



REE profiling in basic volcanic rocks after ultrasonic sample treatment and ICPMS analysis with oxide ion formation in ICP enriched with O₂☆



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ABSTRACT

ICP-MS methods, and its variants, had been extensively used to determine REEs due to their lower detection limits, high sensitivity and dynamic linear range. However, spectral interferences caused by oxide and hydroxide ions always represents an issue regardless the type of sample been dealt. In the present work it was described the study of REEs oxides formation with the introduction of an auxiliary line directly to the cyclonic chamber to generate a mix Ar/O₂ plasma. Plasma conditions were optimized by studying and selecting the best flow rates to induce the formation of REEs oxides. A new analytical method for REE determination was thus proposed using ICPMS with Ar-O₂ mixed plasma to aid the formation of MO ions. This method was validated through CRM analysis and through the analysis of real-world samples. The REE concentrations evaluated and normalized to chondrite REE levels allowed the analysis of basaltic rocks study in terms of their origin.

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1. Introduction

As defined by IUPAC, rare earth elements (REE) are a group of seventeen chemical elements in the periodic table, specifically the fifteen lanthanides plus scandium and yttrium [1]. Scandium and yttrium are considered rare earth elements because they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties. Despite their name, REE are relatively plentiful in the Earth's crust, with Ce being the 25th most abundant element at 68 ppm (similar to Cu). However, because of their geochemical properties, rare earth elements are typically dispersed and not often found concentrated as rare earth minerals in economically exploitable ore deposits [2–4]. REE profiling is a geochemical index used to evaluate origin of certain ores, and other geological information; for instance, Eu abnormality in a chondrite-normalized concentration of REE against atomic number, is a pattern used to distinguish intra or inter plate origin.

Accurate quantification of REE entails a variety of analytical issues according to the analyte to determine and the matrix of the sample itself. In the matter of biological samples, it is not well known which physiological role REE hold in human health, disease and nutrition, although it has

been reported some methods to assess total quantification [5,6]. Difficulties in signal suppression and/or enhancement are often encountered when dealing with these complex matrixes due to organic compounds. Environmental samples are more common targets when researching REEs [4,7–11].

ICP-MS methods, and its variants, had been extensively used to determine REEs due to their lower detection limits, high sensitivity and dynamic linear range. However, spectral interferences caused by oxide and hydroxide ions always represents an issue regardless the type of sample been dealt. Accurate quantification of REE entails a variety of analytical issues according to the analyte to determine and the matrix of the sample itself. Environmental samples are more common targets when researching REEs [4,7–11]. Many alternatives were studied in order to mitigate these overlaps, such as the use of a high resolution instrumentation (HR-ICPMS) [12,13], the application of algebraic corrections with chromatographic separation [14], and the modification of the plasma itself to generate doubly charged ions [15]. Ardini and col. first reported the use of oxygen within a dynamic reaction cell for REEs determination by quadrupole ICP-MS [16]. Their purpose was to make an $m/z + 16$ shift in order to overcome interferences signal contribution. However, they stressed that formation of TmO⁺, YbO⁺ and EuO⁺ was not efficiently achieved under the studied conditions, and the incomplete reaction with oxygen of these elements could give rise to significant spectral interferences at $m/z - 16$. In the present work it was described the study of REEs oxides formation with the introduction of an auxiliary line directly to the cyclonic chamber to generate a mix Ar/O₂ plasma. Plasma conditions were optimized by studying and selecting the best gases flow rates to induce the formation of REEs oxides. In addition, the use of mathematical corrections was also evaluated

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in order to correct minor interfering signals. As a result, a novel method for total quantification of all REEs was developed and applied to the analysis of basaltic rocks. Through the determined REE profile (normalized to chondrite), conclusions about type of magma that generated the studied rocks, and its geochemical features, could be laid out.

2. Experimental

2.1. Instrumentation

An inductively coupled plasma mass spectrometer, Perkin-Elmer SCIEX, ELAN DRC-e (Thornhill, Canada) was used. The argon gas with minimum purity of 99.996% was supplied by Praxair (Córdoba, Argentina). An HF-resistant and high performance perfluoracetate (PFA) nebulizer model PFA-ST, coupled to a quartz cyclonic spray chamber with internal baffle and drain line, cooled with the PC³ system from ESI (Omaha - NE, USA) was used. Tygon black/black 0.76 mm i.d. and 40 cm length peristaltic pump tubing was used. The instrument settings are shown in Table 1. An ultrasonic bath Cleanson 1106 (Buenos Aires, Argentina).

2.2. Reagents and certificated materials

The used water was distilled and de-ionized, with a resistivity of 18.2 MΩ cm, produced by an Easy pure RF system from Barnstead (Dubuque, IA, USA). Concentrated nitric acid (65% v/v) from Sigma-Aldrich (Germany) and hydrofluoric acid (48% v/v) from Merck (Germany) were used throughout. Multi-element calibration standard 2 from Perkin Elmer Pure Plus containing 10 mg L⁻¹ of REEs in 5% HNO₃; and a setup solution containing 10 μg L⁻¹ of Ba and 1 μg L⁻¹ of Mg, Co, Fe, Be, In, Ce, Pb, U and Th in 0.5% HNO₃ from Perkin Elmer Pure, Atomic Spectroscopy Standard, (Norwalk, USA), were used.

The standard reference material used for validation purpose was SRM 2586 from NIST (trace elements in soil containing lead from paint), SRM 2711 from NIST (Montana soil).

For the external calibration against aqueous standards, the standard solutions were prepared in 4.0% v/v nitric acid. The analytes concentrations were 0.5; 1; 5; 10 and 20 μg L⁻¹.

2.3. Sampling, sample treatment and analytical procedure

Approximately 1 kg of basalt samples were collected in two volcanic fields in South America. The first group corresponds to the 'Southern Volcanic Zone of the Andes' (SVZA); with samples of its eastern side (Precordillera at San Juan Province in Argentina) and from the western side (at Republic of Chile). A second group of samples were collected in *Chaján* and *La Garrapata* Hills (limit of San Luis and Cordoba Provinces in the Center of Argentina), an 'olivine basalts volcanic complex' of the higher Cretaceous (−80 ± 5 Ma; [17]).

The basalts were grinded in two steps; first with a metallic rings mortar, and in second term with an agata sphere mortar grinder. A sub-sample of approximately 0.05 g was accurately weighed into a 50 mL volumetric flask (polypropylene), and 2 mL of HNO₃ and 1 mL of HF were added. The flask was closed with a cap and placed in an ultrasound system for 1 h at 40 kHz power with occasional manual stirring. Afterwards, the sample was diluted to 50 mL and analyzed immediately. The analysis was performed by 6-points external calibrations.

3. Results and discussion

3.1. Sample preparation conditions

Standard reference materials were subsampled and accurately weighed in 50-mL polypropylene screw-capped tubes as mentioned above. Dissolution step took place in the same tubes that sub-samples were collected. Soils and sediments are solid samples mainly made of inorganic constituents of the type of silicates, aluminates, carbonates, sulfates, oxides, among others with variable amounts of organic matter. Conventional dissolution is wet acid digestion in closed-vessel assisted with microwave, [3] that is computer controlled and provides safe conditions for operator. However, in some cases it leads to high dilution factors with consequent loses in sensitivity and precision. In previous studies we optimized fast single step procedures for sample wet acid dissolution in hot water bath and ultrasound as energy source providing high reaction rates among acids and sample particles. In this work we evaluated the effectiveness of this approach for basaltic rocks (after grinding) dissolution. Different amounts of HNO₃ acid (0–3 mL) and hydrofluoric acid (0–3 mL) were tested. Visual inspection of resulting solutions allowed arriving to the conclusion that a mixture of 1 + 3 mL of HF and HNO₃ sufficed to dissolve the studied samples totally after soft heating (30 °C) and 1-h ultrasound application (120 W/40 KHz). After that, the resulting solutions were diluted up to 50 mL with ultrapure water. All further experiments were carried out following this procedure. Parallel blank solutions were always prepared to count for reagents contamination.

3.2. Study of plasma conditions

There are several alternatives related to the use of ICP-MS instrumentation to alleviate spectral interferences and/or matrix effects. "Pre-plasma" approaches focus on the manipulation of sample treatment, use of separation and/or preconcentration techniques, or special sample introduction systems (laser ablation, electrothermal vaporization, etc.), in order to eliminate certain interferents from the sample, or enhance the analyte signal before it reaches the plasma. "Post-plasma" approaches are generally based on the addition of a reaction/collision cell between ion optics system and the analyzing quadrupole, which allows the use of a reaction or collision gas, reacting either directly with the analyte to form a new compound, or the interferents. An "in-plasma" alternative was explored with the purpose of generating the oxide species (MO⁺) within the plasma itself. As seen in Table 1, the RF power was lesser (1000 watts) in order to allow better oxide formation efficiency. Lowering even more the RF power was not advisable, because it led to plasma instability. In addition, nebulizer gas flow rate was somehow high favoring this situation.

3.2.1. Ar/O₂ mixed plasma parameters optimization

The optimization of the auxiliary oxygen gas flow rate (AGFR) was assessed with a 5 μg L⁻¹ multielemental standard and blank solutions. The results were plotted as the signal to background ratio (SBR) at the specific *m/z* against the AGFR. Two groups of elements were concluded from the optimization results. The first group (Fig. 1), which includes Sc, La, Ce, Nd, Pr, Eu, Tb, Gd and Sm, shows remarkable reaction yield with O₂ to form MO⁺ ions. The optimum oxygen gas flow rate goes from 0.8 to 1 mL min⁻¹ for this group of elements, which probes good agreement

Table 1
Instrument settings and data acquisition parameters for ICP-MS.

Instrument	Elan DRC-e (Perkin-Elmer SCIEX, Thornhill, Canada)
Sample uptake rate (μL min ⁻¹)	1000
Sample introduction	PFA micronebulizer model PFA-ST, coupled to a quartz cyclonic spray chamber with an oxygen auxiliary gas kit.
RF power (W)	1000/1400 (Ar-O ₂ ICP/ Standard ICP)
Gas flow rates (L min ⁻¹)	Ar gas: Plasma, 13.5; auxiliary, 1.2; nebulizer, 0.75 O ₂ gas: 0.001 (Ar-O ₂ ICP only)
Interface	Ni cones (sampler and skimmer)
Ar-O ₂ ICP conditions	⁴⁵ Sc ¹⁶ O, ¹³⁹ La ¹⁶ O, ¹⁴⁰ Ce ¹⁶ O, ¹⁴¹ Pr ¹⁶ O, ¹⁴² Nd ¹⁶ O, ¹⁶⁴ Dy ¹⁶ O, ¹⁶⁵ Ho ¹⁶ O, ¹⁷⁴ Yb ¹⁶ O, ¹⁷⁵ Lu ¹⁶ O
Standard ICP conditions	⁸⁹ Y, ¹⁵³ Eu, ¹⁵⁸ Gd, ¹⁵⁹ Tb, ¹⁵² Sm, ¹⁶⁹ Tm, ¹⁶⁶ Er
Scanning mode	Peak hopping
Dwell time (ms)	50
Number of replicate	10

in their behavior within the plasma. However, as a consequence of isobaric overlaps (Table 2) advised, it was preferred to determine Eu, Tb, Gd and Sm as M⁺ in standard ICP conditions (Table 1). Sc, La, Ce, Nd

and Pr could be determined as MO⁺ ions with satisfactory SBR and no severe polyatomic interferences.

On the other hand, Y, Dy, Ho, Er, Tm, Yb and Lu showed low yield in MO⁺ ion formation, even at high AGFR. Despite being lesser sensitive,

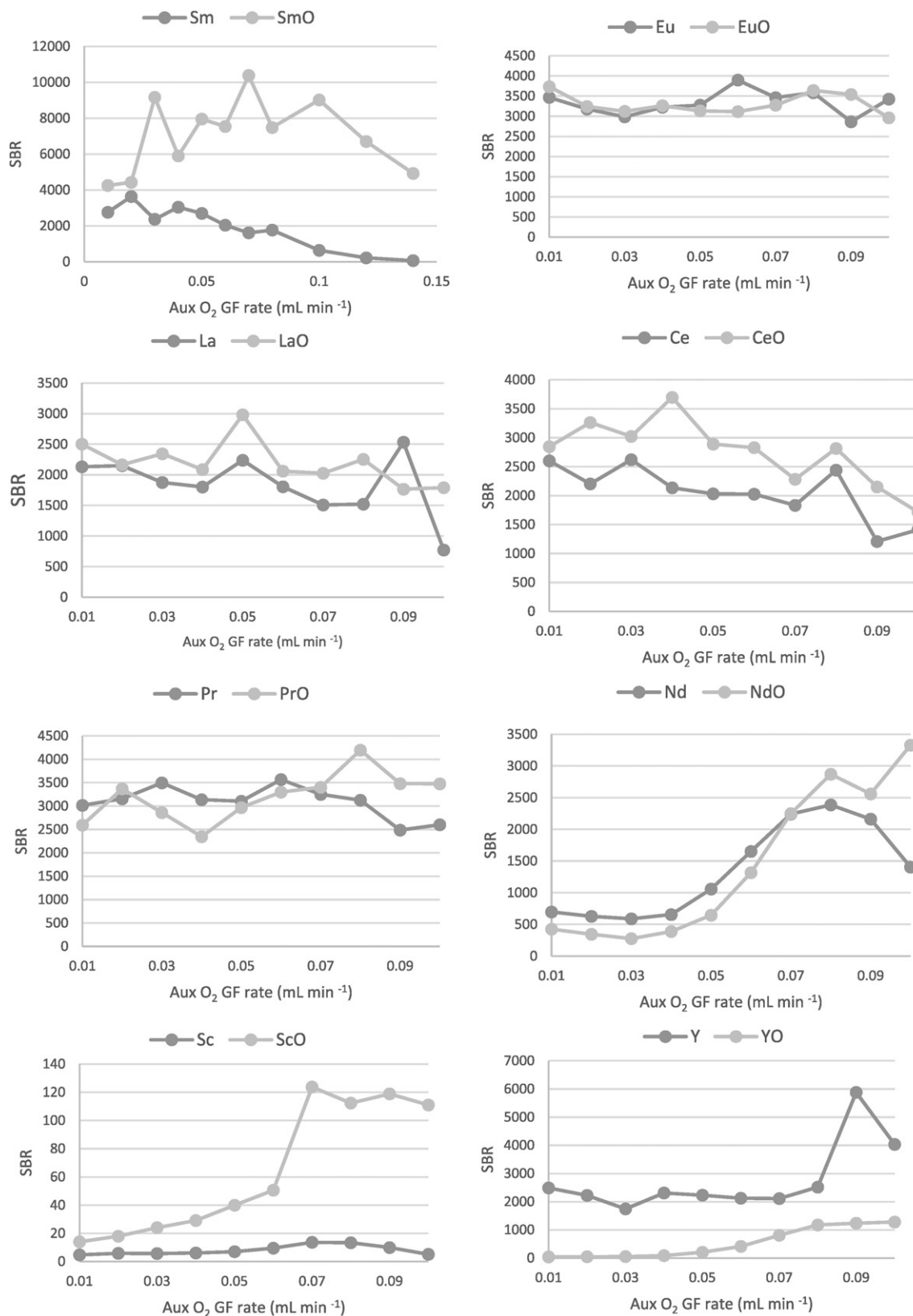


Fig. 1. Effect of O₂ gas flow rate upon light REE ions formation (ScO, YO, LaO, CeO, EuO, SmO, PrO and NdO).

Table 2
Isotopes and major potential interferences.

AMU	Element + abundance (%)	Element + abundance (%)	Element + abundance (%)	O overlap
45	Sc 100			
89	Y 100			
142	Ce 11.08			
143	Nd 12.18			
144		Sm 3.1		
145	Nd 8.30			
146	Nd 17.19			¹³⁰ Ba ¹⁶ O
147		Sm 15.0		⁹⁹ Ru ¹⁶ O ₃
148	Nd 5.76	Sm 11.3		¹⁰⁰ Ru ¹⁶ O ₃ , ¹³² Ba ¹⁶ O
149		Sm 13.8		¹⁰¹ Ru ¹⁶ O ₃
150	Nd 5.64	Sm 7.4		¹³⁴ Ba ¹⁶ O
151			Eu 47.8	¹³³ Ba ¹⁶ O
152	Gd 0.20	Sm 28.7		¹⁰⁴ Ru ¹⁶ O ₃ , ¹³⁶ Ce ¹⁶ O, ¹³⁶ Ba ¹⁶ O
153			Eu 52.2	¹³⁷ Ba ¹⁶ O
154	Gd 2.18	Sm 22.7		¹³⁸ La ¹⁶ O, ¹³⁸ Ba ¹⁶ O, ¹³⁸ Ce ¹⁶ O
155	Gd 14.80			
156	Gd 20.47	Dy 0.06		¹⁴⁰ Ce ¹⁶ O
157	Gd 15.65			
158	Gd 24.84	Dy 0.10		¹⁴² Nd ¹⁶ O, ¹⁴² Ce ¹⁶ O
159			Tb 100	¹⁴³ Nd ¹⁸ O, ¹⁴² Nd ¹⁷ O, ¹⁴¹ Pr ¹⁸ O, ¹⁴⁰ Ce ¹⁷ O, ¹⁴² Ce ¹⁷ O, ¹⁴⁴ Nd ¹⁶ O, ¹⁴⁵ Nd ¹⁶ O, ¹⁴⁸ Nd ¹⁶ O, ¹⁴⁷ Sm ¹⁶ O, ¹⁴⁸ Nd ¹⁶ O, ¹⁴⁸ Sm ¹⁶ O, ¹⁴⁹ Sm ¹⁶ O, ¹⁴⁹ Sm ¹⁶ O, ¹⁵⁰ Nd ¹⁶ O, ¹⁵⁰ Sm ¹⁶ O, ¹⁵¹ Eu ¹⁶ O
160	Gd 21.86	Dy 2.34		
161		Dy 18.9		
162	Er 0.14	Dy 25.5		
163		Dy 24.9		
164	Er 1.61	Dy 28.2		
165			Ho 100	
166	Er 33.6			
167	Er 22.95			
168	Er 26.8	Yb 0.13		
169			Tm 100	¹⁵³ Eu ¹⁶ O, ¹⁵⁴ Gd ¹⁶ O
170	Er 14.9	Yb 3.05		
171		Yb 14.3		
172		Yb 21.9		
173		Yb 16.12		
174		Yb 31.8	Hf 0.162	¹⁵⁷ Gd ¹⁶ O, ⁵⁸ Gd ¹⁶ O, ¹⁵⁸ Dy ¹⁶ O, ¹⁵⁹ Tb ¹⁶ O, ¹⁶⁰ Cd ¹⁶ O, ¹⁶⁰ Dy ¹⁶ O, ¹⁶¹ Dy ¹⁶ O, ¹⁶² Dy ¹⁶ O, ¹⁶² Er ¹⁶ O, ¹⁶³ Dy ¹⁶ O, ¹⁶⁴ Dy ¹⁶ O, ¹⁶⁴ Er ¹⁶ O, ¹⁶⁵ Ho ¹⁶ O, ¹⁸⁶ Er ¹⁶ O, ¹⁶⁷ Er ¹⁶ O, ¹⁶⁶ Er ¹⁷ O, ⁶⁵ Ho ¹⁸ O, ¹⁶⁸ Er ¹⁶ O, ¹⁶⁸ Yb ¹⁶ O, ¹⁶⁹ Tm ¹⁶ O, ¹⁷⁰ Er ¹⁶ O, ¹⁷⁰ Yb ¹⁶ O, ¹⁷¹ Yb ¹⁶ O, ¹⁷² Yb ¹⁶ O, ¹⁷³ Yb ¹⁶ O, ¹⁷⁴ Hf ¹⁶ O, ¹⁷⁴ Yb ¹⁶ O
175	Lu 97.41			
176	Lu 2.59	Yb 12.7	Hf 5.206	
177			Hf 18.606	
178			Hf 27.297	
179			Hf 13.629	
180	Ta 0.012	W 0.13	Hf 35.100	
181	Ta 99,988			
182		W 26.3		
183		W 14.3		
184	Os 0.02	W 30.67		
185			Re 37.40	
186	Os 1.58	W 28.6		
187	Os 1.6		Re 62.60	
188	Os 13.3			
189	Os 16.1			
190	Os 26.4		Pt 0.01	
191		Ir 37.3		¹⁷³ Lu ¹⁶ O, ¹⁷⁶ Hf ¹⁶ O, ¹⁷⁶ Yb ¹⁶ O, ¹⁷⁸ Lu ¹⁶ O, ¹⁷⁷ Hf ¹⁶ O, ¹⁷⁸ Hf ¹⁶ O, ¹⁷⁹ Hf ¹⁶ O, ¹⁸⁰ Hf ¹⁶ O
192	Os 41.0		Pt 0.79	
193		Ir 62.7		
194			Pt 32.9	
195			Pt 33.8	
196	Hg 0.15		Pt 25.3	

adequate SBR could be achieved for YO, DyO, HoO, YbO, and LuO beyond 1.0 mL min⁻¹. On the contrary, TmO and ErO formation is not likely to occur under working conditions. As discussed above, such conditions must be avoided in order to mitigate matrix effects but they are used to advantage this particular situation (see Table 1). In addition, for Dy, Er, Yb and Lu determination as the corresponding MO⁺ ion, algebraic

Table 3
Figures of merit for the rare earth elements determination in digested environmental samples.

Analyte	Instrumental LOD (µg L ⁻¹)	Correlation coefficient for linear fit (R)	Relative standard deviation (n = 3, 1 µg L ⁻¹)
Sc	0.003	0.987	2.4
Y	0.003	0.989	4.6
La	0.005	0.988	0.1
Ce	0.002	0.999	0.4
Pr	0.001	0.998	1.1
Nd	0.002	0.998	1.8
Sm	0.001	0.996	2.4
Eu	0.002	1.000	3.2
Gd	0.002	0.996	3.1
Tb	0.002	0.999	4.3
Dy	0.002	0.989	1.9
Ho	0.001	0.999	0.6
Er	0.0005	0.998	3.1
Tm	0.002	0.998	2.7
Yb	0.004	0.990	4.4
Lu	0.002	0.997	1.5

corrections (Tables 2 and 3) should be introduced to correct for Hf, W, Os and Ir. Table 4 compares the features of this methods with other similar works published recently (Fig. 2).

3.3. Analytical figures of merit

The analytical figures of merit were established in terms of precision (as relative standard deviation) and limits of detection; but also in terms of linearity and good fit of linear regression of calibrations. Accuracy was also assessed through analysis of two certified reference materials (Table 5). The method was established and the determinations were carried out following the recommended procedure.

3.4. REE profiling in volcanic basalt rocks

This method was used for the evaluation of the REE profile of basalt rocks of two volcanic fields of Argentina and Chile (see Section 2.3) as indicated in Fig. 3. The obtained profiles indicated that the two intra plate basalts (Chaján and La Garrapata hills) depicted positive Eu anomaly, as expected. On the other hand, basalts from the Los Andes mountains showed negative Eu anomaly in the case of Chile basaltic rocks (joint of Nasca and South American plates), and no anomaly in the ore of collected in San Juan (border intra plate). Other conclusion that can be laid out is that the light REE are predominant in the case of basalts

Table 4
Recent methods for REE profiling in ores and other related samples.

Determined REE	Ore/sample	Sample treatment	Technique	Ref.
La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, Lu	Carbonatites from Kangankunde Mine	None	INAA	[18]
Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	Indian Kimberlite	Fusion with K ₂ O ₂	ICP-MS	[19]
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	Sandy subterranean estuary (sediment and water)	MW. Acid digestion/ion pair-LC	HR-ICP-MS	[20]
La, Ce, Nd, Sm, Eu, Tb, Ho, Yb, Lu	Ultramafic rock	None	INAA	[21]
Y, Sc, La, Ce, Pr, Nd, Dy, Ho, Yb, Lu, Eu, Gd, Tb, Sm, Tm, Er	Basaltic rock from Los Andes mountains and from San Luis Hills	One-step ultrasound assisted acid digestion	ICP-MS	This work

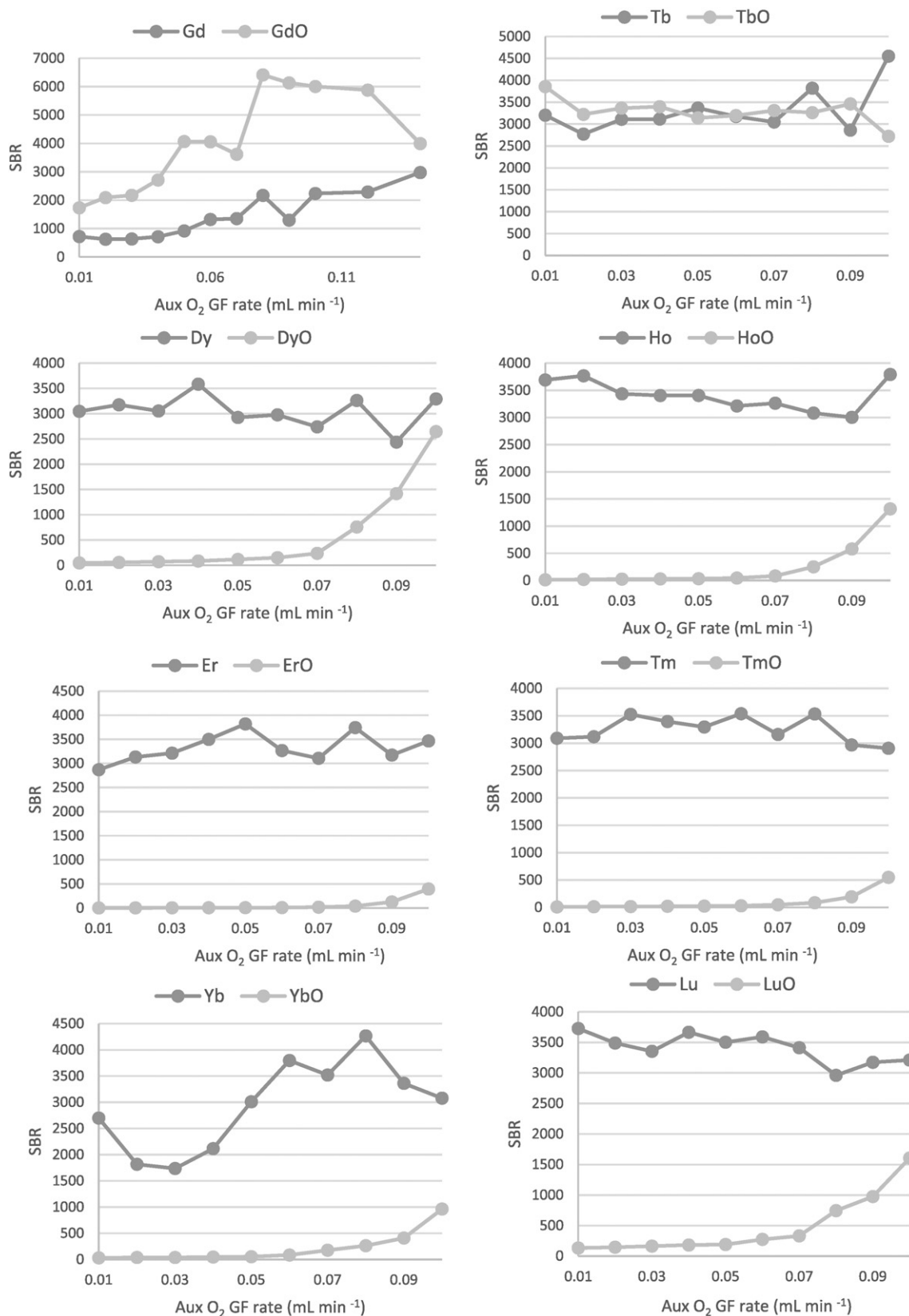


Fig. 2. Effect of O₂ gas flow rate upon heavy REE ions formation (GdO, TbO, DyO, HoO, ErO, TmO, YbO and Lu).

Table 5Analysis of certified reference materials (values in $\mu\text{g g}^{-1}$).

SRM 2586 (soil)			SRM 2711 (Montana soil)		
Analyte	Found ^a	Informed ^b	Analyte	Found ^a	Informed
Sc	20.5 ± 2.1	24	Sc	13.0 ± 2.1	9
Y	19.5 ± 0.8	21	Y	3.0 ± 0.8	–
La	28.5 ± 2.8	29.7 ± 4.8	La	33.0 ± 5.1	40
Ce	59.3 ± 0.5	58 ± 8	Ce	63.8 ± 4.1	69
Pr	39.5 ± 2.2	–	Pr	7.3 ± 0.5	–
Nd	29.5 ± 5.2	26.4 ± 2.9	Nd	25.5 ± 4.1	31
Sm	3.9 ± 0.2	6.1	Sm	7.0 ± 1.0	5.9
Eu	1.5 ± 0.1	1.5	Eu	2.0 ± 0.2	1.1
Gd	3.5 ± 0.2	–	Gd	5.0 ± 0.2	–
Tb	0.5 ± 0.2	0.9	Tb	0.2 ± 0.1	–
Dy	3.5 ± 1.2	5.4	Dy	1.0 ± 0.1	5.6
Ho	0.8 ± 0.1	1.1	Ho	0.8 ± 0.3	1
Er	3.5 ± 0.2	3.3	Er	1.0 ± 0.3	–
Tm	0.5 ± 0.1	–	Tm	N.D.	–
Yb	3.0 ± 0.1	2.64 ± 0.51	Yb	3.01 ± 0.96	2.7
Lu	0.4 ± 0.1	–	Lu	N.D.	–

^a Mean value ± 2 standard deviation (n = 3).^b Certified values in italic.

from La Garrapata, Chaján and Chile, and on the other hand the basaltic rocks from San Juan Province depicted a more balanced ratio between light and heavy REE. These results are a corroboration of well established facts that besides, confirm the goodness of this method for this kind of analysis.

4. Conclusion

A new analytical method for REE determination was established using ICPMS with Ar-O₂ mixed plasma to aid the formation of MO ions. The combination of standard mode and the modification with O₂ allowed the accurate determination of REE in minerals after acid treatment. The validity of this method was assessed through CRM analysis and through the analysis of real-world samples. The REE concentrations evaluated and normalized to chondrite REE levels allowed the analysis of basaltic rocks study in terms of their origin.

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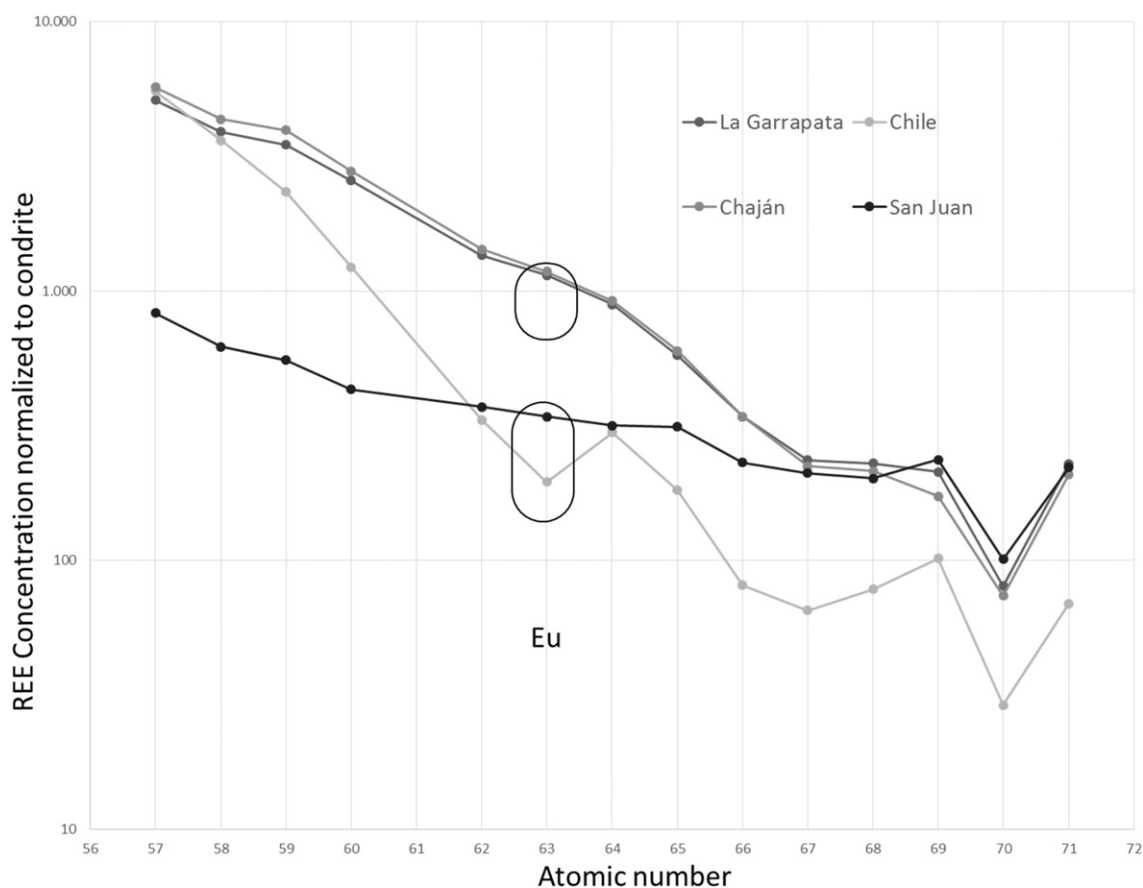


Fig. 3. Plot of REE concentrations normalized to chondrite versus atomic number.

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