In-situ rock slab U-Pb dating of perovskite by laser ablation - magnetic sectorfield ICP-MS: a new tool for diamond exploration

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Introduction

The age of emplacement of kimberlitic rocks can vary considerably within a single cluster (Heaman et al., 2004). Similarly, the abundance of diamonds can vary down to the scale of separate intrusive events within individual composite bodies (e.g. Berryman et al., 2004). Hence determination of ages of kimberlitic rocks is an important tool in diamond prospecting in advance of the costly procedure of diamond separation. Age determinations of hand-screened perovskite separates from kimberlite are routinely carried out using measurements of U and Pb isotopes by ID-TIMS or SHRIMP. However, these measurement techniques are time and cost intensive.

The relatively recent introduction of magnetic sectorfield ICP-MS (SF-ICP-MS) instruments allows accurate and precise in-situ U-Pb dating of a wide range of minerals with high spatial resolution by laser ablation (e.g. Simonetti et al., 2006; Frei and Gerdes, 2008). Currently, the main obstacle for precise and accurate U-Pb dating of perovskite by laser ablation is their usually very high common lead content. However, the high sensitivity of SF-ICP-MS instruments (compared to quadrupole instruments) allows accurate common lead corrections to be performed and hence LA-SF-ICP-MS constitutes a rapid and inexpensive technique for U-Pb dating of perovskite (Frei et al., 2008 *this volume*). Despite reducing analytical costs, the procedure of producing and preparing a mineral separate on which the measurements described in Frei et al. (2008, *this volume*) rely, still contributes a significant time and cost commitment. In order to be a more useful prospecting tool, it is important to minimise both sample preparation and analytical cost whilst maintaining accuracy and precision. Hence in the following we investigate whether minimally prepared rock sections rather than mineral separates can practically be used for the purpose of perovskite age determination.

Sample Selection and Preparation

Kimberlite sample JA-71-20 from Midternæs, located some 15 km north of the Pyramidefjeld igneous complex, South-West Greenland (Emeleus and Andrews, 1975) was chosen for age determination. This is a hand sample from which perovskite mineral separates had previously been prepared for age determination by ID-TIMS and laser-ICP-MS (Frei et al., 2008, *this volume*). Because of its low U and Pb contents (40 and 1 ppm, respectively) and its Jurassic age, this sample represents a well characterised yet challenging kimberlite from which to test the acquisition of accurate and precise in-situ U-Pb ages.

A 15 x 20 mm slab was sawn from JA-71-20 and subsequently polished by hand down to a grade of 6 µm using carborundum paper (Figure 1). Inspection of the slab revealed that perovskites in the sample range from 30 to 100 µm, are orange to tan coloured and typically exhibit light-coloured rims. Emeleus and Andrews (1975) report that perovskite comprises 2 vol% of this sample. The entire polished slab was photographed at high resolution (pixel width of 5 µm) in reflected light using a microscope equipped with motorised stage (Fig. 1). Creating an image of the slab at this resolution greatly facilitates the process of navigating to specific previously chosen grains during analysis.

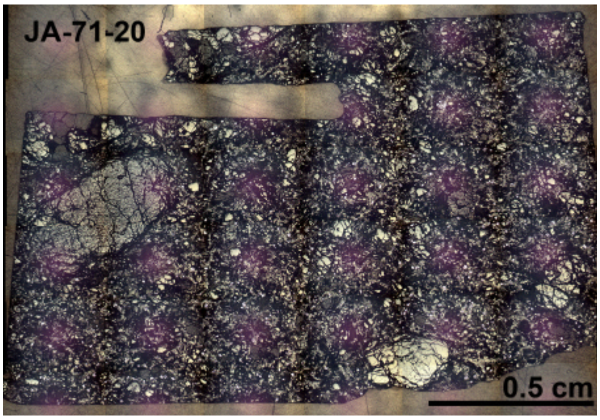

Fig. 1 Composite reflected light image of polished rock slab JA-71-20 (Resampled from a resolution of 5 µm per pixel).

Methodology

As a means to test the extent to which time spent in point selection could also be minimised, grains were chosen for analyses using two methods, scanning electron microscopy (SEM) or simple visual inspection using the reflected light optics of the laser-ICP-MS unit.

Within kimberlitic rocks perovskite grain sizes are typically within the range of 50-200 µm (Mitchell, 1986) and the most likely candidates for confusion with perovskite are oxides, particularly ilmenite. During SEM work, the use of energy dispersive spectrometry where available can provide a definitive identification. However perovskite can be otherwise identified by its higher optical reflectance than ilmenite and is typically slightly darker and often less strikingly zoned in back-scattered electron imaging. Furthermore, perovskite typically crystallises as cubes and hence is usually square in cross-section or slightly rectangular or hexagonal depending on orientation. In contrast, as ilmenite is more cuboid in morphology, sectioned forms are more often rectangular or triangular (Fig. 2).

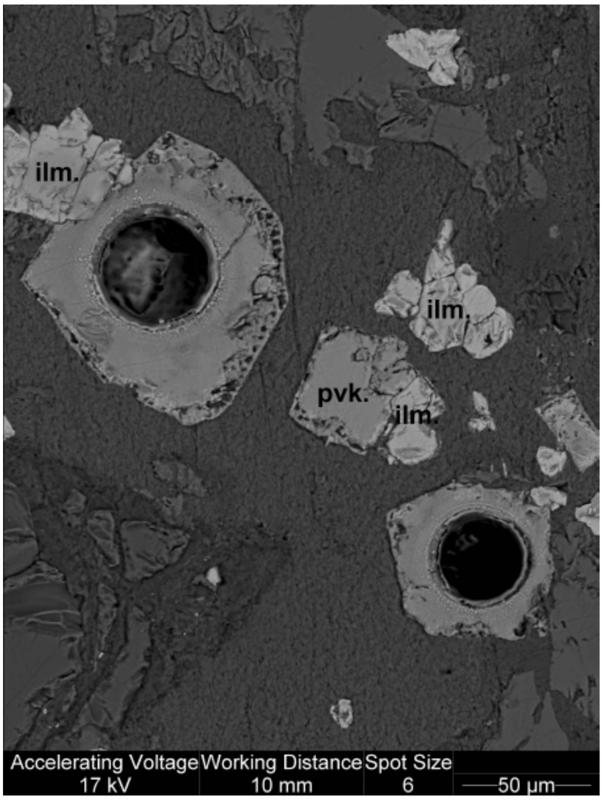

Fig. 2 Back-scattered electron image of 30 µm and 45 µm laser ablation pits in two perovskite grains. Zoned and slightly lighter tone ilmenites (‘ilm.’) are annotated for comparison with perovskite (‘pvk’). Note the morphological and tonal differences between perovskite and ilmenite.

On the basis of grain size, morphology and back-scattered electron intensity 19 grains were picked for laser analysis. A further 13 grains were chosen simply on the basis of size, morphology and reflectance using the reflected light optics in the laser unit.

Analyses were conducted using a ThermoFinnigan Element2 SF-ICP-MS coupled to a NewWave UP213 laser system at the Geological Survey of Denmark and Greenland. A 30 µm (19 analyses) or 45 µm (13 analyses) spot size was used depending on the size of the perovskite grain being measured. A common Pb correction was applied using the interference and background corrected ^{204}Pb signal intensity in combination with a model Pb composition (Stacey and Kramers, 1975). Standardisation was achieved using the GJ1 zircon standard. Quality control was maintained by conducting measurements on perovskite grains from the Ice River alkaline complex, British Columbia acting as a secondary standard.

Results

Multiple measurements of the Ice River secondary standard yielded a concordia age of 357±3 Ma, in excellent agreement with an age of 359±3 Ma acquired in a prior session (Frei et al., 2008, *this volume*). More significantly, this date is also in excellent agreement with independent age determinations by ID-TIMS (356 Ma, Heaman, *pers. comm.* 2007).

Of the Midternæs rock slab grains measured, all grains were confirmed to have been correctly identified as perovskite irrespective of whether they were chosen with the aid of the SEM or by reflected light using the optical system of the laser ablation system. Of the SEM-identified grains, 90% were successfully measured whereas almost 75% of the optically identified grains yielded useable data. Rejected analyses typically arise where the laser burns completely through thinner grains prior to the completion of the analyses. Typical 30 and 45 µm diameter and approximately 20 µm deep ablation pits are shown in Figure 2. The high spatial resolution makes it possible to avoid ablation of partially altered rims and other undesirable areas.

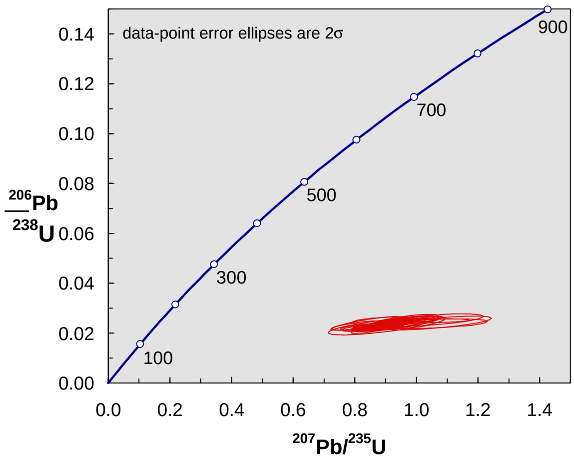

Fig. 3 Not common Pb corrected U-Pb results for kimberlite-hosted perovskite in sample JA-71-20.

The results for 26 analysis obtained *in-situ* in the rock slab of sample JA-71-20 are shown in a Wetherill concordia diagram in Figure 3. In the absence of a correction for common Pb, the results are significantly discordant. Although the data seemingly plots along an array that points to an intercept with the concordia between 100 and 200 Ma, it was not possible to calculate a common Pb anchored intercept age from a Tera-Wasserburg diagram.

However, the high sensitivity of the sectorfield instrument used (compared to quadrupole instruments) allows a meaningful common lead correction to be applied. After common Pb correction, the 26 analysis yielded a concordia age of 152±2 Ma (Fig. 4a; 2s, decay-constant errors included, MSWD of concordance = 3.5, probability of concordance = 0.062) and a common lead corrected ^{206}Pb/^{238}U age of 152±3 Ma (Fig. 4b). These age determinations obtained *in-situ* from a minimally prepared polished rock slab are in excellent agreement with the results from age determinations using more labour intensive mineral separates by ID-TIMS (weighted average ^{206}Pb/^{238}U age of 151.2±1.5 Ma, 2s) and by SF-ICP-MS which gave a common lead corrected weighted average ^{206}Pb/^{238}U age of 152±3 Ma (Frei et al., 2008, *this volume*).

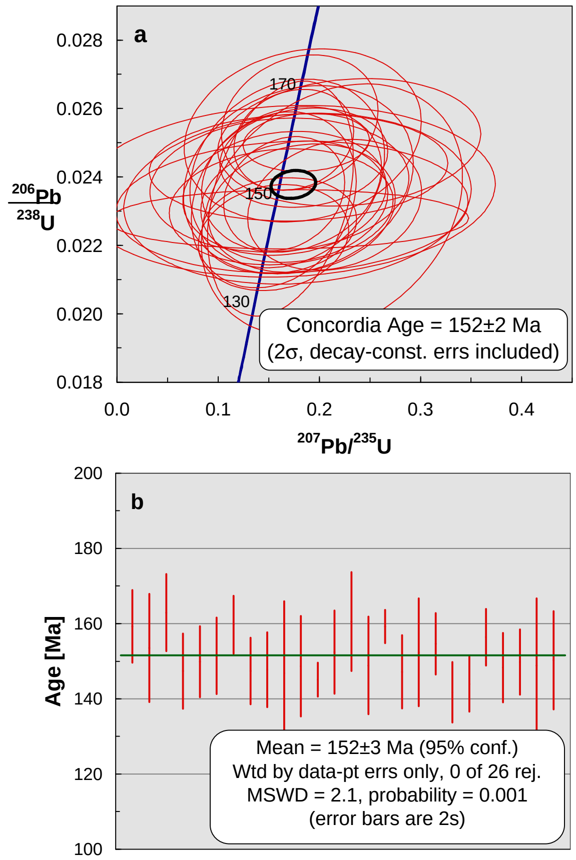

Fig. 4 Wetherill concordia plot (**a**) and weighted average ^{206}Pb/^{238}U age (**b**) for kimberlite-hosted perovskite in sample JA-71-20 from Midternæs.

Conclusions

Our results demonstrate that a minimally prepared rock slab of a sample can be used to identify and successfully measure perovskite grains without grain selection prior to analysis. This represents the least labour intensive and hence cheapest approach to dating of a kimberlitic body described to date. However, in adopting this approach there is a risk of inadvertently consuming U-rich phases such as apatite which would temporarily saturate the detector. Where this risk is deemed significant or for samples with small or sparse perovskite, the procedure of age determination would benefit from prior sample imaging and SEM-assisted phase identification as described. Whether the SEM is employed or not, however, results are shown to maintain the accuracy and precision of significantly more costly techniques.

The data acquired demonstrates that with minimal preparation, robust emplacement ages can be obtained for perovskite-bearing kimberlites using LA-SF-ICP-MS. Given the importance of emplacement age determination in diamond prospectivity, this method constitutes a rapid and inexpensive tool for diamond prospecting.

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