing age is due to the greater participation of supracrustal materials in granite generation with time. This could in turn be a reflection of the increased likelihood of a mantle-derived protolith residing in the crust to become weathered with time, since this will elevate $\delta^{18}$O without changing the Hf model ages. All zircons with $\delta^{18}\text{O} > 9.5$ ‰ are confined to the 450–600 Ma age group, and presumably reflect anatexis of metasedimentary crust. This period coincides with major collisional events along long-lived convergent margins, as exemplified by the Ross–Delamerian and Pan-African orogens, whereupon sedimentary materials are readily tectonically transported to the depths of granite generation.

Two further observations stem from Fig. 9. Firstly, regarding the source rock of the I-type granites, there is scant evidence from the detrital zircons, or indeed the inherited zircons within the plutons themselves, for a mafic precursor being extracted from the mantle at 1.0–1.2 Ga. The Nd model ages of the I-type granites (1.0–1.2 Ga, McCulloch and Chappell, 1982) instead appear to reflect their hybrid origins, with contributions from both older crustal and juvenile mantle-derived materials. If the I-type granites derive from 450 to 600 Ma source rocks, as perhaps implied by the prevalence of inherited zircons of these ages, then the Hf–O isotope systematics suggest that such a protolith contained a significant metasedimentary component. An aged meta-igneous source rock that experienced weathering at the Earth's surface, or a meta-igneous rock that assimilated meta-igneous crust are equally valid candidates. This readily accounts for many other features of the LFB I-type granites, such as their generally low $Na_2O$ contents, and evolved initial $^{87}Sr/^{86}Sr$ and $\varepsilon$Nd values.

Secondly, and on a wider note, Fig. 9 shows that the observed distributions of crystallisation ages in detrital zircons are potentially a poor proxy for the periods of true crustal growth, and thus mantle depletion. Hf isotope-in-zircon data may also be insufficient for revealing episodes of crustal generation, since such data alone are incapable of pinpointing the presence of a recycled or metasedimentary component in the magma from which the zircon crystallised. These episodes can, however, be identified by combining in situ U–Pb ages and Hf isotope data with oxygen isotope data from the same zircon grain, as shown in Fig. 9A. Such studies are essential so that the ages of crustal generation identified by juvenile igneous rocks (Fig. 1) can be integrated with the potentially more representative record provided by detrital zircon suites. The higher resolution record of crustal evolution uniquely provided by in situ U–Pb, Lu–Hf and $^{18}O/^{16}O$ isotope studies should enable more accurate terrane 'fingerprinting', aiding mineral exploration and the reconstruction of tectonic histories of crustal segments. This promises to build on the advances in these areas described by Griffin et al. (2004).

## 5. Conclusions and future directions

Models for the evolution of the continental crust require representative data on the timing of major magmatic events, clear evidence as to which represent periods of significant crustal growth as opposed to reworking of the pre-existing crust, and knowledge of the tectonic setting of crust generation and how that may have changed with time. A key aspect is the extent to which the geological record is representative, particularly for older terranes. Another is that the smooth record of crustal growth and reworking inferred from Nd isotope ratios in sediments has to be reconciled with the marked peaks of crust generation illustrated in Fig. 1 (after Condie, 1998). Magmatic events represent thermal anomalies and as such they occur in relatively restricted areas. However, the igneous rocks are then sampled by sediments which may contain detritus from very much greater areas, and hence offer a more widely representative record of events in the continental crust, even when their source rocks are no longer preserved. Thus, the Nd isotope ratios of fine grained sediments have been used to constrain models of crustal evolution (Allegre and Rousseau, 1984; O'Nions et al., 1983; O'Nions, 1984), and it has been known for some time that zircons, both from sediments and from magmatic rocks, offer an exceptional record of crustal evolution (e.g. Amelin et al., 1999). However, it is only with the development of the latest in situ analytical techniques that the full potential of the zircon record can be exploited.

The combination of high precision ages and Hf and O isotope data distinguishes magmatic events that represent periods of new crustal growth and those that primarily involved the reworking of the pre-existing crust (Fig. 9). It further allows investigation of the evolution of the igneous portion of the continental crust separate from that involved in erosion and sedimentation. In south-east Australia it is very striking that the model ages of the low and high $\delta^{18}$O zircons are very different (Fig. 9), and this is an important initial step in the development of more sophisticated models for the evolution of the crust in this area.

The other topic where the high resolution time series records preserved in zircon have considerable potential is in the age old problem of the origin of granite (sensu lato). The upper continental crust is granitic in composition, and so this in turn links to models for the differentiation of the continental crust, and to the residence times of elements in the lower and the upper crust. In more detail, zircons provide exceptional records of the petrogenetic histories of granitic rocks that are simply not recoverable from whole-rock techniques. Fig. 8 shows the changes in Hf and O isotope ratios, and in trace elements, preserved in zircons from two I-type suites from the Lachlan Fold Belt. Almost none of that information is available from the whole rock compositions, and they highlight the presence of mantle contributions in the generation of these granites, and when the crustal end-member is a partial melt of the local sediments. Such data are a prerequisite for more physically realistic models for granite petrogenesis, better constrained thermal budgets, and much greater insight into the evolution of particular segments of continental crust.

Such detailed studies highlight the considerable potential of integrated Hf, O isotope and trace element data on well dated zircons to more completely chart the growth history of the continental crust, and in particular to assess the extent to which its formation may have been episodic. If it was episodic, it is now possible to investigate how crustal evolutionary processes differ between periods of accelerated versus sluggish crustal growth. Moreover, should episodicity be characteristic of crustal growth, as implied by Fig. 1, then establishing its causes arguably holds the key to understanding planetary differentiation. An important aspect will be the relationship between the trace element inventory of zircon and the composition of the magma from which it precipitated and this requires better knowledge of key partition coefficients. This is so that the contributions from intraplate and subduction settings may be deduced within detrital zircons for which the geological context has been lost. For the most ancient zircons, this may be the only way to ascertain the geodynamic controls of crust formation in the early Earth. However, this approach requires that the original magmatic versus metamorphic paragenesis of detrital zircons can be reliably determined, not always a straightforward task.

Lastly, it is now possible to reassess ambiguities relating to the formation of the Early Archaean continental crust and its complementary depleted mantle reservoir, as highlighted by Amelin et al. (1999), Whitehouse et al. (1999), and Patchett and Samson (2003). Some broad constraints on the size and composition of the residual mantle may even be possible, given that Lu/Hf and Sm/Nd ratios are sensitive to the involvement of garnet in melting. For example, compositions with the Lu/Hf ratio of the bulk continental crust appear to have less than 1% garnet if they were extracted from mantle source regions with Lu/Hf ratios similar to the time-averaged mantle values, at less than 20% melting (modelled using the partition coefficients quoted by Chauvel and Blichert-Toft, 2001). Monitoring the Lu/Hf ratios in juvenile magmatic suites, as identified through coupled Hf–O isotope studies in zircon, may constrain the mineralogy of the residual mantle, and how this varies temporally or regionally within the Earth.

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