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FLUORESCENT *X*-RAY SPECTROGRAPHIC ANALYSES OF AMPHIBOLITE ROCKS

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ABSTRACT

Fluorescent *x*-ray spectrographic analyses have been made for the oxides Fe_2O_3, CaO, MgO, K_2O, TiO_2, and MnO on 27 samples of amphibolite rock. The amphibolites vary appreciably in mineralogical composition but all have a chemical composition approximating that of a saturated basalt. Variations in mineralogy are from hornblende-andesine amphibolites to two pyroxene-labradorite-hornblende gneisses with 0.2 to 5.0 per cent opaque minerals.

Mean deviations of the fluorescent *x*-ray spectrographic analyses from classical wet chemical analyses in per cent of the amount reported are: Fe_2O_3, 3.1; CaO, 1.3; MgO, 3.0, K_2O, 3.2; TiO_2, 3.2; and MnO, 7.7. Precision of the analyses is equivalent to, or better than, that achieved by wet chemical methods.

Preliminary work indicates equivalent precision can be obtained for most common rocks and minerals.

INTRODUCTION

This paper is a report on analytical studies of amphibolites (hornblende, plagioclase, pyroxene-bearing rocks) using fluorescent *x*-ray spectrographic analyses. An earlier report on these studies discusses the basic concept involved in fluorescent *x*-ray spectrographic analysis. Refinements have been made in equipment and the technique has been modified since that report (Chodos, Branco, and Engel, 1957).

Our studies are based upon the obvious need for a rapid, relatively inexpensive method of obtaining precise and accurate chemical analyses of rocks and minerals. Costs and time factors have resulted in a serious reduction in the number of analytical laboratories and of rocks and minerals analyzed by conventional chemical techniques. Moreover, in most analyses that employ classical techniques, neither the precision nor accuracy of the data can be estimated; and the recent studies of the rocks G-1 and W-1 have demonstrated the wide variations in values that may be reported for a given element in these rocks (Fairbairn, *et al.*, 1951). Attempts to reduce the time and costs of silicate analyses include the so-called "rapid" method of chemical analysis developed by Shapiro and Brannock (1952, 1956) and the emission spectrographic techniques formulated by Kvalheim (1947), Ahrens (1950), Dennen *et al.* (1951), Dennen and Fowler (1955), and others. Although the "rapid" method of chemical analysis is more rapid than classical procedures it remains a time consuming technique which requires an enormous amount of "dishwashing." The emission spectrographic methods greatly reduce the time and costs of analyses but at too large a price in precision for the major elements.

The fluorescent *x*-ray spectrographic analytical methods employed in this study permit the rapid determination of total Fe, Mn, K, Ti, Ca, and Mg in rocks and minerals with a precision and accuracy as good as that obtained by a single analyst using classical chemical methods and better than the precision among a number of different analysts (*see* Fairbairn, *et al.*, 1951). The standard working curves used for the determinations have been established by using the values from wet chemical analyses by C. G. Engel. These analyses also included the rock W-1 so that both wet chemical analytical data and those obtained by fluorescent *x*-ray analyses might be keyed to the adjusted mean composition of W-1(Fairbairn 1953). This comparison is particularly significant because the composition of the rock W-1 is very close to the composition of the amphibolites under discussion.

Si and Al can be determined by the fluorescent *x*-ray method but with only limited success due to limitations in techniques and apparatus. Very probably, precise determination of Si and Al can be obtained by slight improvements of the methods we are using. Values for Na may be obtained quickly and with considerable precision by use of the flame photometer. Separate determinations are required for the ratio of ferrous to ferric iron and for total H_2O.

Rock Type

The present work has been confined to amphibolites and pyroxene-bearing "amphibolites" which have the chemical composition of many basalts. In so doing we have eliminated those problems that are inherent in fluorescent *x*-ray spectrographic analyses of rocks of very diverse mineralogy, chemical composition, and texture. Actually any rock or mineral may be analyzed by the fluorescent *x*-ray technique but best results are obtained in analyses of a given rock or mineral for which standard working curves have been constructed.*

The range in chemical compositions of the amphibolites reported in this work are: Fe_2O_3 8–22%; CaO 7–13%; MgO 4–9%; K_2O 0.3–2.5%; TiO_2 1–3%; and MnO 0.12–0.35%.

Variations in mineralogical composition of the amphibolites are shown in Table 1. Modal analyses of these rocks are being published separately in a study of the progressive metamorphism of amphibolite rocks by Engel and Engel. In general, the specimens A 1EF, A 3A, A 4D, A 14B,

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* We have also prepared standard working curves for quartz-biotite-oligoclase gneisses and for the minerals garnet, biotite, and hornblende, with results equivalent to those reported in this paper.

TABLE 1. VARIATIONS IN MINERALOGICAL COMPOSITION OF AMPHIBOLITE ROCKS USED IN FLUORESCENT *X*-RAY SPECTROGRAPHIC AND CHEMICAL ANALYSES

Mineral	Range in volume per cent
Quartz	0 –16.9
Plagioclase*	15.2–57.5
Hornblende	12.4–69.6
Clinopyroxene	0 –31.6?
Orthopyroxene	0 –15.5?
Opaque minerals†	.2– 5.1
Biotite	0 –24.8
K-feldspar	0 – 3.8
Garnet	0 –11.4
Sphene	0 – 1.6

* Partly sericitized.
† Chiefly ilmenite, pyrite, and magnetite.

and A 15DE (Table 2) contain in volume per cent; hornblende 65, andesine 20, quartz 10, and opaque minerals 2. There are gradations in mineralogical composition between these rocks and the remaining specimens in Table 2 which contain as much as 40% combined ortho- and clinopyroxene and as little as 12% hornblende. Sample A 9A is a garnetiferous, pyroxene-rich "amphibolite" with about 11% garnet 35% ortho- and clinopyroxene, 17% hornblende and 28% plagioclase.

It is obvious from comparison of Tables 1 and 2 that these are far greater variations in the mineralogical composition of the amphibolites than in their chemical composition. Iron displays the largest variation in concentration and occurrence among the samples analyzed. Total Fe (as Fe_2O_3) varies from about 8 to 22 weight per cent in the amphibolites and is an important constituent in hornblende, clino- and orthopyroxene, biotite, garnet, ilmenite, pyrite, and magnetite. Despite this diversity in the crystallographic distribution of Fe, its concentration in the rock can be obtained rather precisely by the fluorescent *x*-ray spectrographic technique.

SAMPLE PREPARATION AND PARTICLE SIZE

All samples of amphibolites were reduced to −100 mesh as described elsewhere (Engel and Engel, 1958). These −100 mesh fractions were then split into two parts using a high purity aluminum micro-split. One part, of approximately 10 grams, was used for wet chemical analyses; the other fraction, about 5 grams, was ground to a very fine powder for use in fluorescent *x*-ray analyses.

TABLE 2. COMPARISON OF WET CHEMICAL AND FLUORESCENT *X*-RAY SPECTROGRAPHIC ANALYSES OF AMPHIBOLITE ROCKS

The working curves shown in Fig. 1 to 6 were derived from the wet chemical analyses given in this table.

Sample	Type of Analysis	Oxide (weight per cent)					
		Total Fe as Fe_2O_3	CaO	MgO	K_2O	TiO_2	MnO
A 1EF	Chem.	14.30	9.83	6.59	1.66	1.58	.22
	X-ray	15.14	9.77	7.20	1.71	1.62	.25
A 3A	Chem.	13.14	11.27	7.21	.81	1.20	.23
	X-ray	13.69	11.26	7.40	.75	1.25	.23
A 4D	Chem.	12.53	9.47	7.57	2.29	1.07	.20
	X-ray	13.28	9.38	7.90	2.25	1.18	.24
	X-ray*	12.92	9.38	7.90	2.30	1.15	.24
A 14B	Chem.	19.21	8.93	4.76	1.85	2.64	.31
	X-ray	19.60	8.99	4.88	1.87	2.70	.31
A 15DE	Chem.	16.34	7.86	6.32	1.89	2.05	.24
	X-ray	15.98	7.87	6.58	1.92	2.06	.32
A 19A	Chem.	13.58	8.54	7.63	2.27	1.60	.27
	X-ray	14.61	8.43	7.73	2.34	1.63	.26
	X-ray*	13.90	8.34	7.66	2.37	1.52	.24
A 20A	Chem.	12.46	11.25	8.60	1.19	1.93	.20
	X-ray	12.76	11.25	8.60	1.17	1.86	.20
	X-ray*	12.25	10.96	9.10	1.73	1.80	.19
A 21	Chem.	12.88	9.84	7.14	1.67	1.20	.22
	X-ray	13.35	9.68	7.26	1.73	1.23	.24
	X-ray*	13.20	9.72	7.20	1.73	1.21	.24
A 65A	Chem.	10.59	7.96	3.72	1.38	1.57	.14
	X-ray	10.26	7.93	4.00	1.34	1.63	.13
A 67A	Chem.	10.91	12.77	6.85	.35	.99	.20
	X-ray	10.57	12.63	6.90	.37	1.06	.22
	X-ray*	10.42	12.45	6.91	.36	1.04	.22
A 68	Chem.	12.57	11.17	7.99	1.35	1.18	.20
	X-ray	12.23	11.09	8.13	1.40	1.21	.20
A 104	Chem.	13.57	11.68	7.36	.47	1.60	.25
	X-ray	13.79	11.73	7.16	.47	1.53	.23
	X-ray*	13.68	11.92	7.40	.47	1.53	.23
A 105	Chem.	13.78	11.96	7.43	.57	1.56	.25
	X-ray	13.76	12.72	7.10	.59	1.57	.24
A 10E	Chem.	14.40	11.92	7.46	.58	1.40	.25
	X-ray	14.24	11.95	7.48	.59	1.40	.23
	X-ray*	14.05	12.14	7.77	.78	1.39	.23
A 9A	Chem.	21.06	10.01	5.46	.41	2.73	.35
	X-ray	20.74	10.49	5.43	.44	2.72	.34
	X-ray*	20.81	10.67	5.53	.44	2.77	.35

Note: Mineralogical composition of the rocks is discussed in the text.

* A second split of the sample prepared by A. E. Engel and submitted under a different number to test reproducibility of *x*-ray methods.

Analyses obtained by fluorescent *x*-ray spectrographic techniques may be strongly biased by alternate methods of preparation of samples and by the size of constituent particles. Some of these problems have been discussed by Claisse (1956). Because mineralogical composition and surface homogeneity strongly influences the behavior of the sample during *x*-ray analysis, precision may be increased by very fine grinding. Many grinding problems are presented by different rock types. Minerals such as sulfides and quartz are brittle and powder rapidly; others, such as mica are flexible and resistant to grinding. When all of these minerals coexist in a rock, the resultant powder may show a wide range in particle size that can be correlated with mineral composition. Relatively coarse flakes of mica in a very fine powder of other minerals may induce errors in the analysis of mica-bearing rocks. Obvious analogies may be drawn from other rock types.

The data in Fe are instructive as an example of the relationship of grain size to precision of analyses of elements. Iron occurs in sulfides and silicates (including biotite). Analyses of biotitic amphibolites ground to successively finer fractions below −100 mesh size show an increase in the Fe/Ca intensity ratio which does not level off until the flakes of biotite can no longer be resolved at ×20 magnification. The increase in the ratio Fe/Ca with increased grinding below −100 mesh is from 0.58 to 0.70.

All samples analyzed by the fluorescent *x*-ray spectrographic technique were ground in an automatic agate mortar until the entire sample appeared as a homogeneous powder at ×20 magnification under a binocular microscope. Measurements indicate that the average grain size is about 15 microns and the maximum grain size does not exceed 45 microns. Most of the non-biotitic amphibolites could be ground to this approximate size in 2 to 4 hours. Biotitic amphibolites required from 4 to 10 hours of grinding to reduce the biotite to this size. Similar time requirements have been recorded for other mica-bearing rocks.

Analytical Methods

Each sample of amphibolite analyzed by classical chemical methods and by *x*-ray fluorescent spectrographic methods was handled as an unknown prepared by A. E. Engel. At the outset 15 amphibolites were analyzed by C. G. Engel using analytical methods described in Engel and Engel, 1958. The precision of this analytical work was tested by the introduction of masked splits of the rock W-1 introduced as unknowns along with samples of amphibolites. The results of analyses of W-1 are tabulated in Table 3 and compared with the adjusted mean composition of the rock W-1. They indicate for the elements given the reproducibility of the silicate analyses by classical techniques and any major bias in the determination of the elements relative to the presumed composition of the rock W-1. Inspection of the chemical analytical data in Tables 2 and 4 indicates that the elements, Fe, Ca, Mg, Ti, K, and Mn as determined in the amphibolite are accurate relative to the presumed concentration in the rock W-1. This analytical work suggests that the analyses of amphibolites by classical methods may be used to construct standard working curves for the fluorescent *x*-ray analytical studies.

Wet Chemical Analyses.—Determinations of CaO and MgO were done by conventional gravimetric methods employing a 1.0000 gram sample of rock. This weight of sample was fused in Na_2CO_3 in a platinum crucible and the fusion was dissolved in HCl.

Table 3. Replicate Chemical Analyses of the Rock W-1 Made with Analyses of Amphibolites and Indicative of Precision of Analytical Methods
(Analyst, C. G. Engel)

Oxide	Date										Mean*	Mean deviation
	10/56	1/57	5/57	12/57	1/58	4/58	11/58	4/59	5/59	Mean		
TiO_2	1.05	1.09	1.09	1.11	1.12	1.08	1.09	1.04	1.06	1.08	1.10	.02
Total Fe as Fe_2O_3	10.80	10.74	10.84 10.76 10.88	10.86	—	10.65	—	10.84	—	10.80	11.17	.37
MnO	.17	.15	.16	.17	—	.17	.16	.17	.16	.17	.165	.00
CaO	11.02	—	—	11.00	—	10.90	—	11.04	—	10.99	10.96	.03
MgO	6.55	—	—	6.39	—	6.59	—	6.67	—	6.55	6.63	.08
K_2O	.68 .69	.66	—	.66	—	.66	—	.64	.67	.67	.63	.04

* Arithmetic mean of replicate analyses by 35 laboratories of the rock W-1 (*see* Fairbairn, 1953, table 1, p. 146–147).

Total Fe (as Fe_2O_3), TiO_2, and MnO were determined on a 0.4000 gram sample dissolved in a platinum crucible on a steam bath in sulfuric and hydrofluoric acids. The resulting solution was increased to 200-ml. volume with distilled water. Aliquots were taken to determine Fe_2O_3*, TiO_2, and MnO on the Beckman Model B spectrophotometer using the methods described by Shapiro and Brannock (1956). Another aliquot of

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* Analyses of total Fe as Fe_2O_3 made in this way were checked by 13 analyses with a silver reductor. In this method, iron from the R_2O_3 group, in a HCl solution, was reduced by passing the solution down a column of metallic silver. The determinations of Fe_2O_3 that exceed about 12 weight per cent that are made on the spectrophotometer require a saturated solution of orthophenanthroline. A 0.1% solution of orthophenanthroline is satisfactory where concentrations of Fe_2O_3 do not exceed about 12%.

TABLE 4. COMPARISON OF WET CHEMICAL AND FLUORESCENT X-RAY SPECTROGRAPHIC ANALYSES IN WHICH THE SAMPLES WERE RUN AS UNKNOWNS FOR BOTH ANALYSTS

The analyses are of amphibolite rocks similar in chemical and mineralogical composition to those in Table 2.

Sample	Type of analysis	Oxide (weight per cent)					
		Total Fe as Fe_2O_3	CaO	MgO	K_2O	TiO_2	MnO
AE 317	Chem.	13.15	11.49	7.45	1.20	1.17	.23
	X-ray	13.20	11.37	7.77	1.23	1.23	.23
	X-ray*	13.17	11.29	7.48	1.22	1.23	.23
AE 326	Chem.	15.86	9.54	6.29	.94	2.05	.24
	X-ray	16.08	9.81	6.30	.94	2.14	.26
	X-ray*	16.10	9.84	6.48	.96	2.13	.26
AE 334	Chem.	16.49	9.74	6.32	.88	2.11	.29
	X-ray	16.40	9.84	6.45	.92	2.15	.25
AE 337	Chem.	15.98	9.54	6.51	.98	2.07	.27
	X-ray	16.00	9.76	6.40	.99	2.07	.27
AE 338	Chem.	15.63	9.71	6.04	.99	2.04	.25
	X-ray	16.20	9.84	n.d.	.95	2.04	.25
AE 320	Chem.	8.84	7.78	5.49	2.11	1.11	.15
	X-ray	8.60	7.67	6.20	2.05	1.27	.13
	X-ray*	8.64	7.58	6.00	2.06	1.27	.12
AE 411	Chem.	11.91	n.d.	n.d.	1.76	1.76	.12
	X-ray	11.80	8.40	5.67	1.66	1.77	.14
AE 414	Chem.	8.84	n.d.	n.d.	1.89	1.76	.12
	X-ray	8.74	7.10	5.40	1.92	1.28	.10
AED 404	Chem.	12.44	11.90	8.20	.60	.94	.22
	X-ray	12.18	11.98	8.04	.65	1.04	.20
AC 342	Chem.	15.67	10.65	6.99	.75	1.69	.24
	X-ray	15.60	10.79	7.00	.77	1.71	.25
AC 348	Chem.	14.78	11.46	7.40	.58	1.73	.24
	X-ray	14.67	11.65	7.34	.58	1.78	.23
	X-ray*	14.55	11.59	7.56	.59	1.77	.23
AC 362	Chem.	14.91	10.92	7.38	.47	1.66	.24
	X-ray	15.11	11.37	7.38	.47	1.74	.25
	X-ray*	14.95	11.21	7.14	.46	1.68	.25

Note: Mineralogical composition of the rocks is discussed in the text.

* A second split of the sample prepared by A. E. Engel and submitted under a different number, to test reproducibility of *x*-ray methods.

this same solution was used to determine K_2O and Na_2O on the Perkin-Elmer flame photometer.

Fluorescent X-Ray Spectrographic Technique.—The finely ground rock (or mineral) powder is pressed into the sample aperture of a standard

Norelco sample holder (Zytel boat) and the surface of the powder is smoothed off. After some practice it is possible to make highly reproducible packs of each sample. Tests show that samples prepared by two practiced technicians will yield analytical results which agree within 1%. This sample preparation is used for the analysis of Fe, Ca, Mg, K, Ti, and Mn. As noted below, a modification of this technique is required to achieve adequate precision in the analysis of Si and Al.

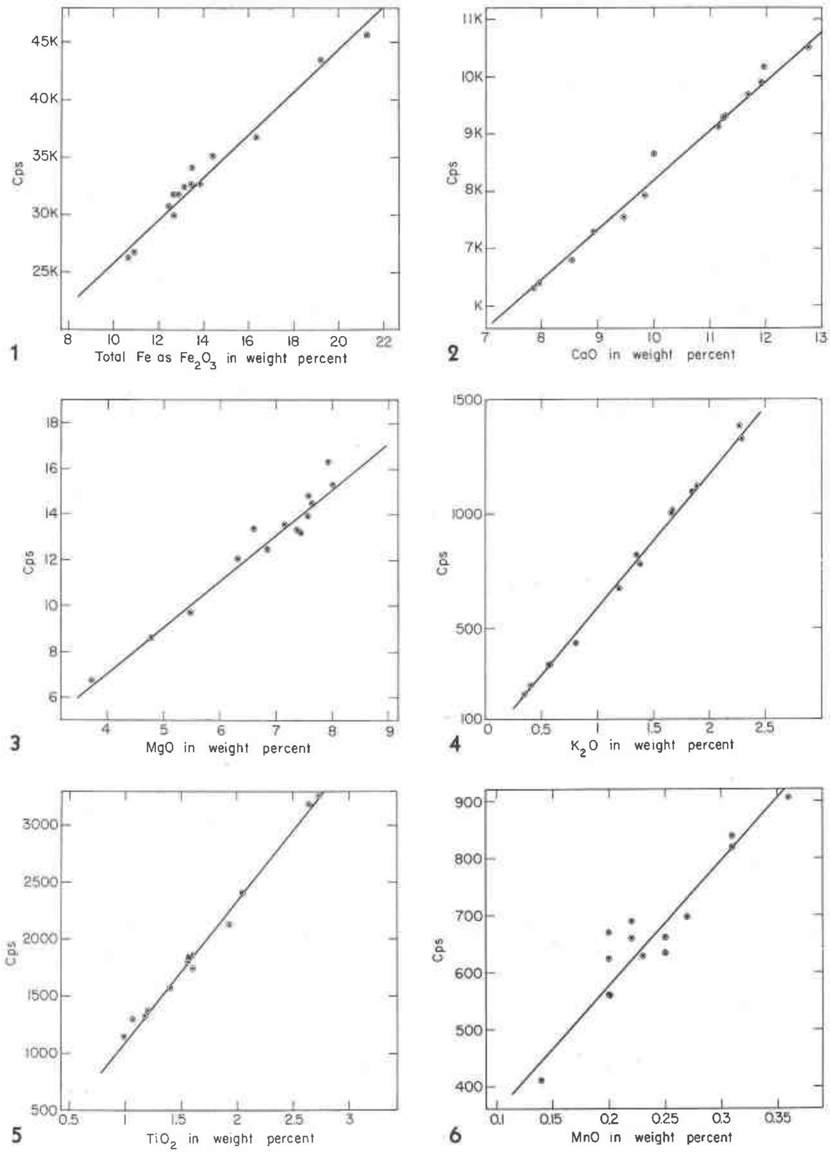
The sample holder is inserted into the *x*-ray spectrograph and the goniometer is set at the proper angular position necessary to measure the peak of the desired elements. This peak position is previously determined by a stepwise scanning of the approximate region in which the peak occurs. A crystal of ammonium dihydrogen phosphate (ADP) is used for the analysis of Mg; all other elements are obtained by use of a crystal of ethylene diamine D-tartrate (EDT). After appropriate crystal and instrumental conditions are chosen, a measurement is made of the time required to accumulate a specific number of counts. The number of counts which must be made for each element is a function of the precision of measurement required for that element. Background readings are made for those elements which require them by counting at some distance from the peak location (Table 5). Counting times are calculated to counts per second (cps) and the background intensity is subtracted from the peak intensity to yield the net peak intensity. The intensity values obtained for the standard samples are plotted against weight per cent of the element to obtain the calibration curves as shown in Figs 1 to 6 inclusive. Values for the unknowns are obtained by interpolation from the calibration curves. This procedure permits the determination of the

TABLE 5. OPERATING CONDITIONS FOR FLUORESCENT *X*-RAY SPECTROGRAPHIC ANALYSES

Element	Crystal	FPC* v	Pulse height analyzer		Element peak	Peak location °2 θ	Back-ground location °2 θ	Counts peak (thousands)	Counts back-ground (thousands)
			Base v	Window v					
Fe	EDT	1825	—	—	Kα	25.45	—	500	—
Mn	EDT	1660	4	9	Kα	27.65	28.75	20	5
Ti	EDT	1750	10	12	Kα	36.46	—	50	—
Ca	EDT	1825	—	—	Kα	44.89	—	100	—
K	EDT	1750	7	9	Kα	50.33	—	20	—
Si	EDT	1825	5	18	Kα	108.10	—	100	—
Al	EDT	1825	5	18	Kα	142.63	—	50	—
Mg	ADP	1825	6	9	Kα	136.90	135.5 138.0	10	1

* Flow proportional counter.

Note: EDT (ethylene diamine D-tartrate).
ADP (ammonium dihydrogen phosphate).



FIGS. 1–6. Calibration curves for fluorescent x-ray analysis.

six elements: Fe, Ca, Mg, K, Ti, and Mn, in approximately one-half hour.

Initial phases of our fluorescent *x*-ray spectrographic studies were begun with a Norelco *x*-ray spectrograph, using its standard electronic panel and a Baird-Atomic pulse height analyzer. It soon became apparent that the desired electronic stability necessary to obtain reproducible values over extended periods could not be obtained with the original electronic panel. Accordingly, an electronic system was constructed from standard components by our colleague E. V. Nenow. The equipment used is commercially available and is listed in Table 6. One of the principal modifications was intended to increase the stability needed for pulse height analysis for light elements. The original system had a pulse height drift of several volts per day. The addition of a high voltage stabilizer, stable to plus or minus 0.01 per cent, decreased this daily drift to less than 0.5 volts per day, and the drift per week on the order of 0.2 volts. This drift may be ignored.

TABLE 6. EQUIPMENT FOR FLUORESCENT *X*-RAY SPECTROGRAPHIC ANALYSES

Norelco standard *x*-ray spectrograph equipped for helium atmosphere
Helium flow rate 2 liters/minute
FA-60 tungsten target *x*-ray tube
50 KV and 35 ma
Flow proportional counter
P-10 gas flow rate 0.02 cu. ft./hr. (air)
EDT and ADP analyzing crystals
0.02″×3″ collimator
Baird-Atomic model 219A preamplifier
Baird-Atomic model 218 linear amplifier
Baird-Atomic model 510 pulse height analyzer
Hamner model N401 high voltage power supply
Baird-Atomic model 134 high speed scaler
Nuclear-Chicago model 1620 rate meter
Norelco interval timer
Leeds and Northrup model G recorder

Initial analytical techniques emphasized speed and simplicity and used only the crystal of ADP as required for analyses of Mg. Use of the ADP crystal is not desirable in the analysis of Si and Al inasmuch as phosphorus from the crystal contributes to the background. The high background increases abnormally the counting times necessary for desired precision and also decreases the reliability of the results. Recently a crystal interchanger has been developed which will permit the rapid change from a crystal of ADP to one of EDT without either shutting off the *x*-rays or opening the helium bag. The crystal of EDT is used for all elements other than Mg.

The pulse height analyzer is not used for determinations of Fe and Ca because there are no interfering lines and the intensity is sufficient to completely eliminate the need for background readings. In the analyses for K, Ti, and Mn, the pulse height analyzer settings were such that more than 95% of the energy of the element lay within the chosen energy range. The settings for Mg are chosen so as to exclude the maximum possible phosphorus energy. This asymmetric setting of the pulse height analyzer is made possible by the use of the stable electronic components added by Nenow. The conditions under which measurements were made are also listed in Table 5, although it must be remembered that these are unique to the apparatus as modified by Nenow.

Both the electronic components and the gas flow to the flow proportional counter are allowed to run continuously. During periods of analysis references are made every hour to a standard rock slab to check intensity and pulse height. During the warmup period of the equipment slight adjustments are made in the milliamperes to keep the intensity at a constant value.

The methods of analysis described above fall short of achieving desirable precision for Si and Al. Analyses of silica are accurate only to within about 3–5% of the amount present and for alumina only to about 5–10% of the amount present. This precision obviously does not compare favorably with results obtained by careful wet chemical analyses. Presumably serious matrix affect reduces the precision of analyses of Si and Al as indicated by the scatter of determinations on our calibration curves. Attempts to compensate for matrix effects by the use of ratios of the elements have proved unsuccessful.

Probably adequate analyses of Si and Al require fusion of the samples. Various alternative methods of fusing samples were tried with limited success. Best results to date have been obtained by sintering one part with one part sodium carbonate. Analyses of freshly sintered samples appear to be quite precise but the sinter appears to be unstable and there is considerable difficulty in reproducing identical sinters of the same sample.

The borax fusion technique described by Claisse (1956) is not entirely adequate because of the loss in intensity of the light elements due to the large dilutions of the sample. At present we are experimenting with types of borax fusions which vary in detail from those described by Claisse.

ANALYTICAL RESULTS

Results of analyses of amphibolites, using both fluorescent *x*-ray spectrographic and chemical techniques are shown in Tables 2 and 4. In Table 2 each of the analyses labelled "chem" represents the results of wet chemical analyses by C. G. Engel. As noted previously these analyses were used to construct the working curves reproduced in Figs. 1 to 6. The fluorescent *x*-ray analyses of these same samples are labelled "*x*-ray" in Table 2.

Comparisons of the two types of analyses indicate the deviation involved. The mean and maximum deviations respectively of the *x*-ray analyses from the chemical analyses in per cent of the amount reported are as follows: Total Fe as Fe_2O_3 3.1, 7.6; CaO 1.3, 6.4; MgO 3.0, 9.3; K_2O 3.2, 7.4; TiO_2 3.2, 10.3; and MnO 7.7 and 33.3. The deviations tend to be fairly symmetrically distributed on either side of the chemical analyses. The mean and maximum deviations in every instance are as small or smaller than deviations in analyses by classical chemical techniques where different analysts are involved. There has been little testing of the precision of a single analyst over long periods of time using classical methods.

X-ray analyses marked with an asterisk in Table 2 represent analyses made at a much later time of identical splits of 8 of the samples. Comparison of these numbers with the earlier *x*-ray data in Table 2 indicate precision over a 4 month time interval. The mean and maximum deviation respectively of *x*-ray analyses of the same samples at 4 months intervals are as follows: total Fe as Fe_2O_3 2.1, 4.9; CaO 1.3, 2.6; MgO 1.4, 3.7; K_2O 7.9, 32.4; TiO_2 2.3, 6.7; and MnO 2.0, 7.7.

Analyses in Table 4 are of samples first run by *x*-ray methods and checked by subsequent wet chemical analyses. A second split was made of 5 of the samples and submitted for *x*-ray analyses under a separate number. This second split was run at the same time and serves as a test of precision of the fluorescent *x*-ray analytical method where there is no time variance.

The chemical analyses obtained after the *x*-ray data were made on masked samples prepared by A. E. Engel so that the analyst did not know the identity of the sample. Duplicate *x*-ray analyses of any sample yields essentially identical results. Accordingly, where two *x*-ray analyses have been made of any sample, the results have been averaged in the comparison made below. The mean and maximum deviation of the *x*-ray analyses from the chemical analyses in per cent are as follows: total Fe as Fe_2O_3 1.2, 3.7; CaO 1.8, 3.4; MgO 2.6, 11.1; K_2O 3.3, 8.3; TiO_2 6.0, 27.3; MnO 7.6, 16.7. With the exception of data from several samples (notably 414, 320), the data in table 4 are very comparable with those in Table 2. Samples AE 320 and AE 414 are biotitic amphibolites in which the flakes of biotite were not reduced to a uniformly small size. This spread in grain size with relatively coarse biotite in a finer matrix appears to be the cause of the rather large errors reported for TiO_2, MnO, and MgO. These results again emphasize the need for fine grinding of the sample to achieve precise analytical results.

CONCLUSIONS

Analyses of rocks and minerals attempted to date point up major advantages and disadvantages to the *x*-ray techniques we have employed. It is obvious that where working curves are available *x*-ray methods permit a rapid analysis and comparison of the compositions of large numbers of samples where data on Fe, Ca, Mg, K, Ti, and Mn are critical.

It is equally obvious that there are important limitations to this method of *x*-ray analysis. Commonly, solution of mineralogical and petrologic problems requires the determinations of Si, Al, Na, H_2O, and the valence states of Fe, and so on. These data cannot be obtained with the equipment and techniques described earlier. At present the most satisfactory method is the classical gravimetric technique.

The working curves necessary for *x*-ray analyses must be prepared by an independent method having a high degree of precision. Moreover, the best working curves usually are obtained on either rock or minerals where there is a rather large continuous variation in chemical composition without major changes in crystal structure (*i.e.*, matrix differences). For this reason working curves prepared for granites are not wholly satisfactory for the analyses of clays or for feldspars. In effect, the *x*-ray technique must be supplemented and constantly rechecked by either wet chemical analysis or some other independent, precise analytical method. We have found (Engel and Engel, in preparation) *x*-ray techniques invaluable as a supplement to classical methods of analysis for a chemical reconnaissance of the concentration of heavy elements in both minerals and rocks. Presumably this is at present where the chief value of the *x*-ray technique lies.

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