THE DETERMINATION AND DISTRIBUTION OF Ti, P, Zr, Mn, AND V IN GRANITIC PLUTONS OF NORTHWESTERN ANATOLIA

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ABSTRACT. — This paper deals with methods of determination and distribution of titanium, phosphorus, zirconium, manganese and vanadium in granitic plutons of Northwestern Anatolia and Thrace. The results are represented graphically as a function of SiO_2. The comparison of the results shows that the rocks in question are actually of the same origin.

INTRODUCTION

Determination and distribution of the minor elements of the Northwestern Anatolian granitic plutons produced a few important results. As it was previously mentioned, the plutons in question are situated in Western Anatolia, but for the sake of comparison the pluton of Demirköy (Thrace) is included in our study. Sixteen plutons were observed in our area of study and at least 20 representative samples were collected from these plutons. These samples were mixed in an equal amount and the mixture was chipped by a jaw crusher and then powdered in a ring mill and an agate crusher. The powdered sample was then divided into four parts and 50 grams of it were separated for further crushing; up to 200-mesh fraction was obtained by using an agate crusher again. The finely powdered sample was further put in a 105°C-oven for four hours and then transferred into a dessicator.

Table - 1

Average petrographic compositions and locations of the plutons mentioned in this study*

Name	*Type of rock*	*Location*
Uludağ	Muscovite and biotite granodiorite	South of Bursa
Sancaktepe	Biotite quartz monzonite	Northwest of Gebze
Oylat	Hornblende and biotite granodiorite	Southeast of Bursa
Kazdağ (Katrandağ)	Hornblende and biotite granodiorite	North of Edremit (Bayramiç)
Kazdağ (Eybekdağ)	Hornblende and biotite granodiorite	North of Edremit
Kozak	Hornblende and biotite granodiorite	Kozak (east of Ayvalık)
Demirköy	Hornblende and biotite granodiorite	Demirköy (Thrace)
Çavuşbaşı	Hornblende and biotite granodiorite	Polonezköy (İstanbul)
Boğazova	Hornblende and biotite granodiorite	South of Uludağ (between Bursa and Keles)
Ilıca	Hornblende and biotite granodiorite	North of Balıkesir
Kapıdağı (west)	Hornblende and biotite granodiorite	Kapıdağı
Eğrigöz	Hornblende and biotite granodiorite	West of Emet
Çataldağ	Muscovite and biotite quartz monzonite	West of M. Kemalpaşa
Kapıdağı (east)	Hornblende and biotite granodiorite	Kapıdağı
Armutlu	Hornblende and biotite granodiorite	Armutlu
Orhaneli	Hornblende and biotite granodiorite	South of Orhaneli

METHOD OF ANALYSIS

Preparation of samples

250 mg of powdered (200 mesh) sample is weighed in a teflone crucible by using a sensitive balance. 5 ml cone. A.R. HNO_3, two drops of conc. A.R. H_2SO_4 and 15-20 ml A.R. HF were added to this powder and then put on a hot plate. When the liquid was completely dried, the remainder was removed by 1 ml A.R. HNO_3 and 15-20 ml pure water and about 250 ml of d.i.w. were stored in a 250 ml conical flask. In this way the samples are prepared for analyses.

Preparation of standards

To eliminate any error that may be introduced by the difference between the composition of the sample and those of the standards, we have prepared a solution which had an analogous composition with the samples. This solution was prepared from the soluble salts of the elements with amounts corresponding to 15.00 % $A1_2O_3$,1.00 % Fe_2O_3, 2.00 % FeO, 1.00 % MgO, 3.00 % CaO, 3.00 % Na_2O and 3.00 % K_2O. Solution containing Ti, Zr, P, Mn and V was then introduced into the main standard solution by means of microliter. This standard solution was later stored in 100-ml volumetric flasks.

DETERMINATION OF TITANIUM

50 ml of a solution of ammonium acetate-acetic acid (1 M acetic acid and ammonium acetate) of pH 4.7 was taken and put in a 100-ml volumetric flask. 5 ml of the previously mentioned standard solution and powder of 130 mg tiron (disodium-1.2-hydroxybenzene - 3.5 disulphate) were added to this solution. The blue-purple color, which is due to iron in the solution, was eliminated by using about 15 mg of powdered dithionite. After one minute the yellow color absorption was measured in a wave length 430 mμ. The obtained reading was then compared with the previously prepared 900, 1000, 1100, 1200, 1300, 1400 ppm Ti standards (prepared from pure metallic Ti-Johnson Matthey JM 431) and the amount of Ti in the unknown sample was calculated (Sandell, 1959).

DETERMINATION OF PHOSPHORUS

Reagents: 5 % ammonium molibdate solution.

Ammonium vanadate: 2.5 gr of ammonium vanadate was dissolved in 500 ml of hot water and then cooled; 20.ml A.R.HNO_3 was added to the final solution and made up to 1 It.

25 ml of dissolved sample was transferred into 100-ml volumetric flask. 10 ml of 6 N(1/2) HNO_3, 10 ml of ammonium vanadate and 10 ml of ammonium molibdate solutions were added to this sample and left for 30 minutes; then yellow absorption was measured in a wave length of 460 mμ. The result was then compared with 400, 450, 500 μg standard solutions and final calculations for the determination of P were performed. (Chariot, 1964).

DETERMINATION OF ZIRCONIUM

Reagents: EDTA: 4 % solution.
Sodium acetate: 272 gr/lt solution.
Pyrocatechol violet: 40 mg/100 solution.

The procedure followed during the dissolution of powdered rock sample is the same as for the Zr determination, but instead of HNO_3, $HClO_4$ was used. After the complete dryness was reached,

the remaining part was redissolved by 1 ml conc. A.R. HCl and the sample dissolved in this way was stored. 50 ml of this solution was then transferred into a 100 ml beaker. 3 ml EDTA was added to this solution and pH of it brought to 5.2. by adding sodium acetate (pH was measured by pH-meter) and 2 ml pyrocatechol violet was added; then this final solution was transferred into a 100-ml volumetric flask and made up to the mark. 250 mg of sodium fluorite was added to 50 ml of this solution and kept for reference. The remainder was used for spectrophotometric determination, using a 590 mμ wave length. The result was compared with 30, 35, 40 μg standards which were prepared from pure $ZrOCl_2$. $8H_2O$ (Johnson Matthey JM 456).

DETERMINATION OF MANGANESE

25 ml of dissolved portion of the sample was transferred into a beaker. Some 25 ml of diw, 25 ml conc. A.R. nitric, 10 ml conc. A.R. phosphoric acid, 0.3-0.4 gram potassium periodate ($K1O_4$) were added to this solution and gently heated to 90°C for 5-6 minutes. The solution then was cooled to room temperature, transferred into a volumetric flask and made up to 100 ml. For this solution which has a purple color (permanganate) a 525 mμ wave length was used in spectrophotometric determination. The result was compared with 12, 13, 14 μg standard solutions which were prepared from Johnson Matthey JM 815 pure manganese oxide (Chariot, 1964).

DETERMINATION OF VANADIUM

100 ml of the previously prepared sample solution was transferred into a 250-ml beaker. The solution was evaporated up to 10 ml. 1 ml conc. A.R. HNO_3 and 1 ml conc. (1/3) A.R. H_3PO_4 and 0.5 ml 0.5 M (16 %) of sodium tungstate solution were added to this solution and boiled. Following the cooling, the solution was transferred into a 25-ml volumetric flask and made up to the mark. Spectrophotometric analysis was carried out in a wave length of 400 mμ. for the existing yellow color. The result was compared with 1, 1.5, 2, 2.5 μg standards which were prepared from Johnson Matthey JM vanadium.

All of these determinations were carried out in Carl Zeiss VSU-1 spectrophotometer.

TITANIUM

It is well known that titanium in granitic rocks forms independent minerals such as sphene, titanomagnetite and rutile; it can be found as an accessory element in mafic minerals—such as biotite and hornblende—in which it usually replaces the major elements.

Titanium content of granitic rocks averages between 23 400-3420 ppm (Wahlstrom, 1950). Titanium content of igneous rocks is given by Rankama and Sahama to be 4400 ppm. In their study of the southern Black Forest plutons, Hahn-Weinheimer and Ackermann (1967) show that these plutons contain 870-5340 ppm Ti.

Granitic plutons of Northwestern Anatolia and the Istranca massif granodiorites show varying Ti contents from 1100 ppm (Oylat) to 1336 ppm (Demirköy). The arithmetic mean of Ti in these plutons is 1263 ppm. Distribution of titanium as a function of SiO_2 shows a regular pattern (Fig. 1). Although the upper and lower limits of the obtained values of Ti are very close, points corresponding to 67 % and lower SiO_2 show some scattering. Moreover, no appreciable change in the SiO_2 and Ti quantities was observed and the hypothetical line connecting these points is approximately horizontal.

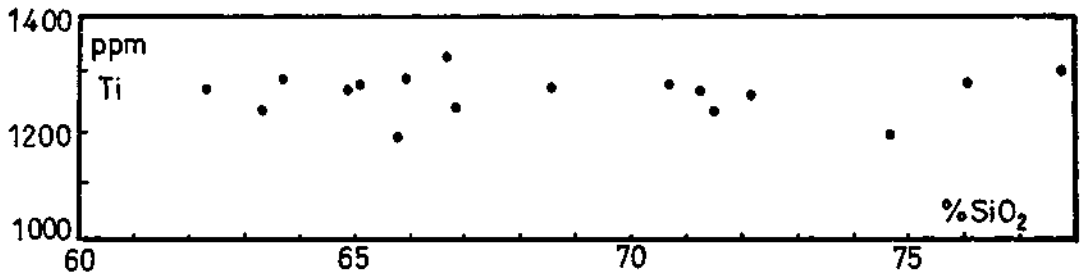

Fig. 1 - Distribution of Ti as a function of SiO_2.

PHOSPHORUS

Phosphorus in this type of rocks is mainly confined to apatite which is known—as well as zircon—to be one of the minerals which crystallize at an early phase of crystallization.

Igneous rocks, on average, contain 1200 ppm phosphorus. Goldschmidt (1958) gives statistical values for P distribution in granitic rocks. According to the same author, the analyzed 340 samples give an average value of 840 ppm P with median and mode being 800 and 650, respectively. 511-1580 ppm P is given by Hahn-Weinheimer and Ackermann (1967) from their study of the southern Black Forest plutons.

The present study, however, shows relatively lower values of P in the Western Anatolian plutons. These values vary between 446 ppm (Uludağ, Çavuşbaşı) and 450 ppm (Gebze, Kazdağ, Armutlu), with arithmetical mean being 448 ppm P. The study of these values as function of SiO_2 of the same rocks ceveals that there is not any apparent correlation between the SiO_2 and P contents of these plutons (Fig. 2).

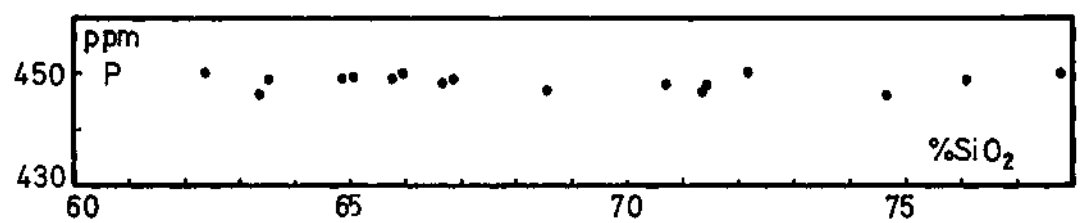

Fig. 2 - Distribution of P as a function of SiO_2.

ZIRCONIUM

This element is mainly confined to zircon ($ZrSiO_4$) which is a very refractory mineral. This mineral also comprises some radioactive elements — e.g. uranium and thorium— in trace amounts. 156 ppm Zr is given by Brooks and Ahrens (1961) as an average value for the earth crust. According to Rankama and Sahama (1954), granitic rocks on average contain 460 ppm Zr. This amount shows a marked drop with rising basicity of the rock from diorite to gabbro and peridotites. Similarly, Ahrens (1954) showed that Canadian granites contain 50-410 ppm Zr and the distribution of this element is lognormal. Hahn-Weinheimer and Ackermann (1967) give 78-281 ppm Zr for the Black Forest granitic plutons.

The Zr content of the granitic plutons in Northwestern Anatolia and Thrace varies between 345 ppm (Kazdağ) and 382 ppm (Kapıdağı), with arithmetical mean being 361 ppm Zr. Distribution of Zr as a function of SiO_2 content of these rocks does not show a very clear trend. There is an indication, however, that acidity of the rock is working towards lowering the Zr content in the rock (Fig. 3). Zirconium reaches its peak values in rocks containing 62-67 % SiO_2.

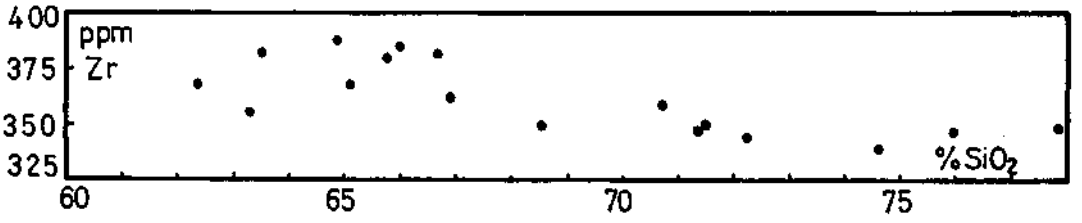

Fig. 3 - Distribution of Zr as a function of SiO_2.

MANGANESE

Manganese does not form independent mineral in granitic igneous rocks, but it is mainly found in mafic minerals to replace elements such as Fe, Ni and Mg. Wager and Mitchell (1951) show that Mn can also be found in plagioclase feldspars. The Mn content of granitic rocks is given by Rankama and Sahama (1950) to be in the order of 965 ppm.

Plutons of Northwestern Anatolia and Thrace contain lower amounts of Mn than given by Rankama and Sahama (1950). The values obtained in this study are very close to each other and varying between 126 ppm (Uludağ) and 129 ppm (in many other plutons). Distribution of Mn as a function of SiO_2 is linear and the graph is parallel to the SiO_2 axis (Fig.4).

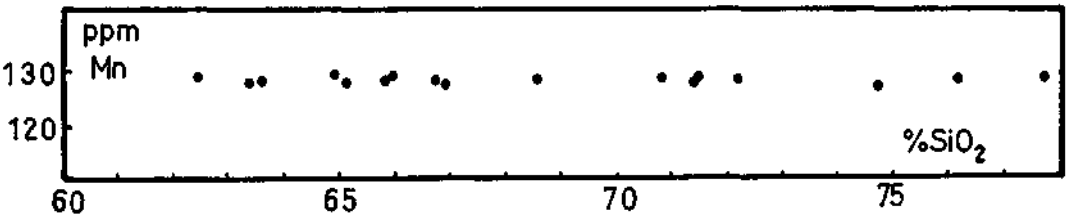

Fig. 4 - Distribution of Mn as a function of SiO_2.

VANADIUM

Many studies indicated that V is mainly located in mafic phases of granitic rocks, such as biotite and hornblende. This element usually replaces Fe, Al and Ti within these minerals. Rankama and Sahama (1950) give values of V in granite and granodiorite to be 1-20 ppm (based on Lentwein, 1941). On the other hand, Ahrens (1954) shows that V has a lognormal distribution in Canadian granites. The values given by the same author vary between 5.5 and 630 ppm. In the earth crust, however, the average value of V is given to be 120 ppm (Brooks & Ahrens, 1961). It is apparent that this value has been affected by the inclusion of sedimentary rocks which show relatively higher V contents.

The plutons of Northwestern Anatolia and Thrace contain 18 to 21 ppm V (see Table 2). The average value of 19 ppm obtained in this study fits very well with the existing data on the V

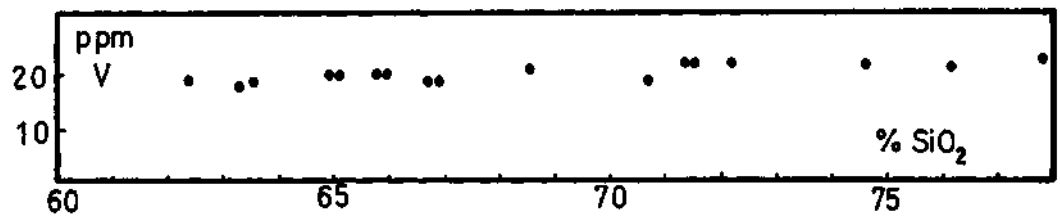

Fig. 5 - Distribution of V as a function of SiO_2.

content of granitic rocks. The distribution of V as a function of SiO_2 closely resembles the distribution of Mn and it can be stated that it has a regular pattern.

Table - 2

Pluton	*SiO_2 (%)*	*Ti (ppm)*	*Zr (ppm)*	*P (ppm)*	*Mn (ppm)*	*V (ppm)*
Uludağ (outer zone)	74.76	1190	365	446	126	21
Uludağ (inner zone)	71.40	1270	380	447	128	21
Sancaktepe	77.76	1300	379	450	127	22
Oylat	65.80	1180	360	449	128	19
Kazdağ (Katrandağ)	65.99	1290	350	450	129	19
Kazdağ (Eybekdağ)	62.43	1270	345	450	129	18
Kozak	66.99	1240	346	449	128	19
Demirköy	66.75	1336	348	448	128	18
Çavuşbaşı	63.42	1230	366	446	128	17
Boğazova	65.13	1280	375	449	128	19
Ilıca	63.58	1290	370	449	128	18
Kapıdağı (west)	70.81	1280	382	448	128	18
Eğrigöz	71.42	1230	350	448	128	21
Çataldağ	76.15	1280	348	449	128	20
Kapıdağı (east)	68.55	1270	349	447	129	20
Armutlu	72.27	1260	355	450	128	21
Orhaneli	64.90	1270	375	449	129	19

RESULTS

The distribution of trace elements Ti, P, Zr, V and Mn in the granitic plutons of Northwestern Anatolia and Thrace show that Zr and V appear to have similar values as given for other granitic rocks in many parts of the world, but Ti, P and Mn have lower values than the average granitic rocks.

The study of distribution of these elements as a function of SiO_2, V, Mn and P shows regular variations, but titanium has scattered values up to 67 % SiO_2. This behavior is also observed in the distribution of Zr.

The regular distribution of these elements indicates that granitic plutons of Northwestern Anatolia and Thrace are of the same origin; in other words they belong to the same magmatic facies.

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