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High resolution-ICPMS in fast scanning-mode: application for laser ablation analysis of zircon

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Abstract The general applicability of a double focusing sector field high resolution-inductively coupled mass spectrometry (HR-ICPMS) is evaluated for the precise and accurate determination of the abundances of rare earth elements (REE) in zircon by LA-ICPMS using a 266 nm UV-laser. “Zircon 91500”, a recently released new reference material for microanalytical work but with contradictory REE data is investigated with both the 266 nm laser and a 1024 nm IR-laser coupled to a quadrupole ICPMS. The data show evidence for a homogeneous distribution of the heavy REE. In contrast, in some “Zircon 91500” chips the trace elements Hf, Th, U are inhomogeneously distributed.

Introduction

The HR-ICPMS on basis of a double focusing sector field instrument was introduced in 1989 [1, 2]. Only recently, sector field instruments with an improved design (inverse Nier-Johnson geometry, laminated magnet technology) [3–6] provide the analytical performance that gives rise to a wider acceptance of HR-ICPMS. Spectral interferences (e.g. molecular ions) from the analyte signal can be resolved up to about 10,000 [M/ΔM], and this may be of analytical significance even under dry aerosol conditions where the formation of molecular ions originating from the solvent is circumvented. High transmission (3% at 10,000 M/ΔM) is a prerequisite that high resolution-measurements can be extended down to low μg g^{-1} concentration levels with laser ablation. Another major benefit of using sector field instruments are very low detection limits in the low ng g^{-1} range for many elements as a consequence of a very low instrumental background and a higher response of the dry plasma.

The principles and merits of laser ablation microanalysis for the direct, in situ-analysis of solids are well known [7–11]. It has been shown that fractionation of elements (e.g. chalcophilic elements) during the ablation process can be overcome by using short wavelength-UV laser-radiation (193–266 nm) [12, 13] and/or cooling of the laser-sampled surface area [14]. Both the ablation process itself and sample compositional heterogeneities generate fast transient analyte signals. The new HR-ICPMS instruments allow wide mass range scans in a fast scanning-mode, i.e. one single scan over the mass range 6–260 m/z takes about 300–500 ms.

Here the general applicability of double focusing sector field HR-ICPMS for the precise and accurate determination of trace element compositions on a micro-scale by LA-ICPMS using a 266 nm UV-laser is evaluated focusing on rare earth element (REE) abundances in a recently introduced zircon mineral reference standard (Zircon 91500, introduced by K. Govindaraju and co-workers [15], originating from a syenite gneiss in Ontario, Canada) which is dedicated for microanalytical investigations. Analytical data for this standard published so far [15] are highly contradictory. In addition, a 1024 nm IR-laser in conjunction with a quadrupole-based ICPMS was used for the investigation of the homogeneity of REE and some other trace elements in five Zircon 91500 chips.

Experimental

A PlasmaTrace 2 HR-ICPMS instrument (PT 2, Micromass, Wythenshawe, UK) was used. The make-up of the Kiel PT 2 instrument is characterized by full mass flow-control for all ICP gases and two separate nebulizer gas lines for the introduction of high-purity argon (99.9990%) and one auxiliary gas. The high performance interface of the PT 2 generates a flat response curve across the whole mass range. The mass resolution can be continuously defined depending on the analytical problem, and quantitative measurements at up to five pre-defined resolution settings can be done during a current sample acquisition (MultiRes). High system response (40×10^6 cps, 1 μg/mL In for solution aspiration, and 8×10^3 cps, 1 μg/g La in NIST 612 glass standard for laser ablation), low background (0.15 cps off-peak) and excellent stability (1–4%, 5 ng/mL solution) even at 10,000 [M/ΔM] in the MultiRes program result in a high analytical performance of the system. Time resolved multielement acquisition was not possible with the PT 2.

A UV-LaserMicroprobe (VG Elemental, Winsford, UK) operating at 266 nm on basis of a quadrupled Nd:YAG laser was applied using a rotatable prism and a revolver with 3 interchangeable apertures for the definition of laser energy and pit sizes (< 10–60 μm pit size), respectively. Target indentification is accomplished by a combined transmitted and reflected light microscope optic with incident illuminator, and a color video system with crossed hair generator (max. 1500 × magnification on the monitor).

During an earlier study on the homogeneity of the zircon standard from which results will be presented here a quadru-

Table 1 Operating conditions and acquisition parameters for laser ablation analysis of NIST 612 glass and Zircon 91500 mineral standard using HR-ICPMS and ICPQMS

Mass spectrometer		HR-ICPMS	ICPQMS
Mass range	[m/z]:	29–175	89–238
No. peaks	:	147	150
Hysteresis settle time high	[ms]:	5	
low	[ms]:	500	
Points per peak	:	20	1
Dwell time	[ms]:	0.1	10
No. sweeps	:	30	200
No. runs	:	3	1
Laser Unit		**266 nm**	**1064 nm**
Pulse energy	[mJ]:	1.2	2
Pulse frequency	[Hz]:	10	10
Pit size	[μm]:	40	50
No. steps	:	5 × 5	1
Pulses per point	:	20	760

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Table 2 Results [µg g^{-1}] of the homogeneity test with 5 chips of Zircon 91500 as measured by LA-ICPQMS

Element	Chip 1		Chip 2		Chip 3		Chip 4		Chip 5		Pooled
	mean (n = 12)	SD	mean (n = 5)	SD	mean (n = 5)	SD	mean (n = 5)	SD	mean (n = 5)	SD	mean (n = 32)
Gd	1.88	2.08	3.36	1.83	2.88	1.26	2.27	1.71	1.79	0.95	2.32
Tb	0.62	0.72	0.64	0.24	0.57	0.18	0.69	0.10	0.63	0.36	0.63
Dy	6.99	0.93	7.59	1.64	7.31	0.92	8.06	1.97	8.17	1.21	7.48
Ho	3.14	0.42	3.39	0.31	2.90	0.43	3.01	0.32	3.13	0.31	3.12
Er	17.2	2.09	19.3	1.73	16.6	0.79	17.4	1.27	17.0	0.68	17.4
Tm	4.67	0.42	4.49	0.40	4.43	0.28	4.51	0.29	4.40	0.33	4.54
Lu	12.1	0.78	12.2	1.58	11.1	1.26	12.2	1.03	11.2	0.73	11.8
Hf	6290	539	5960	330	5450	220	5070	401	5270	432	5760
Th	27.2	3.15	30.7	1.69	26.6	1.65	28.8	1.40	27.1	1.41	27.9
U	71.1	6.66	79.5	4.32	62.4	2.60	75.8	11.1	62.2	4.89	70.4

SD = standard deviation; Zr internal standard

Table 3 Results for rare earth element (REE) concentrations [µg g^{-1}] in Zircon 91500 mineral standard from this study and from literature [15]

Element	LA-HR-ICPMS	LA-ICPQMS	SIMS [15]	ID-TIMS [15]	ID-TIMS [15]	INAA [15]
La	0.17	–	< 0.2	–	0.74	–
Ce	2	–	2	–	39.3	–
Pr	0.05	–	< 0.2	–	–	–
Nd	0.54	–	0.4	–	3.13	–
Sm	0.35	–	0.3	–	4.02	–
Eu	0.18	–	0.2	–	2.49	0.30
Gd	1.6	2.32	1.9	–	9.21	–
Tb	0.61	0.63	–	–	–	0.75
Dy	9.7	7.48	8.0	–	28.1	–
Ho	3.8	3.12	–	–	–	–
Er	20	17.4	20.4	–	31.4	–
Tm	4.7	4.54	–	–	–	–
Yb	52	–	47	–	40.6	74.3
Lu	10	11.2	–	11–13	7.2	11.7

pole based ICPMS system (ICPQMS, up-graded VG PlasmaQuad 1) was used and coupled with a 1024 nm Nd:YAG laser (VG LaserLab 1). Details of this LA-ICPMS system are reported in [10]. Operating conditions and acquisition parameters of both systems used for the investigations in NIST 612 and the Zircon 91500 standard are summarized in Table 1. The original NIST 612 glass beads were used without any further polishing. Chips from the Zircon 91500 standard were mounted on a glass plate by all-purpose glue.

Results and discussion

The nature of the ablation process and the particulate aerosol transport as well as the compositional heterogeneity of the ablated sample generate a transient signal that may change very rapidly with time. Therefore, a simultaneous or a very fast and time resolving system would be required for mass analysis and signal detection of fast transients. Many samples, however, are homogeneous on a microscale, and operating conditions of the laser system can be optimized in order to generate a rather constant particulate aerosol flow. Optimization parameters include pulse energy, pulse frequency, number of pulses per point, ablated sample area, sample preparation, sample cell volume, and tubing diameter. Still remaining fractionation effects between elements during sample ablation – even when using 266 nm laser radiation – can be overcome by e.g. cooling of the ablated sample area [12] or limiting acquisition intervals to time slices without element fractionation. Interelement fractionation, however, poses no serious problem in the analysis of the rare earth elements (REE). Since oxide formation is extremely low and oxide interferences with REE are negligible under dry plasma conditions all measurements with the sector field HR-ICPMS were performed in low resolution mode (400 M/ΔM).

Results from a study on five chips of the Zircon 91500 standard with our former infrared LA-ICPQMS system suggest that the spatial distribution of heavy REE is statistically (t-statistics) homogeneous (Table 2). However, the comparison of the means for Hf, Th, and U gives some indication for inhomogeneity of these elements in the chips. Analytical results were calibrated with NIST 612 using Zr for internal standardization. It was not possible to determine exact values for the very low concentrations of light REE (La-Eu) with this system. This problem could be overcome by the application of the sector field HR-ICPMS instrument.

The most rapid acquisition mode for a sector field analyzer is to hold the magnet at a pre-defined mass and then to perform an electrostatic scan at a very high cycle rate. Nevertheless, the width of the mass window that can be scanned during an electrostatic scan is limited to several percent of the nominal mass. This window is by far not wide enough for most LA-ICPMS multielement applications where matrix and trace elements have to be determined simultaneously. There is, however, another fast scanning mode with the PT 2: This acquisition technique (Sprint) employs both electrostatic and magnetic digital fast scanning. An extremely high accuracy in mass location is

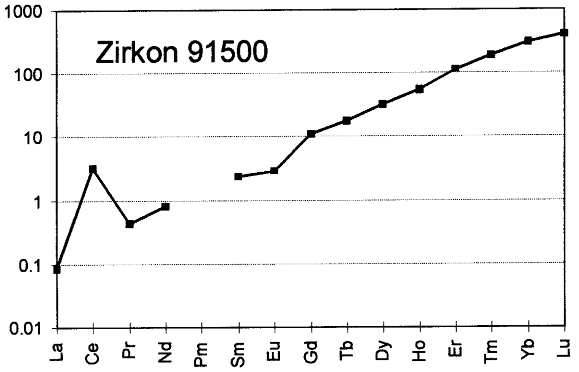

Fig. 1 Rare earth element (REE) abundances in Zircon 91500 mineral standard after normalization to the C1 chondritic meteorite [16]. The smoothness of the pattern indicates good analytical accuracy of the REE data. The REE distribution in this zircon exhibits both a positive cerium and a negative europium anomaly

required. Sprint acquisition allows to scan the mass range 6–260 m/z with approx. 500 ms for one single scan. Our first optimisation steps of the Sprint acquisition technique for the LA-ICPMS application targeted on short dwell (100 µs) and magnet settling times (c.f. Table 1).

The response of the LA-HR-ICPMS system at medium laser energy output was approx. 8000 cps/1 µg/g La in NIST 612 glass (continuous 10 Hz ablation with 40 µm spot size and 1.2 J pulse energy). This is a remarkable increase of instrument response of more than one magnitude with a dry plasma when compared to the quadrupole ICPMS-system under dry plasma conditions. Both systems have a similar response with conventional pneumatic solution nebulization. The reason for this response increase is not clear yet. It may be related to a narrower spread in ion energy in the dry plasma which could be favorable for ion focusing and transmission in a double focusing sector field instrument.

The UV-laser system was optimized for a maximum but constant signal in the mass spectrometer avoiding "spikes" from large particles which originate during catastrophic ablation with too high pulse energy. Automatic active focusing (approx. 10 µm) was used after completion of the first 5 × 5 ablation pattern with 10 pulses per step. Active focusing keeps the ablated sample area (bottom of the ablation pit) within the laser focus and helps to avoid element fractionation. The precision of 3 replicate measurements with HR-ICPMS in the NIST 612 glass bead was in the range of 2–9% RSD. Replicate measurements in the zircon revealed precision of 6–12% for concentrations > 0.5 µg g^{-1}. Detection limits of this procedure for the determination of REE in zircon are estimated to 0.01–0.1 µg g^{-1}. The measurements were calibrated with the NIST 612 standard using Zr as an internal standard.

Our quantitative results show good agreement with some of the previously published results [15] from SIMS and ID-TIMS investigations on aliquots of this standard (Table 3). The smoothness of the REE pattern (REE concentrations in zircon divided by REE concentrations in C1 chondritic meteorite [16]) is further evidence for the good accuracy of our results (Fig. 1).

Conclusion

Five chips of a recently released zircon mineral standard (Zircon 91500) have been analyzed for rare earth elements and Hf, Th, U by LA-ICPMS using either a 1024 nm Nd:YAG IR-laser in conjunction with a quadrupole-ICPMS (ICPQMS), or a 266 nm UV-laser coupled to both ICPQMS or double focusing sector field HR-ICPMS. The laser ablation system was optimized in order to generate a constant particulate aerosol flow with well-defined particle-size distributions over a couple of minutes. Inter-element fractionation was not detectable during the analysis of the elements investigated here. The results demonstrate that a double focusing sector field HR-ICPMS instrument can be used for quantitative laser ablation microanalysis. The acquisition speed is high enough to produce accurate and precise results and the very low background of HR-ICPMS and the significantly increased response from a dry plasma are favorable for very low detection limits and short acquisition times. Nevertheless, time-resolved multielement acquisition is required also with sector-field instruments in order to cope with fast transient multielement data originating from laser sampling.

Our consistent data set for the Zircon 91500 mineral standard points towards a homogeneous distribution of at least the heavy REE. Comparison of the means of Hf, Th, U, however, gives some statistical evidence for inhomogeneity of these elements. It shows that LA-ICPMS is an advanced technique which is equivalent, or superior, to other microanalytical techniques which have been used for the initial characterization of the Zircon 91500 mineral standard.

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