DETERMINATION OF RUBIDIUM BY FLAME ATOMIC ABSORPTION SPECTROSCOPY IN SILICATE ROCKS AND ITS APPLICATION TO IDENTIFY THE TYPES AND TECTONICS OF ROCKS

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ABSTRACT

A new method is described for the determination of Rb^+ concentrations in silicate rocks by FAAS, matrix effect is not observed with Rb. Standard addition method is performed to analyse silicate samples opened by hydrochloric acid and compared with those of the same samples opened by nitric acid. It emphasized that the rubidium does not exhibit any interference from its matrices especially when we use nitric acid for rock sample attack. Chemical analysis of different rocks is carried out and the obtained Rb data are used to identify the incompatible behavior of the rocks and the tectonic setting environment.

1. INTRODUCTION

Rubidium is defined as a member of lithophile elements. It shows an affinity for silicate phase and is concentrated in silicate portion (crust and mantle) of the earth. .Also, rubidium has large ionic radii between 118 to 167 picometers (Pm) and termed large-ion-lithophile element group which have low substitution due to local distortion in the lattice. Consequently, these elements tend to be concentrated in the molten phase. These elements are called incompatible elements.The incompatible elements are good indicators of the degree of the meeting.

From the above we conclude that rubidium can be used to differentiate between the different rocks that formed the earth crust where the rocks of the oceanic crust contain (2.2 ppm) of rubidium and the continental crust contain (32ppm Rb) [1]. Also, the primitive mantle contains (0.7 ppm Rb) [2, 3]. In the same type of rock, by using the rubidium content, we can differentiate between the different tectonic setting environments at which the rock had evolved. Each rock tectonic setting is characterized by its content value of Rb. Basalt in mid-oceanic ridge E-type has Rb content (5.04 ppm), N-type mid-oceanic ridge has (0.56 ppm) and oceanic island has (31ppm) [4]. Also, the oceanic ridge granite has (4 ppm), the rift related granite has (127 ppm), and within plate granite has (94 ppm) [5].

From a structural stand point, Rb^+ ion with an ionic radius intermediate between the radii of Cs^+ and Na^+ forms a chloride (RbCl) with the 8-coordinated cesium chloride structure at high pressures and the more open 6-coordinated structure of sodium chloride at ordinary pressures (polymorphism). Few polymorphs apparently have no true stability range. We can make general predictions about substances will be isomorphous and what compounds will show polymorphism, but the predictions often prove to be inaccurate because our knowledge of the effects of temperatures, pressure, bond type, impurities, and reaction rates is still far from being quantitative.

The distribution of elements in igneous rocks [5] is following the cations with large radii and low electric charges that tend to substitute for potassium, hence are concentrated in felsic rather than mafic rocks. These ions (Rb^+, Cs^+, Ba^+, Pb^+, Ti^+) are often called "the large-ion lithophile" group, their abundance in a rock series is a good indication of the extent to which differentiation has sorted out constituents of the original igneous material.

The rare alkali metal rubidium is so similar to potassium that several tenths of percent can be accommodated as replacements of Rb^+ for K^+ in micas and feldspars. This work aims to

ensure the applicability of FAAS for Rb determination in different rock samples and the obtained data used for identification of the tectonic and type of the rocks.

2. EXPERIMENTAL

2.1. Materials

All chemicals utilised for the preparation of the solutions, were of the analytical grade. Double distilled water is collected from (Kottermnnl034). Standard stock solution were prepared by dissolving accurately weighted amounts of materials as it is known, and finally diluted to appropriate volumes and stored in clean polyethylene bottles. Standard solutions used for obtaining AAS calibration curves were prepared by accurate dilution from thier concentrated stock solutions (Inorganic Ventures).

2.2. Apparatus

A UNICAM Atomic absorption spectrometer model 929, was used for this study The AAS set up, according to the manufacturer specification, is out lined in table (1).

Table (1): Operating conditions of AAS for Rb element

Element parameters	Rubidium (Rb)
wavelength	780.0 nm
Alternative wavelengths	794.8, 420.2 nm
Lamp current	100%
Band width	1.0 mm
Flame type	Air -acetylene
Flame chemistry	stoichiometric
Fuel flow	1.1 L/min

2.3.2. Calibration

After adjustment of the parameters (oxidized ratio and 16 mm burner height) to give max absorbance, standard absorbance values were measured for 0.25, 0.5, 1, 3, 5, 10 ppm Rb⁺ solutions containing 0.2% w/V of K as ionization buffer and the calibration curve was constructed.

3. RESULTS AND DISCUSSION

An oxidizing, lean, blue air-acetylene flame is used, the burner height is 16 mm. Determinations by AAS are simple and straightforward if sample decomposition is completed by using nitric acid as decomposition agent and using 0.2 w/V of K as ionization buffer. The method is assessed by applying the analysis to some types of rocks (serpentinite, basalt, andesites, Qz-diorite and Y-granite) collected from West Fatira area,.NED Egypt [7]. The rubidium content is determined by the developed method in the present work by FAAS and the obtained results of Rb are compared with those obtained by the X-ray fluorescence technique. The results of Rb obtained by FAAS show well agreement with that obtained by XRF as illustrated in table (2).

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Table (2): Rb content of some rocks determined by our AAS compared with XRF technique.

Rock type	AAS	XRF
Serpentite	2	2.10
Basalt	7	7.08
Andesite	14	13.9
Qz-diorite	97	95.0
Y-granite	145	144

Standard addition method is performed on silicate samples (St.5) [6] opened by hydrochloric acid and compared with those of the same samples opened by nitric acid, the obtained results are illustrated in fig (1). It emphasizes that the rubidium dose not exhibit any interference from its matrices especially when we use nitric acid for rock sample attack.

Table (3) contains the chemical analysis data of the studied rocks, it shows an increase in K content parallel to an increasing in Rb content, in the following order (serpentinite > basalt> andesites > Qz-diorite > Y-granite) and these results agreed well with that mentioned above about substitution of K^+ and Rb^+ due to the similarity in charge and approximity in size for both of them. A prediction that agrees well with the observed concentration of Rb^+ in the feldspars and micas of pegmatites[6].
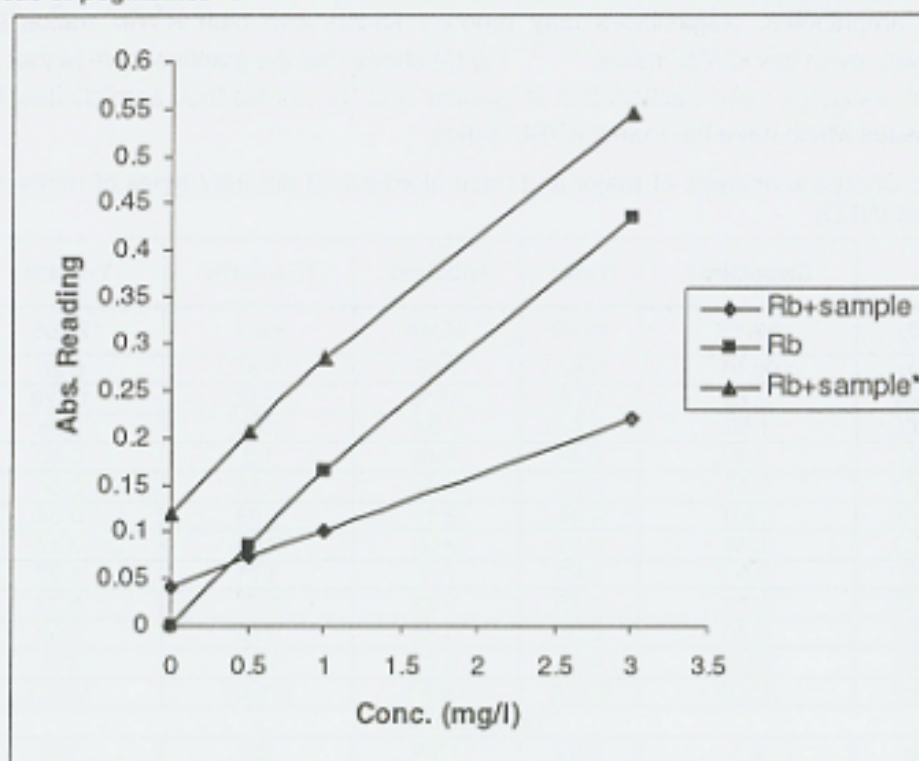

Fig (1): Effect of matrix signal response in the determination of Rb

■   Calibration with aqueous solutions.

▲   Standard additions. Calibration graph – no interference observed from the matrix
         (HNO₃).

♦   Standard additions. Calibration graph showing a depressive effect due to the
            matrix (HCl).
Where sample .... Opened by HCl
         Sample* .... Opened by HNO₃

   In table (3) the serpentines have lower content of Rb (2 ppm), than basalt (7ppm),
andesites (14 ppm) than Qz-diorites (97 ppm) and Y-granite (145 ppm) which emphasizes
that Rb⁺ content can be used as indication of the rock type and also may be used in the
grantic rocks as indication of tectonic setting where Qz-diorite lies in volcanic arc granite and
Y-granite lies within the plate granite tectonic setting as shown in fig (2).
   The elemental ratios of K⁺/ Rb⁺ can provide useful information regarding source regions of
magma generation in the lower crust or upper mantle [9-11]. Also, magma generation
mechanisms can be explained in terms of trace elements behaviour during partial melting or
fractional crystallization processes. In these partial melting of upper mantle materials,
involving amphiboles, plagioclases may produce liquids with high K⁺/Rb⁺ ratios leaving
residues with even low K⁺/Rb⁺ ratios [12, 13]. Fig (3) shows that the granites have higher K⁺/Rb⁺
ratio which indicates more fractionation of granites and Qz-diorites than serpintinites, basalts
and andesites which have the lowest K⁺/Rb⁺ ratios.

Table (3): Chemical analysis of major and trace elements of different types of rocks in West
Fatira area (NED)

	Serpentinite	Basalt	Andesites	Q-z diorite	Y-Granite
SiO_2	38.13	49.62	60.44	68.3	75.05
TiO_2	00.01	0.85	1.05	0.37	0.26
Al_2O_3	2.13	16.6	16.5	15.00	13.28
Fe_2O_3	1.95	3.67	3.34	2.60	0.28
FeO	1.2	7.46	3.48	1.2	0.82
MgO	0.17	0.21	0.1	0.15	0.34
CaO	38.0	4.46	2.61	1.99	0.04
Na_2O	1.80	8.11	3.58	3.99	0.47
K_2O	0.50	3.28	3.3	3.71	4.07
MnO	0.12	0.85	1.39	2.77	3.85
P_2O_5	0.70	0.03	0.23	0.02	0.02
L.O.I	15.25	4.35	3.75	0.26	0.5
Total	99.96	99.78	99.83	100.34	99.98
Trace element					
Rb	2.1	7.08	13.9	95	144
Sr	2	263	453	259	102
Nb	3	8.9	4.37	18	28
Y	4	23	24.3	16	43
Zr	3	109	138	223	160
Ba	10	687	780	757	335
Zn	28	100.2	82	53	37
Th	0.65	1.3	1.88	9	19
U	0.26	0.32	0.62	7.17	2.9
Rb*	2	7	14	97	145

Rb* data determined by AAS

Also Rb^+/Sr^{2+} ratio granitic liquids are significantly affected by the presence of either plagioclase or biotite in the residue. The Rb^+/Sr^{2+} ratio is increased in the melt by the presence of plagioclase and decreased by the presence of biotite in the residue [14]. This ratio is used as discriminating tool to identify the fresh and the weathered rocks and Rb^+-Sr^{2+} variation diagram used to identify the tectonic setting as shown in fig (4) [15]. Fig (4) indicates that the rocks which have higher ratios of Rb^+/Sr^{2+} are more differentiated than the rocks which have lowest ratios. Also, Rb^+/Sr^{2+} isotopes ($^{87}Rb^+/^{86}Sr^{2+}$) are used to determine the age of the minerals and the rocks that are present in the earth.

The Ba^{2+}-Rb^+ variation diagram shown in Fig (5), can be used to signify the degree of the fractionation of the different rocks. The figure shows that the rocks which have lowest values are more differentiated than those having high values.

The Rb^+/U^{+6} variation diagram in fig (6) shows an increasing trend from ultrabasic (serpintinites rocks) to the acidic rocks (Y-granites), confirming the incompatible behaviour of both Rb^+ and U^{+6}.
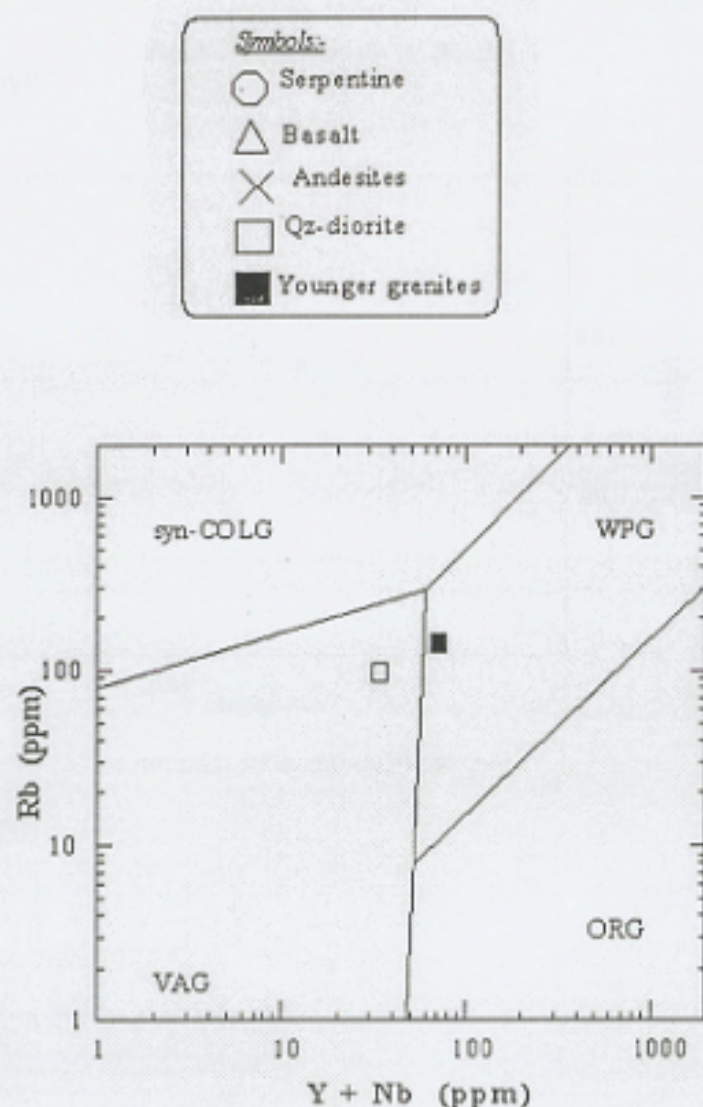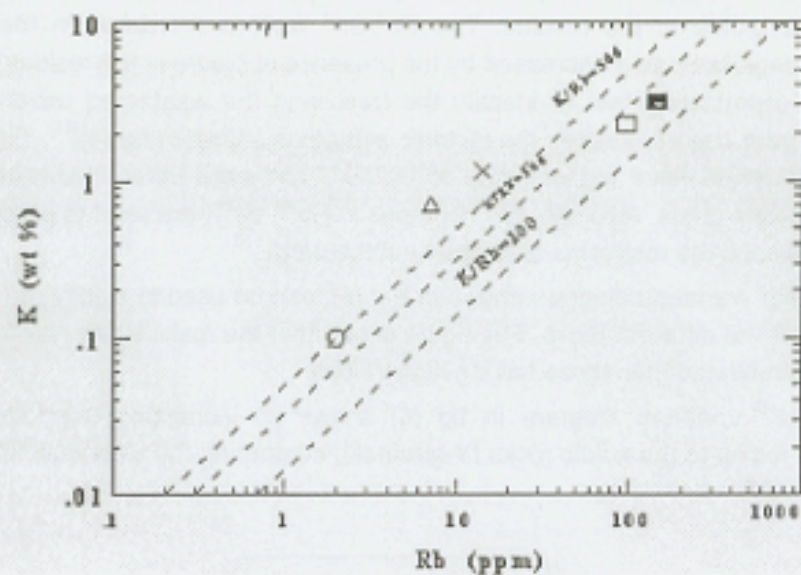

Fig. (2): Rb-Y+Nb variation diagram

Fig. (3): K -Rb variation diagram
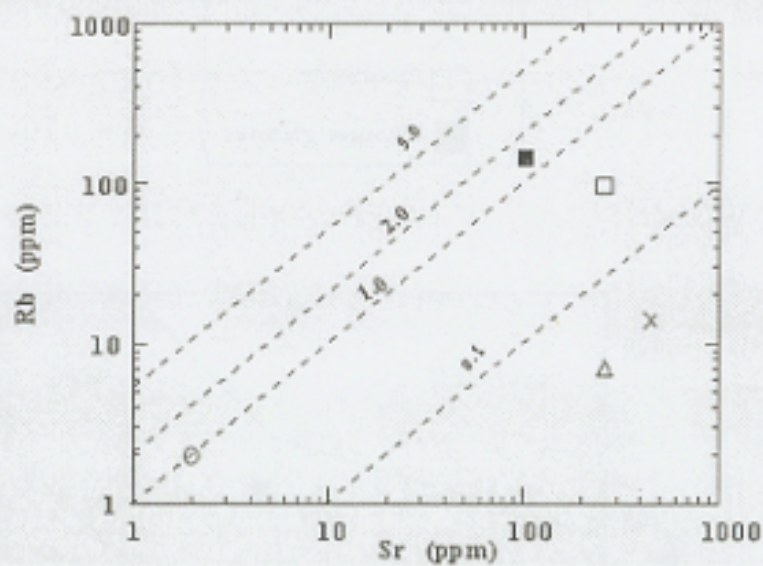
Symbols as in Fig (2)

Fig.(4): Rb-Sr variation diagram
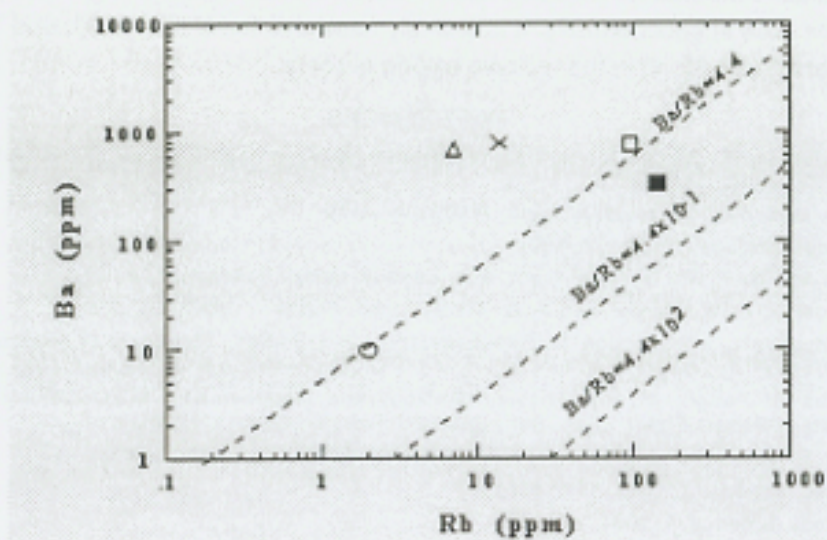
Symbols as in Fig (2)

Fig. (5): Rb-Ba variation diagram
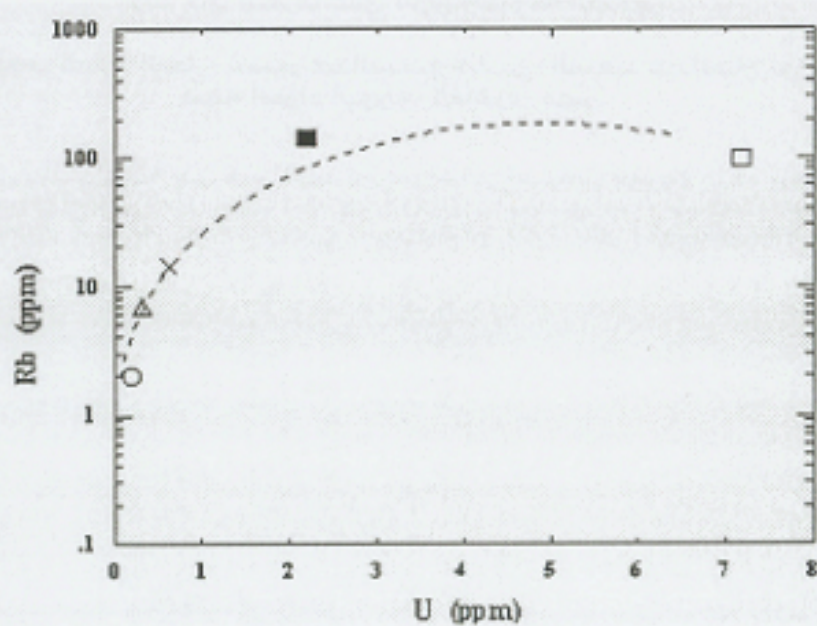
Symbols as in Fig (2)

Fig. (6): Rb-U variation diagram

Symbols as in Fig (2)

4-Conclusion

FAAS is a suitable method for rubidium determination and accurate enough. The Rb data has a main significance in geochemistry. It is strongly related to the K, Ba, Sr, U, and Th, and can have important applications in the tectonic setting of rocks.

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نعيين عنصر الروبيديوم باستخدام جهاز الامتصاص الذري في الصخور السليكانية ونطبيق ذلك في النعرف على أنواع وتكنونية الصخور

وفقي السيد النجار- تيسير عبدالسميع لاشين- السعيد عبدالفتاح نوح
هيئة المواد النووية- الفاهرة- مصر.

يتضمن هذا العمل دراسة إمكانية تعين عنصر الروبيديوم في الصخور السليكانية بواسطة طريقة الإضافات القياسية ودراسة تأثير الأحماض المختلفة على النعين . وقد وجد أن فياسات الروبيديوم لاتتأثر بالتداخلات الخاصة بالوسط خاصة عند فتح العينات باستخدام حمض التتريك وتم نطبيق ذلك في النعرف على أنواع وتكنونية الصخور المختلفة .