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Trace elements analyses of zircon sample by integration of the LA-ICP-MS, EDS and RBS methods

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Abstract

Zircon grains separated from the Mediterranean beach black sands in Northern Egypt were analyzed for their trace elements content using an integrated approach that utilizes the laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), the Rutherford back scattering spectroscopy method (RBS) and the energy dispersive X-ray spectrometry (EDS). For the LA-ICP-MS analysis fused pellets have to be prepared by mixing powdered zircon grains with lithium borate and fusing the mixture at 1050 °C. The homogeneity of these pellets is of crucial importance in the analyses, and therefore, it was checked and assured using the RBS method. On the other hand, the EDS method was used to analyze the zircon grains directly without any fusion treatment.

Data obtained by the depth profiling method on the fused pellets by the RBS method indicate satisfactory homogeneity. Data obtained by the LA-ICP-MS using four NIM standards indicate high precision and accuracy. On the other hand, the precision and accuracy of the analyses carried out by the EDS method are rather poor due to higher limits of detection for most of these elements. (Int J Mass Spectrom 221 (2002) 139–146)

Keywords: Zircon; ICP-MS; EDS; RBS

1. Introduction

Zircon is one of the common accessory minerals that are formed in igneous rocks. It has the general formula ($ZrSiO_4$) with the stoichiometric composition: ZrO_2 67.01%, SiO_2 32.99%. Uranium, thorium and the rare earth elements (REE) occur in zircon as trace constituents replacing Zr in the crystal structure. Economic value of zircon takes in consideration its purity, color and concentration of radioactive elements (the less the better) and other elements, particularly REE inside the grains. Therefore, it is our goal to have reliable direct solids analysis procedures for estimating the concentration of the radioactive and stable elements in the zircon mineral.

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2. Experimental

2.1. Sample preparation

A pure zircon grain sample was separated from black sands deposited at the Mediterranean sea using magnetic separator followed by heavy liquid concentration. Further purification was carried out by hand picking under binocular microscope. Utmost care was given to ensure homogeneity of the sample and absence of grains with anomalous color or morphological features. About 200 mg portion of the picked sample was ground to −200 mesh powder sample from which 100 mg was added to lithium–borate mixture, iron oxide and prepared as fused pellet. Iron oxide was added to improve the absorption of UV laser photons. The fusion of the homogeneous mixture is performed in a muffle furnace at 1050 °C using a Pt–Au crucible twice for 7 min (including an inversion of the target). The preparation procedure of the lithium–borate target is shown in Fig. 1.

2.2. Fused pellets homogeneity

The Van de Graaf accelerator (EG-5) of the Joint Institute for Nuclear Research at Dubna [1,2] was used to check the homogeneity of the prepared pellets. The main parameters of the EG-5 accelerator are typical one for this category of accelerators. The different equipments used for investigating elements content and structure of solid samples by nuclear methods such as Rutherford back scattering spectroscopy (RBS), nuclear reaction (NR), elastic recoil detection (ERD), particle induce X-ray emission (PIXE) and channeling are all installed on the six beam lines of the EG-5 accelerator.

A schematic overview for the (RBS) spectrometer attached to the used Van de Graaf accelerator (EG-5)

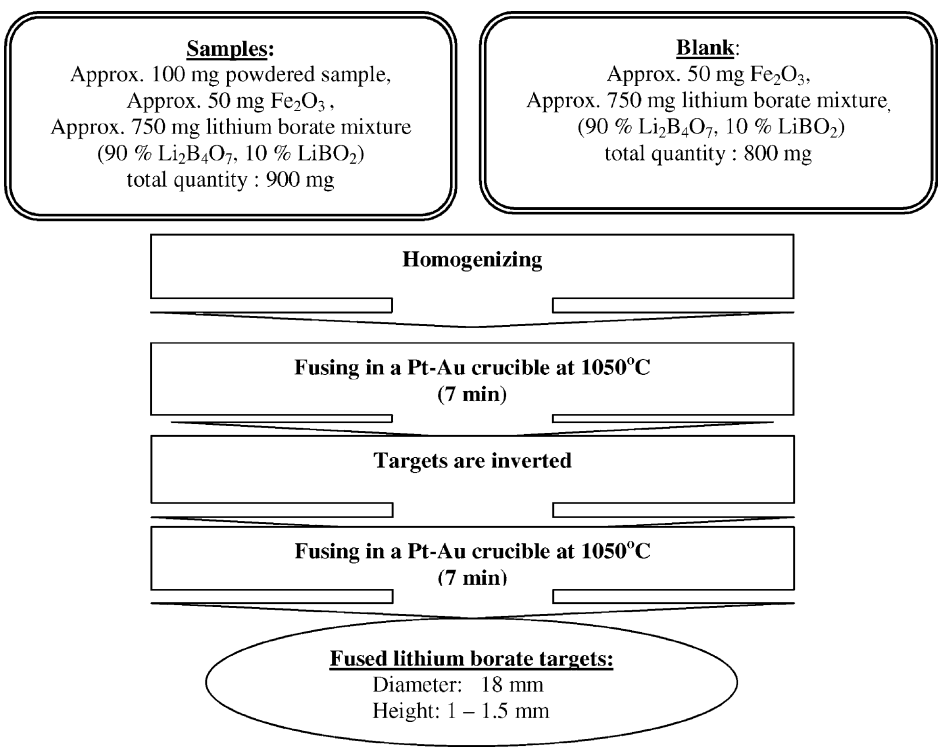
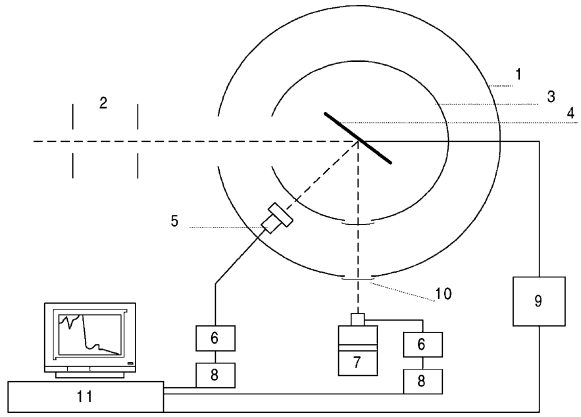


Fig. 1. Preparation of fused pellet lithium–borate target.



1- Experimental chamber.
2- Collimator.
3- Hamper.
4- Target.
5- Detector for RBS.
6- Preamplifier.
7- Si(Li) – detector for PIXE.
8- Amplifier.
9- Integrator.
10- Slits.
11- PC.

Fig. 2. Schematic overview for the Rutherford back scattering spectrometer.

Table 1
The main parameters of the EG-5 accelerator and the operating parameters for Rutherford back scattering (RBS) system

Parameters	EG-5
Energy range	0.8–3.5 MeV
Accelerated ions	^{1}H, ^{2}H, ^{3}He, ^{4}He, ^{12}C, ^{14}N, ^{16}O
Beam current	0.2–20 mA
Energy spread	<500 eV
Accuracy in energy	1 keV
Scattering angle	170°
Detector resolution	15 keV for 5.5 MeV α-particle
Energy of $^{4}He^{+}$ beam	3.04–3.20 MeV

is shown in Fig. 2. The main parameters of the EG-5 accelerator and the operating parameters for (RBS) system are given in Table 1.

RBS, which is discussed elsewhere [1,2] is used to determine light elements in the fused samples. Although this method is useful in the quantification of major elements, it is at most help in the depth profile of the elements, which can indicate the homogeneity of samples. Fig. 3 shows the spectrum of 1.768 MeV protons as scattered by fused target at 170° where an agreement between the experimental spectrum and the stimulated one is observed. Li, B, O and Si are

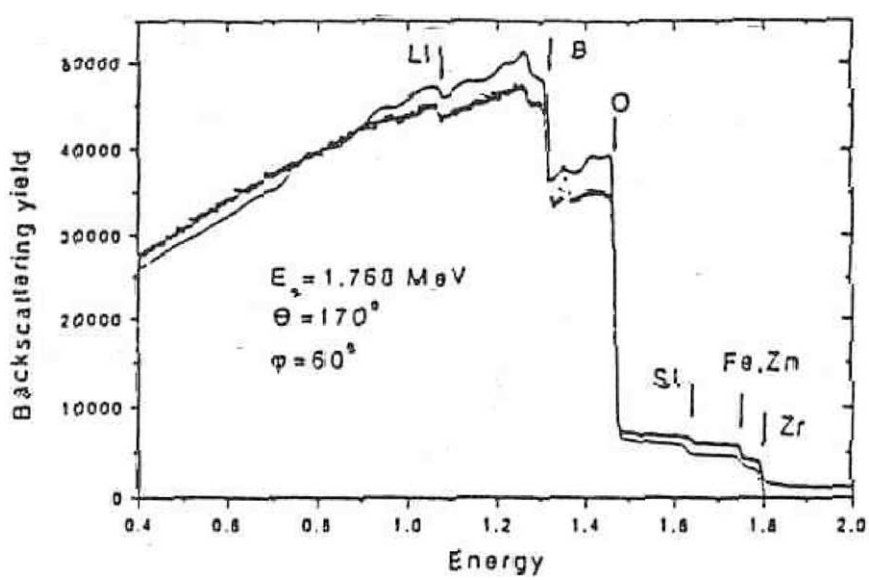


Fig. 3. Experimental (points) and simulated (line) energy spectra of H ions back scattered by zircon sample.

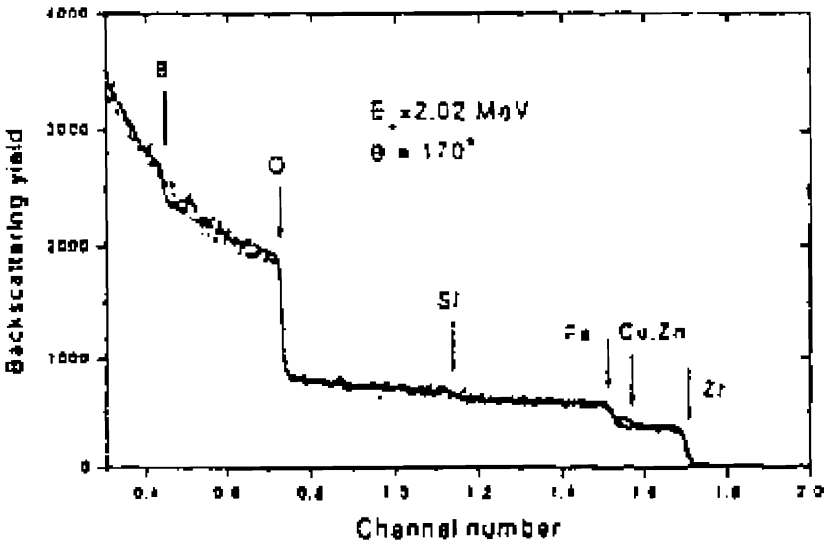


Fig. 4. Experimental (points) and simulated (line) energy spectra of ^{4}He ions back scattered by zircon sample.

determined and their concentrations are derived from this spectrum. Scattering of helium ions at energy of 2.02 MeV and an angle of 170° by atoms in the fused target confirms the spectrum observed by the proton beam. Fig. 3 shows the intensity of most common atoms, however, both Cu and Zn appear in Figs. 4 and 5, which may indicate sulfide inclusions in the zircon. Prediction of these elements and others are considered from the spectrum of PIXE spectrum as shown in Fig. 5, PIXE spectrum is measured from the X-ray of the excited atoms by the impact of protons at 1.94 MeV on the fused surface. PIXE spectrum shows the characteristic lines of some elements, which are not observed in the RBS method, which means that their concentrations are less than 0.1%. The previous measurements are repeated in different spots on the fused

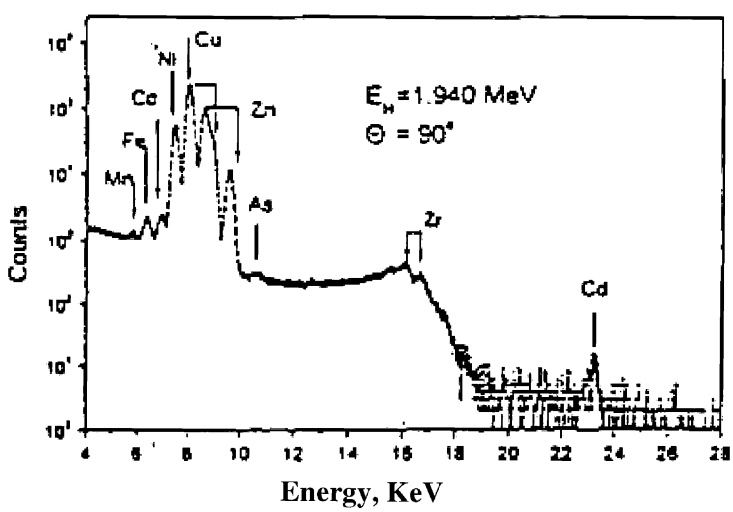


Fig. 5. PIXE spectrum excited by 1.94 MeV protons in zircon sample.

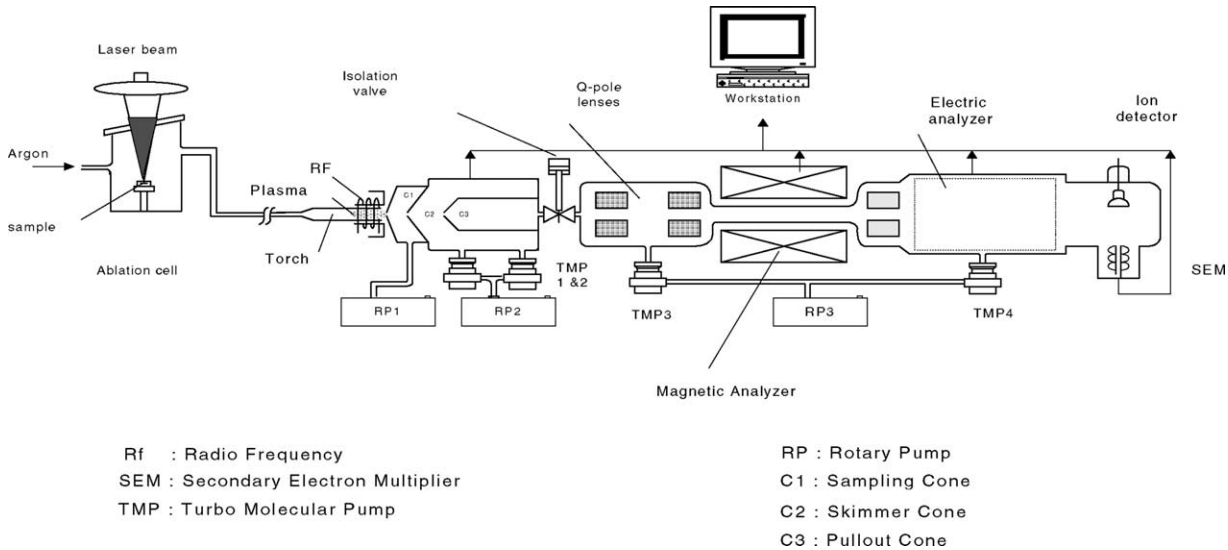


Fig. 6. Schematic overview of the spectrometer.

surface on different places and on different depths up to 2234 nm where the concentration of the major elements are in the same range within the data precision.

2.3. Trace elements measurement

Trace elements measurements are performed using:

1. JEOL high resolution ICP-MS (JMS-Plasmax2) [3–5] connected to Merchantek EO laser ablation unit (GEOLASE) in the ultraviolet range. Fig. 6 is a schematic overview of the used system. The operating parameters for the Nd:YAG laser and the ICP-MS are summarized in Table 2.
2. Energy dispersive X-ray unit (EDS) connected to a scanning electron microscope (SEM JSM-5600LV, JEOL) that permitted the detection and the identification of the X-rays produced by the impact of the focused electron beam on the sample surface, thereby allowing quantitative elemental analysis.

Non-conductive specimens cause charging-up effects, which limit SEM-EDS surface analysis. Therefore, conducting sample surfaces are required in conventional SEM. The LV-SEM allows even non-conductive specimen to be investigated at high accelerating voltage [6]. Therefore, the application of the low vacuum method in SEM (LV-SEM) is of interest. When the vacuum is lowered, incident electrons and molecules (from residual gases, e.g., oxygen, nitrogen, etc.) in the vicinity of the specimen collide with each other, thus ionizing the molecules and neutralizing the electrons collecting on the specimen

Table 2
The operating parameters for the LA-ICP-MS system

Parameters	JMS-Plasmax2
rf power	1200 W
External gas flow rate	14 L/min
Auxiliary gas flow rate	0.8 L/min
Carrier gas flow rate	0.7 L/min
Mass resolution	500
No. of sweeps	30
No. of replicates	6
Sampling cone	Copper with a 1.1 mm orifice
Skimmer cone	Copper with a 0.9 mm orifice
Introduction system	Meinhard Nebulizer
Laser type	Nd:YAG
Wavelength	266 nm
Pulse duration	6 ns
Repetition frequency	10 Hz
Pulse energy	4 mJ
Laser power density	10^{10} W/cm^2

Table 3
Experimental parameters of SEM-EDS system

Condition	JEOL JSM-5600LV
Vacuum	17 Pa
Accelerating voltage	20 kV
Working distance	20 mm
Magnification	200×
Spot size	45 arbitrary unit
Tilt	0°
Live time	100 s
Energy resolution	125 eV
Quantitative analysis	ZAF (five iterations)

[7]. Since the LV-SEM can use high accelerating voltages, composition images with the back scattered electrons and spectrum can be obtained by EDS even from non-conductive specimen, allowing not only specimen observation but also elemental analysis.

A back scattered electron detector is used in low vacuum atmosphere. The electron gun chamber and lens systems of the LV-SEM are constantly evacuated to the high vacuum. In the low vacuum mode, the specimen chamber is differentially evacuated to low vacuum with an additional rotary pump dedicated for the specimen chamber. The high vacuum side and the low vacuum side are separated by the aid of an orifice. The experimental parameters of the SEM-EDS system are summarized in Table 3.

3. Results and discussion

3.1. LA-ICP-MS results

Garbe and Arpe [8] have used the laser abslation attached to high resolution inductively coupled plasma (LA-HR-ICP-MS) to evaluate the abundance of REE in zircon standard sample 91500. Also Chenery and Jennifer [9] have determined the REE in single mineral grain using (LA-HR-ICP-MS). Hirata and Nesbitt [10] have determined ^{238}U, ^{207}Pb, ^{206}Pb and ^{208}Pb abundances in several zircon grains using (LA-ICP-MS).

Relative sensitivity coefficient (RSC) method is used for the quantification of trace elements in zircon fused pellet. Concentration of the trace element C_t in the sample can be estimated from the following equation:

$$C_t = C_r \frac{I_t}{I_r} \frac{A_r}{A_t} \frac{S_r}{S_t}$$

where I_t and I_r are the ion currents measured from an internal reference standard (r) in the sample and the trace element t. A_t and A_r are the respective isotope abundances, S_t and S_r are the respective element sensitivity. The obtained C_t value is used in the following equation to evaluate the RSC.

$$\mathrm{RSC} = \frac{S_t}{S_r} = \frac{C_r}{C_t} \frac{I_t}{I_r} \frac{A_r}{A_t}$$

Taking Ce as an internal reference element, the concentrations of different trace elements are measured by LA-ICP-MS (measurements are carried out for the pellets and tabulated in Table 4).

The calibration curves of some elements gave correlation coefficients R^2 range from 0.9746 up to 0.9999. Comparing the values obtained by the ICP-MS calibration curves and the RSC method, a close similarity is found between the data of both methods (Table 4). This means that it is possible to use this approach with some confidence to estimate the concentration of trace elements in zircon sample.

Table 4
Calculation of elemental concentrations (μg/g) using calibration curves and RSC methods in zircon fused solid sample using LA-ICP-MS

Element	Calibration curve method		RSC method	
	Concentration (ppm)	RSD (%)	Concentration (ppm)	RSD (%)
V	15.0 ± 0.5	3.5	–	–
Co	3.0 ± 0.1	2.1	2.5 ± 0.7	3.6
Zn	33.6 ± 5.5	16.5	22.5 ± 1.9	12
Sr	35.9 ± 0.3	0.8	16.5 ± 1.6	10.5
Y	1557 ± 55.2	3.6	1635 ± 60	3.7
Nb	18.8 ± 0.5	2.7	17.9 ± 0.7	3.7
Ce	842 ± 32	3.8	845.8	–
Nd	287.7 ± 14.3	5	297.1 ± 4.1	1.4
Eu	10.6 ± 0.5	4.8	10.5 ± 0.2	1.4
Sm	77.7 ± 3.7	4.8	74 ± 0.8	1.1
Tb	20.1 ± 0.8	4.2	19.8 ± 0.1	0.5
Lu	56.5 ± 2	3.6	56.7 ± 0.2	0.4
U	231.8 ± 1.9	0.8	268.3 ± 3.6	1.3

Fig. 7. Zircon grains as viewed with electron microscope.

3.2. Electron microprobe energy dispersive X-ray spectrometric method of the grains

The technique is used to analyze the same zircon grains after fixing some of them by sticking papers. These were placed as targets for the electron beam of the electron microscope machine. Fig. 7 shows a micrograph of zircon grains by the scanning electron microscope. Three grains were randomly selected and analyzed for some major and trace elements. The averages of the concentrations obtained are listed in Table 5.

In the EDS method, the machine is already calibrated to make the necessary corrections by a set of internal standards and ZAF software (where Z, A, and F, refer to atomic number, absorbance of X-rays emitted, and fluorescent X-rays, respectively). The standard deviations of the three measurements for all elements are less than 7%.

The presented LA-ICP-MS method, using the fused pellets, has proven itself very useful in giving trace element analysis for a “bulk mineral sample” composed of several grains and hence a better average composition than a single grain analysis. Fine inclusions, however can’t be avoided and hence trace elements determined are not necessarily those taking part in the crystal structure. Also you could adjust the elemental concentration in the pellets by controlling the amount of mineral sample used for fusion to meet limits of detection requirements.

The EDS method is useful in getting major as well as trace elemental composition, analyzing what you see, and hence avoiding inclusions. In zoned zircons it can provide valuable information on the chemical composition of the successive zones and hence environments of different stages in their evolution.

Table 5
Major and trace elements content in zircon grains analyzed by the EDS method (average of three grains)

Major elements oxides	Concentration (%)
ZrO_2	61.83
SiO_2	30.95
Y_2O_3	1.59
Fe_2O_3	0.58
Trace elements	**Concentration (ppm)**
Hf	8667
Cu	2870
Zn	2398
Ru	3000
Ce	712
Sm	90
Ho	785
Er	936
Yb	1770
Th	980

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