Analysis of Rare Earth Elements in Geological Samples by Laser Ablation - Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

Geological

Authors

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Abstract

The unique, coherent chemical properties of the rare earth elements (REE) make them highly suitable for geological studies into the history of rocks. Prior to the advent of reliable laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) methods, the steps required to prepare the rock samples for REE analysis were both time consuming and costly. Now, the same fusion beads prepared for X-ray-fluorescence (XRF) analysis, used for the determination of major and certain trace elements, can also be used for LA-ICP-MS analysis, without additional sample preparation. Data published in the literature [1] for geostandards: BE-N (Basalt), MRG-1 (Gabbro) and MAG-1 (Marine Mud), compares well to the results obtained by LA-ICP-MS.

Introduction

The rare earth elements (REE) belong to the inner transition metals and play an important part in understanding the geological history of rocks. In most cases, the REE content of a geological sample reflects the pristine composition of the rock formation and can, therefore, yield reliable information concerning magmatic processes and the reconstruction of palaeo-tectonic settings. This is because REE are amongst the most immobile elements during diagenesis, metamorphism, hydrothermal alteration and weathering.

In the past, the determination of REE in geological samples was a time consuming and expensive task: sample digestion and separation of the REE via ion exchange was required prior to analysis by ICP-AES or ICP-MS. More recently, the methodology has developed whereby REE can be determined in the same whole-rock fusion glass beads which are used for X-ray fluorescence (XRF) analyses, by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), with two key advantages:

1. Only one chemical sample preparation procedure is necessary, thereby reducing the use of expensive supra pure chemicals.
2. The bulk chemistry and certain trace elements of a rock sample can be determined by XRF prior to analysis of the same fusion bead by LA-ICP-MS.

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Sample preparation

0.6 g very finely (<40µm) ground geological sample (international geostandards BE-N, MRG-1, MAG-1) was added to 3.6 g Spectromelt A12 (66:34 mixture of di-lithiumtetraborate and lithiummetaborate, Merck). Just before melting, 1.1 g NH_4NO_3 was added as an oxidant and merged once again. Fusing was carried out in a Pt-crucible at 1100°C. A different preparation method is described by Becker & Dietze [2]. The bulk chemistry and certain trace elements, as well as the homogeneity of the glass targets, were determined using X-ray-fluorescence (PHILIPS PW1480; Brätz & Klemd, in prep). No further sample preparation is required for additional analysis of the REE in the whole-rock glass target by LA-ICP-MS. At most, the surface of the glass targets can be wiped with alcohol. The measurements were undertaken at the Mineralogisches Institut of the Universität Würzburg by means of a 266 nm Nd:YAG Laser (New Wave Research Inc., Merchantek Products) connected to an Agilent 7500i ICP-MS. Table 1 displays the instrument operating parameters of the LA-ICP-MS, which was tuned for maximum sensitivity.

Table 1. Laser ablation and ICP-MS operating parameters

| Laser ablation adjustment	ICP-MS adjustment
Merchantek 266 LUV	Agilent 7500i
Wavelength: 266 nm	Plasma power: 1390 W
Pulse duration: 6 ns	Carrier Gas (Ar): 1.27 L/min.
Repetition frequency: 20 Hz	Plasma Gas (Ar): 14.9 L/min.
Laser energy: 70% (=1.9 mJ)	Auxiliary Gas (Ar): 0.9 L/min.
Ablation pattern: line, 50 µm spot ⌀	Acquisition Mode: Time Resolved Analysis
Scan speed: 20 µm/sec.	Integration time: Si 0.01 sec.; REE 0.15 sec.
Laser warm-up: 10 sec.	Background: 10 sec.
On delay: 0 sec.	Acquisition time: 40 sec.

Results

Quantification of the REE was undertaken using the GLITTER software [3, 4]. The REE in the glass standard reference material NIST612 were used as calibration standards, and [29]Si as the internal standard. Each prepared geostandard (BE-N, MRG-1, MAG-1) was analysed several times on different days, the relative standard deviation differs from 2 to 14% (the majority from 3 to 8%), and, in agreement with the XRF-measurements of major and certain trace elements, the LA-ICP-MS data highlight an almost homogeneous REE distribution in the glass targets. The mean concentration values for the geostandards, see Table 2, generally show excellent agreement when compared to data from the literature [1]. A graphical representation of the LA-ICP-MS results in comparison to the reference values is shown in Figure 1.

It is important to note that the data presented in this application note has been corrected solely by subtracting the instrument background counts from the counts for each of the elements investigated. While there is the potential for oxide overlaps on the REE - although at much lower levels than would be seen with solution nebulization - the results were in good agreement with the reference values, even when no interference correction was applied. The low level of oxide interferences on the Agilent 7500i is due to the high efficiency of the plasma, which decomposes matrix components efficiently, and thus permits difficult applications to be run without over reliance on correction equations [5].

2

Table 2. Results for REE concentrations [ppm] in lithium borate glasses from this study and comparison data from the literature [1] (underlined data are proposed values, other values are recommended, except those in parentheses which are informative values). LA-ICP-MS results for BE-N are the mean values of at large 53 measured patterns at six days, for MRG-1 the mean values of 44 measured patterns at five days and for MAG-1 the mean values of 20 measured patterns at two days.

| Element	BE-N (Basalt) LA-ICP-MS			MRG-1 (Gabbro) LA-ICP-MS			MAG-1 (Marine Mud) LA-ICP-MS		
	[1]	mean	%RSD	[1]	mean	%RSD	[1]	Mean	%RSD
^{139}La	82	88	3.3	9.8	11	7.1	43	44	5.7
^{140}Ce	152	168	3.1	26	30	9.1	88	81	11.1
^{141}Pr	17.5	18.3	3.1	3.4	4.0	6.4	9.3	9.0	8.9
^{146}Nd	67	70	3.4	19.2	21	5.1	38	40	3.8
^{147}Sm	12.2	12.4	3.7	4.5	5.2	8.0	7.5	8.1	3.1
^{153}Eu	3.6	3.9	3.9	1.39	1.60	8.1	1.55	1.45	10.3
^{157}Gd	9.7	9.3	2.7	4	4.8	11.6	5.8	6.7	4.5
^{159}Tb	1.3	1.2	6.4	0.51	0.58	6.8	0.96	0.86	9.9
^{163}Dy	6.4	6.4	4.0	2.9	3.3	6.6	5.2	5.4	3.7
^{165}Ho	1.1	1.1	3.4	0.49	0.53	6.2	1.02	0.89	7.3
^{166}Er	2.5	2.5	4.9	1.12	1.3	11.3	3	3.1	3.2
^{169}Tm	0.34	0.31	3.5	0.11	0.15	7.9	0.43	0.37	6.8
^{172}Yb	1.8	1.9	3.6	(0.6)	1.0	14.2	2.6	2.9	1.7
^{175}Lu	0.24	0.25	3.8	0.12	0.11	8.9	0.40	0.33	9.1
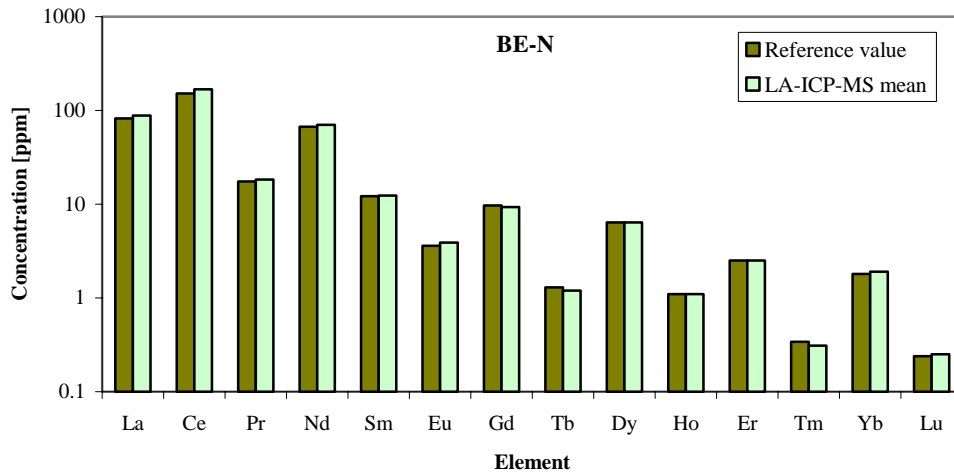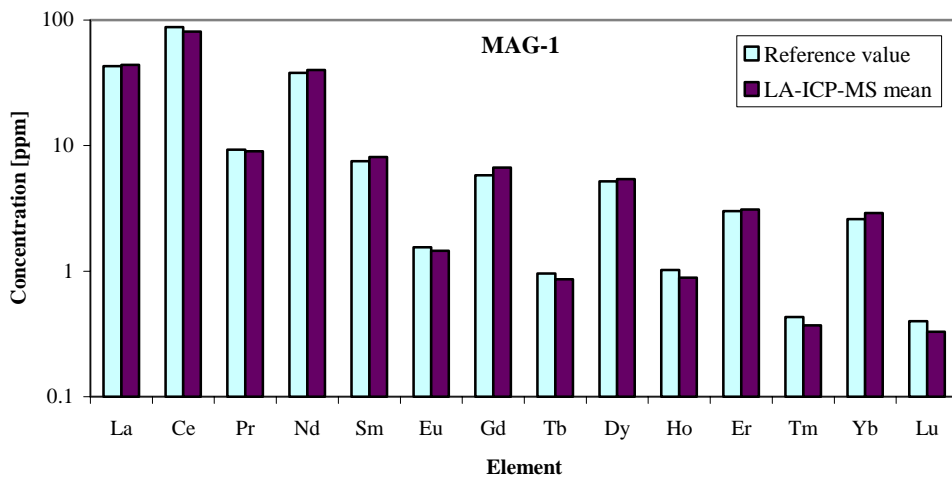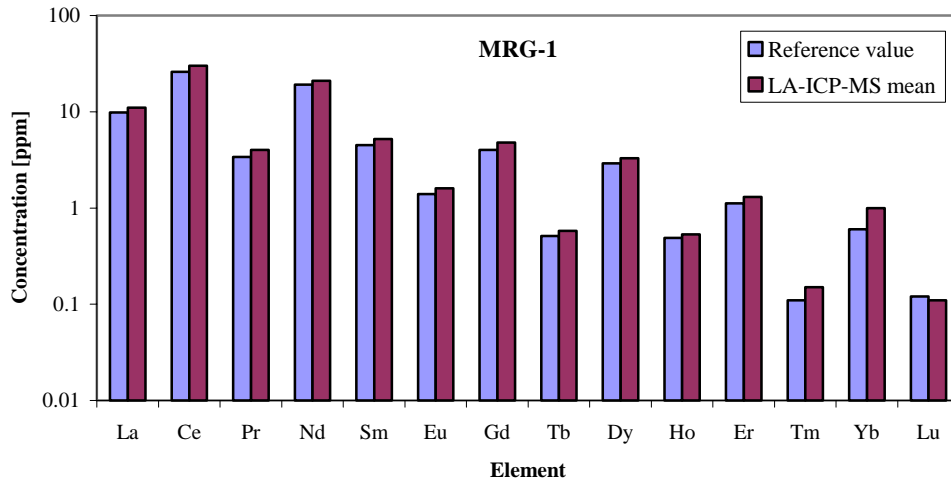
Figure 1. LA-ICP-MS results for REE in comparison to reference values of the international geostandards BE-N, MRG-1 and MAG-1 [1].

Conclusions

The samples prepared for XRF-analysis for the determination of major and certain trace elements (Brätz & Klemd, in prep.) can be used readily for LA-ICP-MS analysis, without additional sample preparation. This way of analysing the REE is fast and relatively inexpensive in comparison to conventional REE-analysis methods. The measured values for the REE in international geostandards are in good agreement with data available in the literature [1]. A disadvantage of the Li borate fusion method of sample preparation is the very high Li-content in the glasses [2], which causes Li contamination of the glassware as well as interface and requires careful cleaning of both the laser ablation and ICP-MS systems in order to permit the subsequent measurement of these elements at trace levels.

References

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Acknowledgement

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