

ANALYSIS OF SPELEOTHEM AND ZIRCON SAMPLES BY LA-ICP-MS

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Abstract

An inductively coupled plasma mass spectrometer (ICP-MS) equipped with a laser ablation (LA) sample introduction device was used to study the element and isotope distribution in a speleothem sample from the Hajnóczy cave (Hungary) and to perform U-Pb zircon geochronology of a drill sample taken from in the Szalatnak area (Hungary). The purpose of the study was to assess the analytical capabilities of the LA-ICP-MS combination in these applications and to obtain data relevant to geochemical research.

Introduction

It was in the mid-1980s that the analytical potential of LA-ICP-MS was first shown by Gray [1]. Subsequent studies by Jackson et al. [2] and Longerich et al. [3] in the 1990s demonstrated that entirely new calibration strategies would have to be developed and significant improvements made in laser technology and ICP mass spectrometry in order to achieve the precision and accuracy required for applications such as isotopic dating of geological samples. The key paper on the application of laser ablation in the Earth sciences came from Jackson et al. [2], who published the first comprehensive work on the use of LA- ICP-MS for analysis of trace elements in minerals. Since then, this analytical methodology is continuously developing, largely determined by the technological advancements made available to the public both in the areas of pulsed lasers and ICP-MS instrumentation. A relatively widespread application of LA-ICP-MS in Earth sciences only started at around the end of 1990s, when suitable calibration standards also became available [4].

The main advantage of LA-ICP-MS geochemical analysis is that the *in-situ* study of minerals and accessory minerals is possible, without separating them from the rock and also without any significant sample preparation for that matter. The elemental or isotopic analysis, as well as dating based on the measurement of isotope ratios by LA-ICP-MS is therefore fast and cheap. The lateral resolution achievable is 5-25 microns.

In Hungary, LA-ICP-MS technology is only available in a couple of research laboratories all located in Budapest (MFGI, ELTE, MTA EK, etc.). Recently, a new, very capable LA-ICP-MS instrument combination was purchased by the Hertelendi Laboratory of the Institute of Nuclear Sciences of the Hungarian Academy of Sciences (Debrecen, Hungary), thus the possibility presented itself to test its performance in some geochemical samples. The present study can be considered as a pilot study.

Experimental

A 8800-type Triple Quadrupole ICP-MS (ICP-QQQ) by Agilent Technologies was coupled to an NWR 213 laser ablation system from ESI & New Wave Research. The Nd:YAG laser was operated at the 213 nm frequency quintupled wavelength. The speleothem sample was from the Hajnóczy cave. The laser operating parameters for the speleothem sample were set to a repetition

frequency of 20 Hz, 15 J/cm² fluence, spot size 100 µm. Surface scans of the sample were recorded for ²⁷Al, ¹³⁷Ba, ⁴³Ca, ²⁴Mg, ⁵⁵Mn, ⁸⁸Sr, ²⁰⁸Pb, ¹³C, ²⁹Si and ⁵⁶Fe isotopes with a spatial resolution of 100 µm. The zircon minerals were presented to the instrument in the form of a thin, micro-polished section (30 µm thickness) affixed to a microscope slide. The sample was a section of a drilled rock sample taken in the Szalatnak area. The section contained 8-10 small (max. ca. 100 µm length) zircon minerals, which were located using optical and cathodoluminescence microscopy. Because of the small size of the zircon particles, we used more gentle conditions in the laser ablation experiments: 40 µm spot size, 10 Hz repetition frequency and 10 J/cm² the energy density. We measured the ²⁰⁶Pb, ²⁰⁷Pb, ²³⁵U and the ²³⁸U isotopes for the purpose of U-Pb dating [5]. A NIST No. 612 glass LA standard was used for the U and Pb calibration on the system.

Results and discussion

As it can be seen in the exemplary data in **Figure 1.**, the Ca content of the speleothem sample was uniformly high (due to the essentially CaCO₃ composition of speleothem formations). The increase of the Mg concentration in certain areas indicates that the calcite form is dominant (over the aragonite form) at these places. In accordance with our expectations, the elemental (isotopic) maps for Fe and Mn recoded on the speleothem sample correlated well with the visually observable colored bands and microscopic features of the sample. A further correlation with the Al content was also revealed, therefore these localized formations are though to be rich in iron alumino silicates.

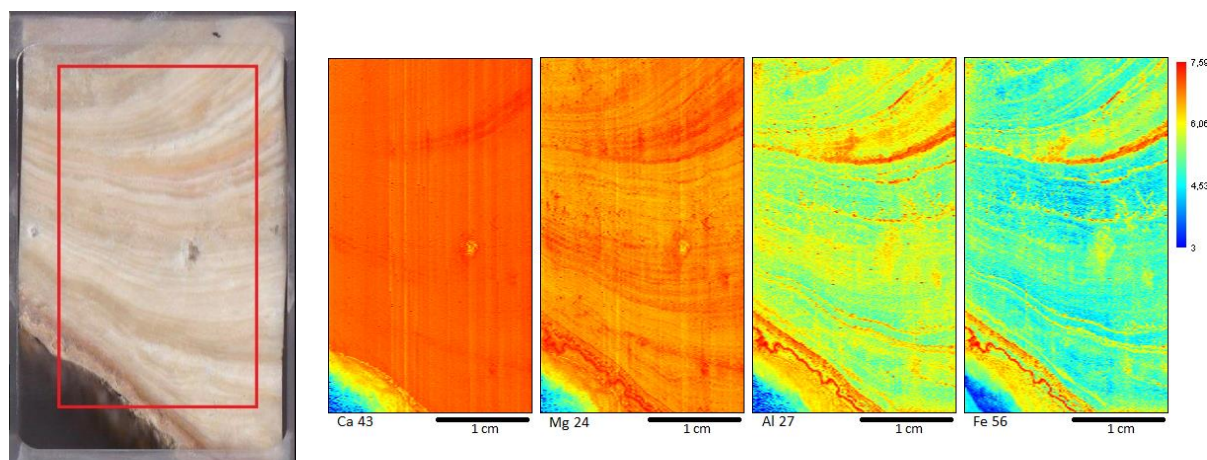


Figure 1. Optical microscopy image (on the left, with the mapped area indicated) and LA-ICP-MS surface maps for ⁴⁰Ca, ²⁴Mg, ⁵⁶Fe and ²⁷Al isotopes of the speleothem sample

Seven zircon mineral particles (grains) were ablated in order to determine the average age of the rock sample (a zircon mineral grain and the effect of laser ablation on it can be seen in **Figure 2.**). As the calculation is based on the concentration ratios of U and Pb (we assessed both the ²⁰⁷Pb/²³⁵U and ²⁰⁶Pb/²³⁸U ages), thus a calibration was performed with the matrix similar NIST 612 sample certified for the U and Pb isotope composition. The laser ablation signal time profiles had to be processed for the calibration and also for the age measurements. The initial part (up to 28 sec) and the tailing part (after 33 sec) of the time-resolved signal profile was discarded identified as transitional, so only the data between 28 and 33 seconds was processed. The result

of the age calculations was 313 Ma (million years) with 16 Ma uncertainty based on the $^{207}\text{Pb}/^{235}\text{U}$ data whereas it was 322 Ma with 29 Ma uncertainty based on the $^{206}\text{Pb}/^{238}\text{U}$ data. As the sample was previously determined by the Rb-Sr method to be 330-320 Ma [6], it can be concluded that the quick and convenient LA-ICP-MS measurement provided well matching results.

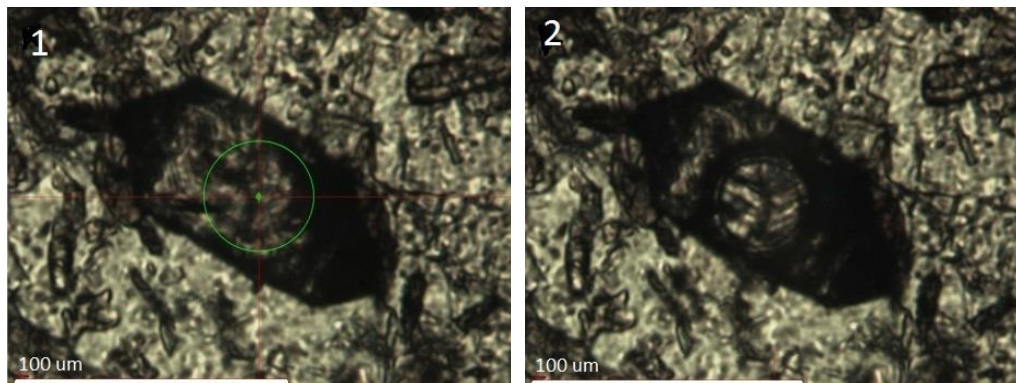


Figure 2. A zircon mineral grain (about 100 µm in length) before (on the left) and after (on the right) of the laser ablation process.

Conclusion

Laser ablation ICP-MS was found to a reliable and convenient method for the recording of element distribution maps and for U-Pb dating of geochemical samples. The achieved U-Pb age result shows a good agreement with the previous Rb-Sr dating result.

References

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