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INSTRUMENTATION, PHYSICS, AND CHEMISTRY

DETERMINATION OF EIGHT LANTHANIDES IN APATITES BY ICP-AES, XRF, AND NAA

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ABSTRACT

In the present work eight rare-earth elements (REEs), Hf, and Th were determined in eight apatite samples from San Luis, Argentina. The determinations were carried out by three methods: inductively coupled argon plasma atomic emission spectrometry (ICP-AES), neutron activation analysis (NAA), and X-ray fluorescence spectrometry (XRF). A new support for a small amount of sample was employed in the determination of La, Ce, and Nd by using XRF technique. The same procedure has proved reliable for the determination of major elements by using small amounts of apatite samples. For the ICP-AES determination, a group separation of the REEs from accompanying elements was required. This was achieved by ion- exchange chromatography and sequential acid elution. For the determination by NAA, a nondestructive instrumental technique (thermal neutron activation) was applied. Conditions of irradiation, decay, and measurements for the determination are described. Good correlation is obtained by these three methods.

Key Words: Rare-earth elements; Apatite; XRF; ICP-AES; NAA

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INTRODUCTION

Over the last few years, apatites of granitic pegmatites have been used, along with K-feldspars and muscovites, as geochemical exploration minerals. Knowledge of the chemical composition of these minerals enables geochemists to characterize the host rocks and to predict the probability of the occurrence of economically interesting ore deposits. Apatite occurs as an accessory mineral in rocks of almost all geneses. It is a fairly common constituent of granitic pegmatites, where fluorapatite is particularly common and where the mineral is regarded as a sensitive indicator of the genetic conditions of the host rocks [e.g. (1, 2)]. To meet current geochemical requirements, a rapid, very low cost of instrumentation and simple sample preparation technique is required. A method utilizing XRF, developed by Perino et al. (3–5), has been employed for determining major, minor, and trace elements in muscovites and K-feldspars. This technique requires a few milligrams of powdered samples, which are compressed to produce pellets. As an extension of our earlier investigations (6), studies on pegmatitic apatite REEs composition are presented. Our XRF technique benefits from the very low amount of solid sample required and from a relatively rapid measurement.

Minor to trace amounts of REEs are commonly hosted by apatite. In spite of their similar chemical behavior, the REEs may be fractionated during mineralogical and petrological processes. This fractionation originates from different types and volumes of coordination polyhedra that can be formed and is also due to the fact that some of the elements occur in oxidation states other than +III. The type and degree of fractionation can therefore be an indicator of the genesis of the rock and provide evidences for the processes involved (7,8).

Several analytical techniques have been developed for the determination of trace amounts of lanthanides in many types of geological samples, including pegmatitic apatites [e.g. (9–13)]. Since the REEs are present in apatites at μg g^{-1} levels, separation of these elements as a group should ordinarily be incorporated in the analysis (ICP-AES determination). This separation not only allows for pre-concentration of the REEs so that lower detection limits are possible, but also simplifies the analytical problem of interference from matrix elements. This separation is achieved by ion-exchange chromatography and sequential acid elution [cation exchange procedure taken from Crock et al. (14)].

MATERIAL AND METHODS

Sample Description

Eight pegmatitic apatites from San Luis, Argentina, have been examined in this study. Details of all samples are given in Table 1. Apatites were separated by handpicking from a 60–70 mesh (0.0212–0.025 cm) fraction under a binocular, and subsequently checked by XRF (4).

XRF Measurements

La_1-lines were measured for La, Ce, and Nd in eight apatite samples (see Table 1 for further details on the origin of the samples). Standard addition procedure was applied and measurements on triplicate apatite samples were performed. Additions were carried out from stock standard solutions according to the expected REEs concentration range. REEs stock standard solutions were prepared by dissolving accurately weighed amounts of high purity (99.99%) oxides (Merck products) in hot nitric acid and diluting with Milli-Q™ purified water to 100 mL. Working solutions were prepared by appropriate dilution of stock solutions in 5 vol% nitric acid. Known amounts of each REE were added to solid samples. These were dried in an oven at 80°C for half an hour and finally mixed in an agate pot to obtain good homogenization. Table 6 shows the results obtained for La, Ce, and Nd concentrations.

Limit of Detection

Although numerous criteria have appeared in the literature regarding the definition of limit of detection, we have used in this paper that proposed by Currie (12). The mathematical definition of this limit of detection, L_D, is given by

$$L_{D(counts)} = t_1^2 + 2t_1(2b)^{1/2} \tag{1}$$

Where b means the background counts (counts seg^{-1}) measured at the Bragg angle position of the element of interest, using a "blank pellet." The parameter t_1 depends on the probability level. For 95% confidence, $t_1 = 1.645$. Hence, Equation (1) becomes

$$L_{D(counts)} = 2.71 + 4.65(b)^{1/2} \tag{2}$$

As a linear relationship exists between intensity and concentration, it is easy to calculate the lower limits of detection. They were calculated from the analytical curves for the elements considered in this study: La, 15 ppm; Ce, 31 ppm; and Nd, 10 ppm. These detection limits are not definitive and could be lowered by using counting periods longer than the 100-s period used in this work.

ICP-AES Determinations

ICP-AES Instrumentation

The measurements were performed with a sequential inductively coupled plasma spectrometer (Baird ICP 2070). The 1-m Czerny–Turner monochromator have a holographic grating with 1800 grooves mm^{-1}. Operating conditions of the ICP emission spectrometer were a) power of RF generator 1 kW; b) frequency of RF generator: 40.68 MHz; c) plasma gas flow rate: 8.5 L min^{-1}; d) observation

Table 2. REE Spectral Interference Correction Coefficients and Detection Limits for Determination by ICP-AES

Element	Wavelength (nm)	Interfering REE and Correction Coefficients		Detection Limit (ng ml^{-1})	
		Refs. (13,16)	This Work	Ref. (17)	This Work
La	333.749			6.7	6.8
Ce	413.765			32	31.8
Nd	401.225			33	33.5
Sm	359.260	Nd (0.0330)	Nd (0.0326)	29	28.8
Eu	381.967	Nd (0.0040)	Nd (0.0045)	1.8	1.75
Tb	350.917			15	14.6
Yb	328.937			1.2	1.3
Lu	261.542			0.67	0.7
Hf	339.980			8	7.7
Th	283.231			47	46.8

height: 15 mm (above load coil). Table 2 lists the analytical wavelengths chosen and the detection limits for the elements considered in this study. The wavelengths chosen offer adequate sensitivity although they are not necessarily the most sensitive analytical lines.

Resin Columns

The columns consisted of 15×1.5 cm borosilicate glass tubes packed with 10 cm of the cation-exchange resin. Before use, the resin column was preequilibrated with 1 *M* hydrochloric acid.

Reagents

REEs Stock Standard Solutions

REEs solutions (1 mg mL^{-1}) were prepared by dissolving accurately weighed amounts of high purity (99.99%) RE-oxides (Merck products) in hot nitric acid and diluting with Milli-Q, purified water to 100 mL. Working solutions were prepared by appropriate dilution of stock solutions in 5 vol% nitric acid and stored in polyethylene bottles. All other solvents and reagents not described were reagent of grade or better.

Ion Exchange Resins

The Dowex 50 W × 8 (100–200 mesh, hydrogen form) cation exchanger used for the column separation was obtained from Aldrich Chemical Co. Colloidal particles were removed by several decantations with deionized water.

Procedures

Sample Dissolution

Accurately weighed (1.000 g) finely powdered samples were decomposed with a mixture of concentrated hydrochloric and nitric acids (5:1). After complete dissolution, the solution was evaporated to dryness on a steam bath. The residue was taken up in 50 mL of 1 M hydrochloric acid.

Ion Exchange Procedure

The elution procedure was as follows: a) load 50 mL of sample solution (in 1 M hydrochloric acid), b) elute with 50 mL of 2 M hydrochloric acid, c) elute with 50 mL of 2 M nitric acid, d) elute with 50 mL of 6 M nitric acid (to be used for REEs analysis), e) elute with 50 mL of 8 M nitric acid (to be used for REEs analysis), and f) regenerate the column by washing with 100 mL of 8 M nitric acid. The REEs were adsorbed on the column, while Fe, Ca, P, and other unwanted elements were eluted with 2 M hydrochloric acid and 2 M nitric acid. The REEs were quantitatively desorbed with 6 and 8 M nitric acids. The REEs eluates [(d) and (e)] were evaporated to dryness on a steam bath and taken up in 10 mL of 5 vol% HNO_3 for subsequent determinations. The same procedure was followed to determine Hf and Th concentrations in (b) and (c) eluates.

ICP-AES Measurements

For each solution, three 1-s signal integrations followed a stabilization time of 20 s. The arithmetic mean of these three readings were used to calculate the results. Relative standard deviation values were generally better than 1%. Primary single-element solution standards of REEs prepared in 5 vol% HNO_3 were used to performed external calibration. The true background under the peak was determined using a 5 vol% nitric acid solution. All intensities were corrected for background so obtained. Table 2 lists the REEs analytical lines selected in this work. Spectral profiles of these lines and experimentally determined correction coefficients for mutual REE interferences are largely dependent on the performance of the ICP-AES spectrometer and vary from instrument to instrument. Among the elements studied in this work only two (Sm and Eu) required interference correction. The factors applied in this study are indicated in Table 2.

Method Validation

In order to determine the validity of the method, 10 g of apatite samples were collected and dividied into 10 portions of 1 g each. Our proposed method was applied to seven portions and the average quantity of the studied elements (REEs, Hf, and Th) obtained was taken as a base value. Then, increasing quantities

of REEs, Hf, and Th were added to the other aliquots of sample and REEs, Hf, and Th were determined by the same method. Standard additions were carried out before applying the acid digestion procedure (volatilizations losses are not possible). Table 3 shows the results obtained.

NAA Determinations

Sample Preparation

Apatite samples were sealed in quartz ampoules and irradiated in an aluminium can together with a multielemental standard (USGS AGV-1 andesite), containing all the REEs.

Table 3. Recovery Tests (Method Validation) for the Determinations in Apatites by ICP-AES, Sample: Ap 1b

Element	Aliquots	Base Value (mg L^{-1})	Quantity of Element Added (mg L^{-1})	Quantity of Element Found (mg L^{-1})	Recovery (%)[a]
La	1	73.73	30.00	103.22	98.3
	2	73.73	60.00	131.09	95.6
	3	73.73	90.00	161.03	97.0
Ce	1	94.2	60.00	151.02	94.7
	2	94.2	90.00	183.57	99.3
	3	94.2	120.00	212.4	98.5
Nd	1	16.6	5.0	21.25	93.0
	2	16.6	15.0	31.33	98.2
	3	16.6	25.0	41.63	100.1
Sm	1	2.89	1.00	3.85	95.7
	2	2.89	2.00	4.88	99.4
	3	2.89	3.00	5.82	97.6
Eu	1	0.66	0.10	0.75	94.3
	2	0.66	0.50	1.14	95.5
	3	0.66	1.00	1.63	96.8
Tb	1	0.23	0.10	0.324	94.5
	2	0.23	0.20	0.43	98.5
	3	0.23	0.40	0.63	99.7
Yb	1	5.42	2.00	7.31	94.5
	2	5.42	4.00	9.26	96.0
	3	5.42	6.00	11.39	99.5
Lu	1	0.86	0.60	1.41	91.5
	2	0.86	0.80	1.62	95.5
	3	0.86	1.00	1.82	96.0
Hf	1	0.05	0.01	0.059	90.0
	2	0.05	0.03	0.077	91.5
	3	0.05	0.07	0.114	92.0
Th	1	2.5	1.00	3.45	95.5
	2	2.5	2.00	4.39	94.7
	3	2.5	3.00	5.47	99.0

[a]$100 \times [(\text{found} - \text{base})/\text{added}]$.

Table 4. Peaks of Υ-Energy Selected for the Measurements

Element	Measured Nuclide	Υ-Energy (keV)	Half-Life Range
La	^{140}La	328.8–815.8–1596.6	40.2 h
Ce	^{141}Ce	145.5	32.5 d
Nd	^{147}Nd	91.1–531.0	11.1 d
Sm	^{153}Sm	103.2	46.8 h
Eu	^{152}Eu	1408.1	12.7 y
Tb	^{160}Tb	879.3	72.1 d
Yb	^{169}Yb	197.8	31.8 d
Yb	^{175}Yb	396.1	4.21 d
Lu	^{177}Lu	208.3	6.74 d
Hf	^{181}Hf	482.2	42.5 d
Th	^{233}Pa	311.9	27 d

*a*h: hours; d: days; y: years.

Irradiation

All the samples and standards were irradiated in the core of the RA-3 reactor at Centro Atómico Ezeiza (CAE), Comisión Nacional de Energía Atómica at a thermal neutron flux of 3.0×10^{13} cm^{-2} s^{-1}.

NAA Measurements

All measurements were performed with a HP Ge detector, having 30% efficiency, 1.8 keV resolution (^{60}Co 1332 peak), coupled to a multichannel analyzer (Canberra Series 85). The peaks selected are shown in Table 4. A software developed in our laboratory (CAE) was used for concentrations calculation. Two measurements at different decay times were performed for each sample, depending on the half-lives of the nuclides: ^{140}La, ^{147}Nd, ^{153}Sm, ^{175}Yb, ^{177}Lu, ^{233}Pa: 7–8 days; ^{141}Ce, ^{152}Eu, ^{160}Tb, ^{169}Yb, ^{181}Hf, ^{233}Pa: 30 days.

Application to Standard Reference Materials

The results for application of the methods (ICP-AES and NAA) to a standard reference material to test their precision and accuracy, compare favorably with the published and accepted values. Table 5 shows the means and 95% confidence limits for analysis of US Geological Survey standard (USGS AGV-1 andesite), based on the triplicate analysis of three splits.

RESULTS AND DISCUSSION

The abundance of REEs in apatites is generally low (μg g^{-1} levels), and most samples contain elements that interfere in the ICP-AES determination. Therefore

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Table 5. Comparative Concentrations of the REE, Hf, and Th in US Survey Standard Andesite AGV-1[a]

Element	ICP-AES[b]	NAA	RV[c]
La	38.5 ± 0.4	38.3 ± 0.3	38 ± 3
Ce	66.8 ± 0.2	64 ± 1	67 ± 5
Nd	35.3 ± 0.5	38 ± 4	33 ± 3
Sm	6.15 ± 0.02	6.00 ± 0.04	5.9 ± 0.4
Eu	1.60 ± 0.03	1.8 ± 0.1	1.64 ± 0.10
Tb	0.65 ± 0.05	–	0.70 ± 0.10
Yb	1.65 ± 0.03	1.3 ± 0.2	1.72 ± 0.19
Lu	0.27 ± 0.03	0.27 ± 0.04	0.28 ± 0.030
Hf	5.0 ± 0.1	5.4 ± 0.3	5.1 ± 0.4
Th	6.39 ± 0.02	6.3 ± 0.2	6.5 ± 0.5

[a] All values as μg g^{-1}.
[b] The presented concentrations are the means of three samples, 95% confidence interval, $n = 6$.
[c] RV = Recommended value (18).

a separation of these elements as a group is incorporated in the analysis. This is achieved by ion-exchange chromatography and sequential acid elution. The group separation allows for preconcentration of the REEs so that lower detection limits are possible. Separating the REE from the mineral matrix removes the bulk of the dissolved salts and also minimizes spectral interferences from non-REE in the ICP-AES determination. After the cation-exchange separation used here, the only important spectral interferences that remain are those from the REE themselves. The results presented in Table 6 indicate the comparative concentrations of REEs, Hf, and Th in apatites by employing ICP-AES and NAA. As demonstrated, an excellent agreement is obtained by using both ICP-AES and NAA.

The mean values obtained by the XRF technique are shown in Table 6 as well. They are also compared with those obtained by thermal NAA and ICP-AES. The concentrations values obtained by XRF spectrometry for the elements studied are almost indistinguishable when compared to ICP-AES or NAA results. However, the mean values obtained for Nd content by using XRF and ICP-AES methods appear to be slightly lower than NAA results. This element is known to be difficult to determine by instrumental NAA. Counting rates for ^{147}Nd photopeak at 531.0 keV are low; the more sensitive 91.1 keV line of ^{147}Nd shows a significant background, whose subtraction from the peak area can introduce a systematic error. This becomes more significant as the Nd contents are lower. Therefore it is possible that the NAA results are overestimated.

From the previous discussion, we may say that the use of small amounts of powdered sample in the XRF method is advantageous to geochemical studies involving minerals that do not occur in great abundance. Since no separation step is needed, this technique allows for a relatively rapid measurement.

Table 6. Comparative Concentrations of Eight REEs, Hf, and Th in Apatite Samples[a]

Element	Ap 1a ICP[b]	Ap 1a NAA	Ap 1a XRF	Ap 1b ICP[b]	Ap 1b NAA	Ap 1b XRF	Ap 2 ICP[b]	Ap 2 NAA	Ap 2 XRF	Ap 3 ICP[b]	Ap 3 NAA	Ap 3 XRF
La	480±0.2	484±5	483±6	737.3±10	740±5	735±8	191.1±3	187±3	185±2	246.8±0.2	247±5	245±4
Ce	698±11	690±20	695±10	942±19	930±20	940±10	498±10	505±8	501±6	299±7	290±20	297±5
Nd	200±3.2	217±10	198±4	155±3	161±10	150±5	319±6.5	330±20	320±7	79±1.2	90±9	71±2
Sm	44.9±0.5	45.0±0.2	ND[c]	28.9±0.3	29.2±0.2	ND	173.2±0.4	173.1±0.5	ND	23.6±0.1	23.8±0.1	ND
Eu	18.9±0.2	18.5±0.7	ND	6.6±0.1	6.9±0.3	ND	41.6±0.2	40±2	ND	1.37±0.09	1.37±0.09	ND
Tb	27.9±0.2	27±3	ND	2.3±0.3	2.8±0.4	ND	32.4±0.2	35±4	ND	1.7±0.02	1.5±0.2	ND
Yb	71.3±0.1	64±8	ND	54.2±0.3	54±7	ND	104.5±0.3	110±10	ND	2.1±0.03	1.9±0.3	ND
Lu	8.6±0.1	8±1	ND	8.6±0.1	9±1	ND	16.4±0.2	17±2	ND	2.1±0.04	1.9±0.2	ND
Hf	ND	ND	ND	0.5±0.01	0.3±0.2	ND	8.4±0.04	8.1±0.3	ND	ND	ND	ND
Th	6.5±0.08	6±2	ND	25±2	24±1	ND	23.3±0.2	23±2	ND	16.2±0.1	15±1	ND

Element	Ap 4 ICP[a]	Ap 4 NAA	Ap 4 XRF	Ap 5a ICP[a]	Ap 5a NAA	Ap 5a XRF	Ap 5b ICP[a]	Ap 5b NAA	Ap 5b XRF	Ap 7 ICP[a]	Ap 7 NAA	Ap 7 XRF
La	395.5±0.2	395±5	397±8	72.2±0.1	72±1	74±2	185.9±0.2	187±2	189±3	18.3±0.2	20±5	17±1
Ce	247±1	240±20	245±5	46.8±0.2	50±10	48±2	287±0.1	290±10	291±6	ND	ND	ND
Nd	111±1.8	120±10	100±3	25±0.1	30±9	18±1	155±2.1	150±10	140±4	64±1.5	71±10	62±2
Sm	31.9±0.2	32.3±0.2	ND	11.25±0.07	11.28±0.09	ND	34.9±0.2	35.9±0.1	ND	22.8±0.3	22.5±0.1	ND
Eu	ND	ND	ND	0.62±0.01	0.62±0.05	ND	ND	ND	ND	ND	ND	ND
Tb	ND	0.33±0.07	ND	ND	0.39±0.07	ND	4.9±0.01	4.6±0.6	ND	0.22±0.001	0.25±0.07	ND
Yb	ND	ND	ND	1.8±0.03	1.5±0.3	ND	19.5±0.2	22±3	ND	1.4±0.02	1.4±0.3	ND
Lu	3.9±0.05	3.4±0.4	ND	0.73±0.1	0.8±0.1	ND	4.8±0.08	4.2±0.6	ND	2.9±0.05	2.5±0.4	ND
Hf	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.6±0.01	0.6±0.1	ND
Th	116.3±0.2	119±6	ND	129.8±0.2	132±5	ND	96.1±0.2	94±3	ND	15.9±0.2	15.5±0.3	ND

[a] All Values as $\mu g\ g^{-1}$ (w/w).

[b] The mean and 95% confidence limit of three splits, each analyzed three times.

[c] ND = not detectable.

Tb	ND	ND	ND	ND	ND	ND	ND
Yb	ND	ND	ND	ND	ND	1.8±0.05	ND	ND
Lu	ND	ND	4.2±0.3	ND	ND	ND	ND	ND
Hf	0.6±0.1	0.6±0.01	ND	4.8±0.08	0.8±0.1	0.73±0.1	3.4±0.4	3.9±0.05
Th	15.5±0.3	15.9±0.2	94±3	96.1±0.2	132±5	129.8±0.2	119±6	116.3±0.2

a All Values as $\mu g\ g^{-1}$ (w/w).
b The mean and 95% confidence limit of three splits, each analyzed three times.
c ND = not detectable.

CONCLUSIONS

The XRF results show the reliability of the concentration values obtained for La, Ce, and Nd. Thus, the most important characteristic of this XRF method is the small amount of powdered sample needed. On the whole, the agreement achieved by using the three techniques (XRF, ICP-AES, and NAA) is reasonably good. By way of concluding it can be stated that the results obtained by these three methods possess the required accuracy and precision for petrogenic studies using REEs. The results obtained for geological reference materials demonstrate that the procedures (ICP-AES and NAA) allow precise and accurate analysis of geological samples for their REE, Hf, and Th content.

ABBREVIATIONS

ICP-AES	inductively coupled plasma atomic emission spectrometry
NAA	neutron activation analysis
ND	not detectable
REE	rare-earth element
RV	recommended value
XRF	X-ray fluorescence spectrometry

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