Evolution of rare earth elements, uranium and thorium in geological samples by ICP-OES and their characterization

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Abstract. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine rare earth elements, uranium and thorium in granitic soils and rock samples collected from Chumporn and Surat Thani provinces, the southern part of Thailand. The effect of digestion temperature (125 °C, 160 °C, 200 °C and 240 °C) on the concentration levels of elements was investigated. It was found that the digestion temperature of 160 °C had an efficient to leach out the elements to achieve the high concentration of elements for soil samples at different horizons such as O-A, A-B, B-C (1) and B-C(2). For rock sample (D horizon), the digestion temperature did not significantly affect to extract the elements. The results of the analytical study were also compared with the results determined by ICP-MS/OES as obtained from Department of Mineral Resources, Thailand (DMR). A good correlation between the determined values digested at 160 °C and the values measured by ICP-MS/OES as obtained from DMR were found for Ce, La, Pr, Nd, Y, Dy, Eu and Th. The SEM-EDS results demonstrated that the samples particles mainly consisted of Si, and Al with varying amount of Fe, K, Mg, Ca, Na and Ti. Quartz and albite were found to exist in all samples that were confirmed by XRD analysis.

1. Introduction

The determinations of rare earth elements, uranium and thorium are of great interest because of their applications in geochronology, as geochemical tracers and economic potential [1,2]. Rare earth elements, uranium and thorium have been found to deposit in granite rock. This igneous rock also consists of quartz, potassium feldspar, sodium feldspar, mica and hornblende. Its chemical composition is typically 75% silica, 12% aluminum, <5% potassium oxide, <5% soda, as well as by lime, iron, magnesia, and titania in smaller quantities [3,4].

There are several analytical techniques, have been used to determine rare earth element, uranium and thorium in geological samples, including neutron activation analysis (NAA), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence spectrometry (XRF) [5-7]. NAA is a non-destructive and sensitive technique for multi-element analysis. However, it has many drawbacks such as severe interferences from the major elements, a long irradiation time (several hours) for determination of rare earth elements and high cost (needs of a nuclear reactor) [7,8]. XRF is an established non-destructive technique to perform elemental analysis in geological samples. It fast speed, stability, relative ease of
low cost sample preparation and easy operation. Unfortunately, it suffers from serious spectral interferences [8,9].

ICP-OES and ICP-MS have become the powerful multi-element techniques for determination of many major and trace elements including rare earths, uranium and thorium. The main benefit of ICP-OES techniques compared to other techniques are the speed of analysis, wide linear dynamic range, operation simplicity, its ability to analyze all elements in a single run and its tolerance to high concentration of major elements [8,10]. ICP-MS provides high sensitivity, low detection limit, fast analysis, broad dynamic linear range, less spectral interference and simultaneous multi element detection [8,11,12]. On the other hand, the limitations of ICP-OES technique are high instrumental detection limits relative to the low rare earths concentration in most samples. Spectra interference caused by high concentrations of matrix elements is the main drawbacks for both ICP-OES and ICP-MS techniques [8].

In this study, the analysis of rare earth elements, uranium and thorium in granitic soil and rock samples collected from different districts of Chumporn and Surat Thani provinces in the southern region of Thailand by ICP-OES techniques was investigated. The determined results were compared with the data results measured by ICP-MS/OES as obtained from DMR laboratory. In addition, the geological samples were characterized by scanning electron microscopy with energy dispersive X-ray (SEM-EDS) and X-ray diffraction (XRD).

2. Materials and methods

2.1. Sample collection and preparation

Four granitic soils at different horizons (O-A, A-B, B-C) and a porphyritic granitic rock (D horizon) were collected from Chumporn and Surat Thani provinces, respectively in the southern region of Thailand. All samples were crushed and grounded to a fine powder approximately 200 mesh using a ceramic mill.

2.2. ICP-OES measurement

A 50 mg of each sample was digested with a nitric acid in a round bottom flask. The flask was fitted with an electric heating mental (Heating mantle, Falc Instruments, model MM 500, Italy) and equipped with a reflux condenser. The samples were digested at various approximately temperatures such as 125 °C, 160 °C, 200 °C, and 240 °C for 6 hr. After completed digestion, the obtained sample solutions were filtrated and diluted for ICP-OES measurement. The ICP-OES instrument used for measurement of rare earth elements, uranium and thorium was an Optima 5300 DV Perkin Elmer, USA).

Six calibration standard solutions at concentration levels of 0.1 μg/mL, 0.25 μg/mL, 0.5 μg/mL, 1 μg/mL, 2.5 μg/mL and 5 μg/mL were prepared by serial diluting single element stock solution (1000 μg/mL) (AccuStandard, Inc., USA) of all determined elements with 1 v/v% nitric acid.

2.3. ICP-MS/OES reference measurement

The soil and rock samples were sent to the SGS Geochemistry Laboratory (Toronto, Canada) by Department of Mineral Resources (DMR), Thailand for analyzing of all elements. Approximately 0.1 g of each sample was fused with sodium peroxide (Na2O2) flux in graphite crucibles and then were dissolved using diluted HNO3. The digested sample solutions were analyzed by ICP-MS using an Elan 6100 and ICP-OES using a Perkin Elmer Optima 5300 DV.

For ICP-MS measurement, Re (50 μg/L) and Rh (10 μg/L) were used as an internal standard to make corrections for instrument drift effects. In addition, the oxide-hydroxide interference correction was observed using single element solutions of barium, cerium and praseodymium under the routine operating conditions. Concentrations, oxide and instrument drift corrections were calculated offline using a spreadsheet. An internal standard of 5 μg/mL Lu was applied for ICP-OES analysis. Three
rock standards namely SY-4, TILL-4 and RTS-3A were employed. All quality control samples were verified using LIMS (Laboratory Information Management System). Ultrapure water used in this experiment was obtained from a milli-Q water purification system (Merck Millipore, Germany), resistivity 18.2 MΩ·cm at 25 °C. All materials were decontaminated with a 10 v/v% HNO₃ solution for 24 h and after that they were rinsed several times with ultrapure water before use.

2.4. Sample characterization
The powder X-ray diffraction (XRD) patterns of samples were recorded on a Bruker, D8 ADVANCE equipped with Cu Kα radiation (λ = 1.5406 Å) operating at 30 kV and 30 mA. The measurements were performed in the 20 angle range of 20-90° with a 20 step size of 0.039° and a step time of 1 sec.

The scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDS) analyses were obtained using a Tescan Vega 3 SEM equipped with an Oxford Instruments X-Max EDS detector, operating at coated with a layer of gold.

3. Results and discussion

Table 1. Concentrations of rare earth elements, uranium and thorium in μg·g⁻¹ at different horizons of granitic soil and rock samples as measured by ICP-OES at experimental conditions; digestion temperature of 125 °C, digestion time of 6 h (n=3).

| Element | O-A horizon Mean (μg·g⁻¹) | O-A horizon RSD (%) | A-B horizon Mean (μg·g⁻¹) | A-B horizon RSD (%) | B-C (1) horizon Mean (μg·g⁻¹) | B-C (1) horizon RSD (%) | B-C (2) horizon Mean (μg·g⁻¹) | B-C (2) horizon RSD (%) | D horizon Mean (μg·g⁻¹) | D horizon RSD (%) |
|---------|---------------------------|---------------------|---------------------------|---------------------|-----------------------------|---------------------|-----------------------------|---------------------|------------------------|---------------------|
| Dy      | 149.74 ± 3.86             | 2.38                | 158.10 ± 1.79             | 1.33                | 170.41 ± 5.30               | 3.11                | 163.01 ± 1.46               | 0.90                | 126.73 ± 1.26          | 0.99                |
| La      | 57.19 ± 0.04              | 0.06                | 65.78 ± 0.18              | 0.28                | 68.59 ± 0.81                | 1.19                | 65.18 ± 0.32                | 0.50                | 50.82 ± 1.27           | 2.49                |
| Pr      | 32.18 ± 0.71              | 2.20                | 35.63 ± 0.62              | 1.75                | 38.02 ± 0.75                | 1.97                | 36.57 ± 0.37                | 1.02                | 28.30 ± 0.32           | 1.11                |
| Nd      | 36.99 ± 0.31              | 0.84                | 44.48 ± 0.42              | 0.94                | 44.42 ± 0.08                | 0.18                | 44.19 ± 0.30                | 0.67                | 35.49 ± 0.67           | 1.89                |
| Sm      | 8.47 ± 0.18               | 2.11                | 10.43 ± 0.23              | 2.21                | 10.39 ± 0.10                | 1.01                | 10.19 ± 0.11                | 1.06                | 8.57 ± 0.27            | 3.19                |
| Gd      | 4.75 ± 0.11               | 2.29                | 6.21 ± 0.01               | 0.13                | 6.24 ± 0.04                 | 0.66                | 6.09 ± 0.03                 | 0.47                | 5.20 ± 0.03            | 0.61                |
| Y       | 18.99 ± 0.27              | 1.40                | 25.07 ± 0.27              | 1.08                | 28.41 ± 0.33                | 1.18                | 28.49 ± 0.33                | 1.16                | 16.22 ± 0.26           | 1.63                |
| Dy      | 2.73 ± 0.07               | 2.72                | 3.83 ± 0.05               | 1.43                | 4.18 ± 0.05                 | 1.18                | 4.08 ± 0.07                 | 1.67                | 2.68 ± 0.07            | 2.70                |
| Eu      | ND                        | ND                  | ND                        | ND                  | ND                          | ND                  | ND                          | ND                  | ND                     | ND                  |
| Yb      | 0.36 ± 0.01               | 2.08                | 0.87 ± 0.01               | 1.30                | 0.99 ± 0.04                 | 4.21                | 0.97 ± 0.00                 | 0.11                | ND                     | ND                  |
| U       | 1.76 ± 0.03               | 1.72                | 1.74 ± 0.01               | 0.14                | 3.97 ± 0.01                 | 4.69                | 4.69 ± 0.05                 | 1.17                | 4.20 ± 0.03            | 0.74                |
| Th      | 67.22 ± 1.93              | 2.87                | 63.87 ± 2.76              | 4.32                | 65.89 ± 1.06                | 1.61                | 64.25 ± 0.12                | 0.19                | 55.68 ± 1.31           | 2.35                |

Table 2. Concentrations of rare earth elements, uranium and thorium in μg·g⁻¹ at different horizons of granitic soil and rock samples as measured by ICP-OES at experimental conditions; digestion temperature of 160 °C, digestion time of 6 h (n=3).

| Element | O-A horizon Mean (μg·g⁻¹) | O-A horizon RSD (%) | A-B horizon Mean (μg·g⁻¹) | A-B horizon RSD (%) | B-C (1) horizon Mean (μg·g⁻¹) | B-C (1) horizon RSD (%) | B-C (2) horizon Mean (μg·g⁻¹) | B-C (2) horizon RSD (%) | D horizon Mean (μg·g⁻¹) | D horizon RSD (%) |
|---------|---------------------------|---------------------|---------------------------|---------------------|-----------------------------|---------------------|-----------------------------|---------------------|------------------------|---------------------|
| Dy      | 172.80 ± 0.60             | 0.34                | 177.51 ± 4.57             | 2.57                | 191.49 ± 5.11               | 2.67                | 195.16 ± 13.11              | 6.72                | 139.73 ± 0.50          | 0.36                |
| La      | 56.41 ± 0.76              | 1.35                | 66.05 ± 2.14              | 3.24                | 69.66 ± 0.41                | 0.58                | 71.05 ± 6.19                | 8.71                | 52.25 ± 0.65           | 1.24                |
| Pr      | 31.17 ± 0.72              | 2.32                | 34.39 ± 1.25              | 3.65                | 36.62 ± 0.44                | 1.19                | 38.14 ± 3.30                | 8.65                | 27.22 ± 0.04           | 0.16                |
| Nd      | 43.79 ± 0.36              | 0.83                | 52.13 ± 1.65              | 3.17                | 54.28 ± 0.14                | 0.25                | 56.18 ± 5.44                | 9.69                | 42.33 ± 0.24           | 0.57                |
| Sm      | 10.81 ± 0.24              | 2.18                | 13.25 ± 0.41              | 3.08                | 13.64 ± 0.02                | 0.16                | 14.44 ± 1.15                | 7.97                | 11.23 ± 0.00           | 0.02                |
| Gd      | 5.99 ± 0.14               | 2.26                | 7.65 ± 0.18               | 2.29                | 8.06 ± 0.17                 | 2.14                | 8.13 ± 0.68                 | 8.40                | 6.70 ± 0.05            | 0.69                |
| Y       | 21.70 ± 0.30              | 1.39                | 28.36 ± 1.09              | 3.84                | 33.05 ± 0.41                | 1.24                | 34.73 ± 3.18                | 9.14                | 18.58 ± 0.26           | 1.41                |
| Dy      | 3.94 ± 0.04               | 1.13                | 5.79 ± 0.23               | 4.03                | 6.37 ± 0.05                 | 0.84                | 6.67 ± 0.64                 | 9.55                | 4.41 ± 0.12            | 2.83                |
| Eu      | 0.04 ± 0.00               | 0.30                | 0.70 ± 0.03               | 4.11                | 0.81 ± 0.02                 | 2.86                | 0.69 ± 0.04                 | 5.97                | 0.21 ± 0.01            | 6.47                |
Uranium and thorium in granitic soil and rock samples at different horizons were measured by ICP-MS. Table 4 presents the concentrations of rare earth elements, uranium, and thorium in µg·g⁻¹ at different horizons of granitic soil and rock samples as measured by ICP-OES at experimental conditions; digestion temperature of 240 °C, digestion time of 6 h (n=3).

### Table 3.

| Element | O-A horizon | A-B horizon | B-C (1) horizon | B-C (2) horizon | D horizon |
|---------|-------------|-------------|----------------|----------------|----------|
| Ce      | 167.93 ± 2.96 | 1.76 | 164.96 ± 4.20 | 2.55 | 195.02 ± 1.17 | 0.60 | 184.79 ± 1.63 | 0.88 | 128.22 ± 0.78 | 0.61 |
| La      | 66.78 ± 0.81 | 1.22 | 64.16 ± 1.32 | 2.06 | 69.29 ± 0.64 | 0.92 | 66.73 ± 0.47 | 0.70 | 50.37 ± 1.05 | 2.09 |
| Pr      | 33.31 ± 1.40 | 4.20 | 31.38 ± 0.75 | 2.40 | 36.72 ± 0.56 | 1.54 | 34.88 ± 0.47 | 1.35 | 24.88 ± 0.39 | 1.56 |
| Nd      | 49.45 ± 0.96 | 1.93 | 53.63 ± 1.66 | 3.09 | 55.83 ± 1.21 | 2.17 | 55.13 ± 1.48 | 2.68 | 40.88 ± 1.45 | 3.54 |
| Sm      | 10.43 ± 0.31 | 2.93 | 11.80 ± 0.40 | 3.40 | 12.74 ± 0.31 | 2.43 | 12.50 ± 0.17 | 1.38 | 9.97 ± 0.29 | 2.92 |
| Gd      | 5.81 ± 0.06 | 1.01 | 6.54 ± 0.08 | 1.15 | 6.75 ± 0.15 | 2.29 | 6.85 ± 0.35 | 5.09 | 5.83 ± 0.23 | 3.96 |
| Y       | 23.44 ± 0.41 | 1.73 | 27.08 ± 0.93 | 3.42 | 32.21 ± 0.79 | 2.44 | 32.36 ± 0.82 | 2.55 | 17.88 ± 0.51 | 2.82 |
| Dy      | 4.65 ± 0.06 | 1.25 | 4.29 ± 0.11 | 2.52 | 5.22 ± 0.35 | 6.73 | 4.96 ± 0.27 | 5.38 | 3.39 ± 0.09 | 2.76 |
| Eu      | ND           | -    | 0.17 ± 0.03 | -   | 0.19 ± 0.03 | - | 0.14 ± 0.02 | 0.00 | ND            | -    |
| Yb      | 0.89 ± 0.00 | 0.11 | 1.06 ± 0.03 | 2.60 | 1.25 ± 0.14 | 11.32 | 1.30 ± 0.04 | 3.27 | ND            | -    |
| U       | 6.04 ± 0.15 | 2.50 | 4.24 ± 0.21 | 4.95 | 6.19 ± 0.07 | 1.12 | 6.23 ± 0.25 | 4.00 | 4.61 ± 0.73 | 15.77 |
| Th      | 65.40 ± 1.77 | 2.71 | 57.27 ± 1.11 | 1.93 | 59.50 ± 1.38 | 2.32 | 58.70 ± 1.68 | 2.86 | 44.45 ± 1.16 | 2.61 |

The concentrations of rare earth elements (Ce, La, Pr, Nd, Sm, Gd, Y, Dy, Eu, and Yb) uranium and thorium in granitic soil and rock samples at different horizons, digested at different temperatures and measured by ICP-OES are illustrated in Table 1, 2, 3, and 4. It can be noted that the concentration values of all measured elements increased with increasing of digestion temperature from 125 °C to 160 °C, except for rock sample (D-horizon). No significant differences were observed in those values when digestion temperature increased up to 200 °C. However, an increase in digestion temperature from 200 °C to 240 °C resulted in a decrease in the concentration of all measured elements. As expect, the
elements can be extracted when digestion temperature increased, however the extraction efficiency was limited at high temperature over 200 °C. It was due to loss of some analytes and contamination problems, despite the use of a reflux condenser. It seemed that the digestion temperature did not affect the determination of elements for rock sample (D horizon as differed from soil samples (O-A, A-B and B-C horizon)). It was due to the lower organic matter in D horizon compared to in O-A, A-B and B-C horizon samples, resulted in the reduction of matrix effect during digestion process using low temperature.

**Figure 1.** Correlation between the data sets of rare earth elements, uranium and thorium measured by ICP-OES and ICP-OES/MS from DMR.
The precisions of the analytical results are presented as the relative standard deviation (RSD) in Table 1, 2, 3 and 4. The RSD of analytical results at digestion temperature of 125 °C were lower than 5% for all elements. For digestion temperature of 160 °C, the RSD values of data sets were below 5% for most elements, except for Eu and U. The analytical errors for Eu might be due to its very low concentration level in the samples. The spectral interferences caused by the overlapping of the analyte lines by rare earth elements and Fe led to the analytical error of U [13]. It can also be noted that the determination of B-C (2) horizon sample generated higher RSD (5-10%) than other samples for most elements, indicating the symmetric error in the sample preparation. At digestion temperature of 200 °C, the RSD of all samples of 0.5% - 5% were achieved for most elements, except for Dy, Yb, Eu and U. For high digestion temperature of 240 °C, large RSD were observed for all samples, revealing the loss of volatile elements and evaporation of reactive mixture during acid digestion process.

Figure 1 shows the comparison of analytical results at digestion temperature of 160 °C and 200 °C and the values measured by ICP-MS/OES as obtained from DMR. A significant high linear relationship between the concentrations digested at 160 °C by ICP-OES and the values measured by ICP-MS/OES as obtained from DMR were obtained with \( R^2 \) ranging from 0.861 to 0.981 for Ce, La, Pr, Nd, Y, Dy, Eu and Th. In case of Sm, Gd and Yb, there were a poor correlation (\( R^2 < 0.850 \)) between the concentration results digested at 160 °C and the concentration obtained by DMR. It can be seen that the concentration values at digestion temperature of 200 °C were in good agreement with the data sets obtained from DMR for Ce, Nd and Y (\( R^2 > 0.850 \)). The linearity was lost in both digestion temperatures for U. The concentrations of all determined elements were lower than that of obtained by DMR, indicating the incomplete digestion of samples.

Figure 2. SEM images of granitic soil and rock at different horizons (a) O-A, (b) A-B, (c) B-C (1), (d) B-C (2) and (e) D.

The SEM images and EDS analyses of the soil and rock samples at O-A, A-B, B-C (1), B-C (2) and D horizons are showed in Figure 2 and Table 5, respectively. It was found that all sample particles mainly consisted of Si, and Al with varying amount of Fe, K, Mg, Ca, Na and Ti. The values obtained from EDS analysis of SiO\(_2\), Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), K\(_2\)O, MgO, CaO, Na\(_2\)O and TiO\(_2\) were 40-68%, 9-27%, 3-6%, 2-6%, 0.3-0.8%, 0.2-1.5%, 0.2-1.3%, and 0.2-0.8%, respectively. This result was in agreement with the XRF results obtained from previous experiment [14]. The high amount of SiO\(_2\) and Al\(_2\)O\(_3\) indicated that these samples were typical of igneous granitic rocks. The presence of K\(_2\)O and Na\(_2\)O
confirmed the alkaline nature of these rocks. The relatively large amount of Fe$_2$O$_3$ associated with biotite. The particle sizes of all samples were ranging from 2-100 $\mu$m with most particles having irregular shapes.

Table 5. EDS analysis of granitic soil and rock at different horizons.

| Element | O-A horizon | A-B horizon | B-C (1) horizon | B-C (2) horizon | D horizon |
|---------|-------------|-------------|-----------------|-----------------|-----------|
| Si      | 52.1        | 60.9        | 62.7            | 46.8            | 68.2      |
| Al      | 27.6        | 23.1        | 20.9            | 26.6            | 8.9       |
| Fe      | 10.3        | 7.9         | 9.6             | 9.9             | 4.0       |
| K       | 8.2         | 5.2         | 4.3             | 12.3            | 7.0       |
| Mg      | 0.8         | 0.6         | 0.3             | 0.4             | 0.8       |
| Ti      | 0.3         | 0.0         | 0.3             | 0.0             | 1.2       |
| Zr      | 0.2         | 0.2         | 0.0             | 0.0             | 1.6       |
| Ce      | 0.2         | 0.1         | 0.4             | 0.2             | 0.1       |
| P       | 0.1         | 0.0         | 0.0             | 0.1             | 0.0       |
| Mn      | 0.1         | 0.3         | 0.1             | 0.2             | 0.0       |
| Ca      | 0.0         | 0.2         | 0.1             | 0.4             | 2.6       |
| Th      | 0.0         | 0.6         | 0.2             | 1.9             | 0.8       |
| Na      | 0.0         | 0.4         | 0.1             | 0.6             | 2.2       |
| La      | 0.0         | 0.0         | 0.1             | 0.6             | 0.1       |
| Y       | 0.1         | 0.0         | 0.9             | 0.0             | 2.0       |
| U       | 0.0         | 0.6         | 0.0             | 0.0             | 0.4       |

Figure 3 shows the XRD patterns of the soil and rock samples at different horizons. All patterns exhibited a mineralogical composition comprising quartz (SiO$_2$) and albite (NaAlSi$_3$O$_8$ or CaAl$_2$Si$_2$O$_8$). In addition, the hexagonal and triclinic crystal structure was observed for quartz and albite, respectively. Consistent with the SEM-EDS and XRF analyses, XRD results indicated that Si and Al were the major components of granitic rocks.
4. Conclusion
The concentrations of rare earth elements, uranium and thorium in granitic soil and rock samples were determined by ICP-OES. The digestion temperature ranging from 125 °C to 240 °C showed a significant effect on the concentration of all elements for soil samples whereas they were no significant influence on those concentrations in rock sample. At digestion temperature of 160 °C, the high concentrations of the most elements were achieved and those values were in good agreement with the values measured by ICP-MS/OES as obtained from DMR, except for U. The SEM-EDS and XRD results showed that all samples contained high amount of silicate and aluminum as related to granitic soil and rock types.

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\textbf{Acknowledgments}

The authors gratefully acknowledge Office of Atoms for Peace (OAP) for help with the analysis of SEM-EDS. The authors would also like to acknowledge the geological samples from Department of Mineral Resources (DMR).