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Recent applications on isotope ratio measurements by ICP-MS and LA-ICP-MS on biological samples and single particles

J. Sabine Becker[a,*], Hagit Sela[b], Justina Dobrowolska[a,d], Miroslav Zoriy[a], J. Susanne Becker[c]

[a] *Central Division of Analytical Chemistry, Research Centre Juelich, D-52425 Juelich, Germany*
[b] *Nuclear Research Centre, Negev, 84190 Beer-Sheva, Israel*
[c] *Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, Centre Technologique Hélioparc, F-64053 Pau, France*
[d] *Faculty of Chemistry, Jagiellonian University, PL-30060 Krakow, Poland*

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Abstract

Inductively coupled plasma mass spectrometry (ICP-MS) and laser ablation ICP-MS (LA-ICP-MS) have proved themselves to be powerful and sensitive inorganic mass spectrometric techniques for analysing stable and radioactive isotopes in different application fields because of their high sensitivity, low detection limits, good accuracy and precision.

New applications of ICP-MS focus on tracer experiments and the development of isotope dilution techniques together with nanoflow injections for the analysis of small volumes of biological samples. Today, LA-ICP-MS is the method of choice for direct determination of metals, e.g., on protein bands in gels after the gel electrophoresis of protein mixtures. Tracer experiments using highly enriched ^{65}Cu were utilized in order to study the formation of metal-binding bovine serum proteins. A challenging task for LA-ICP-MS is its application as an imaging mass spectrometric technique for the production of isotope images (e.g., from thin sections of brain tissues stained with neodymium). In this paper, we demonstrate the application of imaging mass spectrometry on single particles (zircon and uranium oxide). Single Precambrian zircon crystals from the Baltic Shield were investigated with respect to isotope ratios using LA-ICP-MS for age dating. The U–Pb age was determined from the isochrone with $(1.48 \pm 0.14) \times 10^9$ a. Using isotope ratio measurements on 10 nuclear uranium oxide single particles the ^{235}U/^{238}U isotope ratio was determined to be 0.032 ± 0.004.

This paper describes recent developments and applications of isotope ratio measurements by ICP-MS and LA-ICP-MS on biological samples and single particles.

Keywords: Biological sample; Imaging; Isotope ratio; LA-ICP-MS; Single particle

1. Introduction

The determination of the isotope ratios of metals, metalloids and non-metals is a key feature of mass spectrometry. Inductively coupled plasma mass spectrometry (ICP-MS) has many advantages which have led to it becoming a widely accepted method today for isotope analysis with good accuracy and precision. It allows isotope ratios to be measured down to the trace and ultratrace concentration level in a short time [1–6]. However, laser ablation ICP-MS (LA-ICP-MS) is fast becoming one of the most important direct analytical sensitive techniques for the quick and direct determination of isotope ratios and for the isotope analysis of solid surfaces [1,7–9]. Isotope ratio measurements with high precision and accuracy are employed to study fine isotope variations in nature caused by fractionation effects, e.g., for light elements such as Li, B, Mg, S or Si. Isotope variations induced by several physical or chemical processes, or as the result of the nuclear decay of instable radioisotopes, have also been studied and are described for the elements Ca, Fe, Cu, Ni, Cd, Sr, Nd, Hf, Os, Hg, Pb, and U, among others [1,10–26].

Besides advantages of ICP-MS and LA-ICP-MS in isotope analysis there exist a few of limitations. Previous publications have discussed some of these effects and limitations of quadrupole-based and sector-field ICP-MS and LA-ICP-MS with respect to the precision and accuracy of analytical data, e.g., instrumental mass bias, isobaric interferences of analyte

* Corresponding author. Tel.: +49 2461 612698; fax: +49 2461 612560.
E-mail address: s.becker@fz-juelich.de (J.S. Becker).

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ions and isobaric atomic or polyatomic ions, instrumental background, contamination of the solution introduction system, on the sampler, skimmer cone and lens system, mass scale drift effects, plasma instabilities, drifts of ion intensities and matrix effects, etc. [1,2,14,18,19,23]. Nevertheless, ICP-MS including the application of single and multiple collector instruments is applied today to an ever greater extent in isotope analysis. Instrumental progress in ICP-MS has been achieved also over the last two decades especially thanks to the introduction and refinement of the multiple collector system in ICP-MS (MC-ICP-MS), improvements in ion current amplifier technology for ultimate precision and accuracy, increased abundance sensitivity, improved ion optics using zoom optics, enlarged geometry of mass spectrometers, and increased signal-to-noise ratios [27].

The application fields of isotope analysis by inorganic mass spectrometry include biological, geological and cosmological studies, the characterization of medical samples (blood, urine, faeces, hair and tissue analysis), the health control of exposed persons, their use in the human body, and many other applications, such as the determination of long-lived radionuclides for environmental monitoring with a focus on nuclear fallout or radionuclides in nuclear samples [1,10–30]. Moreover, tracer experiments using enriched stable isotopes or radionuclides have been used in combination with isotope ratio measurements, for example, to study the dynamics of biological processes and for the application of isotope dilution analysis [1,3,31].

The aim of this paper is to briefly describe new analytical developments in isotope ratio measurements by ICP-MS and LA-ICP-MS using quadrupole-based and double-focusing sector-field instruments with single ion detection, e.g., in the framework of tracer experiments and single particle analysis in the authors' laboratory.

2. Experimental

2.1. Instrumentation

Different ICP-MS instruments, namely two quadrupole-based ICP-MS (ICP-QMS) with and without a collision cell (Agilent 7500ce with octopole collision cell and Elan 6100, Perkin Elmer Sciex, respectively) and a double-focusing sector-field ICP-MS (ICP-SFMS, ELEMENT, Thermo Fisher Scientific, Bremen, Germany) were used for isotope ratio measurements on aqueous solutions, on protein bands in gels and for the imaging of single particles and biological tissue sections, respectively. For the sample introduction of aqueous solutions in ICP-QMS, a commercial solution introduction system, micronebulizer (MicroMist), was employed together with a cooled Scott spray chamber. In addition a nanovolume flow injection system developed in the authors' laboratory was applied [32]. In order to directly analyze solid samples (single particles) and metal-containing proteins in gels, one of two laser ablation systems CETAC LSX 213 or LSX 200 (CETAC Technologies, Ohama) was used in combination with an ICP-QMS Elan 6100 or ICP-SFMS ELEMENT, respectively. The experimental arrangement of LA-ICP-MS used for analysis, e.g., for the imaging of elements on brain tissues, is detailed elsewhere [33,34]. The nebulized aqueous solution or laser ablated material was transported into the inductively coupled plasma mass spectrometer by argon, which acted as a nebulizer or carrier gas flow in ICP-MS and LA-ICP-MS, respectively. The ions formed in the ICP were extracted in the mass analyzer and separated according to their mass-to-charge ratios. The experimental parameters of ICP-MS and LA-ICP-MS were optimized with respect to the maximal ion intensity of analyte ions [1,34,35].

3. Results and discussion

3.1. Isotope ratio measurements by ICP-MS on biological samples

Tracer experiments using highly enriched stable isotopes are helpful to study dynamic processes in life sciences. For instance, the transport and distribution of mineral elements in plants were investigated in tracer experiments, whereby the nutrient solution and soils were spiked with the highly enriched stable isotopes ^{25}Mg, ^{44}Ca and ^{41}K [35,36]. Whereas the lateral distribution of highly enriched isotopes can be measured by mass spectrometric techniques with spatial resolution [such as secondary ion mass spectrometry (SIMS) or LA-ICP-MS], ICP-MS is employed for isotope ratio measurements of Mg, Ca and K in plants, soils and nutrient solutions [35,36]. Serious difficulties were encountered during the isotope analysis of K and Ca by ICP-MS due to interference problems. Quadrupole ICP-MS without a collision cell and double-focusing sector-field ICP-MS are not suited to measure ^{44}Ca/^{40}Ca and ^{41}K/^{39}K isotope ratios. Therefore, the introduction of the collision cell in ICP-MS represents progress in ICP-MS instrumentation which is relevant for determination of Ca and K isotope ratios with good precision and accuracy. The collision of plasma gas ions with the collision/reaction gas (e.g., He and/or H_2) in the gas cell causes the molecular ions (ArH^+) to dissociate and the atomic argon ions (Ar^+) formed from plasma gas in ICP are neutralized. Recently, Stuerup et al. [37] reported that it was not possible to measure ^{44}Ca/^{40}Ca ratio by ICP-QMS with a dynamic reaction cell (using methane as reaction gas) with a precision only limited by counting system. Therefore, quadrupole-based ICP-MS with an octopole collision cell was evaluated for precise and accurate isotope ratio measurements of magnesium, calcium and potassium. In contrast to the difficulties of K and Ca isotope ratio measurements, the isotope analysis of Mg is simple, and can be performed without the application of collision gases. For tracer experiments with enriched stable ^{25}Mg, ^{44}Ca and ^{41}K isotopes investigating the kinetics of nutrient uptake and transport in plants, an isotope analytical method was created for these three elements using ICP-QMS with an octopole collision cell (Agilent 7500ce) and applied in routine mode in the authors' laboratory. The nutrient solutions investigated contained high amounts of magnesium, calcium and potassium in the mg l^{-1} range. To analyze ^{44}Ca/^{40}Ca and ^{41}K/^{39}K isotope ratios, a gas mix-

ture of H_2/He (2.5 ml min^{-1}/1.5 ml min^{-1}) was inserted into the octopole collision/reaction cell in order to minimize the disturbing isobaric interferences $^{40}Ar^+$ and $^{40}Ar^1H^+$ at $m/z = 40$ and 41 for $^{40}Ca^+$ and $^{41}K^+$ determination, respectively. Mass discrimination factors determined for isotope ratios $^{25}Mg/^{24}Mg$, $^{40}Ca/^{44}Ca$ and $^{39}K/^{41}K$ under optimized experimental conditions varied between 0.044 and 0.075. The precision for $^{25}Mg/^{24}Mg$, $^{40}Ca/^{44}Ca$ and $^{39}K/^{41}K$ was found with 0.09%, 0.43% and 1.4% (R.S.D.—relative standard deviation), respectively. The analytical ICP-QMS technique developed for Ca, K and Mg isotope ratio measurements was routinely applied in long-term mass spectrometric studies (>20 h) with reliable isotope ratio data as part of these tracer experiments using enriched stable Ca, K and Mg isotopes in order to study the dynamics of nutrient uptake and transport phenomena in barley plants at different root temperatures. Significant differences were observed in uptake and translocation patterns between the observed nutrients in dependence on root temperature treatment. Using a tracer experiment, ^{44}Ca enrichment was found in the sprout of the plant after 24 h (for 20 °C root temperature). In contrast, the highest enrichment of ^{41}K was measured at 10 °C [35].

The flow injection (FI) technique, used for solution introduction in ICP-MS, allows small sample volumes to be analyzed in a short time. In our laboratory, we applied FI in ICP-SFMS for ultrasensitive isotope analysis of radionuclides using the nanoflow nebulizer DS-5 (CETAC Technologies, Ohama, USA) [32]. Recently, we developed an isotope dilution strategy in ICP-QMS (Elan 6100, Perkin Elmer Sciex) using nanoflow nebulizer DS-5 in flow injection to analyze small sample volumes of biological samples (e.g., human brain fluids). The principle of the isotope dilution analysis (IDA) for obtaining accurate element concentration is described elsewhere [1,3,32]. Fig. 1 shows the transient signals of $^{63}Cu^+$ and $^{65}Cu^+$ in an isotope dilution experiment (a) in sample, (b) in the isotope enriched spike solution, and (c) in the isotope mixture. The isotope enriched spike was mixed before the third measurement (Fig. 1c) by ICP-QMS. The isotope dilution analysis with flow injection was applied to quantify the Cu concentration in a total sample volume of 400 nl of human brain fluid without dilution. The $^{63}Cu/^{65}Cu$ isotope ratios were measured in the sample, isotopic enriched spike and mixture of sample and spike, e.g., with 2.08 ± 0.04, 0.36 ± 0.03 and 1.21 ± 0.01, respectively. By applying a formula for isotope dilution analysis (IDA), copper concentration could be determined in human brain fluids at low μg ml^{-1} range and below. The development of a mass spectrometric method for the determination of lanthanides at ng g^{-1} levels in small amounts of biological specimens (digested tissues) by nanovolume flow injection ICP-QMS in combination to IDA was described by Pozebon et al. [38]. Due to its advantages as a definitive and accurate analytical method for the determination of element concentration via isotope ratio measurements, IDA is being increasingly applied in ICP-MS and LA-ICP-MS. In addition, the nanoflow nebulizer DS 5 was also inserted directly into the laser ablation chamber for solution-based calibration in LA-ICP-MS, as described in earlier papers [34,39].

3.2. Isotope ratio measurements on biological samples by LA-ICP-MS

In a previous paper, an analytical procedure was proposed for precise uranium isotope ratio measurements in thin uranium layers of certified uranium isotope standard reference materials on a biological surface by LA-ICP-SFMS (Element, Thermo Fisher Scientific) using a cooled laser ablation chamber, whereby an improvement in the precision and accuracy of isotope ratio measurements was observed in comparison to results in the non-cooled laser ablation chamber [33]. Furthermore, LA-ICP-SFMS was utilized for the analysis of uranium in single hair strands in the authors' laboratory [29]. Changes in the uranium concentration of a single hair from very low uranium content up to 200 ng g^{-1} in dependence on the uranium concentration in drinking water (tap water consumed) were observed. The $^{235}U/^{238}U$ isotope ratio measured along the single hair was constant 0.00725 [29].

Recently, isotope ratio measurements were carried out by LA-ICP-SFMS on metal-containing protein spots and bands, e.g., a brain sample with Alzheimer's disease or tau protein in one- and two-dimensional gels after tracer experiments with highly enriched stable isotope tracers [31,40]. In this work, LA-

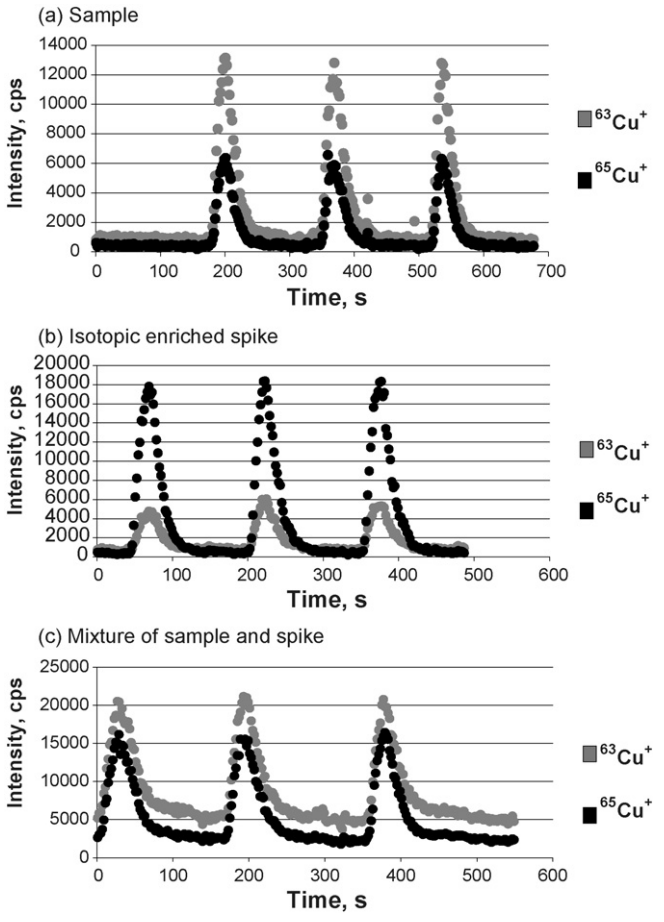

Fig. 1. Transient signals of $^{63}Cu^+$ and $^{65}Cu^+$ for Cu determination in human brain fluids by isotope dilution flow injection ICP-MS in an isotope dilution experiment: (a) in the sample; (b) in the isotope enriched spike solution; (c) in the isotope mixture of sample and isotope enriched spike.

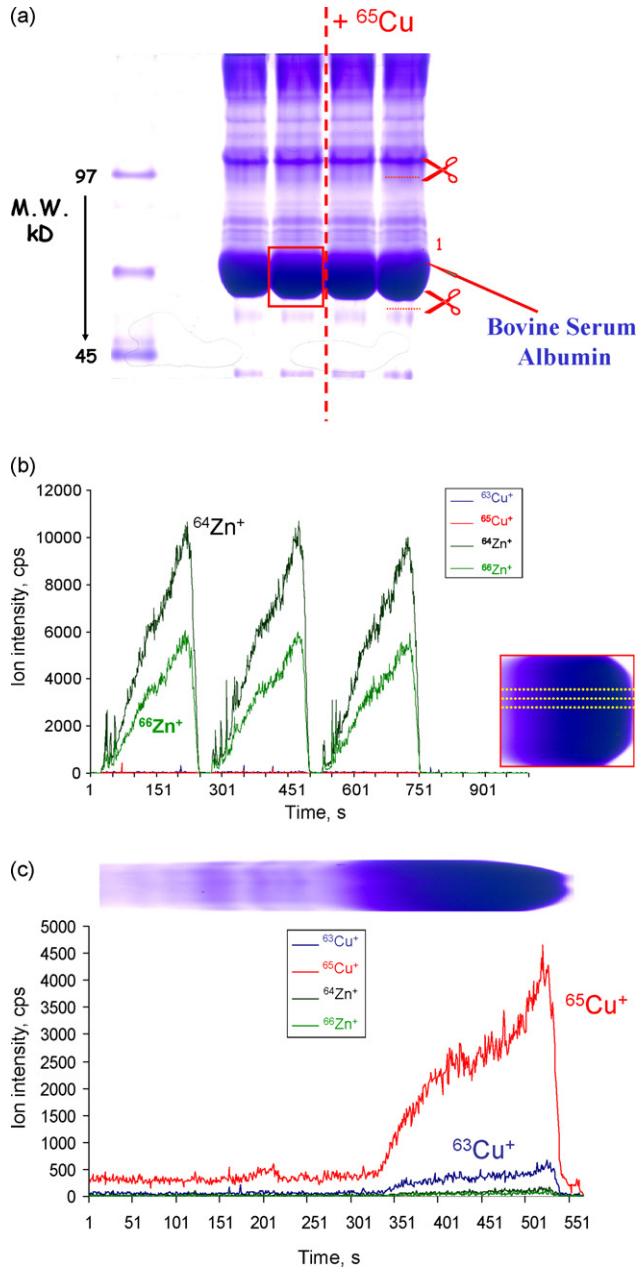

Fig. 2. (a) Part of the blue native gel of bovine serum stained with colloidal Coomassie after one-dimensional gel electrophoresis; (b) signals of $^{64}Zn^+$, $^{66}Zn^+$, $^{63}Cu^+$ and $^{65}Cu^+$ in bovine serum albumin before tracer experiments; (c) after tracer experiments with enriched $^{65}Cu^+$ tracer measured by LA-ICP-MS.

ICP-SFMS was employed to measure metals in bovine serum proteins. Fig. 2a shows a one-dimensional (1D) gel of bovine serum. On this 1D gel tracer experiments with enriched $^{65}Cu^+$ tracer were carried out to study the formation of metal-binding proteins. Zn was detected, for example, in bovine serum albumin before tracer experiments by LA-ICP-MS. The signals for $^{64}Zn^+$ and $^{66}Zn^+$ in bovine serum albumin, measured in three line scans in the 1D gel before the trace experiments, are illustrated in Fig. 2b. The gel was then put in a ^{65}Cu-spiked solution overnight (isotopic abundance in ^{65}Cu tracer was 94.6% compared to 30.8% in nature). After the experiment with enriched $^{65}Cu^+$ tracer, a complete replacement of Zn by Cu was observed

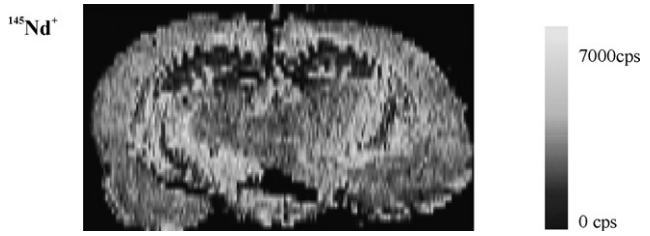

Fig. 3. $^{145}Nd^+$ ion distribution in a rat brain tissue stained in a neodymium solution measured by LA-ICP-SFMS.

(see Fig. 2c). The kinetics of metal exchange – of Zn by Cu using the isotope enriched ^{65}Cu tracer – as a function of reaction time and the identification of metal-containing peptides in tryptic digests of bovine serum albumin and other metal-containing proteins in bovine serum by MALDI/ESI-MS will be discussed in detail in a forthcoming paper [41].

A challenging task for LA-ICP-MS is the imaging of metals, metalloids and non-metals in order to characterize the isotopic distribution in thin sections of tissues [1,34,42,43]. To study the binding or affinity of a heavy metal to tissues, novel staining techniques using heavy metals, e.g., with neodymium on rat brain sections (20 μm thicknesses) were developed. After staining of brain tissue (3 h) in a 100 $\mu g\,ml^{-1}$ Nd solution, the tissue sample was washed and dried. Ion intensities of $^{145}Nd^+$ and $^{146}Nd^+$ were measured within the entire rat brain section by LA-ICP-SFMS (size of sample: 7 mm × 15 mm; measuring time: 5 h). The imaging mass spectrometric measurements were performed by LA-ICP-MS as described in [34]. Fig. 3 illustrates the $^{145}Nd^+$ ion distribution in rat brain tissue stained in neodymium solution, used to study the anatomy of brain. This technique allows fine structures in tissues to be revealed via isotope images, as seen in Fig. 3. Using isotope ratio measurements of $^{145}Nd/^{146}Nd$ in a rat brain tissue section using LA-ICP-MS, the natural isotope ratio of 0.48 was measured. In future, the staining technique developed combined with imaging mass spectrometry will be able to provide additional information for toxicological research, allowing critical substructures to be differentiated within organs.

An improvement in lateral resolution of imaging mass spectrometry in the sub-micrometer range for isotope ratio measurements in biological and medical samples can be achieved in the future by the application of near field LA-ICP-MS [44].

3.3. Single particle analysis by imaging mass spectrometry

Geochronological measurements (isochrone methodology) are based on the radioactive decay of the parent nuclide in the daughter nuclide as described by Becker [1] and Faure [45]. We studied the analytical performance of LA-ICP-MS using a sector-field instrument with a single ion collector (ICP-SFMS, ELEMENT) for the age dating of single Precambrian zircon grains from the Baltic Shield. Single zircon ($ZrSiO_4$) particles were fixed on a sticky tape and an area of 3 mm × 3 mm was examined by imaging mass spectrometry using LA-ICP-MS. Fig. 4a shows the LA-ICP-MS images of $^{208}Pb^+$ and $^{238}U^+$ ion distribution together with the SEM (scanning elec-

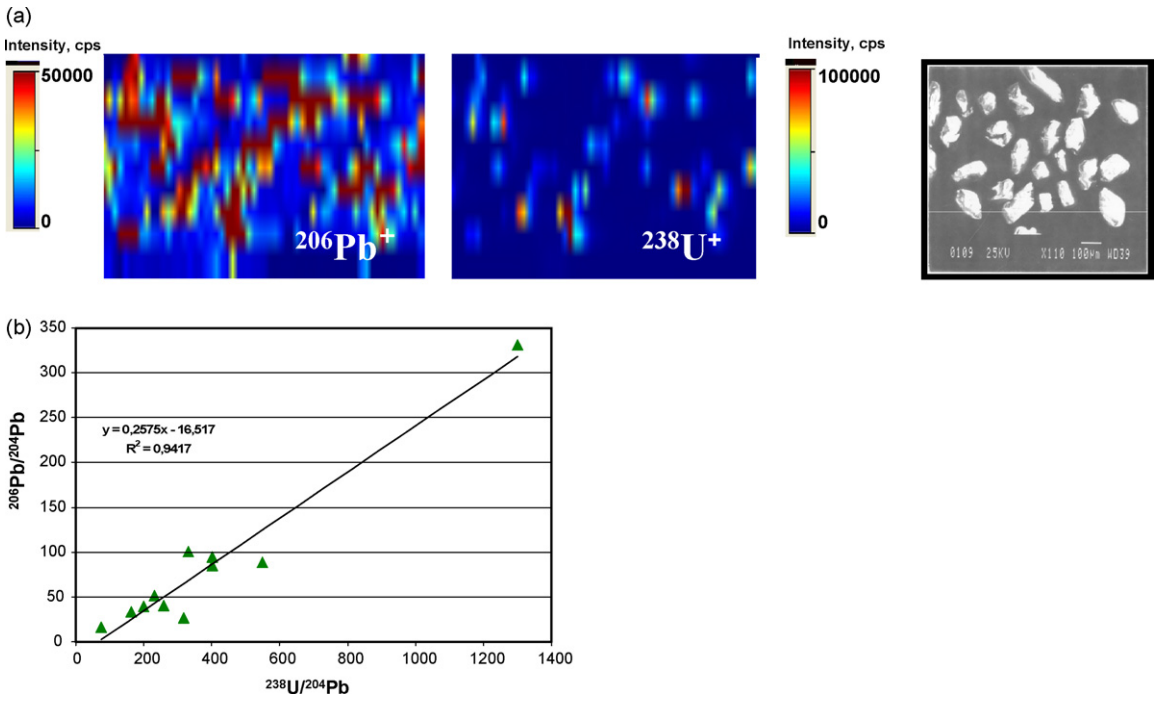

Fig. 4. (a) Images of $^{208}Pb^{+}$ and $^{238}U^{+}$ distribution measured by LA-ICP-MS and a SEM picture (on the right) of single zircon grains from the Precambrian Baltic Shield; (b) graph of $^{206}Pb/^{204}Pb$ isotope ratio versus $^{238}U/^{204}Pb$ (isochrone) for 11 single zircon grains analyzed by LA-ICP-MS.

tron microprobe picture, on the right) of single grains. The single grains in the images of isotopes for $^{208}Pb^{+}$ and $^{238}U^{+}$ measured by LA-ICP-MS were clearly detected. The Precambrian zircon was then characterized using an isochrone technique of the uranium–lead system for age dating [1]. In the graph in Fig. 4b, the $^{206}Pb/^{204}Pb$ isotope ratio (on the ordinate) is plotted against the $^{238}U/^{204}Pb$ isotope ratio. LA-ICP-MS revealed both isotope ratios to be different for selected investigated single zircon grains in the Baltic Shield sediment. This is due to their different origin. The age of the zircons was then calculated from the slope of the isochrone ($e^{\lambda t} - 1$) with λ as the disintegration constant of the radioactive nuclide, whereby the half life of the parent nuclide ^{238}U ($t_{1/2} = \ln 2/\lambda$) was 4.5×10^{9} a. In Fig. 4b, the graph illustrates the $^{206}Pb/^{204}Pb$ isotope ratio versus $^{238}U/^{204}Pb$ for 11 single zircon particles from the Baltic Shield measured by LA-ICP-MS. The U–Pb age was determined

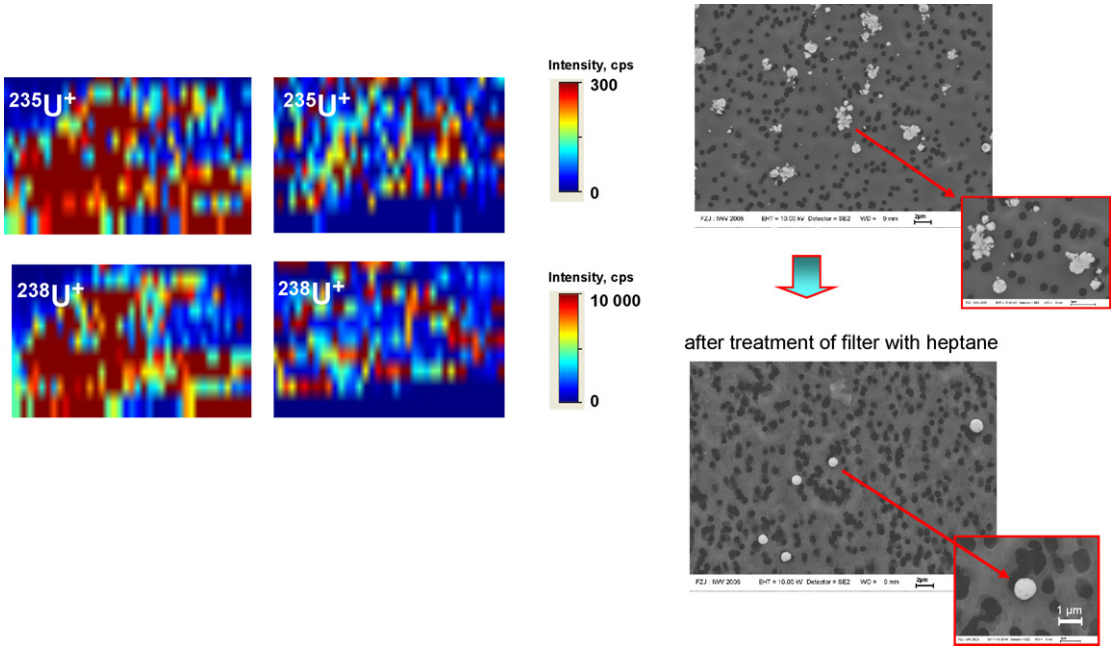

Fig. 5. Images of $^{238}U^{+}$ and $^{235}U^{+}$ distribution on single UO_2 particles measured by LA-ICP-MS and SEM pictures of single particles before and after treatment of filter with heptane (on the right).

from the isochrone at $(1.48 \pm 0.14) \times 10^9$ a. The correlation coefficient of the isochrone was obtained as 0.9417. The age of Precambrian zircons from the Baltic Shield measured by LA-ICP-MS correlated well with the age of this geological material measured by thermal surface ionization mass spectrometry (TIMS: 1.5×10^9 a) more than two decades before [46].

Of special interest in the mass spectrometric determination of transuranium elements is the characterization of microparticles stemming from different radioactivity release scenarios. Such microparticles, which bear radionuclides, in particular uranium, plutonium, neptunium and americium, can enter the environment and therefore the human food chain through different processes that are related to the nuclear fuel cycle as well as to clandestine nuclear activities [22]. Anomalous amounts of ^{233}U, ^{235}U or ^{236}U indicate that artificial isotope enrichment or depletion processes may have been the source of these particles [45]. In the past, several inorganic mass spectrometric techniques (such as SIMS or thermal surface ionization mass spectrometry—TIMS) have been applied for the direct analysis of microparticles with respect to the isotope ratios of radionuclides [22,47,48]. We utilized imaging mass spectrometry using LA-ICP-SFMS to study the isotope composition of uranium oxide single particles with a diameter of 1 μm or less. The distribution of particles on the filter is illustrated in the SEM pictures in Fig. 5 (right). The single UO_2 particles observed after the filter was treated with heptane were analyzed by LA-ICP-MS (analyzed filter area—3 mm × 3 mm). The images on the left in Fig. 5 are the ^{238}U and ^{235}U distribution on single UO_2 particles on two filters measured by LA-ICP-SFMS. Using mass spectrometric measurements on several single particles ($N = 10$), the average ^{235}U/^{238}U isotope ratio was determined as 0.032 ± 0.004. This result demonstrates an enrichment of ^{235}U in the single particles when compared to the isotopic composition in natural samples. In further studies, the lateral resolution for single particles analysis by LA-ICP-MS will be improved.

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