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A fast method for apatite selective leaching from granitic rocks followed through rare earth elements and phosphorus determination by inductively coupled plasma optical emission spectrometry

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Abstract

Rare earth elements (REE) and phosphorus (P) in apatite were determined using inductively coupled plasma optical emission spectrometry (ICP-OES) after partial dissolution of the granitic rocks and pure apatite. The dissolution was performed with nitric acid in an open system and the matrix elements were separated by a cation exchange procedure. Samples of pure apatite from granitic rocks were dissolved with, 0.14 mol L^{-1} nitric acid. The results showed that the release of REE is due to apatite leaching because it could be assessed by comparing the chondrite-normalised pattern corresponding to the rocks and the pure apatite. Similar results were found for absolute REE abundance from the partial dissolution of the rocks and pure apatite.

This simple and rapid method can be applied for the determination of REE in apatite as an indicator for mineral exploration, although its use in petrology could be possible.

Keywords: Apatite; Rare earth elements; Apatite partial dissolution; ICP-OES

1. Introduction

The usefulness of trace element contents in different mineral phases and its use in geochemical exploration is well known [1,2]. Apatite [$Ca_5(PO_4)_3(F,Cl)$] is an accessory mineral in many different types of rocks and particularly in those of granitic composition [3]. Likewise, the presence of chemical elements in apatite and its great potential in geochemical prospecting is due to the fact that a large number of cations and anions may substitute within its structure. Among the better-known substitutions are rare earth elements (REE), whereas light rare earth (LREE) from La to Sm and heavy rare earth (HREE) from Gd to Lu, Sr, U and Th [2,4–6].

In a recent study it has been evidenced that apatites of different types of granite can be distinguished geochemically considering their content in Sr, Y, Mn, REE, enrichment in LREE and the Eu anomaly size [7].

Apatite can be used as an indicator for mineral exploration and particularly in the case of granitic rocks. Besides, apatite grains separated from drainage and soil samples can serve as useful resistate indicator minerals (RIMs) in mineral exploration.

The release of REE from different mineral phases has also been studied including apatite during a sequential leaching of granitic rocks. The release relates the results to measurements

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Table 1
ICP instrumental parameters

ICP conditions	
RF generator power (kW)	1.0
Frequency of RF generator (MHz)	40.68
Plasma gas flow rate (L min^{-1})	8.5
Auxiliary gas flow rate (L min^{-1})	1.0
Observation height (mm)	15
Nebulizer	Meinhard concentric glass
Wavelength of used emission line	
Element	Wavelength (nm)
La	398.852
Ce	418.660
Nd	430.358
Sm	359.260
Eu	381.967
Gd	342.247
Dy	353.170
Yb	328.542
Lu	261.542
P	214.914

of REE distribution patterns in the soil developed on the same granitic rocks. 0.6 mol L^{-1} HCl was used for the leaching in an interaction time that varied from 24 to 800 h [8].

The REE in geological materials have been determined by several methodologies [9,10], being ICP-OES one of the most used so far [11–15]. Besides, the determination of nine strategic REE is enough to determine the very general shape of the REE distribution curve for most rock systems [13].

On the other hand, the dissolution of light REE in apatite is carried out with 7 mol L^{-1} HNO_3 for their the determination by FRX [16].

The aim of the present work was the differential dissolution of apatite in granitic rocks using diverse concentrations of nitric acid. It was controlled throughout the determination of the REE and P. The measurements were performed by ICP-OES and cation-exchange was employed for the separation of matrix elements.

2. Methods and material studied

The measurements were performed with a sequential ICP spectrometer Baird, ICP 2070 (Beldford, MA, USA) and the experimental conditions for measurement are shown in Table 1.

The cation exchange resin Dowex 50WX8 (100–200 mesh) was supplied by Fluka (Basel, Switzerland). Before use, the fine particles were removed by washing with ultra pure water.

All reagents used were of the highest purity and all solutions were prepared in ultra pure water with a resistivity of 18.2 MΩ cm obtained from an EASY pure RF (Barnstedt, IA, USA).

A solution of REE 100 mg L^{-1} from Alfa Aesar, purchased from Johnson Matthey (Hertfordshire, UK) was used as a standard solution from which the working standards were prepared by dilution. A solution of 1000 mg L^{-1} P was prepared from KH_2 PO_4 Fluka (Heidelberg, Germany).

The granite used in this study was extracted from Plutón Las Chacras, which is located in a bigger unit, the Batolito Las Chacras-Piedras Coloradas [17]. It is composed of quartziferous monzonites and pink porphyric granodiorites with potassic feldspar mega crystals up to 16 cm long. It contains biotite and amphibole as mafites whereas the accessories are composed by titanite, apatite, allanite and tourmaline. Apatite (fluorapatite) is present as yellowish green euhedrals crystals of up to 8 mm and it can exhibit zircon and titanite inclusions. The granite sample exhibits a major mineralogical complexity than the granite pegmatite.

The granite pegmatite [18] corresponds to a rock composed by potassic feldspar, apatite, quartz, plagioclase, muscovite, tourmaline and epidote. The apatite is medium green in color with basal hexagonal isotropous sections and it shows a late growth respect of the rest of the minerals. Apatite is the most abundant accessory mineral in this granite pegmatite.

3. Sample preparation and dissolution

The apatites were removed from granite and pegmatite by hand picking. Absence of other minerals inclusions in the apatite was verified with a binocular microscope. Apatite grains with obvious inclusion of others minerals were excluded.

The remaining rock, free of apatite, verified with a binocular microscope, was employed for preparing an artificial mix. Granite and pegmatite samples were ground to 200 mesh in an agate mill. Artificial samples of granite and pegmatite containing 2.88% (w/w) and 18.4% (w/w) apatite, respectively, were also prepared. With this purpose, exactly weighed apatite quantities were mixed with typical minerals of each rock, completely free of apatite, in the proportions mentioned before.

Leaching of apatite from pegmatite and granite was carried out by using different HNO_3 concentrations: 14, 7, 1.4 and 0.14 mol L^{-1}. Nitric acid concentrations below 0.14 mol L^{-1} did not cause a total recovery of the REE contained in the apatite.

For pure minerals, the procedures were as follows: 200 mg of the mineral were treated with 25 mL of nitric acid on a hot plate until complete evaporation to dryness. The final residue was taken up in 25 mL 1.2 mol L^{-1} HCl. In the case of rock samples, 1 g of sample was treated with 25 mL 0.14 mol L^{-1} HNO_3 until complete evaporation to dryness, taking up in 10 mL of H_2O. The floating liquid was separated by filtration and taken in 25 mL with a final HCl concentration of 1.2 mol L^{-1}.

4. Ionic exchange separation

The 1.2 mol L^{-1} HCl attack solution was passed through a column (18 cm × 1 cm) with 100–200 mesh Dowex 50WX8

Table 2
REE (μg g^{-1}) in apatite extracted from granite pegmatite using different HNO_3 concentrations

Elements	HNO_3			
	14 mol L^{-1}	7 mol L^{-1}	1.4 mol L^{-1}	0.14 mol L^{-1}
La	171 ± 11	176 ± 16	172 ± 12	174 ± 16
Ce	436 ± 26	419 ± 24	410 ± 26	425 ± 27
Nd	414 ± 20	397 ± 16	405 ± 18	390 ± 22
Sm	175 ± 17	172 ± 16	179 ± 19	169 ± 17
Eu	31.2 ± 4	29 ± 3	30 ± 4	29.9 ± 4
Gd	168 ± 12	172 ± 14	171 ± 12	174 ± 15
Dy	240 ± 15	238 ± 15	241 ± 12	249 ± 14
Yb	115 ± 10	116 ± 8	115 ± 9	118 ± 9
Lu	18.5 ± 3	19 ± 2	18.6 ± 3	18.2 ± 3

Data are the average of six independent analysis +− the corresponding *s* values at a 95% confidence level.

cation resin preequilibrated with 1.2 mol L^{-1} HCl. The effluent with the elements like Ca, Al, Fe, P, etc. was reserved and additional 30 mL of 1.2 mol L^{-1} HCl were passed through the column to completely separate the elements from the matrix. The eluate was evaporated in order to obtain a final volume of 25 mL, which was used for P determination.

The REE retained on the column were eluted with 50 mL of 6 M HCl. The REE eluate was evaporated to almost 10 and completed to 25 mL with ultra pure water. The REE and P concentrations were determined by ICP-OES using external calibrations and against the reagent blanks.

5. Results and discussion

The concentrations of REE in apatite extracted from granite pegmatite and from Las Chacras granite with different concentrations of HNO_3 are shown in Tables 2 and 3, respectively. In both cases, no difference was observed in the values obtained for each dissolution procedure. Consequently, the procedure adopted as leaching medium was that with 0.14 mol L^{-1} HNO_3 for both rocks. The REE concentrations corresponding to granite pegmatite, either natural or artificial, determinated in the leaching with 0.14 mol L^{-1} HNO_3 are shown in Table 4. In general, the values obtained were in good agreement with the proportion of apatite in the original rock.

Table 3
REE (μg g^{-1}) in apatite extracted from Las Chacras granite with different HNO_3 concentrations

Elements	HNO_3			
	14 mol L^{-1}	7 mol L^{-1}	1.4 mol L^{-1}	0.14 mol L^{-1}
La	1267 ± 87	1303 ± 101	1258 ± 98	1194 ± 81
Ce	2407 ± 130	2240 ± 114	2344 ± 120	2389 ± 126
Nd	1666 ± 88	1635 ± 94	1670 ± 110	1669 ± 118
Sm	241.3 ± 18	241 ± 17	252.6 ± 20	241.6 ± 18
Eu	35.8 ± 3	36.1 ± 4	34.4 ± 3	35.8 ± 4
Gd	145 ± 10	131 ± 9	144 ± 11	147 ± 11
Dy	69.3 ± 5	70.8 ± 4	72.4 ± 5	71.9 ± 4
Yb	19.8 ± 2	24.2 ± 2	23.5 ± 2	22 ± 1.5
Lu	5.2 ± 0.6	5 ± 0.5	4.7 ± 0.6	4.5 ± 0.4

Data expressed as indicated for Table 2.

Table 4
REE concentrations (μg g^{-1}) in natural and artificial granite pegmatite samples

Elementos	Granite pegmatite natural[a]	Granite pegmatite artificial[a]
La	67 ± 3.3	31 ± 1.8
Ce	152 ± 9.8	71 ± 4.9
Nd	139.3 ± 1.7	64 ± 4.8
Sm	61.3 ± 5.8	29.2 ± 2.5
Eu	10.8 ± 0.9	5.2 ± 0.4
Gd	65 ± 6.9	30 ± 2.3
Dy	91.6 ± 7.2	48 ± 5.1
Yb	41 ± 2.4	22.3 ± 1.9
Lu	7 ± 0.5	3.3 ± 0.3

[a] Determined in the leachate with HNO_3 0.14 mol L^{-1}.

The REE concentrations corresponding to Las Chacras granite, either natural or artificial, determined in the leachate with 0.14 mol L^{-1} HNO_3 are shown in Table 5. As in the previous case, the values obtained were in good agreement with the proportion of apatite in the original rock.

The phosphorous concentrations for the different treated rocks and the resultant proportion of apatite in the rock are shown in Table 6. There is a good agreement among the concentrations of P and the quantity of apatite originally placed in the artificial samples so that an extra contribution of P from other minerals can be discarded. Besides, the method shows to be appropriate to determine the quantity of apatite in the samples of treated rocks with comparative purposes.

On the other hand, the ratio $(Ce/Yb)_{cn}$ is indicative of the slope of the REE chondrite-normalised pattern and it can also show changes in the relation of the heavy REE and LREE groups. The Ce/Yb chondrite-normalised relations for the apatites and for the leachates with 0.14 mol L^{-1} HNO_3 of the

Table 5
REE concentrations (μg g^{-1}) in natural and artificial Las Chacras granite

	Granite natural[a]	Granite artificial[a]
La	12 ± 0.7	38.5 ± 2.8
Ce	23 ± 1.4	67.5 ± 4.2
Nd	17.2 ± 1.4	47.5 ± 4.2
Sm	1.9 ± 0.15	7.4 ± 0.35
Eu	0.3 ± 0.03	1 ± 0.06
Gd	1.2 ± 0.1	4.3 ± 0.23
Dy	0.54 ± 0.04	2.1 ± 0.12
Yb	0.22 ± 0.02	0.7 ± 0.05
Lu	0.04	0.14 ± 0.01

[a] Determined in the leachate with HNO_3 0.14 mol L^{-1}.

Table 6
P concentration in the acid-leachate from the treated rocks

Sample	P% (w/w)	Apatite (%, w/w)
Granite pegmatite natural	6.8	37.3
Granite pegmatite artificial	3.4	18.6 (18.4)[a]
Las Chacras granite natural	0.13	0.71
Las Chacras granite artificial	0.53	2.9 (2.88)[a]

[a] In parenthesis, quantity of apatite originally placed.

Table 7
Ratio Ce to Yb chondrite normalised for apatite and acid-leachates from treated rocks

Sample	(Ce/Yb)cn
Apatite (granite pegmatite)	0.92
Apatite (Las Chacras Granite)	25.80
Granite pegmatite acid leach (natural)	0.96
Granite pegmatite acid leach (artificial)	0.82
Las Chacras granite acid leach (natural)	27.2
Las Chacras granite acid leach (artificial)	25.0

Chondrite values are from Taylor and McLennan [19].

analyzed rocks are shown in Table 7. Good agreement among the relations corresponding to the apatites and the leachates with 0.14 mol L^{-1} HNO_3 is observed indicating that there is no contribution of REE from other minerals. Besides, the values obtained were in agreement with those obtained by Belousova et al. [3] for apatites of the same rock types.

The chondrites-normalised patterns for the samples of apatite and leaches with 0.14 mol L^{-1} HNO_3 of the granite pegmatite are shown in Fig. 1. There is an enrichment in HREE that is also reflected in the ratio $(Ce/Yb)_{cn}$ (0.92 on average for apatite). The pattern also exhibits a negative Eu anomaly. There is good coincidence among the patterns for the apatite and the two acid leachates, which make us, conclude that the liberation of REE from the rock only comes from the apatite since other minerals provide very different patterns.

The normalised patterns for the leachates with 0.14 mol L^{-1} HNO_3 of the natural and artificial granite and the corresponding apatite are shown in Fig. 2. In this case, the anomaly of Eu is very weak because of the presence of plagioclase in such rock. In general, a predominance of the LREE over the heavy ones can be observed, also expressed by the ratio $(Ce/Yb)_{cn}$ (25.80 on average for apatite). As with the granite pegmatite, the shape of the standardized patterns were in agreement, showing that the acid leaches come from the apatite, even in this sample of higher mineralogical complexity.

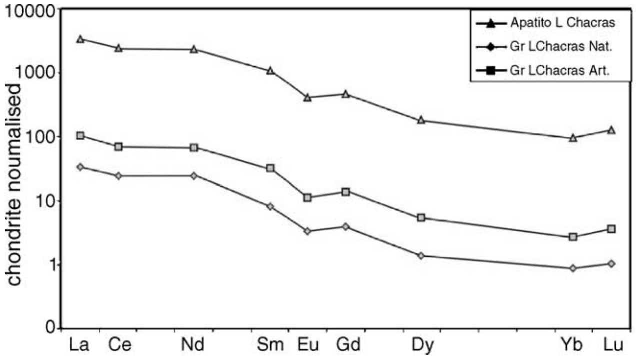

Fig. 1. Chondrite-normalised averaged REE distribution patterns of apatite and acid leachate with 0.14 M HNO_3 from granite pegmatite (natural and artificial). Data from Tables 2 and 4. Chondrite values are from Taylor and McLennan [19].

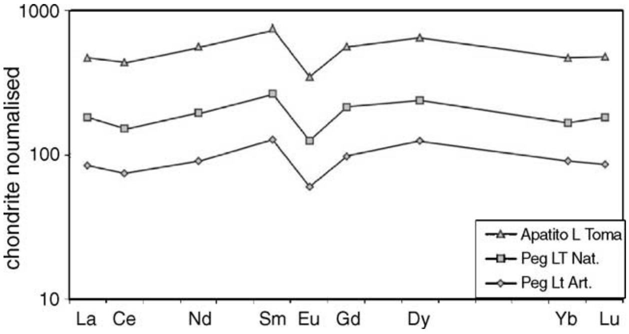

Fig. 2. Chondrite-normalised averaged REE distribution patterns of apatite and acid leachate with 0.14 M HNO_3 from Las Chacras granite. Data from Tables 3 and 5. Chondrite values are from Taylor and McLennan [18].

6. Conclusion

This is the first time that this type of procedure (differential dissolution of apatite with nitric acid) has been carried out.

Under the working conditions previously described (leaching with 0.14 mol L^{-1} HNO_3), a selective dissolution of apatite from granite pegmatite and from granite takes place. Evidence of this is the chondrites-normalised REE patterns of rare soils of the acid leachates and the corresponding apatites as well as the ratio $(Ce/Yb)_{cn}$ and the contents of P. Likewise, the concentrations of REE in the leachates were in agreement with the proportion of apatite added in the artificial samples and detected by the presence of P in the natural samples.

Therefore, we can conclude that the acid leaching with 0.14 mol L^{-1} HNO_3 is appropriate to produce the selective dissolution of apatite of the original sample.

Also, the proposed methodology has advantages such as low cost, rapidness and simplicity compared with the whole analysis of the rock.

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References

[1] A.W. Rose, H.E. Hawkes, H.E. Webb, Geochemistry in Mineral Exploration, Academic Press, New York, 1979, p. 123.
[2] A.A. Levinson, Introduction to exploration geochemistry, Applied Publishing, Alta., Canada, 1980, p. 339 and 776 Supplement 1980.
[3] E.A. Belousova, W.L. Griffin, S.Y. O'Reilly, N.I. Fisher, J. Geochem. Expl. 76 (2002) 45.

[4] M. Fleisher, Z.S. Altschuler, N. Jb, Miner. Mh H10 (1986) 467.
[5] P.L. Roeder, D. MacArthur, X.-P. Ma, G.R. Palmer, A.N. Mariano, Am. Miner. 72 (1987) 801.
[6] J.M. Ronsbo, Am. Miner. 74 (1989) 896.
[7] L.-K. Sha, B.W. Chappell, Geochim. Cosmochim. Acta 63 (1999) 3861.
[8] Y. Harlavan, Y. Erel, Geochim. Cosmochim. Acta 66 (2002) 837.
[9] P. Henderson (Ed.), Rare Earth Elements Geochemistry, Elsevier Science Publications, New York, 1984, p. 467.
[10] V. Balaram, Trends Anal. Chem. 15 (1996) 475.
[11] I. Jarvis, K.E. Jarvis, Chem. Geol. 53 (1985) 335.
[12] I. Roelandts, G. Michel, Geostand. Newslett. 10 (1986) 135.
[13] I. Roelandts, Chem. Geol. 67 (1988) 171.
[14] M.I. Rucandio, Anal. Chim. Acta 264 (1992) 333.
[15] R. Djingova, Ju. Ianova, Talanta 57 (2002) 821.
[16] I. Roelandts, Anal. Chem. 53 (1981) 676.
[17] N. Brogioni, Revista de la Asociación Geológica Argentina 52 (1997) 515.
[18] J.C. Blasco, Mina Loma Blanca (Informe inédito), Dirección Provincial de Minería, San Luis, Argentina, 1997.
[19] S.R. Taylor, S.M. McLennan, The Continental Crust: Its Composition and Evolution, Blackwell Scientific Publications, London, 1985, p. 298.