Use of Laser-Ablation ICP-MS for U-Pb zircon geochronology

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Zircon is the most frequently used mineral for age determination with the U-Pb dating technique, despite its disadvantage of highly complex growth structures, inheritance of older pre-crystallization lead and its tendency to lose some of the radiogenic lead through the further P-T-evolution. Geological processes in deep crustal rocks are known to be very complex and polyphased and in part can be of short duration. The unravelling of such complex evolutionary histories demands for both high precision dating and high spatial resolution of different growth stages that have been visualized by imaging methods such as cathodoluminescence or backscatter electron imaging proir to isotopic dating. Isotope dilution thermal mass-spectrometry (IDTIMS) allows the assessment of highly precise U-Pb ages within a few permil uncertainty. Complex growth structures and/or system behaviour are, however, only resolved by in-situ analyses, e.g. using an ionprobe. Laser-ablation ICP-mass spectrometry now offers a third possibility for accurate, fast and cheap determination of U-Pb ages. The introduction of UV lasers lead to improved ablation behaviour (Günther *et al.*, 1997), reduced inter-elemental fractionation effects and improved accuracy when compared to Nd:YAG lasers (e.g. Hirata and Nesbitt, 1995).

UV-LA-ICP-MS setup at ETH Zürich

ICP-MS instrument: ELAN 6000 (Perkin-Elmer); Detector: dual, pulse counting and analogue detector; Vacuum pressure: 1.45×10^{-5} Torr; 7.6×10^{-6} Torr with 2 additional rotary pumps; Al cone with 0.5 mm diameter; Excimer Laser: Compex 110 I (Lambda Physik); Maximum output energy: 200mJ at 193 nm; Pulse duration: 15 ns; Repetition rate: 1–10 Hz

U-Pb age determinations are performed using NIST 610 and 612 glasses as external calibration standards. LA-ICP-MS data are acquired measuring

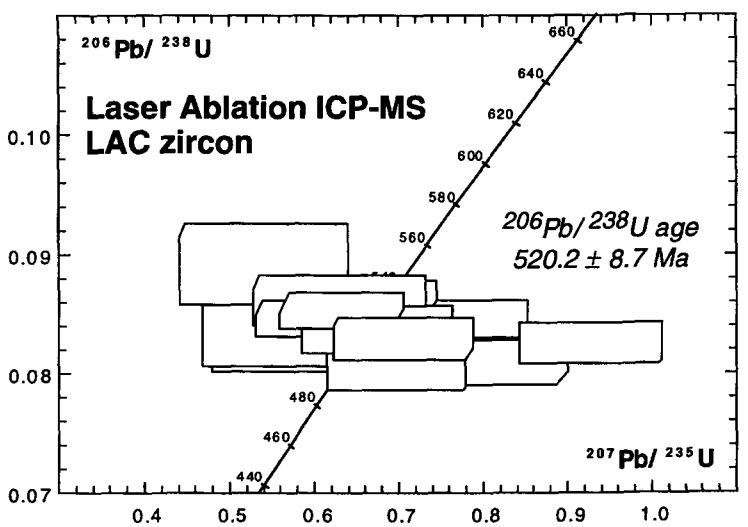

FIG. 1.

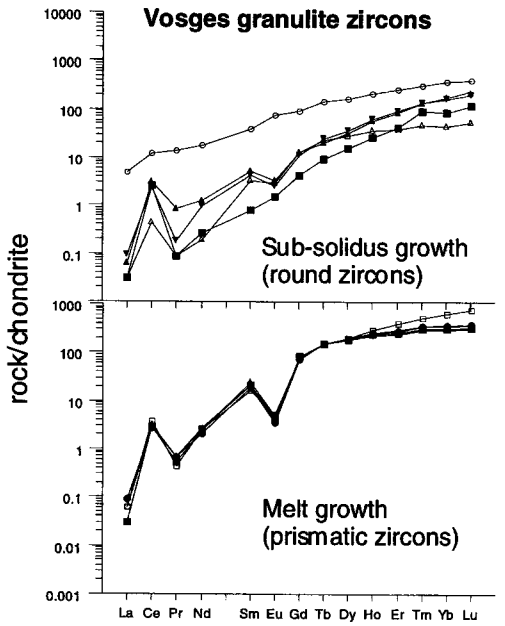

FIG. 2.

^{206}Pb, ^{207}Pb, ^{208}Pb, ^{232}Th, ^{235}U and ^{238}U. Si is used as internal standard to correct for variations in ablation behaviour and the concentrations were calculated on the basis of a theoretical Si concentration in zircon of 32.2 wt.%. A pit diameter of 40μm is mostly used for analysis; data are acquired during a typical ablation period of 30 seconds.

Geochronology

The aim of this paper is to demonstrate that with the present setup we are able to arrive at accuracies of better than 5% and within-run precisions of ± 1% for $^{206}Pb/^{238}U$ ages. Internal and external precisions are anticipated to become comparable to ionprobe data, but with considerably reduced time consumption for sample preparation and actual analysis.

We will present LA-ICP-MS age data on 521 Ma-old low-U LAC zircons (material from MUN St. John's, courtesy of S. Jackson), which serves as ETH internal laboratory standard. A mean $^{206}Pb/^{238}U$ age of 520.2 ± 8.7 Ma (2 sigma) can be calculated from a data set of 18 spot analyses, see Fig. 1.

Granulite-facies zircons with 400 ppm U and 18 ppm Pb from the Variscan Vosges mountains were analysed and serve as a test example, because they are extremely well dated by means of conventional (IDTIMS) and ionprobe (SHRIMP) techniques: A mean $^{206}Pb/^{238}U$ age of 336 ± 20 Ma resulted from a 4-spot run so far, well comparable with a conventional age of 335 ± 1 Ma and a SHRIMP age of 336 ± 4 Ma (Schaltegger *et al.*, submitted).

A third example of the capabilities of this method is given by zircons of a pegmatite from the Lower Swat area of Pakistan (NW Himalaya). Conventional zircon dating yielded a mean $^{206}Pb/^{238}U$ age of 29.28 ± 0.20 Ma. U and Pb concentrations of analysed zircons are ca 300 ppm and 1.1 ppm, respectively. An average of 32 spot ages by our LA-ICP-MS equipment yielded a mean $^{206}Pb/^{238}U$ age of 26.9 ± 4.9 Ma (1 sigma). Isotopes of Si, Pb, Th, U and all *REE*'s were measured within the same analytical run.

Geochemistry

Granulite-facies zircons of the Variscan Vosges mountains reveal a variety of growth structures, which are visible by cathodoluminescence. Different growth zones with sector zoning, planar micro-oscillatory and planar zoning may be attributed to different growth stages with increasing fluid and/or melt proportions under conditions of granulite-facies dehydration melting. Sector-zoned domains that grew in a water-undersaturated environment are characterized by variable *REE* concentrations and distribution patterns (Fig. 2 top). Appearance of small volumes of a fluid or melt phase causes the crystallization of of oscillatory-zoned prismatic zircons with *REE* patterns that are characteristic for equilibrium partitioning between melt and zircon (see Fig. 2 bottom). LA-ICP-MS offers the possibility to determine *REE* patterns on 40μm spots and use them as additional tool (together with cathodoluminescence) for the interpretation of spot ages. The geochemical information can be sampled from the same spots during the same analytical run as the U-Pb ages without considerable loss of performance.

Conclusion and outlook

The data obtained by LA-ICP-MS using a quadrupole ICP-MS demonstrate in a clear way the potential of laser ablation for in-situ geochronology. Much more zircons, however, have to be analysed to evaluate the most reliable parameter set on our instrument for this type of analyses. LA-ICP-MS U-Pb geochronology is anticipated to become a fast evolving technique, complementary to conventional and ionprobe dating methods.