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BIOTITE MICA EFFECT IN *X*-RAY SPECTROGRAPHIC ANALYSIS OF PRESSED ROCK POWDERS

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ABSTRACT

X-ray spectrographic analysis of unfused pelletized rock powders with glass-like surfaces gives high precision and sensitivity enabling quantitative demonstration of the mineralogical effect of biotite mica on the relative intensities of Si, Al, Ti, Fe, Mn, Mg, Ca, K and Na. The abnormal increase and decrease in intensity with decreasing grain size may be explained by the relative increase of the biotite surface and by assuming known differences in the composition of biotite and of granite. When this effect is considered, high accuracy can be achieved in analysis of granitic rocks and mica schists without the necessity of fluxing.

INTRODUCTION

Recent developments in *x*-ray emission analysis have enabled us to analyze for all major elements in rocks (Baird *et al.*, 1962; Henke, 1962, 1963; Volborth, 1963). Fusion techniques (Claisse, 1961; Bertin and Longobucco, 1962; Longobucco, 1962) have helped eliminate particle size (Bernstein, 1961), mineralogic, and homogeneity effects. The heavy absorber technique (Rose and others, 1963) has expanded the method to cover the entire composition range of a sample by one calibration curve. These techniques destroy the original nature of the sample and therefore some workers still adhere to the preparation methods which do not alter the nondestructive nature of the *x*-ray analysis (Chodos, 1960, 1961; Lytle and Heady, 1959; Salmon, 1961; Volborth, 1963).

There are some definite advantages in the truly nondestructive approach to the *x*-ray spectrography. If the sample need not be destroyed, diluted, fluxed, weighed or treated in any way, the precision obtainable will always be better, and the intensities will be as high as possible. Precision will be controlled in this case mainly by the reproducibility of the sample surface and the counter statistics. Intensity is dependent on the intensity of the primary beam, the amounts of the elements present, the grain size, thickness of the sample, and the phase relationships within the sample matrix. This means that similar samples can be analyzed satisfactorily as plain fine-ground powders or pressed pellets if similar standards are available. Speed is obviously also a main asset in this direct approach.

In rock and mineral analysis the feasibility of this approach has been demonstrated on loose powders (Chodos, 1961; Volborth, 1963), as well as on pressed powders, with no binding media (Baird, 1961, 1962; Volborth, 1963).

As pointed out by Chodos (1961), one of the strongest mineralogical effects in *x*-ray analysis is due apparently to the biotite mica, which is difficult to grind and often forms relatively large specks on powder surfaces. Grinding of a rock to a grain size where mica flakes would be invisible is often a tedious process (Baird *et al.*, p. 422, 1961).

The difficulty in obtaining accurate results in granitic rocks of slightly different grain size distribution led this author to collect data on analyzed rock powders of different grain size. This resulted in comparison of intensity trends with relative differences in compositions of granite and biotite.

EXPERIMENTAL

Equipment and instrumental conditions. Standard Norelco Universal *x*-ray spectrograph, control panel, power source, pulse height analyzer with flow proportional counter, EDDT crystal, and tungsten exitation at 35mA and 50KV, were used for elements Si, Al, Ti, Fe, Mn, Ca and K. Aluminum target *x*-ray tube developed by Prof. B. L. Henke (1962), of Pomona College, California, was used for elements Na and Mg. In this latter case a specially built power source delivering 150mA and 10KV, a Vacion vacuum pump to evacuate the demountable *x*-ray tube, and a gypsum analyzing crystal were used. Otherwise the equipment was also standard Norelco built, as described above. Specific instrumental settings and conditions for individual elements have been presented before (Table 3, Volborth, 1963).

Sample preparation. Rock powders G-1 and W-1 were pelletized as received; then 1.5g samples of these powders were reground for specific amounts of time in an automatic Fisher grinder. Granites 24/36 and 16/20, and adamellite 50/50 were crushed by conventional means, then ground to about 100 mesh in Bico pulverizers, and 1.5g samples of these powders were reground similarly as the G-1 and W-1 powders. The original coarse powders are called "as received." All powders on which total rock analyses were made were ground to 95% minus 37 micron size.

Powders were pressed at 30,000 psi against glass plates to obtain smooth surfaces. Buehler Bakelite 1386 AB was used as backing. Pellets so obtained were $1\frac{1}{4}''$ in diameter to fit the standard Norelco sample holders (Baird, 1961; Volborth, 1963). Pellet surface was glassy in appearance.

All data were obtained from the ratios of intensities of a powder in permanent position to the intensities of unknown powders. The same G-1 powder was used as standard at all times throughout the whole experiment.

RESULTS

When intensity readings were taken and compared on rock powders of different grain size, it became obvious that intensities of most elements increased with decrease in grain size and that the intensities of two elements, Si and Ca, decreased with finer grain size. Since we know from theoretical considerations and practice, that in most cases, the intensity of an element increases with decreasing grain size (Claisse, 1961) over a certain grain size region, called the transition zone, an explanation was sought to this abnormal behavior. We know from Bernstein's work (1961) that in certain binary systems when grain size of one component is kept standard while the grain size of another component is decreased, actual decrease in the intensity of the element contained in the coarser powder can result. Obviously different minerals in rock grind differently under similar conditions, but it would be difficult to attribute all the abnormal intensity changes to grain size differences resulting from simultaneous grinding. This is especially true for silica which is the major constituent of most rock minerals. And, therefore, explanation of this effect was sought in the nature and composition of biotite.

TABLE 1. AVERAGE COMPOSITION OF GRANITE AND BIOTITE IN WEIGHT PERCENT

	Granites of all periods	Biotite in Granites and Pegmatites
SiO_2	70.2	36.5
Al_2O_3	14.5	17.2
Fe_2O_3	1.6	8.2
FeO	1.8	14.5
MnO	0.1	0.6
MgO	0.9	8.7
CaO	2.0	1.0
Na_2O	3.5	1.0
K_2O	4.1	8.2
TiO_2	0.4	1.3

A micaceous mineral like biotite will increase its total relative surface more than non-micaceous minerals upon further grinding. This effect is enhanced by pelletizing at 30,000 psi. As a result the elements which compose the biotite will cause higher intensity readings.

A comparison was made of the typical composition of biotite found in granites and pegmatites with the typical composition of granites of all periods (Rankama and Sahama, 1950, p. 156, 166). Table 1 shows that biotite has less SiO_2 and CaO, but much more iron, manganese, and magnesium, than the granite. This corresponds with, and may explain the decreases and increases in intensity. Data on other elements were collected on all powders of different grain size, where the grinding time and sample size were known. In Table 2 the results obtained are given.

TABLE 2. DEMONSTRATION OF BIOTITE EFFECT

Rock	Pellet No.	% Oxide	Grinding Time per 1.5 g	Intensity
G-1, SiO_2	10 pellets	72.65	as received	
G-1, SiO_2	110	72.62	10 min.	decreasing
G-1, SiO_2	111	72.61	10 min.	decreasing
G-1, SiO_2	112	72.00	20 min.	decreasing
G-1, SiO_2	113	72.00	40 min.	decreasing
W-1, SiO_2	10 pellets	52.63	as received	
W-1, SiO_2	114	52.50	20 min.	decreasing
G-1, CaO	4 pellets	1.46	as received	
G-1, CaO	110	1.40	10 min.	decreasing
G-1, CaO	112	1.39	20 min.	decreasing
G-1, CaO	113	1.36	40 min.	decreasing
G-1, Fe_2O_3	9 pellets	1.46	as received	
G-1, Fe_2O_3	110	1.70	10 min.	increasing
G-1, Fe_2O_3	111	1.72	10 min.	increasing
G-1, Fe_2O_3	112	1.86	20 min.	increasing
G-1, Fe_2O_3	113	1.96	40 min.	increasing
W-1, Fe_2O_3	10 pellets	10.64	as received	
W-1, Fe_2O_3	114	11.10	20 min.	increasing
G-1, MnO	7 pellets	0.027	as is, P/B=4	
G-1, MnO	110	0.032	10 min.	increasing
G-1, MnO	112	0.039	20 min.	increasing
G-1, MnO	113	0.043	40 min. P/B=4.5	increasing
Granite, 24/36, MgO	103	0.94	as received	
Granite, 24/36, MgO	104	1.10	30 min.	increasing
Granite, 16/20, MgO	100	1.06	as received	
Granite, 16/20, MgO	99	1.15	30 min.	increasing
G-1, TiO_2	88	0.20	as received	
G-1, TiO_2	113	0.24	40 min.	increasing
G-1, Al_2O_3		14.53	as received	
G-1, Al_2O_3		14.90	10 min.	
G-1, Al_2O_3		15.05	20 min.	
G-1, Al_2O_3		15.13	40 min.	increasing
Adamellite, 50/50, Na_2O		4.11	as received	
Adamellite, 50/50, Na_2O		4.22	30 min.	increasing
G-1, Na_2O		3.32	40 min.	
G-1, Na_2O		3.29	10 min.	
G-1, Na_2O		3.25	20 min.	increasing
G-1, K_2O		5.30	as received	
G-1, K_2O		5.10	40 min.	decreasing

In order to show the influence of the biotite effect on the accuracy of the determination, the intensities are expressed in percentages so that one number, either the highest or the lowest, corresponds to the recommended value (Stevens *et al.*, p. 78, 1960). Where no given value corresponds with the recommended value, the calibration curve has been drawn through more than the two points, G-1 and W-1. In this case the nearest figure to the recommended value is to be used as true value.

When we examine the effect of grinding on each element individually, specific mineralogical and other factors have to be considered in addition to the known absorption and enhancement effects. In silica determination, for example, the biotite effect is stronger in the granite G-1 than in the diabase W-1 which latter has less biotite. To be detectable, the relative intensity decrease has to be of course stronger than the usual increase due to finer grain size. This means that the total biotite effect on silica determination must be stronger than indicated by our results. This is understandable considering that silica is the major oxide in silicate rocks. The total detectable influence of the biotite effect is about 1 per cent of the amount present in G-1.

In calcium oxide determination the intensity decrease is definite but is more difficult to detect because of lower amount of calcium present. This decrease amounts to about 7 per cent of the amount present.

In the case of iron oxide in G-1, the strong biotite effect, expected from composition differences, is contributing to the regular intensity increase with finer grain size. This explains the large total increase of 34 per cent of the amount present. The intensity increase in W-1 is only about 0.5 per cent, indicating relatively insignificant contribution of the biotite effect, due mostly to the fact that in W-1 much of the iron is in other minerals than biotite.

Similarly, manganese intensities and their increase with grinding are due to the contributing factors of decreasing grain size and the biotite effect, resulting in a total intensity increase of 59 per cent.

The same is true for magnesium oxide with a total increase of 8–17 per cent; titanium oxide with a total increase of about 20 per cent; aluminum oxide with a total increase of about 4 per cent; and sodium oxide with a total increase of 2–3 per cent of the amount present.

In the case of sodium one would expect a decrease on the basis of the biotite composition, but apparently the effect of diminishing grain size is greater here, because of the very soft radiation. Besides, most of the sodium is concentrated in the plagioclase and not in the biotite.

Only in potassium oxide an intensity decrease of about 4 per cent was observed. Rather an increase was predicted on the basis of the higher potassium content in biotite. Presently this phenomenon can not be explained satisfactorily. It may be due to some specific filtering properties of biotite mica, and to the fact that most potassium in granite occurs in microcline perthite.

It is clear from the aforesaid that in order to get accurate results all biotite bearing rock powders and the standards have to be ground to exactly the same grain size, and should ideally contain similar amounts of biotite.

An experiment was conducted to establish whether total analyses of granitic rocks of varying biotite content could be made, ignoring the biotite effect, on powders of similar grain size.

Two granites and one adamellite (Volborth, 1962), one quartz monzonite, and one syenite were analyzed using G-1 and W-1 powders as standards in a two-point calibration curve. Because the composition of rocks so analyzed was near the composition of granite G-1, and because no other equivalent standards were available, it was considered permissible to use W-1 as the second point despite the fact that it contains only relatively small amounts of biotite. In Table 3, total *x*-ray spectrographic analyses of these 5 rocks are compared with gravimetric data. In this table, data appearing in parentheses are based on the neighboring column. For example, in "*x*-ray" columns the data on ferrous plus ferric iron are based on the *x*-ray totals for Fe_2O_3 but computed on the basis of the ferrous-ferric ratio in the "chemical" column. Similarly, data on water, fluorine, and other constituents not analyzed for by *x*-rays appear in *x*-ray columns in parentheses. Correction for ferrous iron is made beneath the first totals in "*x*-ray" columns. Correction for fluorine is introduced after the second totals corrected for iron. Data for iron appearing in parentheses are not used in totals.

In the case of the quartz monzonite (Pomona 84) no gravimetric data were available, so that the comparison is between *x*-ray data obtained by Prof. A. K. Baird from Pomona College (priv. comm.), and our *x*-ray data. In this case, one has to consider that Baird's data were obtained by a fusion technique, ours by direct pressing of powders.

In Syenite Rock 1[a], supplied by the Nonmetallic Standards Committee, Canada (1961), the coincidence of results in case of MgO is due to the selection of this point as standard for other rocks here analyzed. The remarkable agreement of magnesium data in all these rocks supports this procedure. If pont W-1 were used, larger, biased deviations from gravimetric values would have been obtained.

It should be pointed out that the total effect of biotite can not be directly determined because of other overlapping effects. However, when we compare the totals of the granitic rocks analyzed with the totals of volcanic rocks analyzed by the same method earlier (Volborth,

TABLE 3. COMPARISON OF *X*-RAY SPECTROGRAPHIC AND CHEMICAL ANALYSES OF GRANITIC ROCKS

Oxide	Granite 24/36 *x*-ray Volborth	Granite 24/36 Chem. Vincent	Granite 16/20 *x*-ray Volborth	Granite 16/20 Chem. Vincent	Q. Monzonite 84 *x*-ray Baird	Q. Monzonite 84 *x*-ray Volborth	Adamellite 50/50 *x*-ray Volborth	Adamellite 50/50 Chem. Vincent	Syenite 1[a] *x*-ray Volborth	Syenite 1[a] Chem. Report, 1961
SiO_2	69.30	68.23	67.85	68.06	66.77	66.60	64.90	64.63	60.65	59.29
TiO_2	0.78	1.26	0.84	1.74	0.59	0.55	1.14	1.78	0.40	0.52
Al_2O_3	13.47	13.99	14.95	13.79	15.06	15.37	13.40	13.71	9.30	9.32
Fe_2O_3, Total	4.68	(4.66)	5.08	(4.20)	2.69	3.46	6.70	(6.26)	8.10	(8.94)
$FeO+Fe_2O_3$	(4.36)	4.34	(4.71)	3.89	—	—	(6.26)	5.85	(7.48)	8.26
MgO	1.08	1.02	1.15	1.11	0.70	1.23	1.29	1.31	4.02	4.02
CaO	2.40	2.36	2.45	2.32	2.92	2.00	2.94	2.98	9.37	10.24
K_2O	4.93	4.90	4.76	5.05	3.12	3.48	4.03	4.11	2.71	2.71
Na_2O	2.68	2.88	2.66	2.94	4.12	4.13	4.11	4.11	3.36	2.99
MnO	0.070	0.04	0.078	0.05	—	0.122	0.087	0.06	0.420	0.42
H_2O^+	(0.47)	0.47	(0.57)	0.57	—	—	(0.94)	0.94	(0.46)	0.46
H_2O^-	(0.06)	0.06	(0.00)	0.00	—	—	(0.30)	0.30	(0.21)	0.21
P_2O_5	(0.27)	0.27	(0.29)	0.29	—	—	(0.49)	0.49	(0.19)	0.19
F	(0.15)	0.15	(0.16)	0.16	—	—	(0.30)	0.30	—	—
BaO	(0.09)	0.09	(0.04)	0.04	—	—	—	—	(0.03)	0.03
SrO	(0.02)	0.02	(0.02)	0.02	—	—	(0.02)	0.02	(0.04)	0.04
Total	100.45		100.90		95.97	96.94	100.65		99.26	
$-Fe_2O_3$ $-(FeO$ $+Fe_2O_3)$	0.32		0.37				0.44		0.62	
Total, corr. FeO	100.13	100.08	100.53	100.03			100.21	100.59	98.64	98.70
$-F=O$	0.06	0.06	0.07	0.07			0.13	0.13		
Total	100.07	100.02	100.46	99.96			100.08	100.46	98.64	

1963) we notice that biotite bearing rocks in general seem to give higher totals than volcanic rocks which contain only insignificant amounts of biotite. This may be explained by comparison of the higher modes for biotite in the granitic rocks analyzed with the modes for G-1 (Table 4). Since for most elements, biotite contributes to relative intensities (Table 2), a relative increase in biotite should cause a total increase in relative intensities in the rock powder, when compared with a standard containing less biotite. Therefore, in volcanic rocks with little biotite the totals should be smaller than in granitic rocks with more biotite, when granitic standard is used. Thus the effect of nondetermination of traces (Volborth, 1963) may be exaggerated in rocks with no biotite, and obscured completely in rocks with more biotite than in the standard used.

TABLE 4. AVERAGE MODES OF MICAS IN VOLUME PERCENT

Rock	Volume Percent	Mineral
W-1	1.8	Biotite
G-1	3.2	Biotite
	1.3	Muscovite
16/20	6.2	Biotite
24/36	(6.2)	Biotite
50/50	(7.0)	Biotite

For some analyzed rocks, modes for biotite and muscovite micas were available. They are compiled in Table 4 to show the range of biotite content in the rocks analyzed. Data in parentheses are estimates based only on one or two thin sections. Unfortunately no modes for Syenite Rock 1[a] were available. This table gives the approximate range of biotite mode in the rocks analyzed as 1.8 to 7.0 volume per cent.

PRECISION AND ACCURACY

Relative standard deviation was determined on groups of ten, eight or four G-1 or other rock pellets, depending on the degree of reproducibility of each determination. G-1 powder was pressed "as received" in most cases and precision for this powder is given in second place under Relative Deviation in Table 5. When reground G-1 and other rock powders gave a much better precision,which is shown as the first figure under Relative Deviation in Table 5. The effect of grain size on precision of standard G-1 is here clearly demonstrated. Because of varying composition of rocks analyzed the Relative Deviation is given in ranges. The best values given are based on actual determinations in the high percentage range.

Accuracy of the method is demonstrated by comparison of individual data in Table 3.

CONCLUSIONS AND DISCUSSION

With the high precision achieved by the glass disc pelletizing method it is possible to study minor changes of intensity due to such factors as grinding or grain size, and biotite or other micas, with high degree of confidence. It is shown that biotite seriously affects the determination of most of the main elements in granitic rocks when the *x*-ray spectrographic analysis is performed on pressed rock powders. This effect can be positive or negative. It can be explained quantitatively by comparison of the composition differences of this mineral with the rock that is being analyzed. When all powders including the standards are ground to equivalent grain size, the contribution of this effect can be ignored in total *x*-ray analysis of similar rocks. Results comparable to gravimetric data can be achieved on rocks whose biotite content varies from about 2 to 7 per cent. If more accurate results are desired, the modal composition of the unknown rock powder and that of the standard rock powder have to be known, and should be preferably close. This would be valid especially in analysis of biotite schists and clay bearing rocks.

TABLE 5. PRECISION OF THE METHOD

Constituent	Concentration Range Percent	Relative Deviation
SiO_2	59–73	0.1 –0.23
Al_2O_3	9–14	0.2 –0.63
Fe_2O_3	2–8	0.1 –2.96
TiO_2	0.4–2	0.5 –5.0
MgO	0.4–4	0.11–
CaO	1.4–10	0.13–0.34
K_2O	2.7–5.4	0.6 –0.74
Na_2O	(10.73, Albite)	0.13–
Na_2O	(4.11, Andesite)	0.10–
MnO	0.027–0.42	0.0 –2.2

Rocks with much biotite, when plotted on standard curves based on rocks with less biotite, seem to give slightly higher totals and vice versa. This may obscure the effect of the nondetermination of traces in spectrographic analysis. Ideally the biotite content of the standard should be the same as that of the unknown.

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REFERENCES

BAIRD, A. K. (1961) A pressed-specimen die for the Norelco vacuum-path *x*-ray spectrograph. *Norelco Reporter* **8,** 108.

———, R. S. MACCOLL AND D. B. MCINTYRE (1961) A test of the precision and sources of error in quantitative analysis of light major elements in granitic rocks by *x*-ray spectrography. *Advances in X-ray Analysis* **5,** 412. Plenum Press, New York.

———, D. B. MCINTYRE AND E. E. WELDAY, (1962) Sodium and magnesium fluorescence analysis. II. *Advances in X-ray Analysis* **6.** Plenum Press, New York, 377.

BERNSTEIN, F. (1961) Application of *x*-ray fluorescence analysis to process control. *Advances in X-ray Analysis* **5,** 486. Plenum Press, New York.

BERTIN, E. P. AND RITA J. LONGOBUCCO (1962) Sample preparation methods for *x*-ray fluorescence emission spectrometry. *Norelco Reporter* **9,** 31.

CHODCS, A. A. AND C. G. ENGEL (1960) Fluorescent *x*-ray spectrographic analyses of amphibolite rocks and constituent hornblendes. *Advances in X-ray Analysis* **4,** 401. Plenum Press, New York.

——— (1961) Fluorescent *x*-ray spectrographic analysis of amphibolite rocks. *Am. Mineral.* **46,** 120.

CLAISSE, F. AND C. SAMSON (1961) Heterogeneity effects in *x*-ray analysis. *Advances in X-ray Analysis* **5,** 335. Plenum Press, New York.

HENKE, B. L. (1962) Sodium and magnesium fluorescence analysis I. *Advances in X-ray Analysis* **6.** Plenum Press, New York, 361.

——— (1963) *X*-ray fluorescence analysis for sodium, fluorine, oxygen, nitrogen, carbon, and boron. *Advances in X-ray Analysis* **7.** Plenum Press, New York (in press).

LONGOBUCCO, RITA J. (1962) Determination of major and minor constituents in ceramic materials by *x*-ray spectrometry. *Anal. Chem.* **34,** 1263.

LYTLE, F. W. AND H. H. HEADY (1959) *X*-ray emission spectrographic analysis of high-purity rare earth oxides. *Anal. Chem.* **31,** 809.

NONMETALLIC STANDARDS COMMITTEE, CANADIAN ASSOCIATION FOR APPLIED SPECTROSCOPY (1961) Applied Spectroscopy **15,** 159.

RANKAMA, K. AND TH. G. SAHAMA (1950) *Geochemistry.* The University of Chicago Press.

ROSE, H. J., I. ADLER AND F. J. FLANAGAN (1963) *X*-ray fluorescence analysis of the light elements in rocks and minerals. *Applied Spectroscopy* **17,** 81.

SALMON, M. L. (1961) A simple multielement-calibration system for analysis of minor and major elements in minerals by fluorescent *x*-ray spectrography. *Advances in X-ray Analysis* **5,** 389. Plenum Press, New York.

STEVENS, R. E. AND OTHERS (1960) Second report on a cooperative investigation of the composition of two silicate rocks. *U. S. Geol. Surv. Bull.* **1113.**

VOLBORTH, A. (1962) Rapakivi-type granites in the Precambrian complex of Gold Butte, Clark County, Nevada. *Geol. Soc. Am. Bull.* **73,** 813.

——— (1963) Total instrumental analysis of rocks. *Nevada Bur. Mines, Rept.* **6**

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