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Comparative Study on the Determination of Rare Earth Elements by ICP-OES

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Abstract: Matrix interference is a problem during the rare earth elements determination by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) in geological rock samples. An international standard rock sample (GS-N) was used to construct the calibration curves and minimize the effect of interference. The physical parameters of the instrument were adjusted, and the most sensitive line was chosen for each element with a detection limit ranging from 5 to 50 ppb and RSD% not exceed to 1.2. On the other hand, the incomplete digestion due to the presence of some acid resistance minerals, including rare earth elements such as zircon, is another problem that was overcome by alkali fusion digestion, international standard rock sample (MA-N) was used to evaluate the results.

The granitic sample was collected from Ras Abdah area, Safaga city, The Red Sea Coast and digested by acids (H.F. and H_2SO_4) and by alkali fusion with (Na_2CO_3 and H_3BO_4) to determine the rare earth elements by using the calibration curves made by (GS-N) classic rock and compare the results, the rare earth contents were normalized to chondrite abundance in each case of digestion to confirm the obtained results.

Keywords: REEs, ICP-OES, Determination, geological sample.

1. Introduction

Rare earth elements (REEs) are groups of fifteen elements in the periodic table, called Lanthanides and yttrium, and scandium. In lanthanide atoms, the configuration of the valence electrons of the outermost shell is the same for all the species, while the 4f orbitals are progressively filled with increasing atomic numbers. This leads to the similarity of the physical and chemical properties of the elements [1].

REEs do not exist as individual native metals like gold and silver because of their reactivity, but they occur in ores or minerals either as major or minor constituents. The principal economic sources of REE minerals are bastnasite, monazite, and loparite. The REE mineralization is also found in layered alkaline complexes and granitic rocks [2].

The abundance of REEs is important to discuss the origin and evolution of igneous rocks [3,4]. Petrogenetic studies of igneous rocks involve determining the history of the source of melts, the conditions of melting, and the chemical composition of the sources during the melt and melting process. Since REEs are the most valuable elements for such a geochemical study. Moreover, the REE patterns do not change through alternation and metamorphism because REEs belong to the group of chemically resembled elements and are resistant to weathering [5,6]. Thus, the behavior of REEs duringthe melting and differentiation of igneous rock is explained mathematically by the Masuda – Coryell plot REE distribution pattern [7], which is the plot of the REE contents normalized to chondrite abundance.

Genetic classification and characterization of igneous rocks are commonly made by primary chemical composition and mineral composition. The survey of minor elements compositions sometimes does [8-10] Such types and descriptions. Among the studies of trace elements for geological rock samples, the REE pattern is the most popular and valuable.

The unique properties of REEs make them irreplaceable materials in modern technologies (cellular phones, computer devices, permanent magnet motors for turbines, etc.) [1,11] So, more resources are required because of the rapid increase in REEs applications [12] and quantitative knowledge of REEs present in rocks and ores is very important for developing effective extraction method for their recovery [13].

To select analytical methods with the multi-elemental capacity to ease the determination of REEs in complex samples like geological and agricultural samples. The use of microwave-assisted acid digestion to prepare the samples for analysis [14].

The inductively coupled plasma spectrometry technique (ICP.) has been extensively used as a convenient and sensitive analytical tool for

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simultaneous multi- elements determination in geological samples [15-19]. ICP-OES can determine various elements with a wide range of concentrations without matrix matching of standard solutions [15]. ICP-OES has improved the analytical sensitivities of rare earth elements (REEs) due to its low detection limits (ng/ml) [16-20]. More accurate measurements for light REEs (La-Gd) than heavy REEs (Tb-Lu) by ICP-MS. The cause was the sample preparation as was suggested [21] so the lower values of REEs in geological samples digested by acid technique were due to incomplete digestion of highly insoluble minerals [22,23].

So, suppose the granitic rock sample contains acid-resistant minerals such as zircon which has some rare earth elements. In that case, it often gives lower results than the recommended values due to the high ability of zircon to capture traces of REEs and Y and incorporates fine inclusions of other REE minerals [24]. Zirconium ion (in zircon)can be replaced by tetravalent cations (M^{4+} = Hf, Th, U), trivalent cations (M^{3+} = REE, Y, Fe), and divalent cations (M^{2+} = Ca, Mg, Mn) [25] and the high resistance of zircon to high temperature and chemicals [26] leads to the incomplete decomposition [27-29]. For this reason, the preparation of the samples for analysis is a critical part of the analytical process. Traditional wet dissolution methods, such as acid digestion or alkaline fusion, are the most common [30], followed by separation by anion [31] or cation exchange [32] and analyzed by I.C.P., or a mathematical correction algorithm was used for the correction of the interference effect [33].

2. Reagents and instruments

All acids were of the grade of atomic absorption spectrometry (Burdick& Jackson, Germany). Na_2CO_3 and H_3BO_4 for alkali flux were high grades (EDWIK).

The standard solutions of REEs used for calibration were prepared in 4% HNO_3 diluted from 1000 µg/ml traditional solutions for atomic absorption spectrometry manufactured in Canada.

Two international rock standard references of granitic rocks were used, (GS-N) to construct the calibration curves and (MA-N) as a reference in the present study. The experimental water was purified by the Millipore system (Human lab InstrumentCo.) with a resistivity >18MΩ and fed with de-ionized water (Aquatron). The ICP-OES instrument used in this work was Prism ICP-OES high dispersion (Teledyne Leeman Labs. U.S.A.)

3. Analytical procedure

Two methods digested 0.5 grams of the granitic rock sample; the first is the usual acid digestion method by 10 ml of 40% hydrofluoric acid (H.F.) and 5 ml of 98% sulfuric acid (H_2SO_4). Then it was heated at 200°C till dryness, and it was dissolved in 10 ml of 20% hydrochloric acid (HCl); the volume was completed to 50 ml by ultrapure water. The second method was the alkali fusion method which was performed by adding 0.5 gm of the same sample in a platinum crucible, ashed using a mecker with a flux of 0.2g of sodium carbonate (Na_2CO_3) and 0.02g of boric acid (H_3BO_4) for about 3 minutes, then heated in an electric furnace at 1000°C for 10 minutes, after cooling; the fused mixture was dissolved by heating with 10 ml 20% (HCl). The solution was filtered, and the filtrate was completed to 50 ml by ultra-pure water [34].

International reference solutions were prepared (GS-N) to construct the calibrationcurves. The second international reference (MA-N) was used to compare and evaluate the accuracy of the analytical data of the sampleunder investigation.

The instrument was washed by drawing ultra-pure water after every measurement to avoid contamination. The operating conditions of the ICP-OES system are listed in Table 1; the sensitivity was adjusted using REEs standard solution to obtain the highest count rates and stable signals.

Table 1. Operating conditions of I.C.P. – OES.

RF current	1200 Watt
Coolant gas	18 L/min.
Neublizer gas pressure	36 L/min.
Replicant	3

4. Application

The applied sample was chosen from the Ra's Abdah area, located in the Egyptian North Eastern Desert, part of the Arabian-Nubian Shield about 20 km Southwest of Safaga City on the Red Sea Coast.

It was digested by acid digestion (Hf and H_2SO_4) and alkali fusion (to dissolute zircon mineral, which includes some REEs). REEs were determined relatively under the optimized conditions on the calibration curves made by the international standard rock reference (GS-N) to overcome the matrix interference effect using ICP-OES (Nuclear Materials Authority, Egypt).

5. Results and Discussion

5.1. Rare earth elements determination

5.1.1. Selection of spectral lines

Firstly, several lines for each element must be chosen, characterized by minimum interference effect with other factors. For this reason, at least threelines were selected for each element and tested with a standard solution of multi-rare earth with a 20 µg/ml concentration. Finally, one line of each component was chosen for determination, giving the nearest result with the standard solution.

5.1.2. Construction of calibration curves and the interference effect

The calibration curves of rare earth elements were constructed using standard synthetic solutions ranging from 0.1 µg/ml to 10 µg/ml, giving calibration curves with acceptable relative standard deviation and detection limit (Table 2).

Table 2. Spectroscopic data and detection limit.

Element	Wavelength (nm)	Det. Limit (M) *10^{-7}	R.S.D.* %
La	379.478	3.60	0.875
Ce	413.765	3.57	0.875
Pr	390.844	2.13	0.900
Nd	399.010	3.47	1.200
Sm	359.260	1.99	1.000
Eu	381.967	1.32	1.100
Gd	342.247	1.28	0.750
Tb	350.917	1.26	0.875
Dy	353.170	1.23	0.875
Ho	348.484	0.60	1.300
Er	326.478	0.68	1.200
Tm	317.283	0.60	1.500
Yb	328.937	0.60	0.900
Lu	261.542	0.60	1.000

It is known that ICP-OES is undoubtedly a very suitable technique for measuring trace levels of element concentration in geological materials. Still, it is often affected by spectral interferences caused by the matrix effect. From the previous work, the interferences are from the existence of some contaminant elements such as Ca, Ba, Fe, K, Na, Al, and Ti, where their concentrations in the matrix are usually orders of magnitude higher than that of the rare earth elements [35]. So, the choice of analytical lines to determine REEs individually is crucial but is not enough to overcome the interference matrix effect.

An international rock sample (MA-N) solution with certified results was measured on the constructed calibration curves prepared from rare earth elements synthetic solutions. The obtained data in Table 3 showed that high interference effects appeared in all aspects due to the matrix effect.

To correct this problem, several methods were usually used internal standardization [22,36,37], standard addition [38], the addition of the interfering elements to the calibration standard (matrixmatching), use of the calibration standard made from a geological standard rocksample [22,] and separation of interfering elements by ion exchange or extraction methods [39,40].

Standard addition and separation of interfering elements require time and chemicals; the internal standardization method is widely used. Still, the degree of the matrix effect may differ from element to element analyzed [41]. Therefore, matrix matching and the calibration made from a geological standard rock sample method were considered the most suitable methods for rapidly obtaining accurate analytical data in the current case. For this purpose, a certified international standard reference (GS-N) was used to construct the calibration curves of REEs on the same selected spectral lines.

The international rock sample (MA-N) solution was measured to test this method, satisfying results (Table 3) and interference minimization.

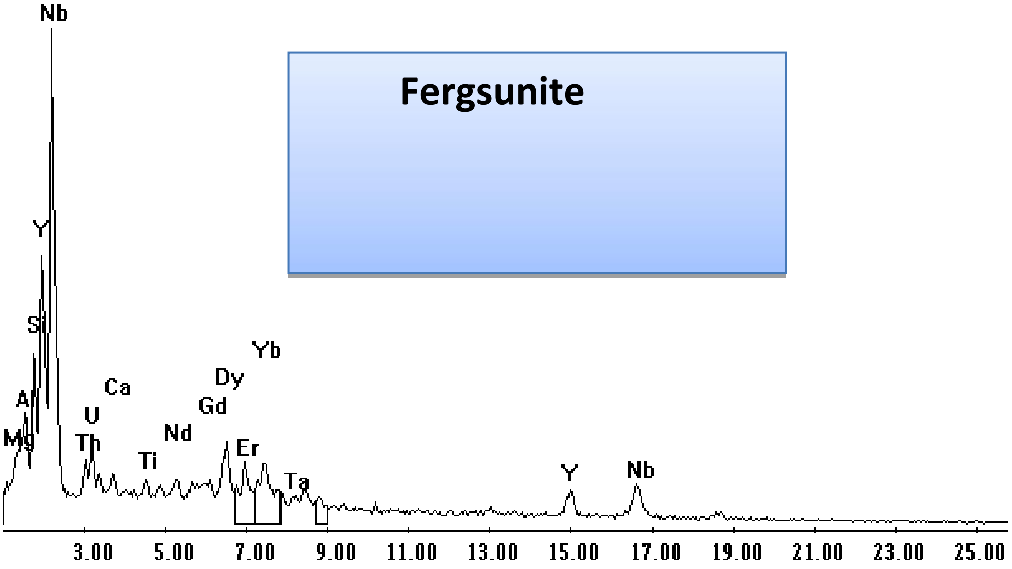
Table 3. Data of certified international standard of granite (MA-N) on calibration curves using synthetic elements (1) and certified international standard reference (2).

Element	Wavelength (nm)	Actual contact. (M) *10^{-}	Measured conc.^{1} (M) *10^{-4}	Accuracy %	Measured conc.^{2} (M) *10^{-4}	Accuracy %
La	379.478	3.599	5.241	54.40	3.750	95.28
Ce	413.765	6.772	6.112	90.26	6.367	94.02
Pr	390.844	0.709	0.167	23.50	0.660	93.00
Nd	399.010	2.773	7.266	62.00	3.071	89.23
Sm	359.260	0.60	0.43	72.56	0.56	93.33
Eu	381.967	0.132	0.047	35.50	0.112	85.00
Gd	342.247	0.509	0.145	28.50	0.4598	90.38
Dy	353.170	0.43	0.115	26.71	0.37	85.74
Ho	348.484	0.103	Not detected	--	0.081	78.82
Er	326.478	0.24	Not detected	--	0.20	56.25
Tm	317.283	0.04	Not detected	--	0.03	75.00
Yb	328.937	0.23	Not detected	--	0.18	79.00
Lu	261.542	0.029	Not detected	--	0.023	82.00

5. 2. Geochemistry of REEs and mineralization

Post-magmatic, deuteric, and hydrothermal processes have significantly affected REEs' distribution. The fluids generated at such stages are highly enriched in complexing agents such as Co$_3^{2-}$, Cl$^-$ and F$^-$ anions. Fluids rich in Cl$^-$ anions can improve LREEs (La-Eu), whereas fluids rich in Co$_3^{2-}$ groups are accompanied by extreme HREEs enrichment (Tb-Lu) [42]. High-temperature fluids may result in both LREEs and HREEs at the expense of the intermediate REES [43], suggested that although the REE group has similar ionic species, they form complexes in the form of Na (REE)F$_4$ at high pressure, with the stability of the HREE-complexes being more significant than those for the LREEs. Thus, the application of REEs geochemistry to hydrothermal systems may be helpful to elucidate its chemical history and the mechanism responsible for metal transport [44,45].

The applied sample in the present study was collected from the altered mineralized zones of syenogranite dikes. These mineralized zones are comprised mainly of iron oxides (ilmenite and magnetite), Nb-bearing minerals (fergsunite), thorite, and zircon minerals (Figures 1 and 2).



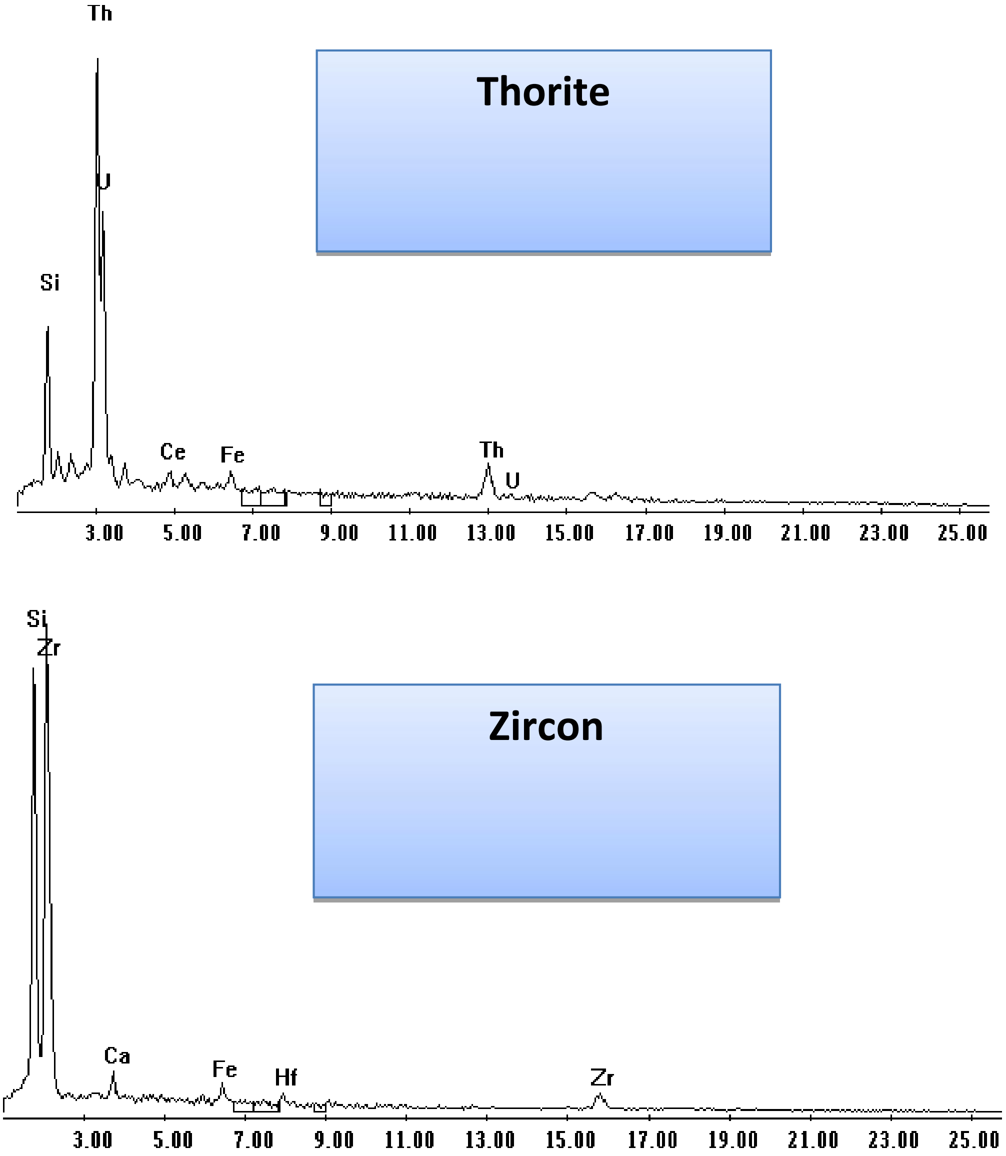


Figure 1. E.D.X. spectrum of the rare metal minerals and zircons in the investigatedsample

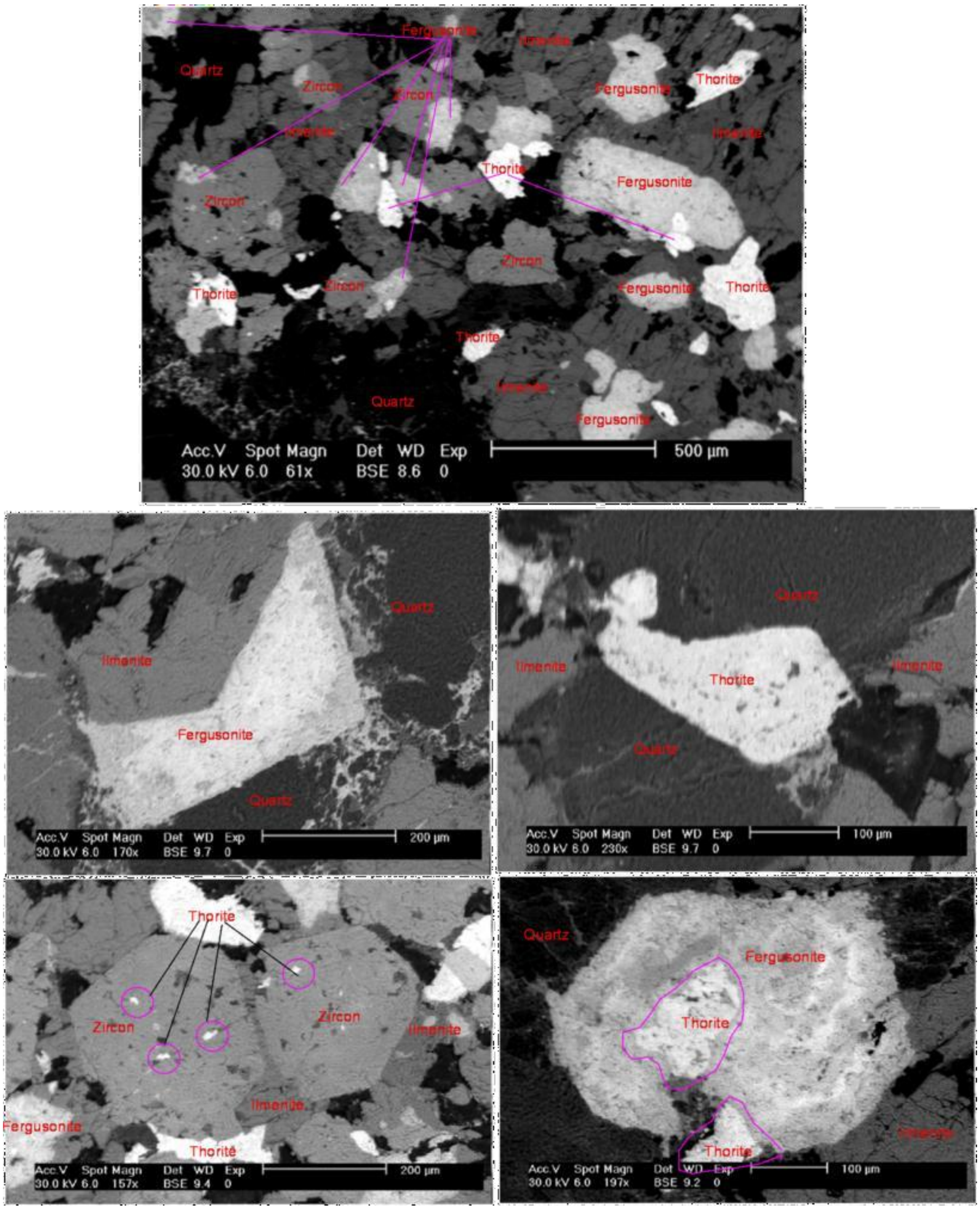


Figure 2. Backscattered electron images of the investigated mineralized altered zones of syenogranite dikes; the dikes compose only iron oxides, fergsunite,thorite, and zircons

5.3. Results of the comparison study

The geological sample, chosen from Ra's Abdah area, Egyptian North Eastern Desert, 20 km Southwest of Safaga City on the Red Sea Coast, was digested by acid digestion (Hf and H_2SO_4) alkali fusion described previously. Rees were determined relatively under the optimized conditions on the calibration curves made by the international standard rock reference (GS-N) to overcome the matrix interference effect using ICP-OES (Nuclear Materials Authority, Egypt). The results and comparative statistics data are described in (Table 4). By comparing the obtained results with that of the expected ones that are analyzed by ICP-MS (Mineral Laboratories,Canada), the measured values obtained from that digested by acids have accurate data in L.R.R.s only due to the incomplete decomposition of the sample because of the existence of zircon mineral which is acid-resistant. In contrast, that digested by alkali fusion gives acceptable results with acceptable accuracy.

The REEs patterns were normalized to chondrite abundance as shown in Figs. 3 and 4 were figured from the analytical data in Tables 3 and 4 to confirm the obtained results. Fig. 3 shows were matching between the resulted data with the certified one and complete matching between results in the case of sample digested by alkali fusion. In the case of acid digestion, the matching was only on the light rare earth elements (La- Gd) (Fig.4).

Table 4. REEs content in granite sample treated by acid digestion and alkali fusion (ppm).

Element	**Expected Conc.***	**Conc. after acid digestion**	**Accuracy %**	**Uncertainty**	**RSD %**	**Conc. after alkali fusion**	**Accuracy %**	**Uncertainty**	**RSD %**
La	6.424	5.992	93.20	0.105	0.14	5.977	93.00	0.035	0.05
Ce	12.385	11.080	89.47	0.11	0.07	10.997	88.79	0.03	0.02
Pr	1.597	1.345	84.22	0.105	0.60	1.457	91.24	0.04	0.21
Nd	5.012	4.999	99.85	0.14	0.19	5.113	97.57	0.055	0.08
Sm	0.751	0.637	84.69	0.11	1.27	0.712	94.69	0.035	0.34
Eu	0.132	0.128	97.00	0.065	3.61	0.141	93.00	0.045	2.43
Gd	0.636	0.693	91.10	0.085	0.78	0.569	89.50	0.04	0.50
Tb	0.113	Not detected	--	--	--	0.079	69.44	0.035	2.88
Dy	0.529	0.113	21.40	0.035	1.96	0.416	78.61	0.015	0.26
Ho	0.103	Not detected	--	--	--	0.117	86.47	0.04	2.26
Er	0.233	0.035	14.87	0.035	6.22	0.187	80.00	0.02	0.64
Tm	0.030	Not detected	--	--	--	0.019	64.00	0.04	13.62
Yb	0.179	Not detected	--	--	--	0.159	88.71	0.03	1.26
Lu	0.023	0.004	17.50	0.02	28.57	0.018	80.00	0.01	6.25

*The analysis of the sample by ICP-MS in mineral laboratories, Canada.

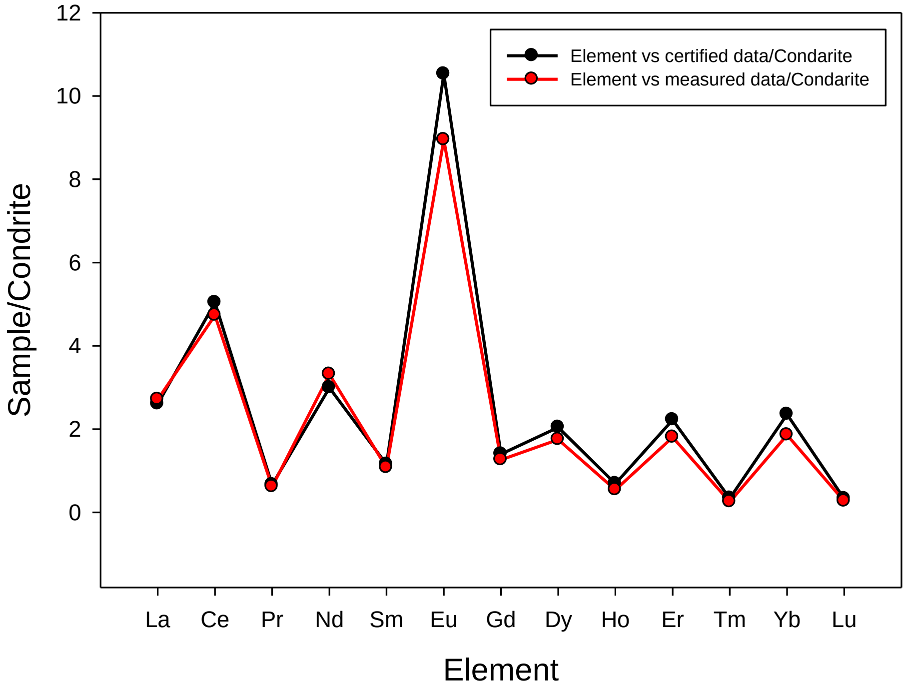


Figure 3. REE patterns of International CRM (MA-N) normalized to chondrite abundance

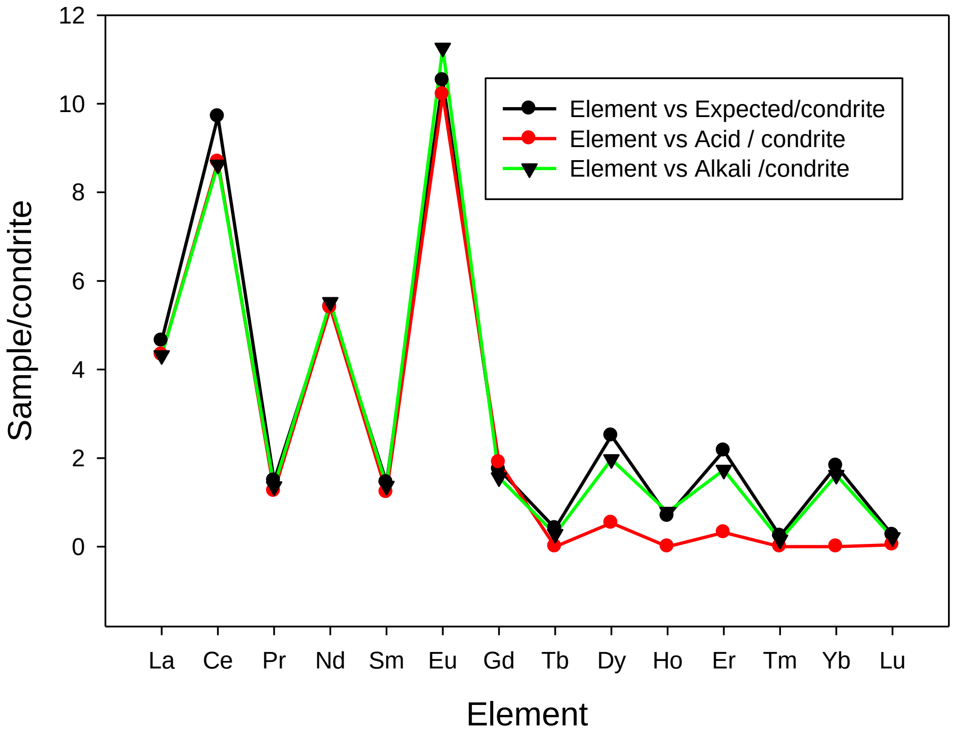


Figure 4. REE patterns of the selected granitic sample normalized to chondrite abundance

6. Conclusion

The analytical method for determining fourteen rare earth elements in granitic and international standard rock samples digested in acid digestion and alkali-fusion using calibration curves made from certified global standard rock samples by I.C.P.-O.E.S. was evaluated and proved to be successful. This method overcomes the problem of matrix interference and incomplete decomposition in the case of acid-resistant minerals such as zircon to give acceptable results with simplicity.

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