REE profiling in basic volcanic rocks after ultrasonic sample treatment and ICPMS analysis with oxide ion formation in ICP enriched with O_2

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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/O_2 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.

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 asses 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 interferents 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/O_2 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 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 PC^3 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% HNO_3; 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% HNO_3 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 Argentine) 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 subsample of approximately 0.05 g was accurately weighed into a 50 mL volumetric flask (polypropylene), and 2 mL of HNO_3 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 HNO_3 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 HNO_3 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/O_2 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 O_2 to form MO + ions. The optimum oxygen gas flow rates 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