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Studies on Granitic Pegmatites

Quantitative Spectrographic Determination of Magnesium and Iron in Biotites and other Minerals by the Means of the Logarithmic Sector.

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Abstract

A method is described for the rapid quantitative analysis of magnesium and iron in biotites requiring only 10mg of powdered samle. The procedure is applicable to the other minerals which contain the above two elements as major constituents in the general ranges of 4–50 per cents Fe_2O_3 and 1–17 percents MgO. The method gives sufficient accuracy and speed for the purpose of studying statistically the variations of the concentrations of magnesium and iron contained in the biotites of the granites of the several regions.

Samples in the form of fine powder are mixed at the ratio of 1 part of sample to 19 parts of cupric oxide which serves as internal control, diluent and buffer. To 1 part of this mixture, 30 parts of carbon dust as diluent and buffer are added.

Introduction

As a part of the study of the granitic pegmatite of which a few papers[1] have been already made public, the writer is desirous of studying statistically the characteristics with regard to the chemical constituents of the biotites contained in the biotite granites of the several regions.

For this purpose, first of all the quantitative analyses of major and minor constituents of a biotite should be done. Hitherto, W. von Engelhardt,[2] J. M. Bray,[3] S. R. Nocholds[4] and R. Allens[4] etc. have applied the spectrochemical quantitative analysis to the minor constituents, but as to the major ones only the wet chemical analysis which is a slow and tedious method has been used in a quantitative analysis of a biotite. It is absolutely necessary to the writer's study to analysis many biotities. Therefore, the following requirements should be satisfied for the analytical method used in

the writer's study : rapidity, the constant accuracy far the analytical results, and the quantity of the sample required for the analysis should be as small as possible. The method which fulfils most of these requirements will be the quantitative spectrochemical analysis.

Furthermore, the spectrograph used in the writer's laboratory is a medium type (Adam Hilger E_2) and a biotite is a mafic mineral of which emmission spectrum has many spectral lines, therefore the writer used the logarithmic sector method in which the width of the slit of the spectrograph may be made smaller than that in the other method.

In this paper, the method of the quantitative spectrochemical determination of magnesium and iron contained in biotites is described. The mode of the variation of these two elements in mafic minerals contained in rocks is generally one of the most interesting problems on petrology and economic geology.

Apparatus

Excitation Source : A direct-current arc source is employed with open circuit voltage of 110 volt, arc current 4.0 amperes. A parallel resistance is used to control and limit the current.

Spectrograph : Adam Hilger E_2 type spectrograph is employed. It is controlled to separate clearly the analytical lines from other lines in the spectrum of the sample in the spectral region 2200 to 3550 Å.

Recording Equipment : The spectra are recorded on Fuji process spectrographic plate.

Logarithmic Sector : The logarithmic spiral sector modified by O'Brien[5] is rotated before the slit of the spectrograph at the constant speed of 500 r. p. m.

Developing Equipment : Emulsions are developed in an open tray with temperature control.

Method of Reading Length of Spectral Lines : The new apparatus designed by the weriter, is used. The details of it will be announced separately.

Procedure

Preparation of samples : Samples are pulverized to a fine powder in a suitable agate mortar. 1 part of sample (10 mg) is mixed thoroughly with 19 parts of cupric oxide for 30 minutes, and then 1 part of this mixture

is mixed again throughly with 30 parts of carbon dust. Thus the expected concentration of the element is about 0.02 percents by weight with respect to the total weight of the buffer (carbon dust) and the internal standard (cupric oxide) used.

Preparation of standards. Pure oxides of the following elements and potassium chloride were used in preparing synthetic standard mixtures : iron, magnesium, silicon and aluminium. These oxides and potassium chloride are mixed thoroughly with one another, according to percentages shown in table 1, and nine standard mixtures are prepared. Afterward 1 part of each standard mixture (10 mg) is mixed with 19 parts of cupric oxide, and then 1 part of this mixture is mixed with 30 parts of carbon dust.

Table 1. Standard mixtures for Fe_2O_3 and MgO

Sample	Fe_2O_3	MgO	SiO	Al_2O_3	KCl
1	50.00	1.00	27.7	13.44	7.86
2	26.00	2.50	40.4	19.60	11.50
3	14.00	6.50	44.9	21.80	12.80
4	7.50	16.00	43.2	21.00	12.30
5	4.00	40.00	31.6	15.40	9.00
6	15.12	11.39	34.0	32.00	7.52
7	18.84	14.91	44.9	10.00	11.35
8	21.46	16.17	48.4	3.20	10.77
9	12.20	8.0	75.0	0.10	4.70

Electrode System : The upper electrode (cathode) is a purified carbon rod 0.5cm in diameter and 3.3cm long with a flat end 0.45 cm in diameter. The lower sample-carrying electrode (anode) is a purified carbon rod 0.42 cm in diameter and 2.6 cm long, with a hole 0.3 cm in diameter, 0.32 cm in depth. The hole is packed level with a sample or a standard.

Arc gap width is maintained at 0.7cm.

Excitation : The samples and the standards are arced in duplicate at D. C. 110V. 4 amperes. After initial setting, further adjustments of current are made by parallel resistance.

Exposure Conditions.

spectral region. 2280 Å—3550 Å
slit width. about 0.015 mm
slit length. 1.8 cm
exposure period. 20 seconds

The spectrograph is illuminated according to the " Kollimatorabbildung " method.

Photographic Processing

Emulsion. Fuji process spectrographic plate.

Development. maximum contrast developer,[6] Open tray, 3 minutes, 18°C.
Fixing. F. F. H-4.
Washing. flowing water, 1 hour.

Preparation of working curve

In Fig. 1 and 2, are shown the working curves for magnesium oxide and iron oxide.

In Fig. 1, the difference in the line length of the magnesium line at 2795.54 Å and copper line at 2766.38 Å is plotted against the log of the magnesium oxide concentration, and in Fig. 2 the difference in the line length of the iron line at 3020.50 Å and copper line at 3010.84 Å is plotted against the log of the iron oxide concentration. The working curves drawn through the points are calculated by the method of least squares.

Analytical reuilts of the samples whose iron oxide and magnesium oxide are known as to their concentrations, and the reliability.

As a test of the reliability and versatility of these methods, one rock, two minerals and nine synthetic samples are analysed. This

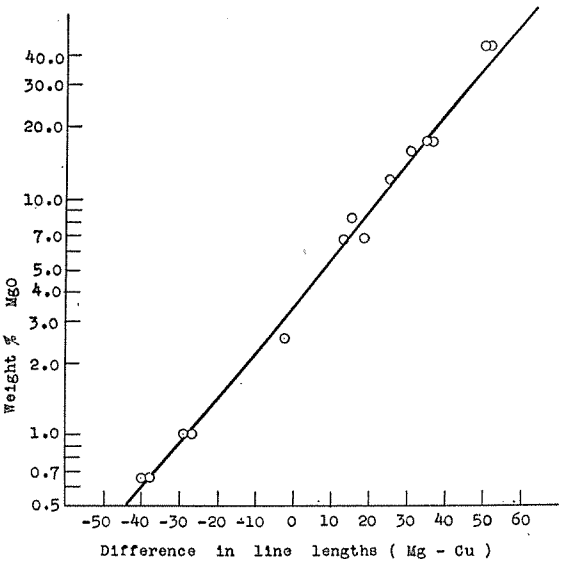

Fig. 1. The working curve for magmesium oxide.

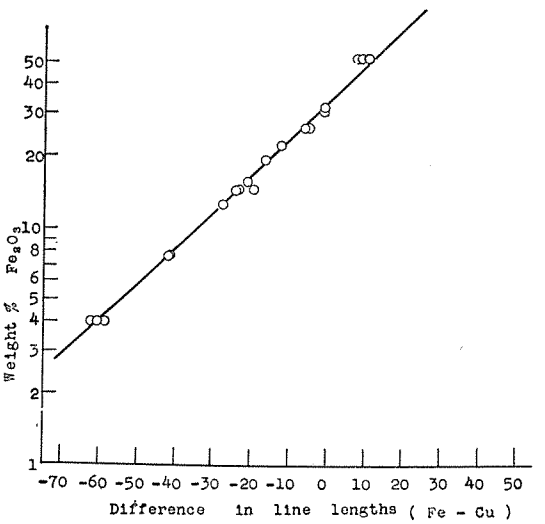

Fig. 2. The working curve for iron oxide.

results of these analyses are given in Tables 2 and 3. In most cases, the correlation between the true value or the chemical value for an oxide and the value found by this methad is very high.

For samples between 1 and 17 % Magnesium oxide, the standard deviation of the spectrochemical results is 1.11, and the average difference between the chemical and spectrochemical determinations is 0.83 %. For samples between 4 and 50 % iron oxide, the standard deviation of the spectrochemical results is 1.57, and the average difference between the chemical and spectrochemical determinations is 0.63 %. For samples between 4 and 26.5 % iron oxide, the standard deviation of the spectrochemical results is 1.03, and the average difference between the chemical and spectrochemical determinations is 0.39 %.

Table 2. Analytical results of a rock and minerals.

Sample	Weight % Fe_2O_3		Weight % MgO	
	Spectrographic	Chemical	Spectrographic	Chemical
Gabbro	12.30	14.82	7.70	8.36
Lievrite	50.20	51.40	0.58	0.66
Tourmrline	16.00	16.99	1.85	1.78

Table 3. Analytical results of artificial samples.

Sample	Weight % Fe_2O_3			Weight % MgO		
	True	Spectrigraphic	Diff.	True	Spectrographic	Diff.
1	3.90	4.00	0.10	1.00	0.98	0.07
2	7.50	7.30	0.20	2.50	2.70	0.20
3	12.20	12.30	0.10	6.50	7.00	0.50
4	14.00	15.00	1.00	8.00	6.60	1.40
5	15.12	15.40	0.28	11.36	10.30	1.06
6	18.84	18.10	0.74	14.91	13.20	1.71
7	21.46	21.14	0.06	16.00	17.50	1.50
8	26.00	26.50	0.50	16.17	16.00	0.17
9	50.00	46.50	3.50			

Analytical results of several biotites contained in granites and a pegmatite

In Table 4, is shown the spectral quantitative analyses of ten biotites whose compositions were entirely unknown to us. Only one of these biotites is the large crystal contained in the pegmatite, others are the small crystals contained in the granite of the Oku-Tango district of Kyoto Prefecture and that of the Kameoka district of Kyoto Prefecture, forming a stock about 10 km in diameter.

Table 4. Analytical results of biotites.

Sample	Weight % Fe_2O_3	Weight % MgO	Ratio Fe_2O_3/MgO
1*	19.3	8.4	2.3
2	20.0	9.6	2.1
3	18.6	10.5	1.8
4	19.4	6.7	2.9
5	29.5	8.2	3.6
6	32.9	9.2	3.6
7	31.0	8.1	3.8
8	21.0	9.6	2.2
9	23.3	8.5	2.7
10	25.4	14.0	1.8

* 1. the biotite of the granite at about 100 m nothwards from the Ôtani mine, Kameoka city, Kyoto Prefecture.
2. the biotite of the granite at the Ôtani mine,
3. do.
4. the biotite of the granite at Kitanosho, Chiyokawa village, Minami-Kuwado district, Kyoto Prefectere.
5. the biotite of the granite at Chozen village, Naka district, Kyoto Prefecture.
6. the biotite of the granite at Morimoto, Mie village, Naka district, Kyoto Prefecture.
7. the biotite of the granite at about 100 m southwards from the Tango-Yura station, Kasa district, Kyoto Prefecture.
8. the biotite of the granite at Takitani, Goka village, Naka district, Kyoto Prefecture.
9. the biotite of the pegmatite at Oro, Goka village, Naka district, Kyoto Prefecture.
10. the biotite of the granite at Yuwaya, Yosa district, Kyoto Prefecture.

Sample numbers 1 and 2 are the biotites which are contained in one and the same hand specimen of the granite. The former is a common-sized pseud-hexagonal crystal (0.1–0.2 cm in diameter) and the latter is a large-sized one (about 1.5 cm in diameter), but analytical results of the two are nearly the same. Sample number 10 is the biotite of the granite which has many sphenes as accessory minerals.

From these analytical results, it seems that the iron would be generally contained much in the biotites of the granite of the Oku-Tango district than in those of the granite of the Kameoka district, but the writer is of course going to statistically ascertain this point analysing many samples by this spectrographic method.

Conclusion

This method is devised with the object of analysing magnesium oxide and iron oxide contained in the small crystals of Biotites of the granite, but it can be widely applied to analyses of any mineral or rock which contains the above two oxides as major constituents. Because, samples prepared for this spectrochemical analyses are diluted as much as 620 times with cupric oxide and carbon dust, and at such strong dilusion the atomic population of the original sample in the arc gases is reduced to such a level that the excitation energy-collision-exchange processes are no longer important in quantitative measurements, therefore the interference between the various elements presented in the original sample, is rendered negligible. The original sample required for the analysis is only 10 mg.

If we want to analyse the sample which contains more than 50 per cents of iron oxide, it is to be diluted with the mixture shown in Table 5 to less than 50 per cents and 10 mg of this mixture is to be mixed with cupric oxide and carbon dust according to the above-mentioned procedure. This procedure is also applicables to the sample which contains more than 17 percents of magnesium oxide, in the same way.

Table 5. Diluent.

KCl	9.0968 g.
Al_2O_3	0.1646 g.
SiO_2	0.3386 g.

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References

1) Takubo, J. and Tatekawa, M.: The distribution of minor elements in pegmatites and granites from the Oku-Tango District, Kyoto Prefecture (Part 1) on the distribution of Barium and strontium. Mineral. Jour. Jap., 1, 301—, (1954).

Tatekawa, M.: Spectrogrophic distribution of minor elements in quartzs and feldspars contrined in granites and pegmatites of the Oku-Tango District, Kyoto Prefecture. Mem. Coll. Sci Univ. Kyoto, Ser. B, 21, 183—, (1952).

Tatekawa, M.: The pegmatites of the Oku-Tango district of Kyoto Prefecture researched chiefly from the viewpoint of trace elements. Mem. Coll. Sci. Univ. Kyoto, Ser. B, 22, 199—, (1955).

2) Engelhard, W. VON: Die Geochemie des Barium. Chemie der Erde, 10, 187-, (1936)

3) Bray J. M.: Spectroscopic distribution of minor elements in igneous rocks from Jamestown, Colorado. Bull. Geol. Soc. Am., 53, 765—, (1942).

4) Nockolds, S. R. and Allen, R.: The geochemistry of some igneous rock series III. Geochim. et Cosmochim. Acta, 9, 34—, (1956).

5) O'Brien, B.: Application of isodensity contouring methods to spectrum photometry. Proceedings of the sixth summer conference on spectroscopy and its application. A publication of the Technology press. (1939).

6) Kikuchi S.: Shashin Kagaku. Kyoritsu Shuppan k. k., 95, (1952).