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Neutron Activation Analysis: a Powerful Tool for Assay of Rare-Earth Elements in Terrestrial Materials

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Neutron activation analysis methods for determination of rare-earth elements in different matrices have been developed at the University of Pavia using the 250 Kw TRIGA Mark II reactor. A critical review of both instrumental and destructive methods is presented, as well as the indication of the best working conditions for irradiation, counting and radiochemical separations. The optimized procedures were utilized in the determination of rare-earth elements in standard reference materials of both mineral and biological origin. The adopted radiochemical procedure is based on the separation of the rare-earth element group by fluoride precipitation.

Results, given as the average of six independent determinations and relative standard deviations, are reported and discussed. Precision of the methods can be deduced from the reproducibility of data, whereas accuracy is evaluated by comparison with existing values in the literature. Sensitivity limits under the described operational conditions are also reported, as are trends and correlations among data.

Introduction

A growing interest is being addressed in the literature to rare-earth elements (REE) on account of their physical, chemical and technological properties. In geochemical systems the knowledge of REE abundance and distribution has been very helpful in defining patterns and trends in the genesis of igneous rocks, the sequence of mineral crystallization, water–mineral interactions, and weathering and hydrothermal alteration of rocks [1–5]. In biological systems REE are known to accumulate in some plants and in mammalian bones and liver [6], to exhibit characteristic distribution patterns and may also provide useful information on the behaviour in the environment of transuranic elements having similar chemical properties [6–8]. An increasing use of rare-earth metals and compounds is being made in chemical, metallurgical, laser, nuclear and electronics industries because of their, optical, magnetic, refractory and mechanical properties.

The enhancement of the peculiar properties of REE has required a great deal of research work. Among chemical investigations, great effort has been devoted to the development of reliable analytical techniques capable of providing accurate data on REE concentrations in terrestrial materials.

Neutron activation analysis is, at the moment, the most used technique for the determination of rare-earth elements on account of its high sensitivity, of the possibility of determining all the elements, and of the undisputed accuracy and reliability of its results [7–13]. Both instrumental (INAA) and radiochemical (RNAA) techniques may be applied, but when the content of all the REE is required the use of destructive methods is compulsory.

The literature reports several separation schemes for the rare-earths, such as solvent extraction, ion-exchange, adsorption on inorganic materials, precipitation, complexation, and high pressure liquid chromatography. The choice of the fluoride precipitation method adopted in the present work is mainly based on the following favorable features: it is simple and rapid; it is applicable to different types of terrestrial samples, either mineral or biological; it conveniently separates the rare-earth group from interfering elements such as scandium, alkaline and alkaline-earth elements; it allows the determination of all the rare-earth elements.

Experimental

Analyzed Materials

The following standard materials were analyzed:
1 - SRM 278, Obsidian rock, provided by U.S. NBS
2 - SRM 1632, Coal, provided by U.S. NBS·

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3 - SRM 1633, Fly Ash, provided by U.S. NBS
4 - SRM 1571, Orchard Leaves, provided by U.S. NBS
5 - NIM G, granite, standard rock provided by National Institute of Metallurgy (South Africa).

Usually 0.5 g samples of Obsidian rock, Fly Ash and NIM G, and 1 g samples of Coal and Orchard Leaves were inserted into polyethylene vials for irradiation.

Reference Standard

A nitric acid solution of the rare-earth elements was used as reference standard. The concentrations of REE in the final solution were in the same ratio as in chondrites [14]. Aliquots of this solution were irradiated with the standard materials samples.

Choice of the Nuclear Reaction

The absolute abundance of rare-earth elements in the solar system is a function of the atomic number: the characteristic saw-toothed pattern reflects the favoured conditions of even numbered nuclides during nucleosynthesis.

The distribution of stable nuclides among REE is the following: five elements (Nd, Sm, Gd, Dy, Yb) with 7 nuclides; four elements (Pr, Tb, Ho, Tm) with 1 nuclide; three elements (La, Eu, Lu) with 2 nuclides; one element (Er) with 6 nuclides and one element (Ce) with 4 nuclides.

The choice of the proper nuclear reaction to be induced by thermal neutrons depends upon the abundance of stable nuclides, their activation cross-sections and the half-life of formed radionuclides. No choice can be made with only 1 stable nuclide; in the other cases not all the stable nuclides are suitable for activation purposes, as they yield another stable nuclide. By taking into account the above cited parameters and the possible interferences in activation and gamma-ray spectrometry, the (n, γ) nuclear reactions reported in Table I have been chosen in the present investigation. Table I also gives some nuclear characteristics of the rare-earth elements.

Irradiation and Cooling

Irradiations were carried out at the 250 Kw Triga Mark II reactor of the University of Pavia.

In the instrumental procedure all standard materials samples (except Orchard Leaves) were irradiated for 20 hours at a thermal flux of about 1×10^{12} n cm^{-2} s^{-1}. Orchard Leaves samples were irradiated for 20 hours at a thermal flux of about 8×10^{12} n cm^{-2} s^{-1}.

After irradiation, samples and reference standards were left to decay for 7 days before counting, which was repeated 15 and 30 days after the end of irradiation.

In the radiochemical procedure all standard materials samples, except Orchard Leaves, were first irradiated for 12 hours at a thermal flux of about 1×10^{12} n cm^{-2} s^{-1}; a second irradiation of 5 minutes was carried out at the end of the radiochemical procedure for the determination of short-lived radionuclides and the evaluation of the chemical yield, at a thermal flux of about 2×10^{12} n cm^{-2} s^{-1}. The Orchard Leaves first irradiation was carried out for 10 hours at a thermal flux of about 8×10^{12} n cm^{-2} s^{-1}, and the second one for 40 minutes at a thermal flux of about 2×10^{12} n cm^{-2} s^{-1}.

After the first irradiation, samples and reference standards were left to decay for 3 days before being processed; after the second irradiation the samples were left to decay for 30 minutes before being submitted to gamma-ray spectrometry.

TABLE I. Nuclear Data on Rare-Earth Elements.

Element	Abundance of stable nuclide (%)	Activation cross-section (barn)	Produced Radionuclide	Half-life	Measured gamma-ray Energy (KeV) and relative intensities
La	99.9	8.9	140-La	1.68 d	1595(100), 487(48)
Ce	88.48	0.6	141-Ce	32.5 d	145(100)
Pr	100	12	142-Pr	19.2 h	1576(100)
Nd	17.18	2	147-Nd	11.1 h	91(100), 531(45)
Sm	26.63	210	153-Sm	1.96 d	103(100), 69.6(20)
Eu	47.7	5900	152-Eu	12.2 y	344(100), 1408(90)
Gd	0.2	125	153-Gd	236 d	98(100)
Tb	100	46	160-Tb	73 d	879(100)
Dy	28.18	800	165-Dy	2.36 h	95(100)
Ho	100	1	166m-Ho	30 y	184(100), 810(66)
Er	14.9	9	171-Er	7.8 h	308(100), 296(42)
Tm	100	125	170-Tm	129 d	84(100)
Yb	0.14	11000	169-Yb	32.6 d	64(100), 198(85)
Lu	2.6	2100	177-Lu	6.75 d	208(100)

Radioactivity Measurements

Induced activity was measured by gamma-ray spectrometry using a 18% efficiency Ge(Li) detector coupled to an analyzer-computer system.

Special care must be addressed to the choice of the proper gamma peak in order to minimize interference. Interferences may derive from the radionuclides of matrix macro- and microconstituents and to the overlapping of gamma peaks from REE radionuclides. The latter is not overcome by the radiochemical group separation of rare-earth elements.

Attention must also be paid to the matrix uranium content: interferences may derive from the fact that some REE radionuclides are simultaneously produced by activation and fission nuclear reactions.

The gamma rays utilized in the present paper, reported in the last column of Table I, have been chosen by taking into account the characteristics of the apparatus used, half-lives of the radionuclides, peak intensities, detector resolution, and the probability of interfering elements being present.

The determination of 7 elements, namely Pr, Eu, Gd, Dy, Ho (184 KeV), Er and Lu, is free from interferences. For La and Ce, interferences occur only in the case of high uranium content. Terbium determination is free from interferences in the radiochemical procedure, whereas the presence of ^{110m}Ag may interfere in the instrumental method. Neodymium-147 activity may be satisfactorily measured after 15 days cooling in the instrumental method, whereas in the radiochemical method a potential but often not significant interference due to ^{169}Yb may be predicted. Samarium activity measurement has to be accomplished within 10 days after the end of irradiation, otherwise a potential interference due to ^{153}Gd (103 KeV) becomes relevant. Interferences due to ^{160}Tb, still not significant, may be predicted in the measurement of ^{170}Tm and ^{169}Yb activities. The latter, however, exhibits the 64 KeV gamma peak, which is free from interference.

Radiochemical Procedure

The irradiated samples, after the decay period, were transferred to a nickel crucible and known amounts (10 mg) of scandium and rare-earth elements (except La, Pr, Nd, Dy and Er) added as carriers. The mixture was then submitted to a basic attack with Na_2O_2 and NaOH in an oven at 380 °C. Soluble silicates were removed from the fused mass by leaching with distilled water. After centrifugation the fused mass was dissolved with 8 *M* HCl solution. The precipitation of rare-earth fluorides was carried out by adding a mixture of 50% HF and 10% NH_4F solutions together with a La^{3+} carrier solution. The fluorides were separated, dissolved with a HNO_3 solution and boric acid saturated solution, and again precipitated as described above without La^{3+} carrier addition. The fluorides were then dissolved as described and brought to a 25 cm^3 volume: an 21 cm^3 aliquot was used for radioactivity measurement and the remaining 4 cm^3 were re-irradiated together with the rare-earth elements reference standard and carrier solutions for the determination of Pr, Nd, Dy and Er and the evaluation of the chemical yield.

Results and Discussion

The rare-earth concentrations in the investigated standard materials are reported in Tables II–VI. They are the average of 6 independent determinations, and are given together with the standard deviation.

TABLE II. Rare-Earth Content (μg/g) of the NBS-SRM 278 'Obsidian Rock'.

Element	This work		Previous
	INAA	RNAA	
La	37.6 ± 0.8	37.8 ± 0.8	27.59[b]; 35.4[c]; 35.8[d]
Ce	54.5 ± 2.2	55.8 ± 0.3	62.2[a]; 56.5[b]; 59.4[c]; 66.5[d]
Pr	–	7.48 ± 0.08	–
Nd	29.5 ± 0.31	33.50 ± 0.02	28.2[c]
Sm	5.85 ± 0.09	5.80 ± 0.03	5.2[a]; 5.69[c]; 5.70[d]
Eu	0.83 ± 0.02	0.78 ± 0.02	0.84[a]; 0.82[b]; 0.764[c]; 0.795[d]
Gd	5.65 ± 0.07	5.70 ± 0.03	5.3[a]; 5.34[b]; 5.28[d]
Tb	1.11 ± 0.1	1.81 ± 0.03	1.0[a]; 1.23[b]; 1.14[c]; 1.12[d]
Dy	6.2 ± 0.1	6.51 ± 0.2	–
Ho	1.23 ± 0.06	1.20 ± 0.04	–
Er	–	3.66 ± 0.07	–
Tm	0.40 ± 0.02	0.33 ± 0.03	0.30[b]; 4.54[c]
Yb	4.79 ± 0.04	5.04 ± 0.08	4.5[a]; 3.58[b]; 5.09[d]
Lu	0.947 ± 0.002	0.934 ± 0.002	0.72[a]; 0.745[b]; 0.836[c]; 0.820[d]

[a] Ref. [15]; [b] ref. [16]; [c] ref. [17]; [d] ref. [18].

TABLE III. Rare-Earths Content (μg/g) of the NBS-SRM 1632 'Coal'.

Element	This work		Previous
	INAA	RNAA	
La	11.4 ± 0.4	10.8 ± 0.3	10.7[a]; 7.89[b]; 11.3[c]; 11.4[d]; 10.5[e]
Ce	20.4 ± 0.3	20.6 ± 0.2	19.5[a]; 19.6[e]
Pr	–	4.9 ± 0.5	–
Nd	9.7 ± 0.4	9.9 ± 0.4	–
Sm	1.7 ± 0.3	1.8 ± 0.1	1.7[a]; 1.66[b]; 1.8[c]; 1.38[d]; 1.66[e]
Eu	0.34 ± 0.05	0.35 ± 0.03	0.33[a]; 0.37[b]; 0.41[c]; 0.299[d]; 0.34[e]
Gd	3.0 ± 0.9	3.1 ± 0.2	–
Tb	0.31 ± 0.04	0.34 ± 0.02	0.23[a]; 0.23[e]
Dy	1.2 ± 0.2	1.1 ± 0.1	1.38[b]; 1.3[c]; 1.12[d]; 1.45[e]
Ho	0.26 ± 0.03	0.27 ± 0.04	0.24[d]
Er	–	9.3 ± 0.2	–
Tm	0.30 ± 0.04	0.30 ± 0.02	–
Yb	0.81 ± 0.04	0.79 ± 0.02	0.7[a]; 0.78[e]
Lu	0.13 ± 0.02	0.14 ± 0.03	0.14[a]; 0.13[e]

[a] Ref. [14]; [b] ref. [20]; [c] ref. [21]; [d] ref. [22]; [e] ref. [23].

TABLE IV. Rare-Earths Content (μg/g) of the NBS-SRM 1633 'Fly Ash'.

Element	This work		Previous
	INAA	RNAA	
La	85 ± 3	84 ± 2	82[a]; 79[b]; 74[c]; 64[d]; 84.3[e]
Ce	153 ± 4	153 ± 6	146[a]; 154[b]; 152[c]; 149[e]
Pr	–	92 ± 1	–
Nd	69 ± 4	67 ± 2	64[b, c, e]
Sm	12.9 ± 0.3	12.3 ± 0.4	12.4[a]; 13.6[d]; 12.6[e]
Eu	2.72 ± 0.07	2.8 ± 0.3	2.5[a]; 2[b]; 2.6[c]; 2.74[e]
Gd	11.9 ± 0.2	11.6 ± 0.1	–
Tb	2.4 ± 0.1	2.5 ± 0.1	1.9[a]; 2.0[b]; 2.62[c]; 2.1[d]; 1.98[e]
Dy	9.1 ± 0.1	9.0 ± 0.1	10.9[e]
Ho	1.99 ± 0.07	1.98 ± 0.01	–
Er	–	89 ± 3	–
Tm	1.43 ± 0.04	1.36 ± 0.02	–
Yb	6.8 ± 0.1	6.77 ± 0.06	7[a]; 6.5[e]
Lu	1.68 ± 0.06	1.56 ± 0.01	1.0[a]; 0.98[e]

[a] Ref. [19]; [b] ref. [24]; [c] ref. [25]; [d] ref. [20]; [e] ref. [23].

Average precision in the instrumental method is about 9%, with some unusually high values as for Gd content in NBS-SRM 1632 'Coal' (30%), La and Ce content in NBS-SRM 1571 'Orchard Leaves' (26 and 33% respectively), and Eu content in NIM G (25%).

Average precision in the radiochemical method is about 5%: also in this method there are some high values as in the case of Lu content in NBS-SRM 1632 'Coal' (21%), and La, Ce and Yb content in NBS-SRM 1571 'Orchard Leaves' (14, 14 and 18.5% respectively).

The results obtained by INAA and RNAA agree quite well within experimental error, except for Nd and Tb content in NBS-SRM 278 'Obsidian rock' and for Nd and Tm content in NIM G. An evaluation of the accuracy may be obtained by comparing the data reported in the present paper with the existing values in the literature (last column of Tables II–VI): it is possible to observe a general agreement within experimental error. Minor discrepancies occur: i) for NBS-SRM 278 'Obsidian rock' in the case of La and Yb content reported by Ammad *et al.* [16], and Lu content [15–18]; in the latter case the obtained values appear to be somewhat higher; ii) for NBS-SRM 1632 'Coal' in the case of La content reported by Nadkarni [20], and Tb content reported by Ondov *et al.* [19] and Nadkarni [23]; iii) for NBS-SRM 1633 'Fly Ash' in the case of La content reported by NBS Certificate of Analysis [25], and by Nadkarni [20], Eu content reported by Gladney *et al.* [24], Tb

TABLE V. Rare-Earths Content (ng/g) of the NBS-SRM 1571 'Orchard Leaves'.

Element	This work		Previous
	INAA	RNAA	
La	1270 ± 330	1440 ± 200	$1200^{a,b}$; 1000^{c}
Ce	1250 ± 410	1280 ± 180	1000^{a}; 900^{c}
Pr	–	65 ± 3	60^{a}; 230^{c}
Nd	407 ± 20	423 ± 9	400^{a}; 570^{c}
Sm	–	114 ± 1	110^{a}; 100^{c}
Eu	–	91 ± 5	90^{a}; 300^{b}; 21^{c}
Gd	–	12 ± 1	$1.64–100^{a}$; 100^{c}
Tb	–	72 ± 6	$1.2–80^{a}$; 13^{c}
Dy	–	80 ± 7	81^{a}
Ho	–	22 ± 2	20^{a}; 13^{c}
Er	–	31 ± 4	$<100^{c}$
Tm	–	7.0 ± 0.5	7^{a}; $<10^{c}$
Yb	–	27 ± 5	27^{a}; 33400^{b}; 25^{c}
Lu	–	8.4 ± 0.7	$6.1–10^{a}$; 60^{b}; 3.3^{c}

^{a}Ref. [26]; ^{b}ref. [27]; ^{c}ref. [28].

TABLE VI. Rare-Earths Content (μg/g) of the South Africa granite NIM G.

Element	This work		Previous
	INAA	RNAA	
La	103 ± 5	107 ± 3	115^{a}; 119^{b}; 114^{c}; 114^{d}
Ce	190 ± 3	195 ± 3	224^{b}; 195^{e}; 190^{f}; 192^{c}; 216^{g}
Pr	–	21.4 ± 0.9	19.8^{a}; 21^{c}
Nd	85 ± 3	73 ± 2	71^{g}; 67^{a}; 72^{c}; 110^{f}
Sm	19.4 ± 0.8	17.3 ± 0.4	18^{g}; 14.6^{a}; 16.7^{c}; 13^{f}
Eu	0.4 ± 0.1	0.43 ± 0.2	0.4^{f}; 0.41^{a}; 0.47^{b}; 0.39^{c}
Gd	13.2 ± 0.3	12.1 ± 0.3	11^{a}; 11^{b}; 17.2^{c}; 13.8^{f}
Tb	2.87 ± 0.06	2.9 ± 0.3	1.9^{a}; 2.1^{c}
Dy	15.4 ± 0.7	17.1 ± 0.6	17^{g}; 15.4^{a}; 15.9^{c}
Ho	2.9 ± 0.2	3.0 ± 0.2	5^{g}; 3.0^{a}; 4.6^{c}
Er	–	9.4 ± 0.3	13.5^{g}; 9.6^{a}; 13.7^{c}
Tm	1.66 ± 0.07	1.91 ± 0.03	1.9^{g}; 1.6^{a}; 1.91^{c}
Yb	10.6 ± 0.5	11.5 ± 0.4	12.2^{g}; 12.8^{a}; 13^{c}; 14.2^{d}; 12.6^{e}; 12.8^{f}
Lu	1.49 ± 0.06	1.54 ± 0.04	1.58^{a}; 1.59^{c}

^{a}Ref. [29]; ^{b}ref. [30]; ^{c}ref. [31]; ^{d}ref. [32]; ^{e}ref. [33]; ^{f}ref. [34]; ^{g}ref. [35].

content reported by Ondov *et al.* [19], Dy content reported by Nadkarni [23] and Lu content reported by Ondov *et al.* [19] and Nadkarni [23]; iv) for NBS-SRM 1571 'Orchard Leaves' in the case of Lu content reported by Nadkarni *et al.* [27] and by Laul *et al.* [28]; for NIM G in the case of Ce content reported by Pol *et al.* [30] and by Sen Gupta [34], Nd and Sm content reported by Sen Gupta [35], Gd content reported by Voldet *et al.* [31], Tb content reported by Strelow *et al.* [29] and by Voldet *et al.* [31], Ho, Er and Tm content reported by Voldet *et al.* [31] and by Sen Gupta [35], Tm content reported by Strelow *et al.* [29] and Yb content reported by Steele *et al.* [32].

Few major discrepancies occur in the case of Tm content of NBS-SRM 278 'Obsidian Rock' reported by Graham *et al.* [17] and for NBS-SRM 1571 'Orchard Leaves' in the case of Pr, Nd, Eu, Gd and Ho content reported by Laul *et al.* [28] and of Eu, Yb and Lu content reported by Nadkarni *et al.* [27]. The occurence of large discrepancies for 'Orchard Leaves' may be ascribed to the very low REE abundance (quite close to the sensitivity limits of the used analytical methods) and, in some cases, to contamination.

As already mentioned, a possible source of error in the determination of rare-earth elements is the presence of significant amounts of fissile nuclides

TABLE VII. Sensitivities for Rare-Earth Elements with Instrumental and Radiochemical Neutron Activation Analysis.

Element	Radionuclide used	Measured gamma ray (KeV)	Sensitivity (μg)*	
			INAA	RNAA
La	140-La	1595	2E-3	8E-4
Ce	141-Ce	145	1E-3	2E-3
Pr	142-Pr	1576	–	4E-3
Nd	147-Nd	91	1E-2	9E-4
Sm	153-Sm	103	6E-4	7E-5
Eu	152-Eu	1408	3E-5	5E-5
Gd	153-Gd	98	2E-2	5E-5
Tb	160-Tb	879	4E-4	1E-4
Dy	165-Dy	95	4E-5	8E-6
Ho	166m-Ho	810	4E-4	5E-5
Er	171-Er	308	–	1E-4
Tm	170-Tm	84	2E-4	4E-5
Yb	169-Yb	198	2E-4	4E-4
Lu	177-Lu	208	3E-4	4E-5

*Evaluated under the experimental conditions described in this paper.

(^{235}U, and ^{233}U deriving from ^{232}Th) as some of the REE nuclides, especially among the light rare-earth elements (La to Sm) are produced both by activation and fission. In the present work with U and Th content ranging from 0.029 μg/g (U in Orchard Leaves) and 0.064 μg/g (Th in Orchard Leaves) to 16.8 μg/g (U in NIM G) and 56.7 μg/g (Th in NIM G), no interferences were observed.

The sensitivities for all the rare-earth elements with INAA and RNAA are reported in Table VII. In almost all cases no meaningful differences between sensitivities or an increase of sensitivity with the radiochemical method are shown; only in one case (Yb) is sensitivity better in the instrumental method. The reported sensitivities clearly indicate that both procedures, except INAA for biological materials, can be safely applied to the determination of low levels of rare earth elements in environmental matrices.

The main goal in developing rare-earth group separation schemes is the removal of ^{46}Sc and alkaline and alkaline-earth radionuclides interfering in the high resolution gamma-ray spectrometry. In a previous paper [13] two procedures had been set up and applied to REE analysis in geological samples. Both procedures are highly satisfactory for the separation of the rare-earth elements from interfering elements. However, in the present paper, the rare-earth separation by fluoride precipitation was preferred on account of a greater versatility and of a highly reproducible chemical yield: (86 ± 2)%. This procedure takes care of: i) difficulties encountered when samples with high silica content are submitted to analysis, by employing a basic attack which involves the formation of soluble sodium silicates; ii) ^{46}Sc removal by fluoride precipitation with a mixture of HF and NH_4F: scandium is kept in solution by the formation of the soluble ScF_6^{3-} complex ion, thus obtaining decontamination factors of about 100.

The working conditions have been preliminarily optimised by checking each step by tracer experiments. Fluoride precipitation is thus carried out in such conditions to have the lowest solubility of all the REE fluorides. No meaningful differences among the precipitation yields of different REE fluorides were observed so that the procedure chemical yield can only be easily evaluated on lanthanum.

For purposes of comparison, measured rare-earth abundances are usually normalized to those in chondritic meteorites, which are supposed to have the same composition of primordial matter, and plotted against REE atomic number or ionic (+3) radius. In geological samples the REE patterns thus obtained are characteristic of the type of sample and can be used to infer mineralogy and melting history of source rocks (1, 3, 7, 28). Laul *et al.* (7, 28) have shown that also in the case of vegetal samples, REE patterns are similar to those of secondary minerals, such as apatite, and to the patterns of host soils, thus indicating that no REE fractionation occurs during their uptake by plants.

The REE patterns for the examined matrices are given in Fig. 1. The rock samples (NBS-SRM 278 'Obsidian rock' an NIM G granite) show typical patterns of geological samples with a steep slope from La to Lu and a negative anomaly for Eu. A similar but less marked trend is shown by NBS-SRM 1571 'Orchard Leaves': Eu anomaly is less deep and the slope from La to Lu is quite smooth. Different patterns are shown by NBS-SRM 1632 and 1633 ('Coal' and 'Fly Ash'); the slope from La to Lu is steep but the Eu negative anomaly is not quite evident and two unusual enrichments (Pr and Er) are present.

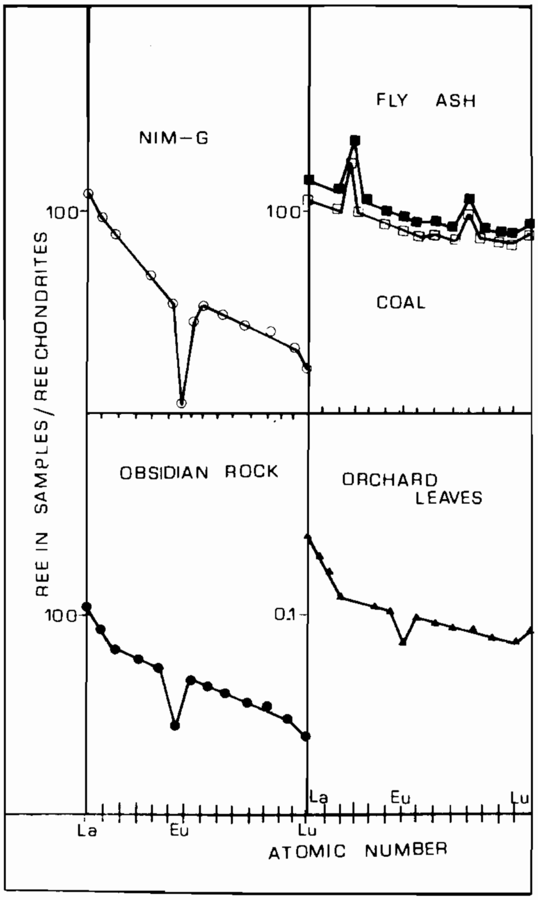

Fig. 1. Rare-earth elements patterns for the investigated standard materials.

TABLE VIII. Comparison of REE Data in the Investigated Materials and in Chondrites.

Material	L-REE/H-REE	La/Lu
NBS-SRM 278 'Obsidian Rock'	5.41	40
NBS-SRM 1632 'Coal'	3.01	77
NBS-SRM 1633 'Fly Ash'	3.22	46
NBS-SRM 1571 'Orchard Leaves'	9.50	171
NIM G	6.90	70
Chondrites	1.80	10

The ratio of abundances of light rare earths (L-REE, La to Sm) to heavy rare earths (H-REE, Eu to Lu) and the La/Lu abundance ratio can be used to characterize different matrices and to evidentiate possible fractionations. The ratios for the investigated materials and for chondritic meteorites [7] are given in Table VIII. All materials show a H-REE depletion with respect to chondrites: 'Coal' and 'Fly Ash' present a small depletion (by a factor less than 2), rock samples ('Obsidian rock' and NIM G) are depleted by factors in the range 3–4, and 'Orchard Leaves' by a factor of 5. H-REE depletion is more evident if the La/Lu ratios are considered. All materials, except 'Orchard Leaves', have ratios 4 to 8 times higher than chondrites. In 'Orchard Leaves' the factor is as high as 17.

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