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Recent advances in *in situ* U–Pb dating of geological events by laser ablation inductively coupled plasma mass spectrometry

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A little over a century ago, Marie Curie, Pierre Curie and Henri Bequerel discovered radioactivity, winning them the Nobel prize for physics in 1903. Their discovery paved the way towards the first determinations of the radiometric age of the Earth. In the decades that followed, improvements in mass spectrometer design[1] enabled the measurement and understanding of more isotope systems. A key discovery in this new field was the radioactive decay of uranium and thorium to lead, with long decay half-lives (in billion years: $^{238}U = 4.468$, $^{235}U = 0.7038$ and $^{232}Th = 14.01$). This discovery prompted the early pioneers to attempt to date natural rock and mineral samples to determine the age of the Earth, thereby creating the science of geochronology.

World War II and the so-called "Cold War" promoted great effort in the burgeoning field of nuclear physics and chemistry. A by-product of this effort was an advance in chemical techniques for separating elements within dissolved rocks and minerals via ion-exchange. Isotope ratio measurements improved as a consequence of the decreased spectral interferences observed and the increased ionisation efficiency in thermal ionisation mass spectrometry (TIMS). The creation of non-naturally occurring isotopes for use as tracers and spikes led to the development of the isotope dilution (ID) method to measure isotopic concentrations. Coupled with advances in dissolution techniques via acid attack in high-pressure "bombs" that allowed complete homogenisation of the spike with dissolved refractory minerals, the IDTIMS method became, and remains, the most precise method used in geochronology.

With the aim of reducing the amount of material required, a concentration of effort in the 1980s resulted in the possibility of measuring precise and accurate U–Pb ages within single crystals of the mineral zircon ($ZrSiO_4$). Zircon is an extremely robust mineral, capable of retaining both its parent and daughter isotopes, even when heated to extreme temperatures (>900°C) and subjected to extreme pressures and stresses. This means that single crystals can act as a repository of geological information over timescales spanning the entire Earth history (4.57 billion years). However, this also means that single crystals may contain discrete growth zones of different U–Pb isotopic age. This realisation led some workers to investigate measuring *in situ* ages within crystals mounted in resin and polished down so that an entire cross-section through the crystal was exposed. Imaging of polished zircons, particularly by cathodoluminescence (CL), see Figure 1, allows growth zones to be characterised and, therefore, guide subsequent *in situ* analysis. In the early 1980s, ion microprobe developments led to the reality of *in situ* zircon geochronology at the 20–30 µm scale. A decade later, as laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) techniques improved (see below),
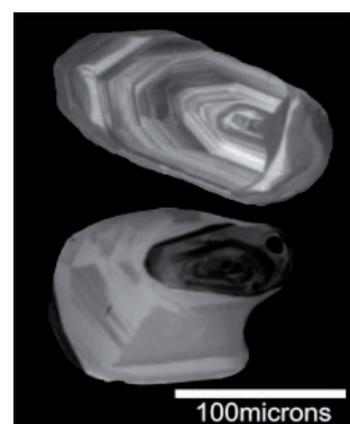

Figure 1. Cathodoluminescence images of zircon. Top image displays a typical well-formed igneous zircon with oscillatory zoning. Note, however, that the right-hand end has been affected by a later phase of alteration and the zoning in this area truncates the igneous zoning. Lower image displays a zircon containing an inherited core of older zircon (darker) surrounded by a later overgrowth of igneous zircon.

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so did the possibility of *in situ* U–Pb geochronology by this technique. In this article, we look at some recent further advances in LA-ICP-MS geochronology.

LA-ICP-MS

The technique of laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) was developed in 1985 when Gray[2] had the idea of coupling a ruby laser to an ICP-MS to enable the direct determination of trace elements in solid samples. In the 20+ years that have intervened, laser ablation accessories used, and ICP-MS instruments to which they are connected, have undergone much development, but the principles of the technique have remained the same: a laser is fired at a sample which is held in an airtight cell and flushed with a transport (carrier) gas. As the energy of the laser is transferred to the sample, particles are removed (ablated), picked up in the carrier gas flow and transferred to the inductively-coupled plasma of the ICP-MS where they are ionised. The ions are transmitted through the ICP-MS, separated and counted in the usual way, see schematic in Figure 2. Early commercial laser ablation systems employed Nd:YAG lasers operating in the near infrared (NIR) at 1064 nm. Although this laser proved to be stable and fairly easy to incorporate into a laser ablation system, many materials are poorly absorbing in the NIR and proved difficult to ablate controllably. This problem was resolved by simply placing two frequency-doubling harmonic generators in the beam path to create the 4th harmonic of the Nd:YAG laser at 266 nm in the ultraviolet (UV). Most materials are strongly absorbing in the UV and ablation at this wavelength could be controlled and focused to achieve a much higher spatial resolution. The frequency-quadrupled 266 nm laser became instantly popular and remained the industry standard until the introduction of the frequency-quintupled Nd:YAG laser operating at 213 nm and the excimer gas laser operating at 193 nm during the late 1990s. Alongside developments in laser technology, ICP-MS manufacturers have developed ever more sensitive and stable instruments with an array of mass analysers and detector systems bolted onto the ICP source. From the fairly crude bulk-sampling device of 20 years ago, the LA-ICP-MS technique is now one capable of sampling solid materials at a spatial resolution of a few microns, and providing precise isotopic information and determination of trace elements at the ppb level.[3]

Much of the development of LA-ICP-MS has been driven by the needs of the geological and earth science community and most instruments in academic institutions are still to be found in earth science departments. The Natural History Museum, London was the first of such institutions to develop a LA-ICP-MS facility for use across all of its science disciplines: mineralogy, palaeontology, botany, entomology and zoology. The advantages of using LA-ICP-MS in the field of natural history are clear. Natural materials often require lengthy and complex dissolution procedures prior to wet-chemical analysis but often little or no sample preparation is required for LA-ICP-MS. Spatial information, for example chemically zoned minerals, growth bands in shells, speleothems, teeth, wood etc., which is usually lost on dissolution, is retained in the solid material and can be discretely sampled with the laser. Typically, 40 or more trace elements spanning the periodic table can be determined in a single analysis taking no more than a minute or two. Rare or precious materials can be analysed without the need for sample preparation in an essentially non-destructive way. The disadvantages of the technique are perhaps less obvious. The development of applications for the technique has far outpaced the characterisation of suitable reference materials. Although matrix matching of samples and reference materials is frequently unnecessary to obtain high quality data, there is no doubt that the lack of these materials is to the detriment of some applications, for example, the determination of platinum group elements in sulphides, the direct analysis of fluid inclusions in minerals and the analysis of soft tissues. The processes involved in laser sample interaction are complex and still poorly understood. They are thought to include true ablation, volatilisation, electron stripping, plasma erosion and melting. In some circumstances, the laser may preferentially volatilise some elements from a sample giving rise to laser-induced element fractionation (LIEF).

Signals arising from the laser ablation of solids are considered to be transient. As the laser penetrates deeper into a sample, different chemical zones, alterations, inclusions or cracks may be sampled and cause the signal to fluctuate and change, and fractionation may start to develop. For these reasons, it is essential that, during analysis, data are
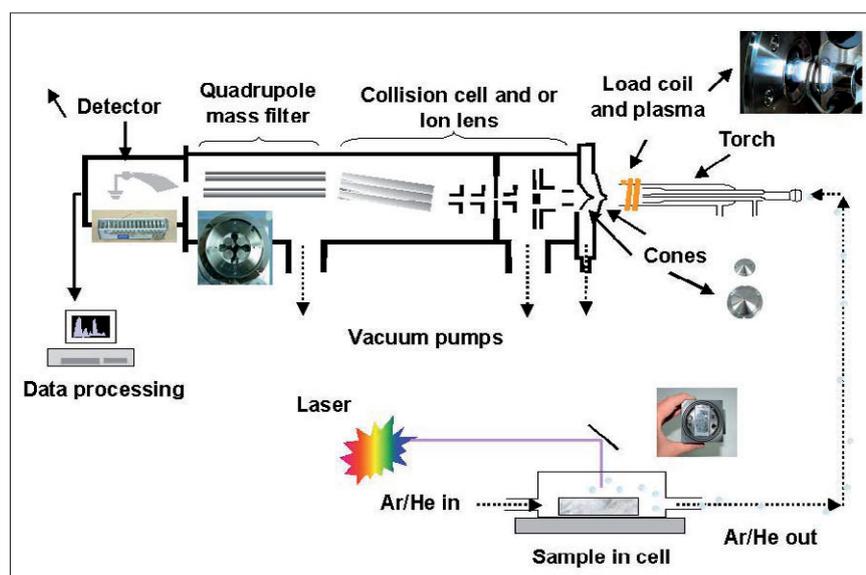

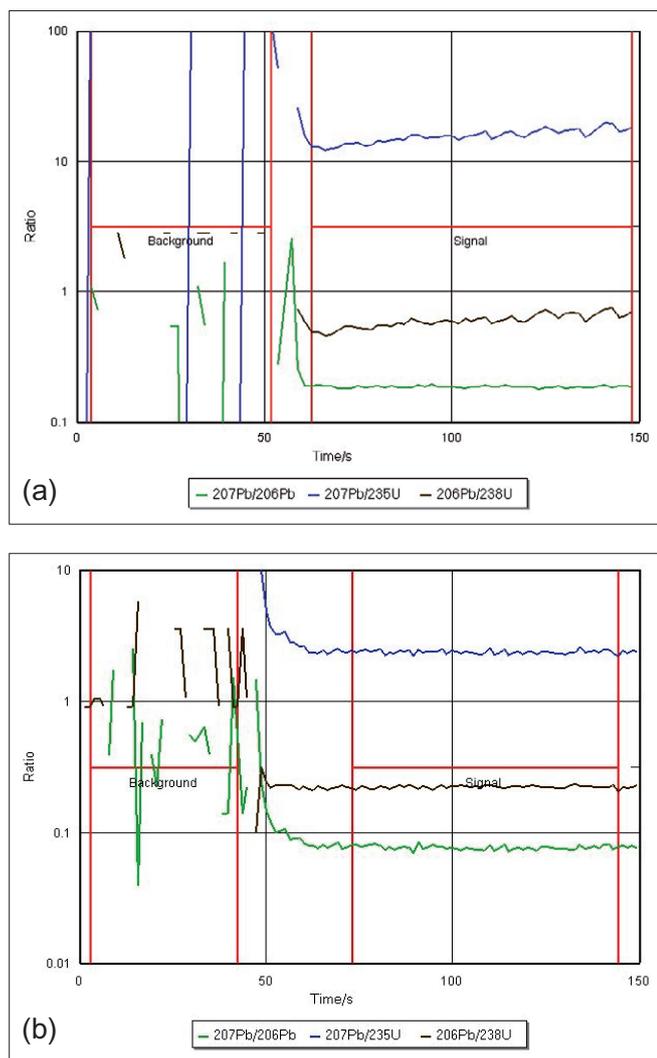**Figure 2.** Schematic of a laser ablation ICP-MS (quadrupole) system.

(a)

(b)

Figure 3. Time-resolved plots during single analyses of zircon. (a) Single spot analysis; note severe fractionation of Pb/U ratios whilst Pb/Pb ratio remains unfractionated. (b) Line raster analysis. Note the apparent lack of fractionation between Pb and U during this analysis. (Green, $^{207}Pb/^{206}Pb$; Black, $^{206}Pb/^{238}U$; Blue, $^{207}Pb/^{235}U$.)

collected, monitored and processed as a function of time; time during the analysis being loosely equivalent to depth within the sample or position along a traverse. This process is known as time-resolved analysis.

The Natural History Museum, London currently houses three quadrupole-based ICP-MS instruments and one multicollector magnetic sector ICP-MS. A 213 nm laser has been used in conjunction with these instruments on a diverse array of projects including the determination of heavy metals in preserved tiger skins, the analysis of parasitic wasp mandibles, determination of Sr/Ca ratios in teeth and bones and the focus of this article: U–Pb dating of zircons and other accessory minerals.

In situ zircon geochronology by LA-ICP-MS

As with many analytical techniques, to obtain accurate and precise data, LA-ICP-MS relies on normalising measured U and Pb signals
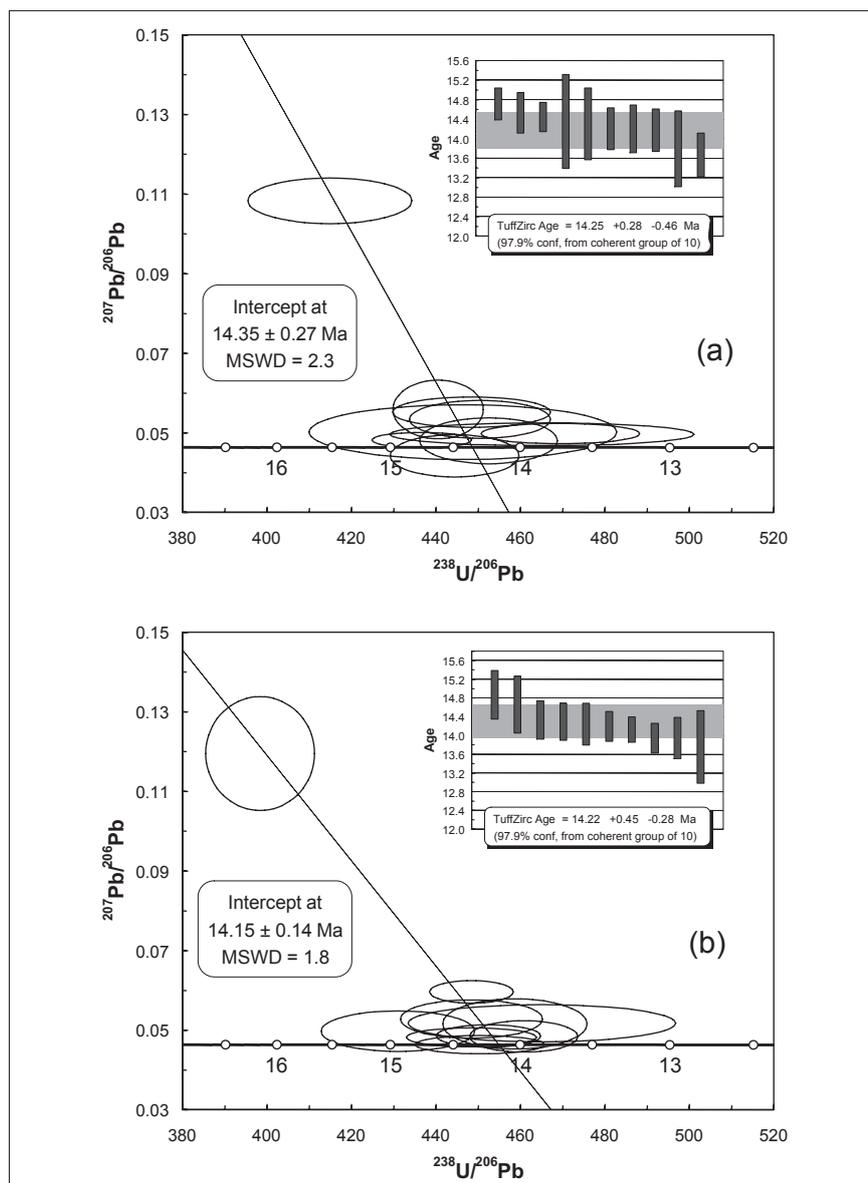
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Figure 4. Tera–Wasserburg concordia plots for tephra zircon analyses. Error ellipses and boxes all 2σ. (a) Sample Tephra1, lower intercept of regression gives age shown. Inset shows a weighted average treatment of indvidual ages. (b) Sample Tephra2.

LIEF is a more sensible approach than trying to characterise and correct for it, thereby introducing another uncertainty. Therefore, although we compromise some spatial resolution, our U–Pb analyses are conducted by rastering along a single line.

Naturally, as analysts, we have to work within the detection limit of the technique. So one of the limiting factors for U–Pb dating by LA-ICP-MS is the often low abundance of radiogenic daughter Pb isotopes to be determined. Their abundance is a function of the initial abundance of U in the mineral and the age since isotopic closure. In practice, most laboratories (both LA-ICP-MS and ionmicroprobe) tend to deal with samples that are at least as old as Mesozoic [>65 million years (Ma)] and more usually Palaeozoic (>251 Ma) or Precambrian (>542 Ma). With the aim of moving the technique forward, we have recently investigated *in situ* dating of very young (Neogene <23 Ma) zircons.

Zircons were collected from tephra (volcanic rock fragments) from two separate geographic localities, but thought to be the from the same stratigraphic horizon. Figures 4(a) and 4(b) display U–Pb data plotted on Tera–Wasserburg concordia ($^{207}Pb/^{206}Pb$–$^{238}U/^{206}Pb$) from the two samples, Tephra1 and Tephra2, respectively. This diagram is particularly useful for young samples, since the radiogenic Pb signals are very low and, hence, the small amount of common Pb (Pb that was incorporated into the crystal as it grew) present in zircon is elevated. On this diagram, U/Pb and Pb/Pb ratios that have the same age plot on the solid line known as concordia. Deviation from concordia can be produced by a number of mechanisms but, in this case, the small spread of data away

to a homogeneous reference material of well-known U–Pb isotopic ratio. Demand for such materials is high and availability low. Various reference materials have been tested and are in use in laboratories worldwide. Here, we use the zircon standard 91500[4] as this provides us with the best long-term reproducibility for our set-up. A major challenge in measuring U–Pb isotopic ratios in zircon by LA-ICP-MS is minimising the amount of material sampled whilst maintaining a measurable and stable signal for all of the isotopes of interest (^{206}Pb, ^{207}Pb,

^{235}U and ^{238}U). Of equal importance is reducing the influence of LIEF, either by its effective elimination or by its characterisation and correction.

Laser ablation, using a single spot, can induce fractionation between U and Pb [Figure 3(a)] and this will strongly influence the calculated U–Pb age (though a Pb–Pb age should not be affected). However, LIEF can be controlled by keeping the aspect ratio (depth vs diameter) of the pit small by rastering the laser beam repeatedly over an area [Figure 3(b)]. We find that controlling

Figure 5. Gold trap attached in-line to carrier gas line to scrub Hg.

from concordia is entirely due to small amounts of common Pb. The regression through these data to the Y-axis gives the common $^{207}Pb/^{206}Pb$ composition, which is identical to the known modern-day composition of terrestrial Pb. Therefore, a regression through these data can be performed to give an intercept age on concordia for both samples. The two ages are within error of each other and are interpreted as crystallisation ages of the zircon during the same volcanic eruption. The insets in Figures 4(a) and 4(b) are common Pb-corrected data based on stripping of common Pb from the total Pb signal of a known $^{207}Pb/^{206}Pb$ composition. The data are plotted as common Pb corrected $^{207}Pb/^{206}Pb$ age and error (2σ) and a final weighted average age is calculated based on the algorithm of Ludwig.[5] These ages are in close agreement ($14.25+0.28/-0.46$ Ma and $14.22+0.45/-0.28$ Ma). These data demonstrate the applicability of this technique to dating Neogene zircons to a reasonable analytical precision.

In situ dating of common Pb bearing minerals by LA-ICP-MS

Generally, zircon does not incorporate excessive common Pb into its lattice during crystallisation and for this reason many laboratories do not perform a common Pb correction to their zircon U–Pb data. For LA-ICP-MS, the correction is difficult and relates to measurement of the stable isotope ^{204}Pb. In minerals with very high radiogenic/common Pb ratios, such as zircon, the ^{204}Pb signal is very low. Furthermore, an isobaric interference at amu 204 from Hg, which is present in the carrier gases and through atmospheric entrainment, masks the signal. As ^{204}Pb is the only stable Pb isotope, it must be accurately and precisely measured in order to make an optimal common Pb correction. If the amount of ^{204}Pb counts per second (cps) is very low (<1–200 cps), it will be difficult to measure precisely and this problem is exacerbated when the ^{204}Hg background is far greater than this. With the aim of dating common Pb-bearing minerals and making this correction, we have developed a method of reducing the Hg background so that it is not so far in excess of the ^{204}Pb signal. We have incorporated gold traps (Figure 5) in our carrier gas lines in order to adsorb Hg from the gases and reduce this source of contamination. This has effectively reduced the Hg background by 70% and this allows us to make a reasonable ^{204}Pb measurement in minerals with elevated common Pb concentration.

Titanite ($CaTiSiO_5$) is a common mineral in igneous, metamorphic and sedimentary rocks and often contains reasonably elevated U content (50–100 ppm). It also has a fairly high Pb isotopic closure temperature (around 650°C) making it a useful mineral for U–Pb geochronology. It can, however, incorporate common Pb into its lattice and this needs to be assessed and corrected for. This mineral seems an ideal choice on which to test the LA-ICP-MS method of in situ geochronology and, due to the lack of a well referenced homogeneous titanite standard, we decided to investigate the potential of using a zircon standard to normalise the Pb/U ratios. The sample chosen was from a coarse-grained granite vein in Scotland, containing well-formed and good quality titanite grains. First of all, we measured the U–Pb age of the titanites by TIMS at the NERC Isotope Geoscience Laboratory in Keyworth, UK. The calculated U–Pb age of the sample was 437±6 Ma. We then mounted the grains in resin, polished them and then analysed one laser raster line per grain, using the same protocols as for zircon. The results, uncorrected for common Pb and plotted on Tera–Wasserburg concordia [Figure 6(a)], regress through the correct age of the sample, within error, on the X-axis
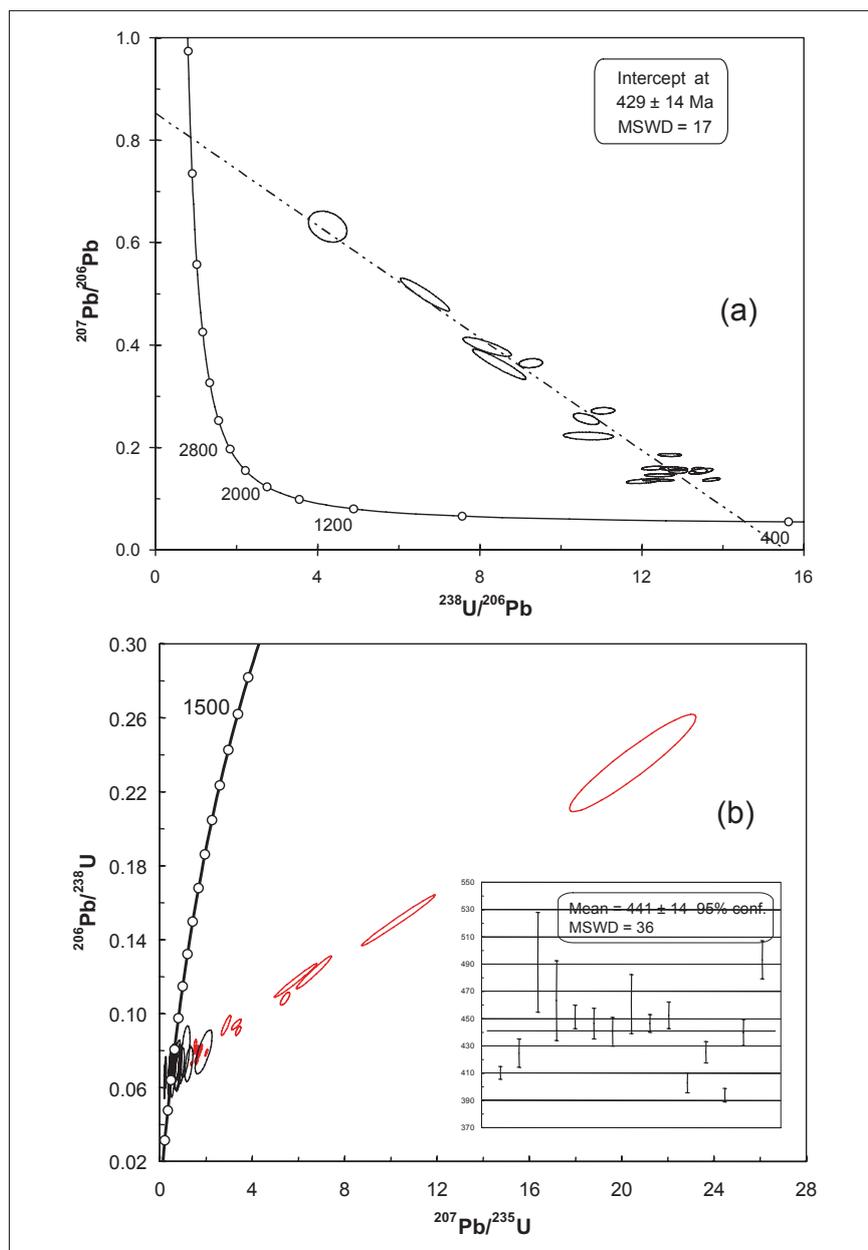
Figure 6. U–Pb titanite data. All ellipses and error bars at 2σ. (a) Tera–Wasserburg concordia plot of uncorrected analyses. (b) Wetherill concordia plot of uncorrected (red) vs corrected (black) analyses. Inset shows weighted average of corrected $^{206}Pb/^{238}U$ ages.

effective the common Pb correction. The ^{204}Pb corrected $^{206}Pb/^{238}U$ age (which is the least sensitive to common Pb) can be shown to be accurate, since a weighted average of all corrected analyses yields the correct age [see Figure 6(b) inset]. In this case, we have demonstrated that we can perform accurate common Pb corrected U–Pb geochronology on titanite, but there is a lower limit on Pb signal strength below which an effective ^{204}Pb correction cannot be made. For more information see Storey et al.[6] We are exploring other common Pb bearing minerals, such as allanite, rutile, apatite, perovskite and columbite and, for most of these minerals, the same approach seems to work and encourages further effort in the future.

Summary

LA-ICP-MS is an ideal technique for in situ analysis of a variety of matrices for trace element concentrations at the micron scale. LA-ICP-MS, with a quadrupole mass analyser in this study, can also be used for in situ U–Pb isotope ratio analysis of zircon, as now performed by many laboratories worldwide. We have also shown that it is possible to use a fairly simple analytical set-up to further utilise LA-ICP-MS for in situ U–Pb geochronology of young (Neogene) zircons and common Pb bearing minerals. This highlights the flexibility and, as yet, unrealised potential of LA-ICP-MS as an in situ analytical tool.

References

1. A.O. Nier, Rev. Sci. Instrum. **11,** 212 (1940).
2. A.L. Gray, Analyst **110,** 551 (1985).
3. T.E. Jeffries, in Non-Destructive Microanalysis of Cultural Heritage Materials, Ed by K. Janssens and R. Van Grieken. Elsevier, Amsterdam, The Netherlands, p. 313 (2004).
4. M. Wiedenbeck, P. Alle, F. Corfu, W.L. Griffin, M. Meier, F. Oberli, A. Vonquadt, J.C. Roddick and W. Spiegel, Geostand. Newslett. **19,** 1 (1995).
5. K.R. Ludwig, Berkeley Geochron. Cent. Sp. Publ. **4,** 1 (2003).
6. C.D. Storey, T.E. Jeffries and M. Smith, Chem. Geol. **227,** 37 (2006).

($^{238}U/^{206}Pb$ age = 429 ± 14 Ma) and the model terrestrial common $^{207}Pb/^{206}Pb$ composition on the Y-axis. This gives a great deal of confidence that the data are accurate and, therefore, that strict matrix matching may not be necessary for U–Pb geochronology by this method. Performing a ^{204}Pb-based common Pb correction on these analyses moves the ellipses towards concordia. This is best seen on Wetherill (or conventional) concordia [$^{206}Pb/^{238}U$–$^{207}Pb/^{235}U$;

Figure 6(b)], where the uncorrected data are plotted in red and the corrected ellipses in black. The ^{204}Pb corrected ellipses are enlarged as the error from the Hg-stripped ^{204}Pb correction has been propagated. Not all ellipses overlap concordia and some have, therefore, been under-corrected. This, we discovered, was a function of signal strength and, therefore, counting statistics; the lower the signal strength for the Pb isotopes (particularly ^{207}Pb), the less