

Advanced *in situ* geochronological and trace element microanalysis by laser ablation techniques

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was developed in 1985 and the first commercial laser ablation systems were introduced in the mid 1990s. Since then, LA-ICP-MS has become an important analytical tool in the earth sciences. Initially, the main interest for geologists was in its ability to quantitatively determine the contents of a wide range of elements in many minerals at very low concentrations (a few ppm and below) with relatively high spatial resolution (spot diameters of typically 30–100 μm). The potential of LA-ICP-MS for rapid *in situ* U–Th–Pb geochronology was already realised in the early to mid 1990s. However, the full potential of LA-ICP-MS as the low-cost alternative to ion-microprobe techniques for highly precise and accurate *in situ* U–Th–Pb age dating was not realised until the relatively recent advances in laser technologies and the introduction of magnetic sectorfield ICP-MS (SF-ICP-MS) instruments. In March 2005, the Geological Survey of Denmark and Greenland (GEUS) commissioned a new laser ablation magnetic sectorfield inductively coupled plasma mass spectrometry (LA-SF-ICP-MS) facility employing a ThermoFinnigan Element2 high resolution magnetic sectorfield ICP-MS and a Merchantek New Wave 213 nm UV laser ablation system. The new GEUS LA-SF-ICP-MS facility is widely used on Survey research projects in Denmark and Greenland, as well as in collaborative research and contract projects conducted with partners from academia and industry worldwide. Here, we present examples from some of these ongoing studies that highlight the application of the new facility for advanced geochronological and trace element *in situ* microanalysis of geomaterials. The application of LA-SF-ICP-MS based *in situ* zircon geochronology to regional studies addressing the Archaean geology of southern West Greenland is presented by Hollis *et al.* (2006, this volume).

Zircon U–Pb geochronology using LA-SF-ICP-MS

In situ U–Th–Pb geochronology was developed in the mid-80s with the introduction of ion-microprobe techniques, most commonly referred to as secondary ion mass spectrometry (SIMS) and sensitive high resolution ion microprobe (SHRIMP). The advantage of *in situ* U–Th–Pb geochronol-

ogy over conventional chemical dating by isotope dilution thermal ionisation mass spectrometry (ID-TIMS) is the capability to analyse different domains in heterogeneous single zircons with high spatial resolution (spot diameters of typically 10–30 μm). This allows resolution of igneous and metamorphic events separated by intervals of only a few tens of million years from polychronic zircons. The disadvantages of ion-microprobe techniques are the very high purchasing and operating costs for the instrument. The rapid improvements in laser based U–Th–Pb geochronology makes it now possible to obtain *in situ* U–Th–Pb geochronological data with comparable spatial resolution as well as analytical precision and accuracy at only a fraction of the costs of ion-microprobe techniques (e.g. Jackson *et al.* 2004; Janoušek *et al.* 2006).

Dating of magmatic and metamorphic events

The capabilities of LA-SF-ICP-MS for the precise and accurate U–Pb age dating of relatively young igneous zircons are demonstrated by the analysis of a population of 40 zircons extracted from a gabbro from the Coastal Cordillera at Tregualemu, central Southern Chile. The gabbro is believed to have been formed by regional extension during the late Triassic to early Jurassic (Charrier 1979). Three zircons proved to be too small for analysis (< 30 μm). The results for the remaining 37 zircons (Fig. 1) define a highly precise igneous concordia age of 203 ± 2 Ma (2σ ; MSWD = 1.7) and indicate a Late Triassic (Rhaetian) intrusion age of the gabbro. An even

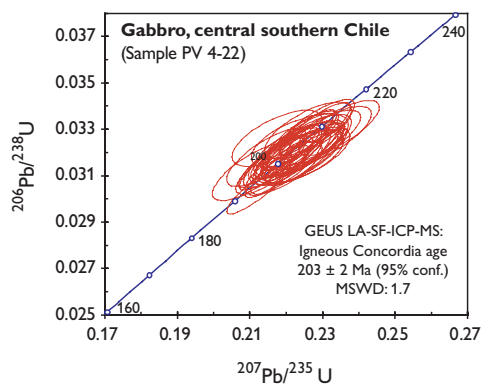


Fig. 1. Concordia diagram for igneous zircons from a gabbro from the Coastal Cordillera in central Southern Chile.

younger igneous age of 158 ± 2 Ma was recently obtained for a zircon xeno- or phenocryst derived from a newly discovered carbonatite in southern West Greenland (Steenfelt *et al.* 2006, this volume).

The high sensitivity of the Element2 SF-ICP-MS allows U–Pb zircon age dating with a laser spotsize of 30 μm or less, depending on the Pb content of the zircons. This makes it feasible to analyse different age domains in polychronic zircons, e.g. igneous cores and metamorphic rims. For example, zircons from an orthogneiss from the Nuuk region, southern West Greenland, display characteristic textures in back-scattered electron (BSE) and cathodoluminescence (CL) pictures that are interpreted as igneous cores surrounded by rims grown during a metamorphic event (see inset in Fig. 2). The U–Pb age data of the cores suggest an emplacement of the igneous protolith at *c.* 3660 Ma, while the rim data indicate metamorphism close to 2700 Ma (Fig. 2).

Dating of detrital zircons

Analyses of the crystallisation ages of detrital zircons in clastic sediments are a powerful tool in sedimentary provenance analysis. Accurate and precise U–Pb ages of >100 detrital zircon grains in a sample are needed to detect all major sedimentary source components with statistical confidence (cf. Vermeesch 2004; and references therein). The relatively high costs and the limited capacities of ion microprobe techniques (*c.* 75 zircon age analyses per day) impose restrictions on the number of samples that can be studied. Because LA-SF-ICP-MS provides very high capacities (in excess of 300 zircon age analyses per day) without compromising accuracy and preci-

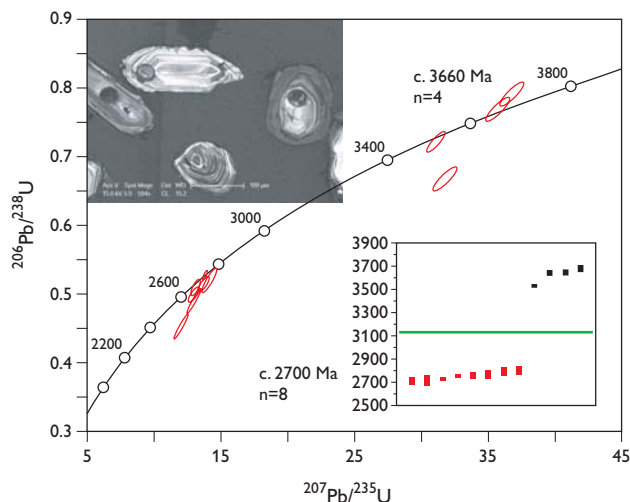


Fig. 2. Concordia diagram and inset of $^{207}\text{Pb}/^{206}\text{Pb}$ age plot for polychronic zircons from an orthogneiss in the Nuuk region, southern West Greenland. **Inset** CL image shows laser ablation pits (pit diameter = 30 μm) in igneous cores and metamorphic rims of polychronic zircons. Note the shallow depth (usually < 20 μm) of the laser ablation pits.

sion, it constitutes the economic method of choice for provenance studies based on detrital zircon U–Pb ages.

An example for detrital zircon age data obtained by LA-SF-ICP-MS is shown in Fig. 3, where the ^{207}Pb – ^{206}Pb age distribution for a population of 100 zircon grains separated from a Cambrian sandstone from Torekov, southern Sweden, are shown in a combined histogram and probability density distribution (PPD) diagram. The concordance filtered zircons (dark shaded area; 90–110% concordance, defined as $100 \times [^{206}\text{Pb} - ^{238}\text{U} \text{ age} / ^{207}\text{Pb} - ^{206}\text{Pb} \text{ age}]$) show a polymodal age distribution with a minor peak at ~ 1000 Ma and two major peaks at *c.* 1150 Ma and 1650 Ma. The presence of two older sedimentary sources (*c.* 2150 Ma and *c.* 3050 Ma) is indicated by discordant grains (lighter shaded grey areas) that most likely suffered lead loss during their petrogenetic evolution.

Figures of merit

The short and long term precision and accuracy of LA-SF-ICP-MS for U–Pb zircon age dating has been assessed using two zircon reference materials, Plesovice (with an ID-TIMS age of 338 ± 1 Ma; Aftalion *et al.* 1989; provided by Jan Kosler, University of Bergen) and 91500 (ID-TIMS age = 1065 ± 0.4 Ma; Wiedenbeck *et al.* 1995). The PL zircon is routinely analysed as unknown for quality control purposes in every analytical session in the GEUS laboratory. The results for 16 analyses of the zircon from a typical single analytical session are shown in Fig. 4A. They define a concordia age that is in excellent agreement with the ID-TIMS age reported by Aftalion *et al.* (1989). Long-term precision (2σ) based on 109 analyses of the Plesovice zircon by two different operators was 2%, 2.3% and 1.1% for the $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios, respectively. The widely used 91500 zircon has so far only been analysed during one analytical session. The results for all seven analyses carried out

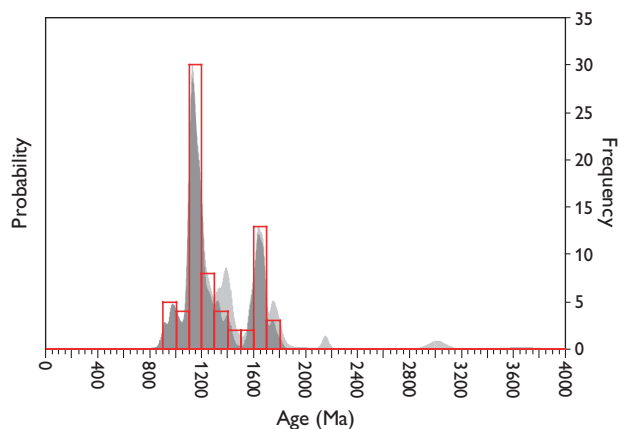
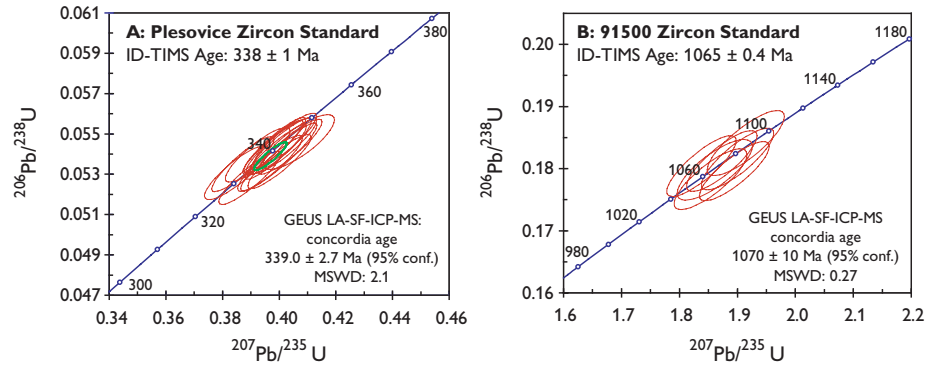


Fig. 3. Combined display of histogram and probability density distribution (PPD) diagram for zircons from a Cambrian sandstone from Torekov, south-western Sweden. See text for explanations.

Fig. 4. Concordia diagrams for 16 analysis of the Plesovice zircon reference material obtained during a single analytical session (A); and 7 analysis of the 91500 zircon reference material obtained during a single analytical session (B).



during this session (Fig. 4B) define a concordia age which is in excellent agreement with the ID-TIMS age reported by Wiedenbeck *et al.* (1995).

Trace element analysis using LA-SF-ICP-MS

Due mainly to the introduction of LA-ICP-MS techniques, the trace element signatures of individual minerals (e.g. garnet, clinopyroxene, epidote, rutile, calcite) are now frequently being used to deduce the petrogenetic evolution of magmatic rocks, unravel water–rock interactions, identify geotectonic settings and sediment sources, track down the pathways of potentially health-damaging pollutants, and to unravel the change of seafloor and atmospheric temperatures. Furthermore, LA-ICP-MS is an important tool for the characterisation of synthetically produced geomaterials.

Water–rock interaction

Fluid-mediated mass transfer during metamorphism and metasomatism is a hotly debated issue. Mobility of geochemically important trace elements during fluid flow has far-reaching implications for e.g. ore-forming processes and mass transfer during subduction. Detailed investigation of the mechanisms of element mobility during fluid–rock interaction on a grain-scale are pivotal for an understanding of the processes that lead to the characteristic element enrichments and depletions observed in nature.

In the Söndrum stone quarry in Sweden, a localised dehydration zone of 2.5 to 3 m width occurs in garnet-bearing granitic gneiss around an approximately 1 m wide pegmatoid dyke. Whole-rock chemistry suggests that the solid-state dehydration of the granitic gneiss to charnokite via low H₂O activity fluids consisting principally of CO₂ and a minor brine component was predominantly isochemical (Harlov *et al.* 2006). Exceptions include Y and the heavy rare earth elements (HREE), which are markedly depleted throughout the dehydration zone. In order to assess the mechanism of Y and

HREE depletion, the trace element geochemistry of garnet was studied in a traverse across the dehydration zone. Garnets from the pristine, unaltered granitic gneiss are characterised by a strong negative Eu-anomaly and the steep, HREE enriched pattern typical for garnet (sample SD45-600 in Fig. 5). In contrast, garnets from within the dehydration zone show a less pronounced Eu-anomaly and are characterised by dramatic Y and HREE depletions, leading to almost flat REE pattern (sample SD9-120 in Fig. 5). This observation provides direct evidence for massive release of Y and HREE from garnets, the principal hosts of these elements in the granitic gneiss, via solid-state fluid–rock interaction which was also accompanied by dehydration of hornblende and biotite to ortho- and clinopyroxene.

Analysis of synthetic geomaterials

Another application of LA-ICP-MS is the trace element analysis of synthetic geomaterials, e.g. products of experiments carried out for petrogenetical purposes. Since the experimentally produced mineral phases are usually very small, *in situ* microanalysis with high spatial resolution is needed. This was traditionally achieved by SIMS techniques. Because LA-ICP-MS analyses are much cheaper and facilities are much

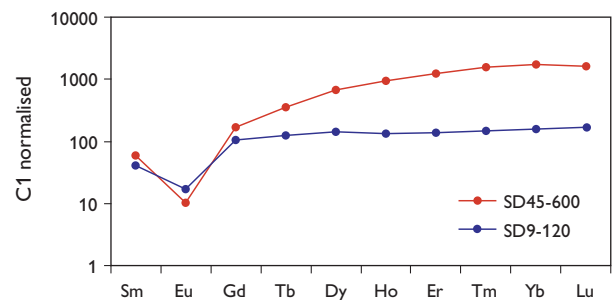


Fig. 5. Average chondrite-normalised REE-pattern of garnets from the unaffected granitic gneiss (SD45-600) and the dehydration zone (SD9-120). Note the depletion in HREE of garnets from the dehydration zone.

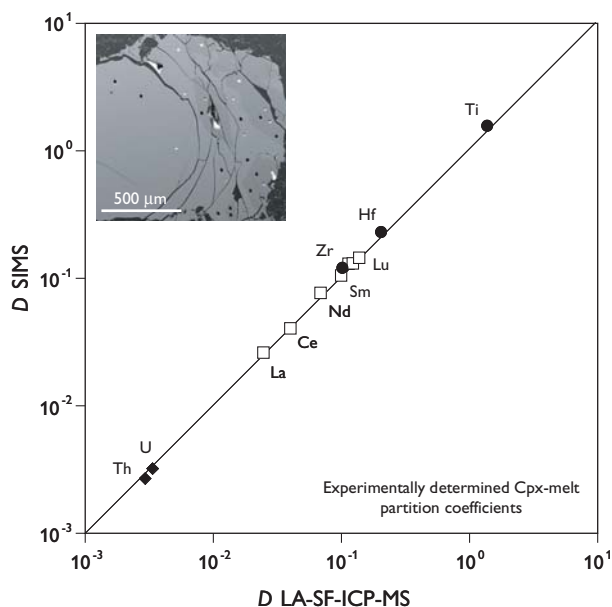


Fig. 6. Comparison of clinopyroxene-melt trace element partition coefficients (**open symbols**: REE; **solid symbols**: HFSE) determined from synthetic run products by SIMS and LA-SF-ICP-MS. **Inset** shows a BSE photomicrograph of synthetic, euhedral clinopyroxene coexisting with a glassy melt produced experimentally at high pressure and temperature. Shallow, bright spots are SIMS ablation pits (c. 20 μm diameter), while deeper, dark spots are laser ablation pits (c. 30 μm in diameter).

more widely available, LA-ICP-MS is increasingly used for the trace element analysis of synthetic geomaterials.

The inset in Fig. 6, for example, shows a back-scattered electron photomicrograph of an experimental charge containing euhedral clinopyroxene and a coexisting anhydrous silicate melt. The experimental charge was synthesised in order to determine the clinopyroxene-melt trace element partition coefficients D_i (defined as $D_i = [\text{concentration of } i]_{\text{cpx}} / [\text{concentration of } i]_{\text{melt}}$), knowledge of which is important for geochemical melt modelling purposes (Landwehr *et al.* 2001). In order to test the ability of laser ablation techniques to correctly determine partition coefficients from such experimental charges, we have analysed clinopyroxenes and coexisting silicate melts from a number of experiments with both SIMS (at the NERC ion-microprobe facility in Edinburgh) and LA-SF-ICP-MS (at GEUS). The resulting partition coefficients determined by SIMS and LA-SF-ICP-MS are graphi-

cally compared in Fig. 6 for a representative sample. For all investigated samples, the partition coefficients determined by SIMS and LA-SF-ICP-MS are in excellent agreement, clearly demonstrating the reliability of laser ablation techniques for the characterisation of synthetic geomaterials.

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