ADVANCES IN ISOTOPE RATIO DETERMINATION BY LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (LA–ICP–MS)

Jon Woodhead[1], Matthew S.A. Horstwood[2], and John Cottle[3]

ABSTRACT

LA–ICP–MS has proven to be an extremely important analytical tool within the Earth, environmental, and archaeological sciences. New developments in both instrumentation and methodology now provide the ability to extract age and isotopic tracer information in situ at a variety of scales (from nm to cm), in 2- and 3-dimensions, quickly and cost-effectively, providing considerable analytical flexibility compared to other micro-analytical techniques. Here we review the current state of the art in LA isotope ratio determination and provide some insights into future developments.

KEYWORDS: laser ablation, radiogenic isotopes, non-traditional stable isotopes, geochronology, geochemical mapping

INTRODUCTION

The advent of laser ablation (LA) micro-sampling has revolutionized many research fields. The first isotope ratio measurements by this method were made only two decades ago but, since that time, the technique has seen tremendous advances in the design of mass spectrometers and lasers, driven by researchers and by instrument manufacturers. It is now routine to obtain age and isotope ratio information from many minerals at the scale of just a few tens of microns. Initially, many of these advances were achieved using so-called quadrupole inductively coupled plasma mass spectrometry (ICP–MS) technologies that used only a single detector. The subsequent development of 'multiple collection' instrumentation (MC–ICP–MS) now allows the simultaneous detection of multiple atomic masses countering some of the previous analytical problems associated with plasma noise. This development now enables researchers to obtain high-precision isotope ratio data for

---

[1] The University of Melbourne
School of Earth Sciences
Melbourne, VIC 30101, Australia
E-mail: jdwood@unimelb.edu.au
[2] NERC Isotope Geosciences Laboratory
British Geological Survey
Keyworth, Nottingham NG12 5GG, UK
E-mail: msah@bgs.ac.uk
[3] University of California, Santa Barbara
Department of Earth Science
Santa Barbara CA 93106-9630, USA
E-mail: cottle@geol.ucsb.edu

many elements, from lithium to uranium. Importantly, laser-ablation techniques differ from most other micro-analytical methods of isotopic analysis. The equipment is relatively inexpensive, analyses are rapid, and can be performed over a range of spatial resolutions. The ICPMS technique also permits measurements spanning a very large dynamic range, allowing quantification at concentrations ranging from percent levels down to parts per billion (ppb) and, with MC–ICP–MS instruments, isotope ratio determinations can now be made down to ppm levels of precision. In the sections that follow, we describe the features that make LA–ICP–MS a desirable measurement tool for isotopic analysis, review some of the inherent analytical challenges and identify areas of future development.

FLEXIBILITY AND SPEED: THE HALLMARKS OF LA–ICP–MS

For many years after the introduction of quadrupole ICP–MS instruments, laser ablation sampling was seen purely as a means of undertaking in situ trace element analyses or obtaining U–Pb age determinations. Although these capabilities were already well established in the geoscience arena using secondary ion mass spectrometry (SIMS), the relative affordability and speed of the laser ablation platform provided an attractive alternative and resulted in the generation of many very large datasets and subsequent ground-breaking research programs. Perhaps the most prominent of these have been dating studies of the mineral zircon, which has led to new insights into the growth of the continental crust. For example, Parman (2015) interrogated literature U–Pb age distributions for some ~200,000 zircon grains in order to document the complex interplay between crust production and destruction over the course of Earth history. Availability of the very large quantities of data required to undertake such studies would have been unthinkable prior to the arrival of ICP–MS technologies.

The appearance of MC–ICP–MS instruments, however, was the pivotal moment in the development of the technique for isotope ratio measurements. Researchers were quick to recognize the potential of being able to perform relatively straightforward investigations of the isotope systematics of many different elements, including those with high ionization energy that had previously proved problematic both for thermal ionization MS (TIMS) and for secondary ion MS (SIMS) methods. The most prominent application has been the use of Hf isotopes in zircon as a tracer of source character and evolution to complement the age information provided by the zircon U–Pb chronometer: this has been an enduring 'isotopic partnership' and remains a mainstay of many LA–ICP–MS laboratories. Today, however, laser ablation sampling methods are far more widely applied for both dating and isotope tracer purposes. It is difficult to convey the magnitude and speed of this recent expansion, but TABLE 1 shows the first recorded application of laser ablation isotope ratio studies to various minerals and is an attempt to illustrate this growth. This is by no means an exhaustive list, but there are two clear messages to be derived from such a compilation – one is the inherent flexibility of a method that is so readily adaptable to many different isotope systems and mineral types, and the other is the remarkable uptake of the method over the past decade.

Although the inductively coupled plasma is a highly efficient ion source, with the potential for near 100% ionisation, the efficacy with which the resultant ions are transmitted into the mass spectrometer is less than perfect, something that limits the detection efficiency (the proportion of ions generated that are actually detected) of MC–ICP–MS instruments to around 1% in most cases. Importantly, the laser ablation platform allows the analyst to circumvent this deficiency, at least in some cases, by varying laser spot size, varying the repetition rate and/or the energy (fluence) and thus carefully controlling the amount of material ablated into the plasma. This in turn allows optimization of the ion count rates measured up until such time as the ionisation capacity of the plasma becomes saturated. In addition, many lasers offer the potential to mask (i.e. control the shape of) the laser beam, providing a range of ablation geometries from circular spots to narrow rectangles. The latter, for example, can be extremely useful for characterising thin growth layers in samples with complex zonation, such as corals, speleothems, and even tree-rings. This ability to control the count rate and ablation geometry, coupled with the high dynamic range of ICP–MS (especially with mixed Faraday cup–ion counter detector systems), provides opportunities for the simultaneous monitoring of isotopes that have either a high or a low abundance in complex materials and that could not be detected using other micro-analytical methods. Thus, for example, the feasibility of using LA–ICP–MS for U-series dating of corals, speleothems, molluscs, and bones and teeth have all been demonstrated (e.g. Eggins et al. 2005). The relative speed of analysis and scanning capabilities of laser systems also now allow for the generation of U–Th isotope maps (FIG. 1). Most recently, the ability of laser ablation methods to operate with very low concentration samples has been exploited to allow in situ U–Pb dating of carbonates, where Pb contents are in the ppb range. Promising results have been obtained for a variety of samples including speleothems lying beyond the range of the U–Th chronometer and carbonate-filled fractures in hydrothermally altered oceanic crust (e.g. Coogan et al. 2016).

The ability to remove a sample relatively rapidly and analyse it in a time-resolved sequence opens another important niche for LA–ICP–MS: that of depth-profiling measurements tens to hundreds of microns into different materials to delineate growth zonation or diffusional gradients. For example, Woodhead et al. (2004) demonstrated the feasibility of measuring Hf isotope ratios in holes, drilled by the laser, 120 microns deep into magmatically zoned zircon. With appropriate model corrections for ‘down hole’ elemental fractionation effects, it is now entirely feasible to conduct U–Pb dating in a similar fashion. Smye and Stockli (2014) measured U–Pb age depth profiles down to 35 μm to determine the thermal histories in rutile from the Ivrea Zone (a tectonic belt within the Southern Alps in northern Italy), whilst Cottle et al. (2009) constructed depth profiles in zircon with individual bursts of the laser, each removing successive ~130 nm slices. Ironically, one of the original perceived shortcomings of laser ablation – that the laser beam penetrated too quickly, limiting depth resolution – has now turned into one of the method's greatest assets. Modern laser systems can be very precisely controlled and provide an extremely high depth resolution, on the nanometre scale. This means that ICP systems may, thus, employ signals from individual laser pulses to interpret geochronological and geochemical information as thin mineral zones are ablated. Recently, Stearns et al. (2016) used this capability with the laser ablation 'split stream' (LASS) approach (described below) to acquire multiple data sets from single signal pulses.

Increasingly, LA–ICP–MS is now being used to exploit its true capabilities in high spatial resolution rather than as a micro bulk-sampling tool. Modern ablation cells have been designed to take advantage of this capability and are characterised by having fast responses (the time required for the analyte to enter/leave the system at the start/end of the analysis respectively) of ~0.5 s. This enhances signal-to-noise ratios and requires less material to be ablated, and for less time, to achieve the same precision, thereby improving spatial resolution. Decreasing the volume of material required for analysis is a major growth area for geoscience LA–ICP–MS research. For now, the application of this technology to isotope studies is limited by instrument efficiency, because higher ion yields are usually required to achieve the precision necessary for isotope ratio analysis.

In many areas of microbeam analysis, the last decade has seen a shift in emphasis from single spot determinations to the generation of 2-D compositional images that preserve the spatial context of the analyses. Initial laser ablation developments in this area were hampered by the fact that the LA–ICP–MS technique involves two different analytical systems: the laser and the mass spectrometer. Unfortunately, these were often produced by different manufacturers, and the systems did not necessarily communicate well with each other. With the advent of improved hardware and software for intersystem communications, however, the field of elemental and isotopic mapping is now growing rapidly. Applications are diverse (FIG. 2) and include mapping Sr-isotope distributions in fish otoliths (calcium carbonate 'ear stones') (Woodhead et al. 2007), age zonation in zircon (Gehrels 2008) and titanite (Spencer et al 2013), U alteration processes in fossil teeth (Duval et al. 2011) and B isotope variations in coralline algae for the investigation of ocean pH and temperature changes (Fietzke et al. 2015). Recent developments in the arena of LA trace-element analysis have demonstrated the feasibility of imaging multiphase assemblages (Paul et al. 2014) and also of producing 3-D reconstructions (van Elteren et al. 2013); applications to isotope analysis are sure to follow.

High ionisation efficiency, coupled with simultaneous detection in MC–ICP–MS instruments, has placed the technique at the forefront of measurements of so-called 'non-traditional' stable isotope systems (e.g. Fe, Mg, and Si). The biggest challenge here is that there are only minor differences in the relative isotopic ratios between samples: some can be as low as <1 per mil (‰) per atomic mass unit (amu). Therefore, measurements must be made to very high levels of precision and accuracy in order to identify and distinguish the subtle natural variations. The majority of such measurements, to date, have been made using solution-mode MC–ICP–MS. The advantage here is that the element of interest can be separated from the bulk sample via chromatography, thereby minimizing analytical interferences and sample–matrix effects. The major disadvantage of this approach is the effective compositional averaging of samples that occurs through bulk sampling. Increasingly, LA–MC–ICP–MS approaches are being applied to non-traditional stable isotope systems to achieve higher spatial resolution. For example, Graham et al. (2004) used Cu and Fe isotope measurements as indicators of both source and process in the formation of porphyry copper deposits. Shahar and Young (2007) used Si isotope data measured in situ in calcium aluminium inclusions (CAIs) from the Leoville (Kansas, USA) carbonaceous chondrite meteorite to show that these CAIs were originally molten for no longer than 70 days. Steinhoefel et al. (2009) measured micron-scale variations in Fe and Si isotope ratios, providing new insight into the sediment flux and diagenetic history of banded iron formations. Sio et al. (2013) demonstrated that LA Fe-isotope measurements could be used in olivine to distinguish diffusion-controlled from growth-controlled zoning, with important implications for the field of diffusion-based geospeedometry.

CHALLENGES AND OPPORTUNITIES

The field of LA–ICP–MS is continually evolving in terms of the hardware, software and methodologies being established. Some of the many exciting developments that are underway are now described.

Relationships between Mineral Structure, Chemistry, and Isotope Ratio Analyses

As laser ablation methodologies achieve higher and higher levels of precision, the need to correct for very subtle differences in ablation behaviour between samples (so-called 'matrix effects') becomes more acute. In the context of U–Pb geochronology of relatively radiogenic minerals (such as zircon, baddeleyite and monazite), matrix-related fluctuations in the measured U/Pb ratio now form the dominant component of analytical uncertainty (Horstwood et al. 2016). There is a general understanding emerging that these effects may relate to radiation damage in the crystal lattice (Allen and Campbell 2012), which will affect laser penetration rate (Marillo-Sialer et al. 2016). As yet, there are no easy ways to correct for such effects during analysis, and the simplest solution appears to be to anneal samples prior to ablation to remove lattice defects (Solari et al. 2015). Such annealing will harmonise, as far as possible, the relative ablation behaviour between two materials of the same nominal composition. Clearly, however, annealing can only be performed on mineral separates, and the issue of matrix-dependence remains for in situ analysis of phases within thin sections or rock slabs.

Unfortunately, matrix effects are not limited only to U–Pb geochronology. They are also likely to be exacerbated in lower-mass isotope systems. For example, in a study using synthetically produced target materials, Norman et al. (2006) demonstrated the importance of matrix effects when analysing Mg isotopes in olivine. In their own words, 'the magnitude of this effect is surprisingly large and could lead to erroneous conclusions if not recognized and properly corrected'. In the last decade, matrix effects have come to be recognised as perhaps the most significant phenomenon limiting the attainment of accuracy in laser ablation methodologies.

This is an area of intense research and is currently moving in at least two parallel directions. On the one hand, there is a push to generate new suites of 'matrix matched' reference materials to minimise calibration biases (e.g. Garbe-Schönberg and Müller 2014). Simultaneously, others are experimenting with femtosecond pulse–length lasers which deliver light pulses ~4 orders of magnitude shorter (~100 fs versus ~4 ns) than the more widely employed nanosecond devices. This huge decrease in laser pulse duration essentially eliminates any time for thermal effects to occur within the sample material. Inter-element and isotopic fractionation is correspondingly reduced to a level unresolvable outside the uncertainty of the analysis. For LA analysis of non-traditional stable isotope systems that are otherwise prone to laser-induced isotopic fractionation, this is especially advantageous (e.g. Horn et al. 2006), and even U–Pb fractionation appears to be significantly reduced to the point at which 'down hole' correction of fractionation during static ablations may not be required. Although the operational reliability of femtosecond systems has improved as the technology has matured, for most laboratories, the cost is still prohibitive. In time, no doubt this situation will improve – and maybe femtosecond laser ablation will then become routine.

Combining Multiple Geochemical Data Sets

Interpretations based on multiple independent data sets, related by the same causal mechanism, are inherently more robust than isolated analyses. As a result, it is now commonplace to combine analyses of U–Pb, Hf and O isotopes in zircons to investigate processes of magma generation and crustal evolution where O isotopes are first determined using SIMS, and this is followed by U–Pb geochronology using SIMS or LA–ICP–MS, and finally Hf isotopes are analysed using LA–MC–ICP–MS. If each of these data sets is collected from a separate analytical volume of a heterogeneous sample material, however, the results may not relate directly to one another. It is for this reason that recent efforts have sought to analyse the same material, synchronously, by splitting the sample aerosol between two different ICP instruments. This laser ablation 'split stream' (LASS–ICP–MS) methodology (e.g. Kylander-Clark et al. 2013) harnesses the strengths of MC–ICP–MS, which is capable of measuring isotope ratios to high precision (e.g. for U–Th–Pb, Hf and Nd), and quadrupole- or single collector sector field–ICP–MS, which is capable of rapid measurement over a large mass range (e.g. for element abundance analysis). Thus, the LASS technique simultaneously provides complementary geochemical information. This new approach enables much easier pairing of measured radiometric ages to specific geologic processes, a field of research termed 'petrochronology'. The processes involved could be melt crystallization or the responses of minerals to changes in pressure, temperature, and/or fluid/melt infiltration (with or without accompanying deformation). Whatever the process being investigated, ultimately, the methodology seeks to improve the geological interpretation of radiometric ages (FIG. 3).

Enhancing Data Quality

The measurement uncertainty ('precision') and accuracy of results from LA–ICP–MS methods are fundamentally limited by detection efficiency, by the stability of both the laser and the mass spectrometer system, and by the homogeneity of the reference material and its match to the sample composition and physical structure. Detection efficiency ('sensitivity') is constantly under refinement by instrument manufacturers. Currently, efficiencies for ICP–MS (for U) range from 0.01%–0.1% for quadrupole ICP–MS, 0.1%–0.3% for single collector sector field ICP–MS and 0.6%–2% for multiple collector ICP–MS, although with special tuning and/or set-up conditions these figures can be further improved. Other instrumentation characteristics (e.g. amplifier noise, stability of detector calibrations, mass bias stability, laser energy and beam profile stability) can also contribute significantly to the uncertainty budget in higher precision isotope ratio measurements. Improvements to the amplifier noise and to the stability of the detector calibrations are currently under development, with higher resistance amplifiers and improved Daly ion counting systems being produced. However, the trade off is often a slower response time when trying to improve the noise characteristics on Faraday detector systems and this reduces the spatial resolution in laser applications. An implication is that higher resistance amplification circuitry may have more limited applications in this area. Of course, the desire to achieve the highest spatial resolution possible also produces an inevitable decrease in measurement precision, which is correlated with the smaller volume of ablation. For applications requiring inter-element calibration (e.g. U–Pb, Lu–Hf), increased laser-induced 'down hole' fractionation effects in high aspect ratio ablation pits may further contribute to this reduced accuracy. Conversely, increasing the amount of material analysed to improve the measurement precision increases the risk of sampling multiple domains, potentially causing a biased result. Designing an ablation protocol can, therefore, be a delicate balancing act; improving detection efficiency and/or signal-to-noise ratio of analyses will remain a key development area for improving the spatial resolution of LA–ICP–MS methods.

LA–ICP–MS requires well-characterised reference materials to achieve accurate quantification. Due to variations in ablation behaviour and plasma loading, reference materials should match the composition and physical structure of the unknowns as closely as possible. Particularly in the case of high-precision isotope ratio measurements, interference- and mass bias corrections must be monitored and their accuracy validated via periodic analysis of reference materials interspersed throughout the analytical session. Failure to use an appropriate reference material can lead to systematic biases in sample data. This problem is more acute for the lower mass, non-traditional stable isotope systems (e.g. Fe and Si) where variations in the matrix have a greater impact on instrumental mass bias. A realistic assessment of the uncertainties associated with individual sample measurements also requires routine measurement of multiple secondary/tertiary reference materials run under identical analytical conditions to monitor both short- and long-term accuracy and reproducibility. An assessment of these effects for LA–ICP–MS U–Pb geochronology by Horstwood et al. (2016) can be used as a model for uncertainty assessment in other isotope systems, such as Hf, Sr, and Nd isotopes.

Demonstrating that the calibration material is homogeneous at the sampling scale is also a significant factor in the overall uncertainty assessment. As spatial resolution improves, this requirement becomes increasingly challenging for natural materials and contributes a greater proportion of uncertainty to the determination for the unknown. Ultimately, at the finest scale, all materials are heterogeneous; but knowledge of the sampling scale at which the primary reference material is quantified is an important factor when considering accuracy and uncertainty. Improvements in the documentation and quantification of the total uncertainty assigned to LA–ICP–MS isotope measurements will result in better discrimination and confidence when interpreting data, particularly between laboratories. Improving these metrics is a key focus for the LA–ICP–MS community as the scientific questions become ever more challenging with finer spatial constraints.

New Technologies

Two new 'hardware' developments offer great potential to change the analytical capabilities of LA–ICP–MS systems. The first of these is a fundamental shift in the design of laser ablation systems. For many years, analysts have favoured the use of large ablation cells (to accommodate multiple samples) coupled with a variety of 'sample smoothing' devices that can produce more stable signals at the mass spectrometer and, thus, improve analytical precision. These have been very successful, but they come at the cost of reducing the 'response time' of the system, which thus impacts the temporal (hence spatial) resolution, e.g. when performing depth profiling tasks, or when producing images. Now, prompted largely by the needs of the biosciences community where extremely high-resolution images are required, a new generation of small, ultra-fast ablation cells are being developed, without signal smoothing, providing millisecond response times (e.g. Van

Malderen et al. 2015). These offer the prospect of much higher-resolution analytical capability, especially when combined with small laser spots (many systems are now offering spot sizes approaching a minimum of one micron). Furthermore, when combined with analytical systems employing simultaneous detection, such as time-of-flight analysers (ToF), the capability to analyse relatively large areas of sample at speed makes 3-D imaging of materials eminently practical, e.g. Burger et al. (2015). This is a technology that will quickly filter into the geoscience arena, opening up the possibility of 3-D imaging, and ultra–high resolution geochemical analysis. When applied to isotope ratio and age data and combined with other information sets, the 3-D imaging and the new resolutions achievable are likely to be a significant growth area for LA–ICP–MS in the coming years, albeit with the caveat of somewhat reduced data quality due to inherently shorter signals produced.

New ICP–MS instruments are also appearing. For many years, ‘collision cells’, where unwanted analytes can be removed by collisions with a reaction gas prior to entry into the mass spectrometer, have been employed in routine trace-element analysis instruments. Now, for the first time, collision cells are being used with tandem quadrupoles in ICP–MS instruments, allowing interfering elements to be combined with a variety of reaction gases and ‘mass shifted’, rather than being removed entirely. In this way, the analyte and its interfering element can both be measured. While these single collector instruments are not likely to produce high-precision isotope analyses, multiple collector versions of this technology are in development and are being tested. This powerful capability should allow, for example, in situ Lu–Hf dating of heavy rare earth element–rich minerals, something that had previously been impossible and, potentially, for in situ Rb–Sr dating of minerals such as biotite. These prototype instruments are poised to add important new capabilities to the field of LA–ICP–MS. Finally, a ‘next generation’ of ToF analysers are being developed coupled to plasma source instruments. These are showing great promise for the simultaneous measurement of key isotope ratios (e.g. for U–Pb geochronology) together with full trace element profiles.

CONCLUSIONS

These are exciting times in the field of LA–ICP–MS isotope ratio determination. For some, this is seen as a mature technology because we do have a very good understanding of the physics and chemistry behind the processes involved, and many applications of the method are commonplace in geoscience laboratories worldwide, e.g. U–Pb zircon geochronology. Important steps are being taken to reduce uncertainties and to increase both lateral and depth resolution, both of which are now comparable to SIMS instruments. Laser ablation is also moving rapidly away from a simple micro-sampling technique, prompted by a much greater integration with other systems, particularly those allowing improved visualisation of data in two and three dimensions. Simultaneously, there are countless new applications being pursued by pioneering analysts, motivated by intractable or intriguing problems in science and new hardware systems rapidly coming on line. For these people, LA–ICP–MS is still very much a bold new frontier….

ACKNOWLEDGMENTS

We thank David Chew, Mark Norman, and Janet Hergt for thoughtful and constructive reviews.

REFERENCES

Allen CM, Campbell IH (2012) Identification and elimination of a matrix-induced systematic error in LA–ICP–MS ^{206}Pb/^{238}U dating of zircon. Chemical Geology 332-333: 157-165

Burger M and 9 coauthors (2015) High-speed, high-resolution, multielemental LA-ICP-TOFMS imaging: Part II. Critical evaluation of quantitative three-dimensional imaging of major, minor, and trace elements in geological samples. Analytical Chemistry 87: 8259-8267

Cottle JM, Horstwood MSA, Parrish RR (2009) A new approach to single shot laser ablation analysis and its application to in situ Pb/U geochronology. Journal of Analytical Atomic Spectrometry 24: 1355-1363

Coogan LA, Parrish RR, Roberts NMW (2016) Early hydrothermal carbon uptake by the upper oceanic crust: insight from in situ U-Pb dating. Geology 44: 147-150

Duval M, Aubert M, Hellstrom J, Grün R (2011) High resolution LA-ICP-MS mapping of U and Th isotopes in an early Pleistocene equid tooth from Fuente Nueva-3 (Orce, Andalusia, Spain). Quaternary Geochronology 6: 458-467

Eggins S and 10 coauthors (2005) In situ U-series dating by laser ablation multi-collector ICPMS: new prospects for Quaternary geochronology. Quaternary Science Reviews 24: 2523-2538

Fietzke J and 7 coauthors (2015) Century-scale trends and seasonality in pH and temperature for shallow zones of the Bering Sea. Proceedings of the National Academy of Sciences of the United States of America 112: 2960-2965

Garbe-Schönberg D, Müller S (2014) Nano-particulate pressed powder tablets for LA-ICP-MS. Journal of Analytical Atomic Spectrometry 29: 990-1000

Gehrels GE, Valencia VA, Ruiz J (2008) Enhanced precision, accuracy, efficiency, and spatial resolution of U-Pb ages by laser ablation–multicollector–inductively coupled plasma–mass spectrometry. Geochemistry, Geophysics, Geosystems 9: doi: 10.1029/2007GC001805

Graham S, Pearson N, Jackson S, Griffin W, O'Reilly SY (2004) Tracing Cu and Fe from source to porphyry: in situ determination of Cu and Fe isotope ratios in sulfides from the Grasberg Cu–Au deposit. Chemical Geology 207: 147-169

Horn I, von Blanckenburg F, Schoenberg R, Steinhoefel G, Markl G (2006) In situ iron isotope ratio determination using UV-femtosecond laser ablation with application to hydrothermal ore formation processes. Geochimica et Cosmochimica Acta 70: 3677-3688

Horton F, Hacker B, Kylander-Clark A, Holder R, Jöns N (2016) Focused radiogenic heating of middle crust caused ultrahigh temperatures in southern Madagascar. Tectonics 35: doi: 10.1002/2015TC004040

Horstwood MSA and 12 coauthors (2016) Community-derived standards for LA-ICP-MS U–Th-Pb geochronology – uncertainty propagation, age interpretation and data reporting. Geostandards and Geoanalytical Research, doi: 10.1111/j.1751-908X.2016.00379.x

Kylander-Clark ARC, Hacker BR, Cottle JM (2013) Laser ablation split-stream ICP petrochronology. Chemical Geology 345: 99-112

Marillo-Sialer E and 6 coauthors (2016) An investigation of the laser-induced zircon 'matrix effect'. Chemical Geology 438: 11-24

Norman MD, McCulloch MT, O'Neill HStC, Yaxley GM (2006) Magnesium isotopic analysis of olivine by laser-ablation multi-collector ICP-MS: composition dependent matrix effects and a comparison of the Earth and Moon. Journal of Analytical Atomic Spectrometry 21: 50-54

Parman SW (2015) Time-lapse zirconography: imaging punctuated continental evolution. Geochemical Perspectives Letters 1: 43-52

Paul B and 5 coauthors (2014) Towards a method for quantitative LA-ICP-MS imaging of multi-phase assemblages: mineral identification and analysis correction procedures. Geostandards and Geoanalytical Research, 38: 253-263

Scolari LA, Ortega-Obregón L, Bernal JP (2015) U–Pb zircon geochronology by LAICPMS combined with thermal annealing: achievements in precision and accuracy on dating standard and unknown samples. Chemical Geology 414: 109-123

Shahar A, Young ED (2007) Astrophysics of CAI formation as revealed by silicon isotope LA-MC–ICPMS of an igneous CAI. Earth and Planetary Science Letters 257: 497-510

Sio CKI and 5 coauthors (2013) Discerning crystal growth from diffusion profiles in zoned olivine by in situ Mg–Fe isotopic analyses. Geochimica et Cosmochima Acta 123: 302-321

Spencer KJ and 7 coauthors (2013) Campaign-style titanite U–Pb dating by laser-ablation ICP: implications for crustal flow, phase transformations and titanite closure. Chemical Geology 341: 84-101

Stearns MA, Cottle JM, Hacker BR, Kylander-Clark ARC (2016) Extracting thermal histories from the near-rim zoning in titanite using coupled U–Pb and trace-element depth profiles by single-shot laser-ablation split stream (SS-LASS) ICP-MS. Chemical Geology, 422: 13-24.

Steinhoefel G, Horn I, von Blanckenburg F (2009) Micro-scale tracing of Fe and Si isotope signatures in banded iron formation using femtosecond laser ablation. Geochimica et Cosmochima Acta 73: 5343-5360

Smye AJ, Stockli DF (2014) Rutile U–Pb age depth profiling: a continuous record of lithospheric thermal evolution. Earth and Planetary Science Letters 408: 171-182

van Elteren JT and 6 coauthors (2013) 3D laser ablation-ICP-mass spectrometry mapping for the study of surface layer phenomena – a case study for weathered glass. Journal of Analytical Atomic Spectrometry 28: 994-1004

Van Malderen SJM, van Elteren JT, Vanhaecke F (2015) Development of a fast laser ablation inductively coupled plasma mass spectrometry cell for sub-um scanning of layered materials. Journal of Analytical Atomic Spectrometry 30: 119-125

Woodhead J, Hergt J, Shelley M, Eggins S, Kemp R (2004) Zircon Hf-isotope analysis with an excimer laser, depth profiling, ablation of complex geometries, and concomitant age estimation. Chemical Geology 209: 121-135

Woodhead JD, Hellstrom J, Hergt JM, Greig A, Maas R (2007) Isotopic and elemental imaging of geological materials by laser ablation inductively coupled plasma mass spectrometry. Geostandards and Geoanalytical Research 31: 331-343

FIGURE AND TABLE CAPTIONS

TABLE 1 A literature survey indicating the first recorded publication of laser ablation determinations for various minerals and isotope systems.

FIGURE 1 Laser ablation U–Th concentration and isotope ratio data obtained on a fossil horse tooth from the Fuente Nueva-3 archaeological excavation in Spain. The data reveal complex pathways of U remobilization after burial, providing the means to target optimal domains most suitable for radiometric dating. REDRAWN FROM FIGURE 4 OF DUVAL ET AL. (2011).

FIGURE 2 Examples of isotopic imaging by LA–ICP–MS. (**A**) Sr isotope map of a Barramundi fish otolith showing how growth layers record different stages of the life history spent in marine and brackish environments. Data such as these are widely used to track migration of commercially important fish stocks, but they can equally be applied to palaeoenvironmental and archaeological research. (**B**) Boron isotope variations (in colour) in high-latitude coralline algae (*Clathromorphum nereostratum*) are used to help interpret rates of ocean acidification (years shown are derived by counting annual growth increments). Isotope data are overlain on electron microprobe secondary electron images, providing a spatial context that greatly assists in data interpretation. REDRAWN FROM WOODHEAD ET AL. (2007) AND FIETZKE ET AL. (2015).

FIGURE 3 An example of laser ablation 'split stream' (LASS) analysis of a monazite contained in the matrix of a garnet-sillimanite-spinel metapelite from Madagascar. Such analysis provides simultaneous U–Pb age and trace element compositional data (colour coding refers to element ratios as indicated). A) Tera-Wasserburg concordia diagram for monazite with individual analyses colored by Th/U ratio B) Concordant data from the same sample plotted on a Tera-Wasserburg concordia diagram and colored by Gd/Yb ratio. C) Two-dimensional maps of a monazite crystal showing distribution of apparent U-Pb age, Gd/Yb and Th/U ratios constructed using a 10 µm laser spot. D) Chondrite-normalized Rare Earth Element diagram where lines represent individual analyses colored by apparent U-Pb age.

Taken together, the data illustrate partial recrystallization of a ca. 1.9 Ga monazite to a ca. 540-500 Ma Yb-poor rim, suggestive of growth in the garnet stability field. Modified from Horton et al. (2016).

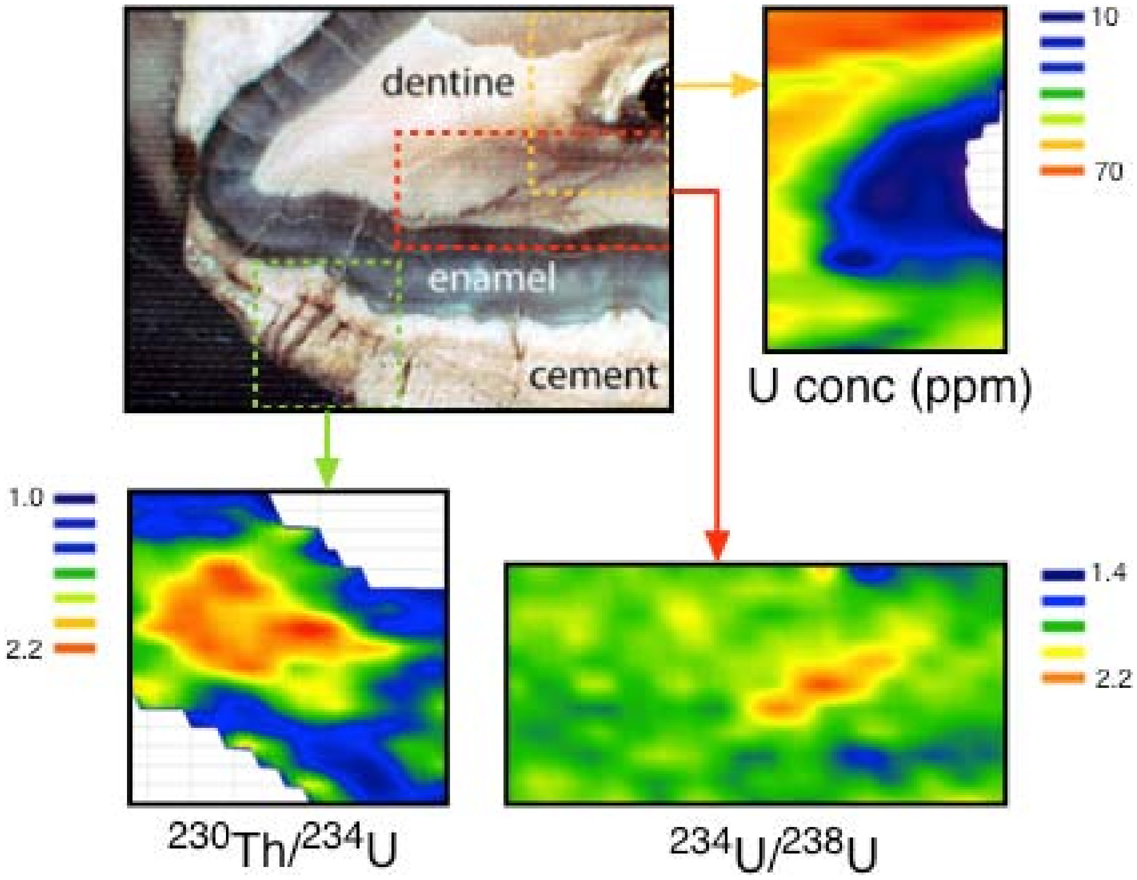

Figure 1

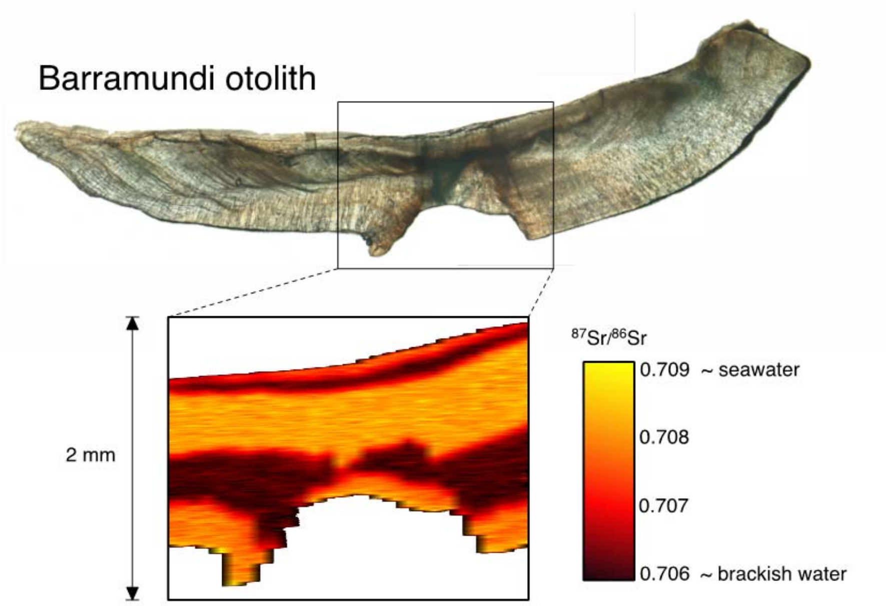

Figure 2a

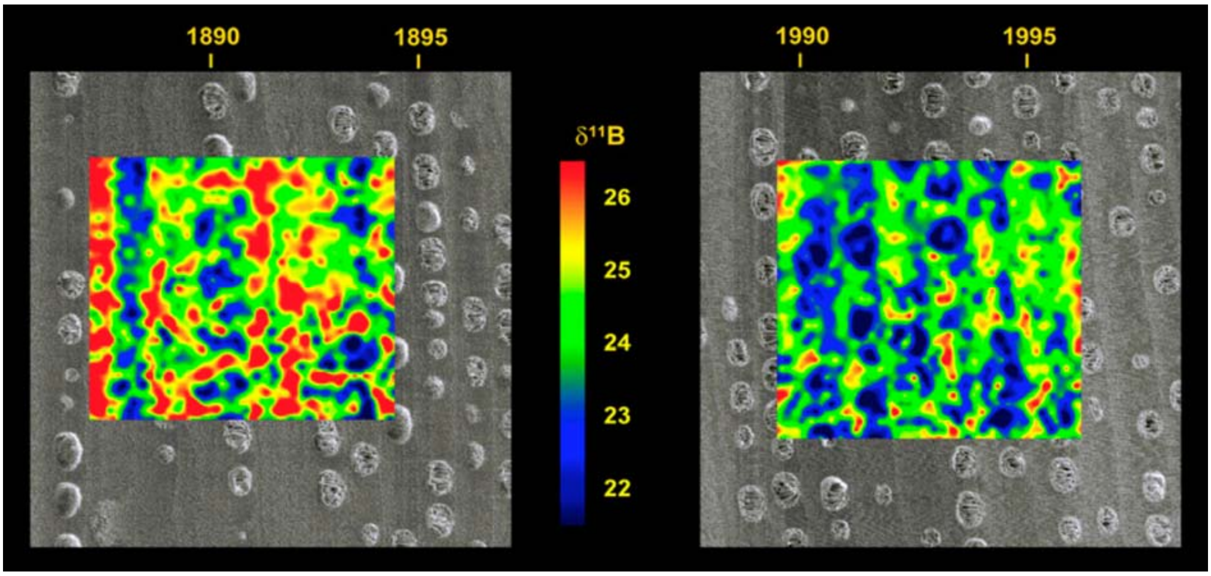

Figure 2b

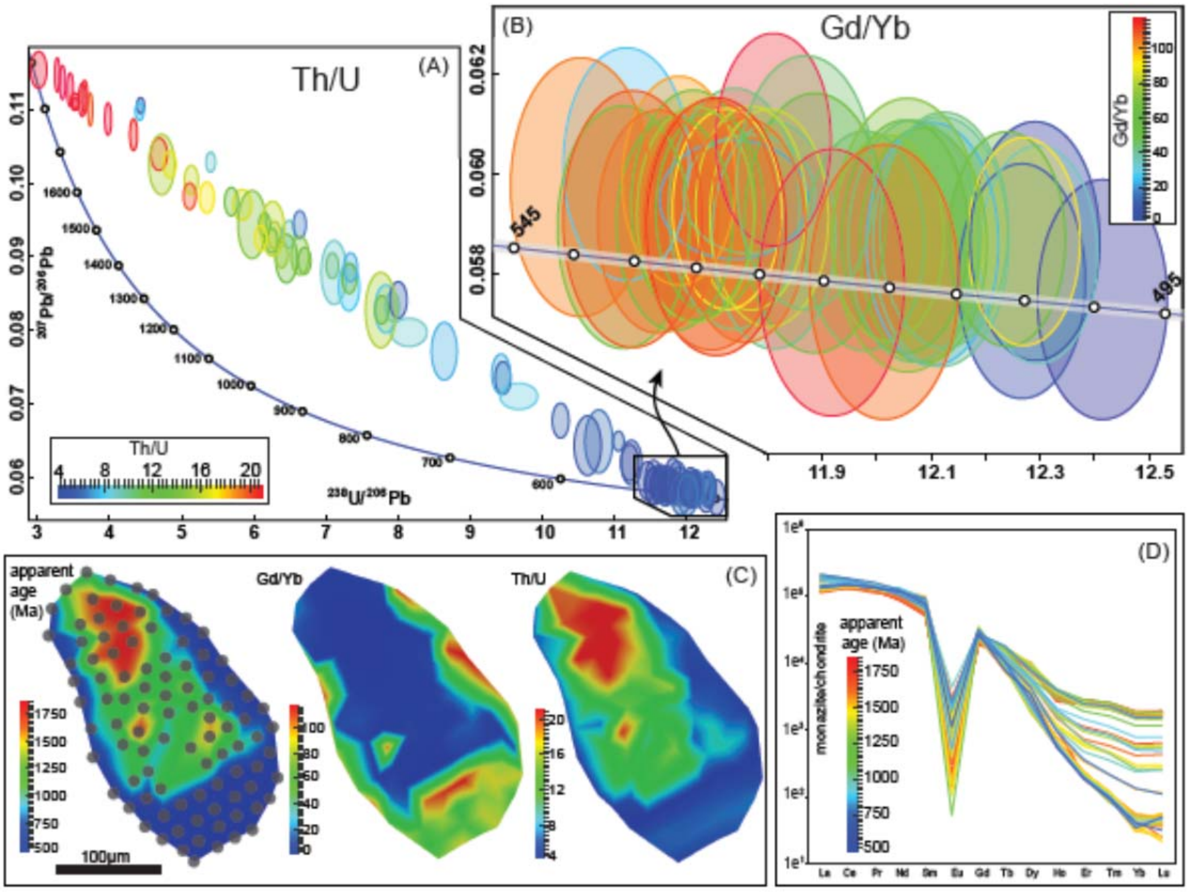

Figure 3

Table. 1. Selected literature references applying LA-ICPMS studies for isotope tracer and dating purposes.

Mineral	**Geochronology - selected references**	**Tracer applications - selected references**
Allanite ([LREE]2(Al,Fe+3)3(SiO4)3(OH))	**U-Pb:** Cox et al., 2003; Gregory et al., 2007	**Sm-Nd:** McFarlane & McCulloch 2007
Apatite (Ca5PO43(F,Cl,OH))	**U-Pb:** Willigers et al., 2002; Thomson et al., 2012	**Sm-Nd**: Foster and Vance 2006; **Sr:** Horstwood et al., **Pb:**Willigers et al., 2002; **Ca:** Tacail et al., 2015
Baddeleyite (ZrO2)	**U-Pb:** Horn et al., 2000, Xie et al., 2008	**Lu-Hf:** Xie et al., 2008; Ibanez-Mieja, 2014
Basnaesite ((LREE,Y)CO3F)	**U-Pb:** Yang et al., 2014;	-
Calcite (CaCO3)	**U-Pb:** Li et al., 2014; **U-Th:** Eggins et al., 2005**;** Potter et al., 2005	**Sr:** Christensen et al., 1995; Woodhead et al 2003; **B:** Fietzke et al., 2010
Cassiterite (SnO2)	**U-Pb**: Yuan et al., 2011	-
Celestine (SrSO4)	-	**Sr:** Giuliani et al., 2013
Columbite-Tantalite (Fe2+Nb2O6 - (Fe,Mn)Ta2O6)	**U-Pb**: Smith et al., 2004	-
Feldspar ([K-Na-Ca]AlSi3O8)	-	**Sr:** Christensen et al., 1995; Davidson et al., 2007
Glasses	-	**Pb:** Paul et al, 2005; Kent et al., 2008; **B**: Le Roux et al., 2004; **Li:** Le Roux et al., 2010
LIMA minerals (e.g. [Mg,Fe]2[Ti,Fe,Cr, Al]18O38)	**U-Pb:** Giuliani et al., 2014	
Metals (e.g. meteorites etc)	-	**Fe:** Hirata et al., 2001; Kosler et al., 2005
Molybdenite (MoS2)	**Re-Os**: Selby et al., 2004	-
Monazite [(LREE]PO4)	**U-Pb:** 2000	**Sm-Nd:** McFarlane & McCulloch 2007; Fisher et al., 2011
Perovskite (CaTiO3)	**U-Pb:** Cox & Wilton 2006	**Sr:** Paton et al., 2007**; Sr-Nd:** Yang et al., 2009
Pyrite (FeS2)	-	**Pb:** Woodhead et al., 2009
Rutile /Anatase (TiO2)	**U-Pb:** Vry & Baker, 2006; Zack et al. (2011)	**Lu-Hf:** Ewing et al. 2012
(urano)Thorite ((U)ThSiO4)	**U-Pb:** Cottle, 2014	-
Titanite (CaTiSiO5)	**U-Pb:** Willigers et al., 2002; Spencer et al., 2013	**Sr-Nd:** Foster and Vance, 2006
Tourmaline ([Ca,K,Na][Al,Fe,Li,Mg,Mn]3[Al,Cr, Fe,V]6 (BO3)3[Si,Al,B]6O18[OH,F]4)	-	**B:** Tiepolo et al., 2006; Mikova et al., 2014
Uraninite (UO2)	**U-Pb:** Chipley et al., 2007	-
Xenotime (Y[HREE]PO4)	**U-Pb:** Liu et al., 2011	**Sm-Nd:** Hammerli et al., 2014
Zircon (ZrSiO4)	**U-Pb**: Hirata & Nesbitt, 1995; Scaltegger et al., 2015	**Lu-Hf**: Griffin et al., 2000; Woodhead et al., 2004
Zr-bearing silicates (e.g., zirconolite, [Ca,Ce]Zr[Ti,Nb,Fe]2O7)	**U-Pb:** Wu et al., 2010	**Sr-Nd-Hf:** Wu et al., 2010