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Proficiency testing programs – a tool in the validation process of an analytical methodology for quantification of rare earth elements by ICP-MS

SUMMARY

ICP-MS is the widely used instrumental method for rare earth elements (REE) quantification. Nevertheless, its applicability to the analysis of geological samples exhibits some constraints, since the accuracy of the data is largely dependent, on both complete sample dissolution and adequate correction of polyatomic species, MO⁺ and MOH⁺. In this work six well-studied geological Reference Materials (RM), BHVO-1, JB-3, AC-E, NIM-G, JGb-1, JG-1a and JA-1, were employed for method development. In order to validate the options made for sample decomposition and polyatomic corrections nine samples of the Geopt proficiency-testing program have been analysed and revealed that analytical results, obtained in very different matrices, presented the required quality for further application in studies of petrological and mineralogical processes.

KEYWORDS

Analytical methodology, ICP-MS, rare earth elements, validation

Essais interlaboratoires — un outil pour la validation d'une méthodologie analytique dédiée à la quantification de terres rares par ICP-MS

RÉSUMÉ

L'ICP-MS constitue aujourd'hui la technique analytique la plus utilisée pour l'analyse des terres rares. Toutefois son application à l'analyse d'échantillons géologiques doit tenir compte de plusieurs contraintes. L'exactitude des données produites dépend étroitement du mode de dissolution mis en œuvre et surtout du mode de correction utilisé pour minimiser l'influence des interférences provenant des ions poly-atomiques du type MO⁺ ou MOH⁺. Pour les travaux rapportés dans cet article, nous avons utilisé le frittage avec Na₂O₂ pour la solubilisation des échantillons ; les coefficients de correction des interférences ont quant à eux été évalués expérimentalement après l'optimisation du système instrumentale. La méthodologie a été mise au point en utilisant six matériaux de référence bien caractérisés BHVO-1, JB-3, AC-E, NIM-G, JGb-1, JG-1a et JA-1, elle a ensuite été validée par la participation du laboratoire au programme de contrôle externe de qualité – Geopt. La qualité analytique des résultats, obtenus pour toutes les matrices testées, vérifie les critères internes d'acceptation/rejet, normalisés pour une erreur maximum admissible de 10 %. La méthodologie développée permet la quantification de l'ensemble des terres rares.

MOTS-CLÉS

Méthodologie analytique, ICP-MS, terres rares, validation

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Essais interlaboratoires - un outil pour la validation d'une méthodologie analytique dédiée à la quantification de terres rares par ICP-MS

I - Introduction

The significant growth of interest in the geochemistry of REE has come about because of the recognition that the observed degree of their fractionation in a rock or mineral can be a pointer to its genesis. By the evaluation of REE abundances, processes such as partial melting of crustal and mantle materials, fractional crystallization, and/or mixing of magmas could be better understood (1).

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) has found popularity in earth science field, mainly because of the very low detection limits available for most elements in the periodic table. However, problems associated with the ICP-MS technique, such as low resolution of quadrupole and occurrence of polyatomic/isobaric overlaps, and even sample preparation, imposed some analytical constraints, which cause some limitations on the acquisition of accurate and precise analytical data (2).

For the quantification of REE it is important that a complete dissolution of the sample is achieved because any insoluble residue may retain undetermined amount of these elements. When acid mixtures containing HF are used, insoluble fluorides of REEs may remain in the precipitate, then the sample decomposition by acid attack in open vessel must be avoided, unless a previously and detailed knowledge of the sample matrix is available (3). In fact, refractory minerals such as zircon, tourmaline, chromite, rutile, garnet, spinel and corundum are incompletely decomposed by an acid attack (4).

Decomposition by lithium metaborate and tetraborate fusion procedure has been adopted by several authors (2, 5-7). However complete decomposition of silicate phases and accessory minerals causes high levels of total dissolved solids (TDS) in the aspirated solution and high blank levels too. The dissolution of fused sample with HF followed by a treatment with HNO₃ has been recently proposed (8) to overcome the main problems caused by the use of high dilution factors and strong adsorption phenomenon in the sample introduction devices, due to the high levels of Li and B in the aspirated solutions. Matrix removal by solvent extraction or with chelating resins is also proposed (9, 10).

For several types of geological matrices, sintering with Na₂O₂ is a very attractive analytical decomposition procedure, because it is highly effective in attacking minerals quickly and the resulting sinter residue is easy to dissolve, additionally it does not introduce elements that cause significant memory effects (11). However, the lack of ultra-pure reagents may preclude the use of sodium peroxide sinter method for the measurement of geological samples if others low trace elements have to be analysed too (12).

Refractory oxide formation can be a significant problem in the quantification of REE by ICP-MS,

particularly if the light REE (LREE) to heavy REE (HREE) ratio is high, then ions of the LREE-oxides and/or LREE-hydroxides may produce significant interferences on some of the HREE. The identification of oxide and hydroxide ions and the instrumental parameters related to their formation have been fully discussed (13, 14, 15, 16, 17). Instrumental parameters such as Rf Power, nebulizer argon flow, distance from load coil to sampler cone and changes in the orifice of the sampler and skimmer cones have been identified as the most important in the formation of MO⁺ and MOH⁺ species. These types of polyatomic interferences are particularly significant in all isotopic masses of Gd, Dy, Er and Yb, which may sustain the diversity of isotopic masses used in their quantification (2, 11, 14, 18).

In such circumstances, this work aims at developing a robust methodology that, when applied to different geological matrices, leads to reliable results for petrogenetic studies. For that reason, sample decomposition and quantification steps were fully validated by analysing several geological Reference Materials and samples of the Geopt proficiency-testing program.

II – Sample decomposition

A decomposition procedure that minimizes incomplete dissolutions of hard minerals has been chosen on account of the high probability that samples with different matrices will appear in the same analytical batch. Sintering with Na₂O₂ was the option because sample decomposition can be achieved in only thirty minutes and therefore solubilization and quantification steps can be performed in the same working day.

Sodium peroxide (Merck p.a.) finely powdered in an agate ball mill, ultra pure water (18.2 MΩ.cm⁻¹) produced by MilliQ Elemental system (Millipore) and ultra pure HNO₃ and HCl, obtained by double sub-boiling distillation in a Duopor system (Milestone), were used on the entire analytical procedure. Sintering was performed in a Carbolite muffle (CWF 1200), with periodical external control of thermal gradients, Mettler PC400 and AE160 balances, externally calibrated, were used to weight both Na₂O₂ and sample material. Disposable polypropylene 50 mL tubes and PFA volumetric flasks were employed in samples and standards preparation.

100.0 mg of sample grounded to pass a 200-mesh sieve were mixed with 0.60 g of Na₂O₂ in a porcelain crucible (30 x 30 mm²) lined with aluminium sheet and mixture sintered at 480 ± 10 °C for exactly 30 minutes. After cooling, the sinter residue was gently removed from the crucible with ultra-pure water drop-wise into a 50 mL polypropylene tube; when the reaction finished 3 drops of concentrate HCl and 2 mL of concentrate HNO₃ were added; the tube was filled to the mark with H₂O. Before quantification, this solution was diluted 1:10 with

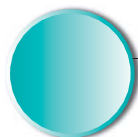


Table I
Instrument operating conditions.

Instrumental settings		Data acquisition settings	
Instrument	VG PQ ExCell	Detector	Multiplier ETP AF214
Nebulizer type	Cross-flow	Scan mode	Peak jumping
Spray chamber	Cooled at 4 °C by Peltier effect	Channel per mass	1
Cones	Nickel	Dwell time per peak	10 ms
Typical ¹¹⁵ In sensitivity	> 80000 cps per µg ⁻¹	Sweeps per read	250
Plasma power	1350 W	Total acquisition time	64 sec
Coolant gas flow	13 L min ⁻¹	Uptake time	100 sec
Auxiliary gas flow	0.78 L min ⁻¹	Wash time	50 sec
Nebulizer gas flow	0.85 L min ⁻¹	Internal Standards (In, Ir)	2 µg ⁻¹

2 % HNO₃ blank solution to a final volume of 10 mL and 10 µL of In and Ir standard solutions with, 2 mg/L for each one, were also added.

III – Instrumental optimisation

1. Operating Conditions

The ICP-MS system used was the PQ ExCell (ThermoElemental) equipped with a peristaltic pump (Spetec Perimax 12) and an auto-sampler (50/60 Cetac ASX500). The operating conditions, ensuring that the equipment runs under the factory specifications, are summarized in Table I. These conditions are properly adjusted everyday, in order to achieve a sensitivity better than 80000 cps for ¹¹⁵In, BaO⁺/Ba ratio better than 0.3 % and, for ten consecutive measurements, RSD values better than 1 % for all elements, aspirating a multi elemental solution with 1 µg⁻¹ of Li, Be, Co, In, Ba, Bi and U in 2 % HNO₃.

2. Calibration curve

Rare Earth Elements (1 mg/L La; 2 mg/L Ce and Nb; 0,2 mg/L Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) and Internal Standards (2 mg/L In and Ir) stock solutions in 2 % HNO₃ were prepared from 1 g/L single standard certified solutions (Alfa Aesar).

At the beginning of each analytical sequence, four calibration standards (*table II*) and one blank were prepared in 100 mL PFA volumetric flasks, using automatic calibrated pipettes (Eppendorf) to spike the appropriate volumes of the above-mentioned REE solution. To all calibration solutions, 100 µL of the stock internal standard solution were added. The flasks were filled to the mark with a 2 % HNO₃ + 1.2 g/L Na₂O₂ solution.

Sodium peroxide was introduced in the calibration standards in order to reproduce in the standards solutions the sample matrix after decomposition. Like that, spatial charge phenomena in the skimmer cone are similar for all the solutions to be aspirated and modifications in transmission of the ionic beam were therefore minimized.

The stability of the calibration curves was under a tied survey during an entire month. The data obtained from 16 independent analytical calibrations clearly show : (i) values without any statistic significance for the intercepts. (ii) RSD values higher than 5 % for the corresponding slopes. These results point out a low contamination level in REE from the sodium peroxide and that it is not advisable to work with fixed calibration curves.

Even with internal standards drift correction, the unavoidable strong deposition of solid material on cones surfaces determines several recalibrations through the working period. Thus, a periodical analytical calibration after each twelve samples has been adopted and a quality control (QC) low concentration standard is used to check the reference curve robustness between recalibrations. For this QC a bias lower than ±10 % of the nominal concentration value has been always achieved.

IV – Interferences identification and correction

With an optimized set of instrumental parameters, allowed by the new generation of ICP-MS instruments, it is possible to reduce and control the amount of oxide/hydroxide formation to very low levels (<2 %) (19, 20). Values better than 0.3 % for BaO⁺/Ba⁺ and 1.5 % for CeO⁺/Ce⁺ can be achieved. Nevertheless, the identification and subsequent correction of such interferences are

Table II
Concentration of the standard calibration solutions in µg⁻¹.

Standard	Final concentrations (µg ⁻¹)													
	La	Ce	Pr	Nd	Sm	Eu	Tb	Gd	Dy	Ho	Er	Tm	Yb	Lu
Std 1	0.25	0.5	0.05	0.5	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Std 2	5	10	1	10	1	1	1	1	1	1	1	1	1	1
Std 3	12.5	25	2.5	25	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Std 4	25	50	5	50	5	5	5	5	5	5	5	5	5	5

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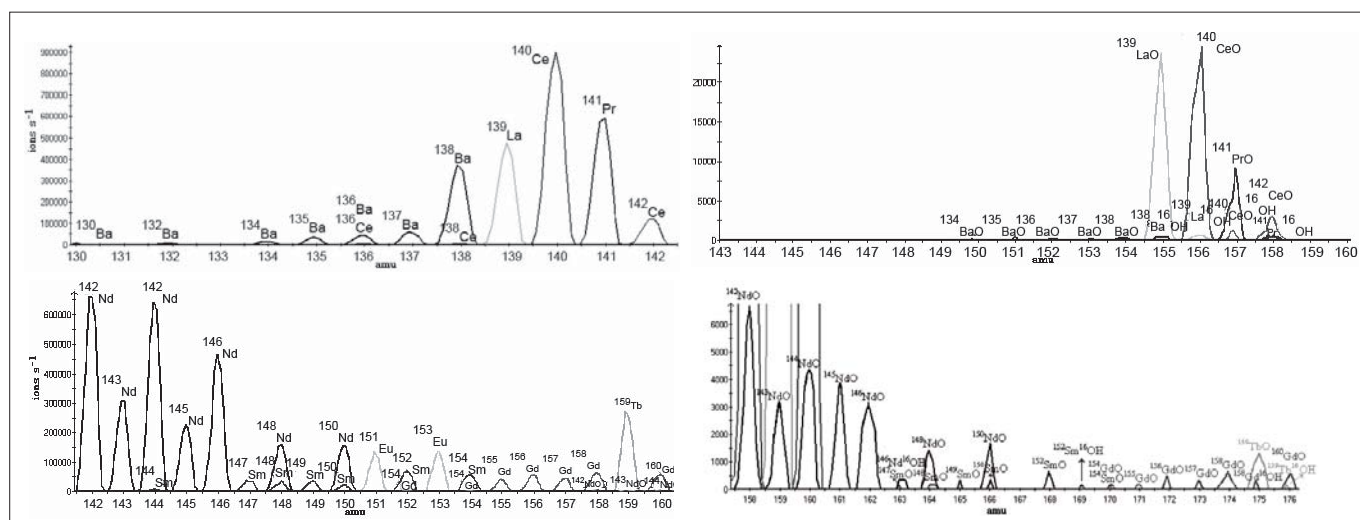


Figure 1

Isobaric and polyatomic MO^+/MOH^+ interferences identified in 130-178 amu range. Spectrum obtained in Survey Run mode (sweeps: 20; dwell time: 300 μ s, channels per mass:10; acquisition time: 15 sec; mass range: 80.59–245.5 amu) with mono-elemental solutions of Ba, La, Pr, Sm, Eu, Gd and Tb (5 μ g.L⁻¹), Ce (10 μ g.L⁻¹) and Nd (50 μ g.L⁻¹) in 2% HNO₃ medium.

necessary in routine schemes of REE analysis in geological materials.

For that reason, the mass spectra of several mono-elemental solutions (Ba, La, Ce, Pr, Nd, Sm, Eu, Gd and Tb), for which oxides and hydroxides species strongly affects the analyte intensities in the range 150-176 amu, have been studied (figure 1) in order to evaluate the better isotopic mass for quantification purpose.

The isotopic masses were selected (table III) based on their relative abundance and incidence degree of isobaric and polyatomic (MO^+ and/or MOH^+) interferences.

For the operating conditions (table I) it has been found that : (i) MO^+ and MOH^+ formation are strictly related to the isotopic relative abundance

as pointed out by several authors (14, 21, 22) ; (ii) their incidence degree are element nature-dependent.

For analytical purposes, it is important to clarify if the nature of the element is in fact one of the parameters that control the polyatomic formation (MO^+ and MOH^+ type). In such circumstances oxides and hydroxides formation will follow particular stoichiometric reactions, which enables their correction by a fixed numerical coefficient.

With this propose the MO^+/M^+ and MOH^+/M^+ ratios for all the REE, as well as for Ba, have been evaluated for different concentrations along the selected calibration curve. Analytical data (figure 2 see next page) clearly show : (1) % MO^+ and % MOH^+ are better than 1.5 and 0.06 %, respectively

Table III

Selected isotopic mass for quantification and corresponding equations for interfering corrections.

Isotope	Abundance (%)	Interferences		Correction Equation
		Isobaric	MO^+/MOH^+	
¹³⁹ La	99.9			139M + 1,000* ¹⁵⁵ Gd
¹⁴⁰ Ce	88.5			140M + 1,000* ¹⁵⁶ Gd
¹⁴¹ Pr	100			141M + 1,000* ¹⁵⁷ Gd
¹⁴⁴ Nd	23.8	¹⁴⁴ Sm(3.2%)		144M - 0,2067* ¹⁴⁷ Sm
¹⁴⁶ Nd	17.3			
¹⁴⁷ Sm	15.1			
¹⁵¹ Eu	47.8		¹⁵¹ BaO(6.6%)	151M - 0,0001* ¹³⁸ Ba
¹⁵⁵ Gd	14.7		¹⁶⁰ O + ¹³⁹ La(99.7%), ¹⁶⁰ O ¹ H + ¹³⁸ Ba(71.5%)	155M - 0,6738* ¹⁶⁰ Gd
¹⁵⁶ Gd	20.5		¹⁵⁶ CeO(88.3%), ¹⁶⁰ O ¹ H + ¹³⁹ La(99.7%)	156M - 0,9364* ¹⁶⁰ Gd
¹⁵⁷ Gd	15.7		¹⁶⁰ O + ¹⁴¹ Pr(99.8%), ¹⁶⁰ O ¹ H + ¹⁴⁰ Ce(88.3%)	157M - 0,7173* ¹⁶⁰ Gd
¹⁵⁹ Tb	100		¹⁶⁰ O + ¹⁴³ Nd(12.1%)	159M - 0,0046* ¹⁴⁴ Nd
¹⁶⁰ Gd	21.9	¹⁶⁰ Dy(2.3%)	¹⁶⁰ O + ¹⁴⁴ Nd(23.8%)	160M - 0,0082* ¹⁴⁴ Nd - 0,081* ¹⁶⁴ Dy
¹⁶³ Dy	25.0		¹⁶⁰ O ¹ H + ¹⁴⁶ Nd(17.2%), ¹⁶⁰ O + ¹⁴⁷ Sm(15.0%)	163M - 0,0004* ¹⁴⁴ Nd - 0,0023* ¹⁴⁷ Sm
¹⁶⁴ Dy	28.2	¹⁶⁴ Er(1.6%)	¹⁶⁰ O + ¹⁴⁸ Sm(11.2%), ¹⁶⁰ O + ¹⁴⁸ Nd(5.7%)	164M - 0,0467* ¹⁶⁶ Er
¹⁶⁵ Ho	100		¹⁶⁰ O + ¹⁴⁹ Sm(13.8%)	165M - 0,0023* ¹⁴⁷ Sm
¹⁶⁶ Er	33.4		¹⁶⁰ O + ¹⁵⁰ Sm(7.5%), ¹⁶⁰ O + ¹⁵⁰ Nd(5.6%)	166M - 0,0020* ¹⁴⁴ Nd - 0,0013* ¹⁴⁷ Sm
¹⁶⁹ Tm	100		¹⁶⁰ O ¹ H + ¹⁵² Sm(26.6%)	169M - 0,0007* ¹⁴⁷ Sm
¹⁷⁴ Yb	31.8		¹⁶⁰ O + ¹⁵⁸ Gd(24.8%)	174M - 0,0056* ¹⁶⁰ Gd
¹⁷⁵ Lu	97.4		¹⁶⁰ O + ¹⁵⁹ Tb(99.8%), ¹⁶⁰ O ¹ H + ¹⁵⁸ Gd(24.8%)	175M - 0,0006* ¹⁶⁰ Gd - 0,0048* ¹⁵⁹ Tb

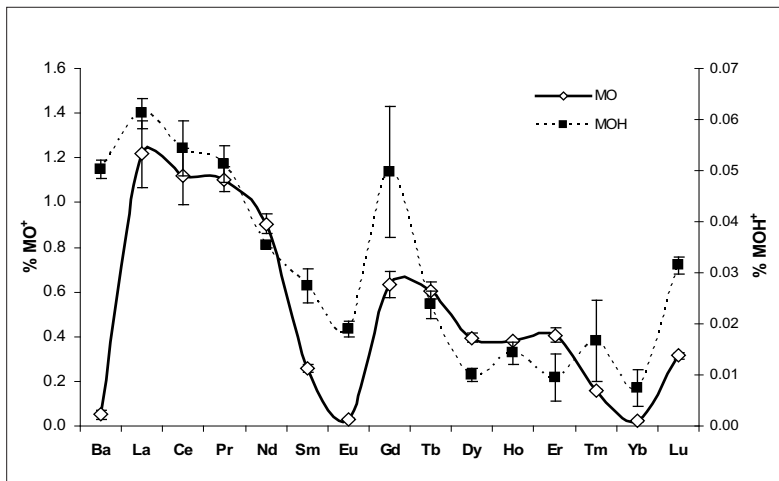
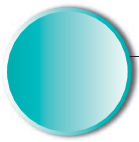


Figure 2
Percentages of oxide and hydroxide formation for the entire group of REE (values obtained with $0.88 \text{ L} \cdot \text{min}^{-1}$ for argon flow on the nebulizer).

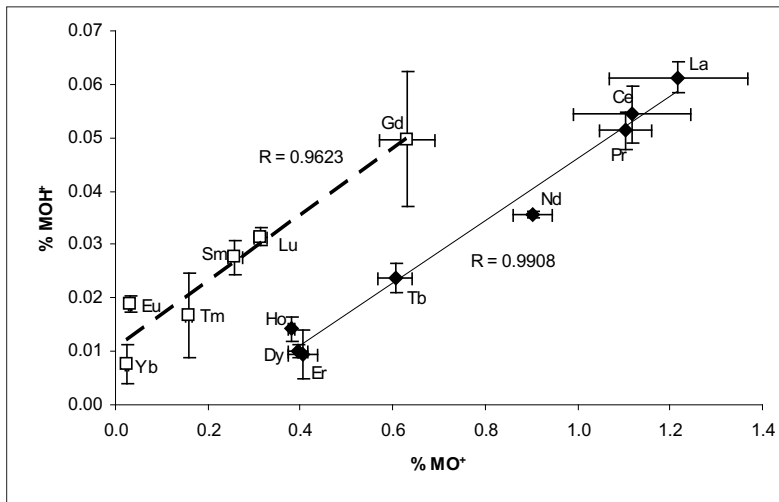


Figure 3
Relationship between the percentages of oxide and hydroxide formation for the entire group of REE.

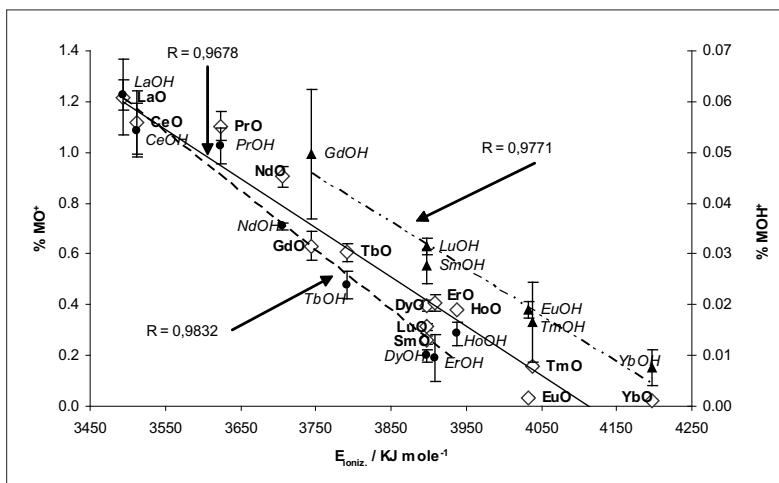


Figure 4
Variation on formation percentage of MO^+ and MOH^+ species with ionization energy of the REE ($E_{\text{ioniz}} = E_1 + E_2 + E_3$; see ref. (23)).

for all the studied elements. (2) The distribution for oxides is identical to the before reported data (14). (3) The formation degree of both polyatomic species (MO^+ and MOH^+) seems directly related with atomic number of each element (17).

The last conclusion does not mean, however, that the formation of MO^+ and MOH^+ follows the same mechanism. In fact, such a statement is only legitimated if experimental data for $\% \text{MO}^+$ versus $\% \text{MOH}^+$ presents a significant linear correlation for all the REE.

Figure 3 reveals the existence of two significant correlations, one for La, Ce, Pr, Nd, Tb, Dy, Ho and Er, and another for Sm, Eu, Gd, Tm, Yb and Lu, which possibly indicates the existence of several mechanisms, that controls the formation of both species. On the other hand, the observed REE separation in the two series may sustain, in our opinion, the hypothesis that the manifestation of oxides and hydroxides species is controlled by different parameters. Although such behaviour is not yet completely understood, the oxide formation seems to be directly dependent of element ionisation energies ($E_{\text{ionis.}} = E_{1\text{st}} + E_{2\text{nd}} + E_{3\text{rd}}$) while, for the hydroxides, its formation is enhanced for some REE of high ionisation energy, like Sm, Eu, Gd, Tm, Yb and Lu (figure 4).

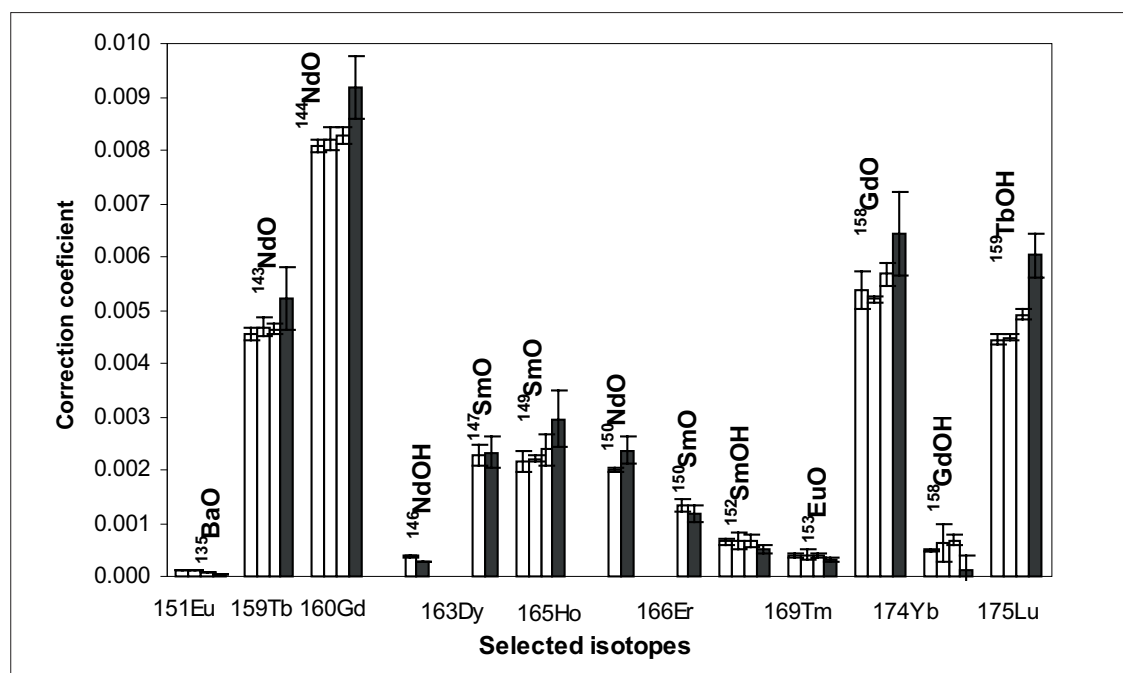
According to the results of this preliminary study, we have decided to use two elements to control these species formation. Monitoring CeO and GdOH, a properly optimization of the instrumental operation conditions is achieved when values for $\% \text{CeO}/\text{Ce} \leq 1.4$ and $\% \text{GdOH}/\text{Gd} \leq 0.06$ are obtained. Correction factors directly related to each oxide were also introduced in La and Ce selected isotopic masses to minimize the possible effects from oxides formation variability along the working day.

1. Correction coefficients

Coefficients for correction of oxide and/or hydroxide interferences were experimentally evaluated from the overcharges caused by single standard solutions of the different interfering elements on each isotopic mass that have been selected for quantification. These overcharges were evaluated in different routine situations, three of them in consecutive working days and the fourth, six months later, after a technical maintenance of the system.

The good agreement exhibited by the coefficient values (figure 5) confirms that small instrumental adjustments are not a source of important modification of MO^+ and MOH^+ species formation. As expected, small variations on coefficient values due to different cones and modifications on the argon pressure at the nebulizer have been observed. Nevertheless, these variations, in accordance with our accepted/rejected criteria, did not introduce any significant degradation on the analytical quality for RMs results.

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**Figure 5**

Mean values for the correction coefficient obtained in different analytical routine situations (□ in consecutive working days with 0.85 Lmin⁻¹ for argon flow on the nebulizer; ■ after cone change and 0.88 Lmin⁻¹ for argon flow on the nebulizer; | standard deviation). Several coefficients are the mean of the results obtained for three different concentrations of single standard solutions from each interfering element.

V – Detection and quantification limits

Detection and/or quantification capabilities of an analytical methodology may be inhibited by several analytical factors. Figures of merit quoted for any analytical technique usually include analyte detection limits, typically evaluated with dilute acid solutions. Obtained from three times the

standard deviation of acid blanks (3sB), these figures will represent the technique at its best and, for that reason, indicate the methodology potential for determination of very low elemental levels in samples.

However, for analytical purposes, the smallest amount that can be evaluated with an acceptable reproducibility, using a selected analytical methodology, is best represented by the quantification li-

Table IV

Detection and Quantification limits for the entire REE group (values obtained with a population of 61 sample blanks) and typical REE concentrations in three different types of rocks (see ref. (14)).

Element	in solution mg/L		in samples mg/kg	Concentration mg/kg		
	LD=3*sB	LQ=10*sB	LQ= 5000*10*sB	Basalts	Intermediate	Granites
La	0.062	0.19	1	6.1	31	55
Ce	0.197	0.6	3.3	16	60	104
Pr	0.011	0.04	0.2	2.7	7.4	12
Nd	0.11	0.34	1.8	14	31	47
Sm	0.018	0.06	0.3	4.3	6.2	8
Eu	0.016	0.05	0.3	1.5	1.3	1.1
Gd	0.016	0.05	0.3	6.2	6.8	7.4
Tb	0.011	0.04	0.2	1.1	1.1	1.1
Dy	0.011	0.04	0.2	5.9	6.1	6.2
Ho	0.013	0.04	0.2	1.4	1.5	1.5
Er	0.013	0.05	0.2	3.6	3.9	4.2
Tm	0.012	0.04	0.2	0.6	0.65	0.69
Yb	0.014	0.05	0.2	3.2	3.8	4.3
Lu	0.009	0.03	0.1	0.55	0.62	0.68



Element	BHVO-1 Basalt - USGS (n=4)					JB-3 Basalt - GSJ (n=7)					AC-E Granite-GIT-IWG (n=2)				
	Mean	stdev	RSD	Ref	M/ref	Mean	stdev	RSD	Ref	M/ref	Mean	stdev	RSD	Ref	M/ref
La	15.1	0.8	5.0	15.5	0.98	8.3	0.2	2.1	8.3	1.00	56.3	0.8	1.5	58.0	0.97
Ce	37.9	2.0	5.4	38.1	0.99	20.8	0.5	2.6	21	1.00	152.5	0.7	0.5	153	1.00
Pr	5.3	0.2	4.5	5.59	0.95	3.1	0.1	3.7	3.3	0.96	21.2	0.3	1.2	22.0	0.96
Nd	24.3	0.8	3.4	24.5	0.99	15.3	0.6	4.2	15.1	1.01	89.2	0.9	1.0	92.0	0.97
Sm	5.9	0.2	3.4	6.0	0.99	4.1	0.2	4.6	4.1	1.01	23.88	0.02	0.1	25.0	0.96
Eu	2.0	0.1	4.3	2.1	0.98	1.3	0.1	5.4	1.28	1.02	1.92	0.03	1.6	2.00	0.96
Gd	5.8	0.2	3.9	6.6	0.88	4.3	0.2	4.5	4.7	0.92	24.5	0.9	3.6	27.1	0.90
Tb	0.91	0.04	4.1	0.94	0.96	0.74	0.02	2.6	0.71	1.04	4.5	0.1	2.0	4.90	0.92
Dy	5.0	0.2	3.6	5.4	0.93	4.4	0.1	3.4	4.4	0.98	28.9	0.9	3.0	30.0	0.96
Ho	1.0	0.1	5.7	0.98	0.98	0.91	0.02	2.6	0.90	1.02	6.0	0.2	3.3	6.30	0.96
Er	2.4	0.1	4.9	2.55	0.94	2.5	0.1	3.6	2.6	0.97	17.1	0.3	1.7	19.0	0.90
Tm	0.33	0.02	6.6	0.34	0.97	0.40	0.06	15.1	0.38	1.06	2.59	0.02	0.7	2.70	0.96
Yb	1.9	0.1	3.7	2.1	0.92	2.5	0.1	4.4	2.44	1.02	16.9	0.4	2.1	17.90	0.94
Lu	0.27	0.02	8.3	0.28	0.98	0.39	0.05	12.6	0.37	1.05	2.32	0.05	2.1	2.50	0.93
Element	NIM-G Granite - MINTEK (n=4)					JGb-1 Gabro - GSJ (n=4)					JA-1 Andesito - GSJ (n=3)				
	Mean	stdev	RSD	Ref	M/ref	Mean	stdev	RSD	Ref	M/ref	Mean	stdev	RSD	Ref	M/ref
La	114.8	0.8	0.7	109	1.05	3.42	0.05	1.5	3.4	1.01	4.8	0.2	4.6	5.1	0.95
Ce	215.4	2.4	1.1	199	1.08	7.9	0.2	3.0	8	0.99	12.5	0.7	5.8	13.5	0.93
Pr	22.2	0.1	0.5	21.7	1.02	1.13	0.02	1.9	1.13	1.00	2.03	0.08	4.0	1.98	1.02
Nd	75.3	0.5	0.6	74	1.02	5.1	0.4	7.1	5.0	1.01	10.4	0.3	3.2	11.0	0.95
Sm	14.7	0.1	1.0	14.5	1.01	1.38	0.02	1.5	1.33	1.04	3.2	0.2	7.0	3.52	0.92
Eu	0.35	0.01	3.2	0.37	0.94	0.60	0.05	7.5	0.61	0.99	1.07	0.06	5.7	1.17	0.92
Gd	2.7	0.0	1.5	2.9	0.95	1.53	0.02	1.2	1.67	0.92	3.9	0.2	5.0	4.36	0.89
Tb	15.2	0.4	2.7	14.8	1.03	0.29	0.02	5.5	0.266	1.07	0.68	0.03	4.4	0.77	0.88
Dy	19.1	0.1	0.6	18.8	1.02	1.67	0.03	1.6	1.69	0.99	4.4	0.2	4.4	4.53	0.98
Ho	4.2	0.0	0.9	4.3	0.99	0.35	0.04	11.3	0.344	1.01	0.96	0.05	5.7	0.94	1.02
Er	13.6	0.1	1.0	14	0.97	0.97	0.05	5.4	1.00	0.97	2.8	0.2	5.7	3.01	0.93
Tm	2.16	0.02	1.0	2.09	1.03	0.13	0.02	16.6	0.14	0.90	0.42	0.03	7.1	0.48	0.86
Yb	14.6	0.2	1.7	14.4	1.01	0.91	0.08	9.3	0.91	1.00	2.8	0.2	5.9	2.92	0.95
Lu	2.11	0.04	1.9	2.11	1.00	0.14	0.02	13.2	0.139	1.03	0.42	0.02	4.8	0.47	0.89

Table V

Average values found for the analysed RMs without prior dryness (in mg/kg), relative standard deviations, reference values and M/ref ratios (n- number of independent digestions).

mit (10sB). For solid materials, these values must be recalculated into concentrations, taking in account the dilution factor of sample preparation (2).

Quantification limits were evaluated monitoring sample blank solutions over six months. Thus, the lower level of measurement for the developed methodology was estimated from a population of 61 independent values, obtained in very different routine situations. Quantification limits, although higher than chondritic abundances, potentially allow the quantification of the entire REE group

(table IV see previous page) in non-depleted geological materials.

VI – Results and discussion

Six well-characterized RMs, covering three of the most representative geological matrices, have been used for method development. In Table V, are represented analytical data and some statistic parameters obtained for these samples.

Essais interlaboratoires - un outil pour la validation d'une méthodologie analytique dédiée à la quantification de terres rares par ICP-MS

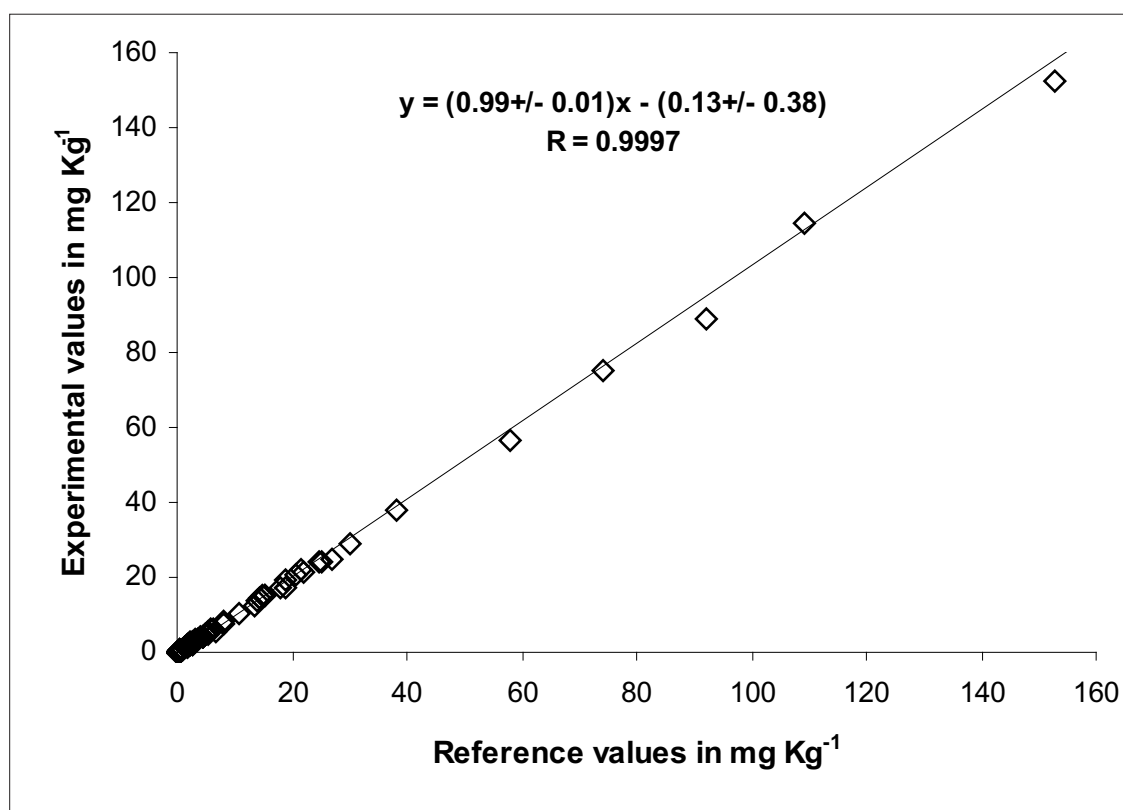


Figure 6

Correlation of REE between measured results obtained by Na_2O_2 sinter method and reference values for BHVO-1, JB-3, AC-E, NIM-G, JGb-1 and JA-1.

Relative standard deviation (RSD) values less than 5% were achieved for most elements with the described method. These values are evenly distributed and almost independent of REE concentrations. For some heavy REE poorer precisions were obtained (Tm and Lu in BHVO-1; Ho, Tm and Lu in JGb-1; Tm in JA-1). For such low-level measurement, close to the methodology quantification limits, RSD of about 15 % can be expected.

The agreement between our results and reference values are clearly illustrated in Figure 6. A high correlation was found (correl coef. = 0.9997) for the two data sets, which indicates that systematic errors have been minimized and that Na_2O_2 sintering is an efficient method for total decomposition of hard minerals. The accurate evaluation of correction coefficients for polyatomic interferences is also revealed, since all the experimental values fall on the line that represents exact agreement (slope = 1 and intercept = 0).

According to some authors (24) the percentage of recovery of the reference values calculated, as the ratio between laboratory results and reference values (M/ref), is an effective way to evaluate the accuracy of the data. In fact, analyte losses during decomposition step, matrix influence in quantification step and even the correction coefficient efficiency for minimization of polyatomic interferences may be studied in a semi-quantitative approach. For calculation of these ratios (M/ref) reference values from Dulski (2001) compilation and from Govindaraju (1994, for the Andesit JA-1) were used (25, 26).

For most of quantified REE ratios varying between 0.95 and 1.05 (figure 7 see next page) were obtained and recoveries within this range for light REE (La-Eu) have been achieved in all the six analysed MRs. For heavy REE these ratios lie between 0.90 and 1.10. Ratio values for Tb, Dy, Ho, Er, Tm, Yb and Lu seem straight connected to the amount of these elements in analysed samples, while a quotient systematically lower than 0.92 was observed for Gd.

MO^+ and MOH^+ polyatomic interferences are particularly significant for Gd and for minimizing their influence high correction coefficients must be used. In these circumstances, low recoveries may signify a possible use of inappropriate coefficients. Such hypothesis, however, needs a confirmation, by analysing Gd in a very wide type of matrices, before any attempt to change coefficient values or, even, the selected isotopic mass.

Data from RMs have been used to estimate accuracy and mean precision of the developed methodology (table VI see next page). In fact, a comparison with certified and/or literature values, acquired using different analytical methodologies, allows the demonstration of the accuracy obtained with the described method, while RSD(s) associated to the averages estimate the methodology reproducibility, since the results came from independently sample decompositions, different daily calibration curves and variable tuning parameters. The attained results for all REE are within the laboratory quality criteria

Prior to be launched in routine, this methodology has been submitted to a roughness test by

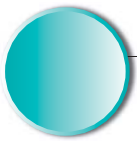
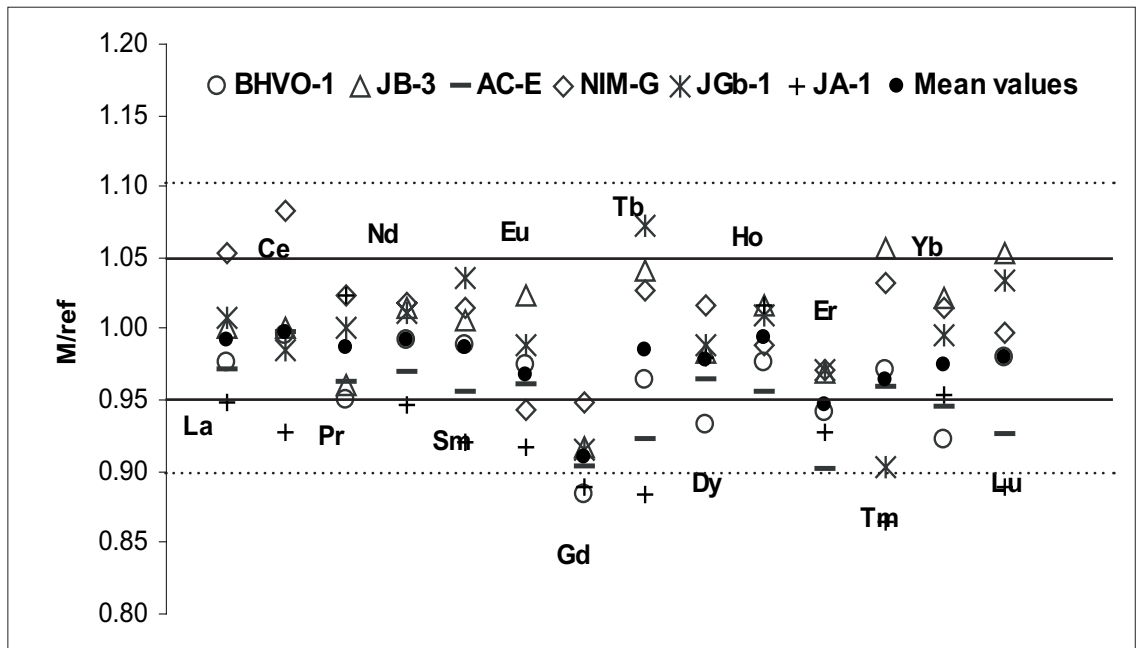


Figure 7
M/ref ratios obtained for the analyzed RMs (black circles represent the ratios mean value for each REE).



	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Precision (%)	2.6	3.0	2.6	3.3	2.9	4.6	3.3	3.5	2.8	4.9	3.7	7.9	4.5	7.2
(M/ref) mean	0.99	1.00	0.99	0.99	0.99	0.97	0.91	0.99	0.98	0.99	0.95	0.96	0.98	0.98

Table VI

Mean precision and accuracy for REE group quantified with the developed methodology.

analysing several distributions from Geopt proficiency-testing program as unknown samples. Geopt numbers 3, 4, 5, 6/1, 7, 8, 9, 10, 11 and 13 with a wide range of concentrations and a variety of geological matrices were selected for the test and REE quantification was made from a single decomposition, without previous sample dryness. To evaluate the analytical quality, Z-score was adopted as the appropriated parameter. Calculated according to the organization criteria for laboratories operating to pure geochemistry fitness-for-purpose (27), the results achieved for Z-score lie, without any exception, in +2 to -2 range (table VII), which means that our data agree quite well with the recommended reference values.

Nevertheless, the presence of a negative sign for most part of these Z-score values (table VIII see page 38), indicate the possible incidence of a small systematic error, probably due to the omitted drying operation before sample weighting. Actually, moisture will provide a false mass for the small aliquot weighed, which increases with the use of high dilution factors.

This hypothesis is sustained by the results obtained in Geopt13, a sample without a store period, for which Z-score values do not exhibit any particularly tendency (figure 8 see page 38).

VII – Conclusions

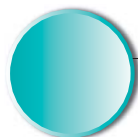
The potentialities of the developed methodology for the quantification of REE were fully explored by analysing very different types of geological matrices. Results with appropriate analytical quality for further petrogenetic studies were always attained. Our initial intent of setting up a robust and practical analytical method for routine analysis has been accomplished therefore.

Since indoor results intercomparisons for REE obtained with other analytical techniques were not possible, the use of geological Reference Materials revealed to be an essential tool to evaluate the performance degree of the several options that have been made and, therefore, to achieve a robust methodology.

Our laboratory has been participating in the GeoPT proficiency-testing scheme since 1996. This participation and the analysis of various samples from the Geopt program have contributed to the enlargement of analysed matrices and, therefore, an accurate checking of methodology capabilities, to provide REE results with good analytical quality for very different types of non-depleted geological materials.

Essais interlaboratoires - un outil pour la validation d'une méthodologie analytique dédiée à la quantification de terres rares par ICP-MS

Geopt 3				Geopt 4			Geopt 5			Geopt 6/1																								
Element	VREF ^a	Target Precision	VEXP.	VREF ^a	Target Precision	VEXP.	VREF ^a	Target Precision	VEXP.	VREF ^a	Target Precision	VEXP.																						
La	63.40	2.72	61.06	27.71	1.34	26.20	15.87	2.45	15.63	94.64	3.82	85.72																						
Ce	129.5	4.98	131.86	60.2	2.6	59.35	33.03	4.7	33.26	196.34	7.09	194.00																						
Pr	15.01	0.80	14.67	7.92	0.46	7.62	4.21	0.3	4.14	22.7	1.13	22.28																						
Nd	56.66	2.47	54.33	33.35	1.57	32.30	17.69	2.21	16.74	87.0	3.55	82.80																						
Sm	11.44	0.63	10.85	8.7	0.5	8.20	3.68	0.28	3.43	18.72	0.96	17.44																						
Eu	1.63	0.12	1.61	2.23	0.16	2.21	1.16	0.09	1.14	1.15	0.09	1.15																						
Gd	10.85	0.61	9.70	7.26	0.43	6.48	3.34	0.22	3.04	18.07	0.94	16.62																						
Tb	1.71	0.13	1.62	1.11	0.09	1.04	0.51	0.05	0.49	3.08	0.21	2.99																						
Dy	9.93	0.56	9.37	6.09	0.37	5.82	2.84	0.29	2.58	18.87	0.97	18.90																						
Ho	1.96	0.14	1.83	1.21	0.09	1.14	0.57	0.09	0.54	4.01	0.26	3.92																						
Er	5.30	0.33	5.00	3.06	0.21	2.84	1.52	0.15	1.37	11.45	0.63	11.33																						
Tm	0.74	0.06	0.70	0.427	0.039	0.38	0.21	0.01	0.19	1.73	0.13	1.72																						
Yb	4.73	0.30	4.54	2.52	0.18	2.36	1.37	0.14	1.28	11.37	0.63	11.27																						
Lu	0.69	0.06	0.66	0.372	0.035	0.35	0.21	0.02	0.21	1.63	0.12	1.59																						
Geopt 7				Geopt 8			Geopt 9			Geopt 10																								
Element	VREF ^a	Target Precision	VEXP.	VREF ^a	Target Precision	VEXP.	VREF ^a	Target Precision	VEXP.	VREF ^a	Target Precision	VEXP.																						
La	52.95	2.33	50.73	24.96	1.23	24.26	33	1.56	31.63	31.10	1.48	30.87																						
Ce	103.2	4.1	101.7	55.7	2.4	55.9	74.42	3.11	77.28	60.5	2.6	61.45																						
Pr	11.45	0.63	11.46	6.85	0.41	6.70	7.8	0.46	7.76	7.07	0.42	6.86																						
Nd	43.3	1.96	41.47	27.9	1.35	27.1	29.01	1.4	28.86	26.24	1.28	25.71																						
Sm	6.79	0.41	6.38	6.94	0.41	6.66	5.92	0.36	5.67	5.04	0.32	4.87																						
Eu	1.79	0.13	1.72	1.64	0.12	1.57	1.36	0.1	1.33	1.029	0.082	1.02																						
Gd	4.74	0.3	4.25	7.39	0.44	6.82	5.27	0.33	4.85	4.39	0.28	4.06																						
Tb	0.6	0.05	0.59	1.25	0.1	1.22	0.85	0.07	0.83	0.675	0.057	0.68																						
Dy	3.26	0.22	3.05	7.81	0.46	7.37	4.99	0.31	4.70	3.88	0.25	3.85																						
Ho	0.69	0.06	0.67	1.63	0.12	1.57	1.01	0.08	0.95	0.796	0.066	0.80																						
Er	2.01	0.14	1.94	4.83	0.3	4.52	2.98	0.2	2.78	2.15	0.15	2.19																						
Tm	0.3	0.03	0.29	0.72	0.06	0.66	0.44	0.04	0.42	0.325	0.031	0.33																						
Yb	2.03	0.15	2.03	4.7	0.3	4.42	3.0	0.2	2.93	2.09	0.15	2.15																						
Lu	0.31	0.03	0.32	0.71	0.06	0.66	0.45	0.04	0.44	0.316	0.03	0.34																						
Geopt 11				Geopt 13			Table VII <i>Results obtained in a single decomposition without previous sample drying for several geological samples from the Geopt Program (concentrations in mg.kg⁻¹).</i> <table border="1" style="margin-top: 10px;"> <thead> <tr> <th>Designation</th> <th>Lithologic type</th> </tr> </thead> <tbody> <tr><td>Geopt 3</td><td>Yewrangara Granite</td></tr> <tr><td>Geopt 4</td><td>Bamford Dolerite</td></tr> <tr><td>Geopt 5</td><td>USGS andesite</td></tr> <tr><td>Geopt 6/1</td><td>Nahoron Microgranite</td></tr> <tr><td>Geopt 7</td><td>Garnet-biotite-plagionesse</td></tr> <tr><td>Geopt 8</td><td>Penmaenmawr microdiorite</td></tr> <tr><td>Geopt 9</td><td>Penrhyn Slate</td></tr> <tr><td>Geopt 10</td><td>Marine sediment</td></tr> <tr><td>Geopt 11</td><td>Leaton Dolerite</td></tr> <tr><td>Geopt 13</td><td>Köln Loess</td></tr> </tbody> </table>						Designation	Lithologic type	Geopt 3	Yewrangara Granite	Geopt 4	Bamford Dolerite	Geopt 5	USGS andesite	Geopt 6/1	Nahoron Microgranite	Geopt 7	Garnet-biotite-plagionesse	Geopt 8	Penmaenmawr microdiorite	Geopt 9	Penrhyn Slate	Geopt 10	Marine sediment	Geopt 11	Leaton Dolerite	Geopt 13	Köln Loess
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Geopt 13	Köln Loess																																	
Element	VREF ^a	Target Precision	VEXP.	VREF ^a	Target Precision	VEXP.																												
La	18.1	0.94	17.99	25.54	1.25	25.7																												
Ce	44.17	2	44.31	53.00	2.32	53.4																												
Pr	6.29	0.38	6.18	6.24	0.38	6.3																												
Nd	28.47	1.38	29.05	24.32	1.20	24.5																												
Sm	7.64	0.45	7.45	5.01	0.31	4.9																												
Eu	2.35	0.17	2.39	0.888	0.072	0.89																												
Gd	8.64	0.5	8.25	4.465	0.285	4.5																												
Tb	1.46	0.11	1.43	0.687	0.058	0.70																												
Dy	9.04	0.52	8.85	4.02	0.26	4.2																												
Ho	1.92	0.14	1.88	0.80	0.07	0.85																												
Er	5.49	0.34	5.21	2.382	0.167	2.5																												
Tm	0.789	0.065	0.77	0.339	0.032	0.38																												
Yb	5.1	0.32	4.99	2.42	0.169	2.4																												
Lu	0.767	0.064	0.75	0.370	0.034	0.38																												



Element	Geopt 3	Geopt 4	Geopt 5	Geopt 6/1	Geopt 7	Geopt 8	Geopt 9	Geopt 10	Geopt 11	Geopt 13
La	-0.86	-1.12	-0.10	-2.33	-0.95	-0.57	-0.88	-0.16	-0.12	0.13
Ce	0.47	-0.33	0.05	-0.33	-0.37	0.09	0.92	0.37	0.07	0.17
Pr	-0.42	-0.65	-0.23	-0.37	0.02	-0.36	-0.08	-0.50	-0.30	0.16
Nd	-0.94	-0.67	-0.43	-1.18	-0.93	-0.57	-0.11	-0.41	0.42	0.15
Sm	-0.93	-1.00	-0.89	-1.34	-0.99	-0.68	-0.69	-0.54	-0.41	-0.35
Eu	-0.20	-0.13	-0.20	-0.05	-0.50	-0.57	-0.31	-0.05	0.23	0.03
Gd	-1.88	-1.82	-1.37	-1.54	-1.64	-1.30	-1.28	-1.18	-0.78	0.12
Tb	-0.73	-0.79	-0.42	-0.42	-0.16	-0.29	-0.26	0.02	-0.28	0.22
Dy	-0.99	-0.73	-0.89	0.03	-0.97	-0.95	-0.94	-0.13	-0.36	0.69
Ho	-0.89	-0.79	-0.30	-0.35	-0.30	-0.49	-0.77	0.09	-0.32	0.71
Er	-0.91	-1.07	-0.99	-0.19	-0.50	-1.04	-1.02	0.29	-0.83	0.71
Tm	-0.70	-1.13	-1.57	-0.07	-0.23	-0.94	-0.54	0.16	-0.27	1.28
Yb	-0.63	-0.88	-0.66	-0.16	-0.03	-0.94	-0.35	0.37	-0.34	-0.12
Lu	-0.54	-0.68	-0.25	-0.34	0.44	-0.77	-0.26	0.64	-0.32	0.29

Table VIII

Values for Z-score parameter evaluated for target precision figuring in table 7. These values have been calculated with a Horwitz function modification ($h(a)=0,01.(Xa)^{0,8495}$, Xa robust mean of participants).

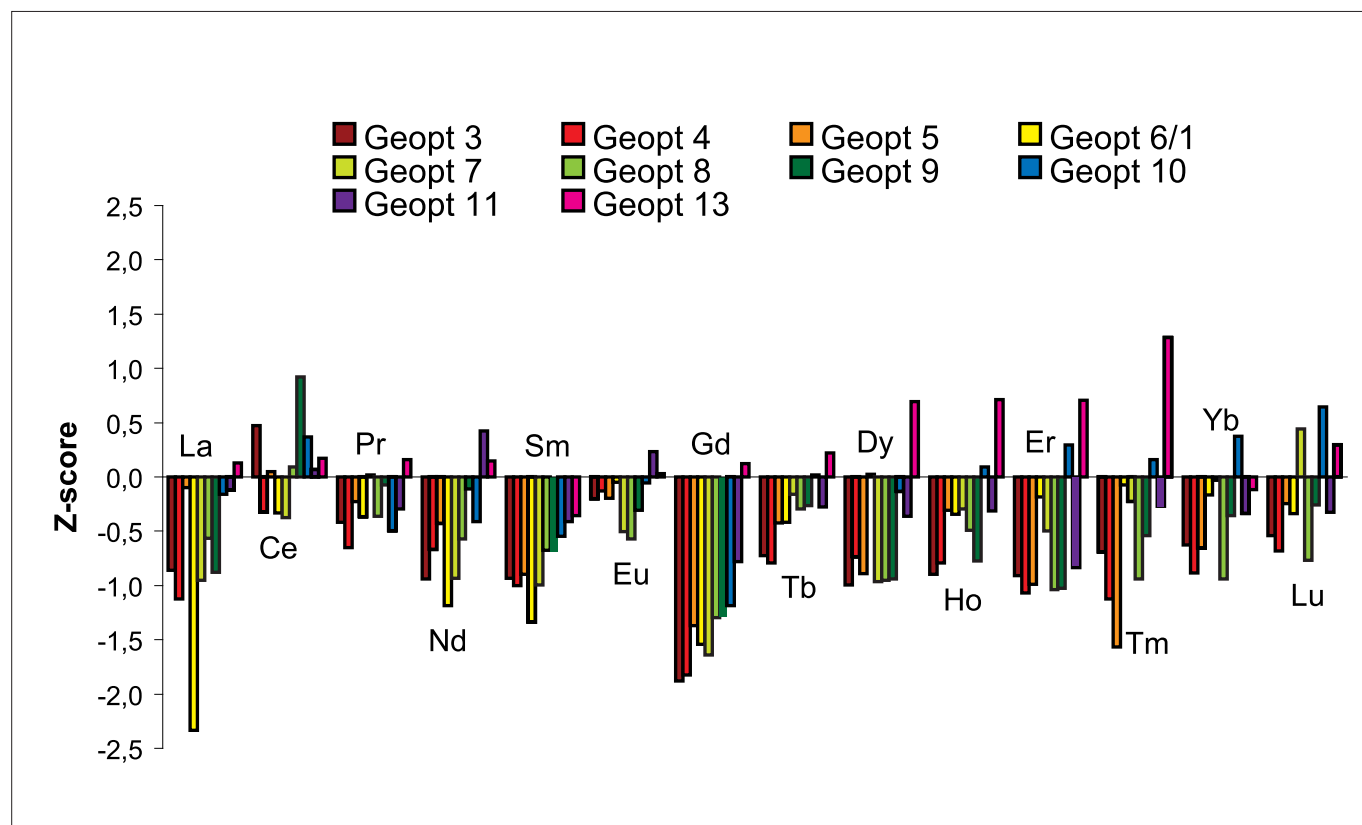


Figure 8

Z-score distribution of all REE group for ten samples of the Geopt proficiency-testing program.

Essais interlaboratoires - un outil pour la validation d'une méthodologie analytique dédiée à la quantification de terres rares par ICP-MS

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