THE ACCURACY OF CHEMICAL ANALYSES OF AMPHIBOLES AND OTHER SILICATES

ESPER S. LARSEN.

ABSTRACT.

Analyses were made on each of six amphiboles by from two to four of the better chemists upon whom mineralogists and geologists depend. For every amphibole the analysts failed to agree on one or more constituents by as much as one and one-half per cent. The lack of agreement was not confined to a few of the oxides but was present in every major constituent, including TiO_2. This failure to check may have been partly due to the fluorine (up to 2.18 per cent) of the amphiboles but cannot all be explained in that way.

The accuracy of silicate analyses, some checks on analyses and the sampling of a rock for analyses are discussed.

SOME DUPLICATE ANALYSES OF AMPHIBOLES.

In the course of a study of a series of amphiboles from Libby, Montana, through a combination of circumstances several of the amphiboles were analyzed by two different chemists. The pairs of analyses of the same amphiboles differed greatly from each other and failed to fit into any reasonable amphibole formula, so a third analysis was made. Through a misunderstanding the third chemist failed to take into account the fluorine content, and finally analyses were made by F. A. Gonyer taking all the precautions required for a silicate containing fluorine. These latter results are believed to be reliable.

For the purpose of showing something of the possible errors in an analysis of an amphibole or other silicate containing fluorine where the method for an ordinary silicate analysis was used, the results of analyses on six amphiboles from Colorado and Montana are shown in tables 1 to 6. The two analyses listed first in each table were made on powder from the same tube, but as the two analyses exhausted the powder it was necessary to prepare new samples for the other analyses. These new samples were made from the specimen that supplied material for the original powder, and in each case the two samples were essentially the same both in the optical properties of the amphibole and the small amount of impurities present.

In the last column of each table are given the results of analyses by F. A. Gonyer using the methods required for a fluorine mineral.

The data show a surprising lack of agreement. The writer has never believed that a very high degree of accuracy for ordinary rock or mineral analyses is attained, but the differences shown here were disconcerting. They show that minerals or even rocks with any appreciable amount of fluorine must receive special consideration if reliable results are expected.

TABLE I.

Comparison of Four Analyses of an Amphibole (Libby, Mont. 16948).

	Analyst A	Analyst B	Analyst D	Gonyer
SiO_2	56.40	56.04	56.28	56.97
TiO_2	.14	tr	.36	.28
Al_2O_3	.43	1.76	.90	.71
Fe_2O_3	4.14	4.11	4.94	4.71
FeO	1.28	1.65	.57	.87
MnO	tr	.10	.08	.07
MgO	21.82	20.63	22.22	21.95
CaO	8.08	6.56	6.46	6.15
BaO	none	none	....	....
SrO	....	.02	....	....
Na_2O	5.01	5.45	5.04	5.15
K_2O	1.86	2.30	1.74	1.80
H_2O-	.20	.06	.02	....
H_2O+	.48	1.02	1.08	.87
NiO	....	.23	....	....
CuO	....	tr	....	....
S	....	....	.02	....
P_2O_5	....	.01	nd	....
CO_2	....	none	nd	....
Cr_2O_3	....	.06	nd	....
F	nd	nd	nd	1.30
				100.83
Less O for F	....	....	....	.54
	99.84	100.00	99.71	100.29

The five analysts who contributed analyses of the amphiboles are believed to be among the more reliable rock and mineral analysts in the world; two were Europeans and three Americans. In comparing the results, SiO_2, TiO_2, and Al_2O_3 show differences as great as 2.5 per cent, Fe_2O_3 as much as 1.8, FeO up to 3.2, MgO up to 2.5, and CaO up to 4.0.

TABLE II.

Comparison of Three Analyses of an Amphibole (Iron Hill 39).

	Analyst C	Analyst D	Gonyer
SiO_2	53.58	54.07	54.30
TiO_2	.23	none	.04
Al_2O_3	1.48	1.12	2.02
Fe_2O_3	8.40	8.33	7.37
FeO	2.65	3.17	2.96
MnO	.51	.56	.52
MgO	17.57	17.88	17.71
CaO	4.12	2.76	3.30
BaO	.14	....	none
SrO	tr	....	none
Na_2O	7.95	7.60	7.80
K_2O	2.71	1.96	2.10
H_2O-	.07	....	.08
H_2O+	.64	.69	.61
P_2O_5	.20	....	....
F	....	....	2.14
	100.25	98.14	100.95
Less O for F & S	.05		.90
	100.20		100.05

TABLE III.

Comparison of Two Analyses of an Amphibole (Iron Hill 87).

	Analyst C	Gonyer
SiO_2	52.79	52.94
TiO_2	1.51	1.32
Al_2O_3	3.17	3.30
Fe_2O_3	10.08	9.87
FeO	4.29	4.24
MnO	.25	.15
MgO	15.50	15.02
CaO	3.24	3.98
BaO	.16	.12
SrO	....	none
Na_2O	5.70	7.01
K_2O	2.92	.48
H_2O-	.03	....
H_2O+	.60	1.24
S	tr	....
F	....	.78
		100.45
Less O for F	....	.33
	100.24	100.12

TABLE IV.

Comparison of Three Analyses of an Amphibole (Iron Hill 1954).

	Analyst A	Analyst B	Gonyer
SiO_2	49.66	49.90	52.14
TiO_2	.32	2.40	.47
Al_2O_3	4.60	4.39	4.03
Fe_2O_3	6.23	4.98	6.71
FeO	9.05	9.62	6.40
MnO	.26	.36	.33
MgO	14.50	13.09	15.52
CaO	6.18	5.02	4.49
BaO	....	none	none
SrO	....	.03	.03
Na_2O	6.75	7.81	7.31
K_2O	.60	1.19	.76
H_2O-	.60	.10	....
H_2O+	1.20	1.26	1.60
Cr_2O_3	....	none	....
NiO	....	tr	....
CuO	....	tr	....
P_2O_5	....	tr	....
V_2O_3	....	none	....
CO_2	....	none	....
F	....	....	.41
			100.20
Less O for F	....	....	.17
	99.95	100.15	100.03

TABLE V.

Comparison of Three Analyses of an Amphibole (Iron Hill 1993).

	Analyst A	Analyst B	Gonyer
SiO_2	37.70	37.86	40.18
TiO_2	3.10	.60	1.79
Al_2O_3	12.36	14.83	14.26
Fe_2O_3	4.74	4.37	4.73
FeO	5.80	5.97	5.76
MnO	.14	.25	.22
MgO	14.55	13.11	14.87
CaO	16.86	14.96	12.88
BaO	doubtful tr	.15	none
SrO	....	.15	.03
Na_2O	2.35	2.20	2.22
K_2O	1.24	1.70	1.86
H_2O-	tr	.34	....
H_2O+	1.20	1.82	.60
F	....	....	.79
Cr_2O_3	....	none	....
NiO	....	.10	....
CuO	....	.05	....
P_2O_5	....	.63	....
CO_2	....	1.00	....
			100.19
Less O for F	....	....	.33
	100.04	100.09	99.86

TABLE VI.

Comparison of Two Analyses of an Amphibole (Iron Hill 1994).

	Analyst C	Gonyer
SiO_2	55.26	56.00
TiO_2	.34	.26
Al_2O_3	.58	.30
Fe_2O_3	5.97	3.91
FeO	2.49	2.44
MnO	.67	.55
MgO	20.97	20.37
CaO	5.43	5.08
Na_2O	5.55	5.39
K_2O	2.35	3.01
H_2O-	.02	....
H_2O+	.43	2.40
S	tr	....
F	....	none
BaO	.17	....
	100.23	99.71

ACCURACY OF SILICATE ANALYSES.

The failure of the several analyses for each amphibole to check cannot be attributed entirely to the presence of fluorine. From my experience if duplicate analyses are made on the same silicate powder by the same chemist or by two chemists, differences as great as 0.5 per cent are common and larger differences are too numerous. I have long advocated that chemists should report ordinary analyses only to the nearest tenth of a per cent, as the figures in the hundredths of a per cent column mean nothing, except possibly for some of the minor oxides. Many geologists who are not familiar with the probable errors in chemical analyses draw unwarranted conclusions from a small difference between the analyses of two rocks.

Analyses made with special care and with little regard to the time required or the cost may have a greater accuracy, and in such analyses the hundredths of a per cent may have real significance.

In most rock analyses, for the constituents that are present to the extent of half a per cent or more, there are six independent determinations that enter into the summation: SiO_2, $Al_2O_3+TiO_2+P_2O_5+$etc., MgO, CaO, total alkalies, and H_2O. An analysis is considered satisfactory if the summation is 100.00 ± 0.50. Since the errors may be either positive or negative, and are therefore partly compensating, it is inevitable that many of the determinations are out as much as

0.10 per cent and some are out much more. We know that the errors in the determination of some of the oxides are much greater than those in others.

In my own work, if the facts could be reasonably assured that the chemical analyses made for me were correct to within a few tenths of a per cent for most of the oxides and to within half of one per cent for the few oxides that are in large amount (especially SiO_2 and Al_2O_3), I could have much more assurance in the conclusions that were drawn from analyses and groups of analyses than I do, and therefore could make more use of chemical analyses.

SAMPLING A ROCK FOR ANALYSIS.

Mining engineers give very careful consideration to the problem of supplying the chemist with a sample that represents a body of rock. Petrographers and geologists have seriously neglected this, and it is not uncommon for a petrographer to send a chemist a sample of a coarse-grained rock that weighs 20 to 30 grams. This is far too little.

To reach some approximation to the size of sample required for rocks of different grain size, first assume loose grains, each of a single mineral. In sampling a rock the fragments, especially the larger ones, may contain more than one mineral and this will improve the sample somewhat. To attain a probable error of 0.1 per cent for the minerals, on a sample made up of loose grains, the largest of which are cubes whose edges are given in column 1, table VII, the length of a channel or cylinder required for the sample is given in column 2, the area of a thin slab in column 3, the volume of a sample in column 4 and the weight of the sample (assuming a specific gravity of the large grains as 2.7) in column 5. The data in the table assume perfect mixing of the sample.

TABLE VII.

Size of samples required for rocks of given maximum grain size to sample the minerals with a probable error of 0.1%.

Maximum grain size, edges of cubes centimeters	Length of channel or cylinder centimeters	Area of thin slab square centimeters	Volume of cube Cubic centimeters	Weight grams
0.1	100	10	1	2.7
0.5	500	250	125	340.
1.	1000	1000	1000	2700.

An average rock, either granular or porphyritic, will have some grains equal to about 0.5 centimeter cubes. To sample such rocks with a probable error in the minerals of 0.1 per cent requires about an ordinary hand specimen. To sample a rock whose largest grains are 1 centimeter cubes with the same error requires about eight average hand specimens. Such a rock is not unusually coarse grained.

Column 3 gives the size of a thin section required to give a probable error in a Rosiwal determination of 0.1 per cent. To give an error of one per cent where the largest grains are 1, 5, and 10 millimeters across, the thin section should be 100, 2500, 10,000 square millimeters in area respectively. An average thin section has an area of about 300 square millimeters and a very large one under 500 square millimeters.

Assayers advocate for the most favorable ores—very low-grade or very uniform ores such as iron ores—much larger samples. Where the largest grains are 1 millimeter in diameter they advocate a sample of one half a pound or about 226 grams; where the largest grains are 4.6 millimeters in diameter they advocate a sample of ten pounds or 4530 grams; and where the largest grains are 10.7 millimeters in diameter they advocate a sample of 50 pounds or 22,650 grams.[1] They thus advocate samples from 9 to 100 times as large as those indicated in table VII.

Many samples of medium-grained rocks sent to a chemist for accurate analyses probably do not sample the minerals of the rock closer than within one per cent, and many samples of coarse-grained rock are much poorer samples. The sampling of the oxides is much better unless the extra grains happen to be of a constituent that is in small amount. In an ordinary granite an extra per cent of quartz in the rock would increase the SiO_2 content approximately 0.35 per cent, while an extra per cent of alkaline feldspar would decrease the SiO_2 by about 0.10 per cent, and would increase the alkalies by about 0.07 per cent and the alumina by about 0.08 per cent. An extra per cent of a mineral like amphibole or pyroxene would introduce a greater error in most rocks. In a granodiorite an additional per cent of pyroxene would introduce approximately the following errors:

SiO_2 — 0.2 per cent. $CaO + MgO + FeO$ 0.4 per cent.

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[1] Bugbee, E. E.: A textbook of fire assaying, John Wiley & Sons, p. 43, 1926.

SOME CHECKS OF CHEMICAL ANALYSES.

The petrographer and mineralogist have some checks on chemical analyses that it is their duty to apply. For rock analyses the best check is a comparison of the norm and the mode, and an experienced petrographer can find any large error in an analysis by this method. He must remember that some potash goes into the plagioclase, considerable soda goes into the orthoclase and microcline, and much soda goes into sanidine. In lavas, even where the groundmass is submicroscopic in crystallization, it is possible in most cases to estimate approximately its composition. In my experience considerable errors have been found in more than one out of ten rock analyses tested by this method, and a redetermination of one or two constituents checks my finding.

For minerals, the judgment of an experienced mineralogist is a check. The law of Gladstone and Dale ($K=\frac{n-1}{D}$), which gives a relation between mean index of refraction, chemical composition, and density, serves as a check in some cases; for instance, fluorine gives a very low value for K, BaO gives a low value, TiO_2 gives a very high value. It is wise to calculate the value of K before sending a sample of an unknown mineral to the chemist, as it may give a clue to the presence of some unusual constituent that may introduce difficulties into the analysis. In this way the chemist will be enabled to furnish an analysis on a smaller sample.

X-ray data give several checks on the chemical composition. Some chemical combinations are associated with some structures. The relation between the size of the unit cell, the specific gravity, and the average index of refraction give a clue to the chemical composition. The molecular weight of the compound may be exactly determined by the X-ray method, and the chemical analysis must conform to this independent determination.

After a mineral sample is prepared for analysis it should be powdered, and a part of the powder sent to the chemist should be examined carefully under the microscope for impurities, zoning, and other irregularities. It is surprising how much impurity can be found in a carefully hand-picked sample or even in powdered crystals.

An unusually instructive example of the value of some of these checks recently came to my attention. A mineral that could not be identified was found in a rock specimen, and the optical properties and specific gravity of the mineral were determined. A part of the small rock specimen was then powdered and a sample prepared for the chemist. Owing to a desire to expedite the work, the powder was not examined with the microscope before it was sent to the chemist. In due time, the chemist furnished an analysis that was an excellent analysis of a garnet. The low indices of refraction and high specific gravity of the unknown mineral showed on checking by the law of Gladstone and Dale that such a composition was impossible and that the mineral must have a considerable amount of some element like fluorine. A new study of the original specimen showed that an unknown mineral was present in addition to the abundant garnet. By taking special precautions a new sample of the unknown mineral, checked with a microscope, was given to the chemist with the information that the mineral probably contained much fluorine. The final analysis gave a composition that checked with all the other data and showed much fluorine.

CONCLUSIONS.

In justice, a few words in defense of the chemist are required. We mineralogists and petrographers nearly always need more chemical analyses than we can afford. We therefore "shop around" to find some chemist who will make analyses for as little as possible. We not uncommonly pay Twenty Dollars or less for a complete silicate analysis. By the time the analyst pays for his materials, allows for accidents, and other items he cannot make a first-class analysis for Twenty Dollars and make a modest living.

Hillebrand says:

> "If there is a competent assistant to do the grinding and specific-gravity determinations are not required, it is quite possible after long experience for a quick worker to learn to so economize every moment of time in a working day of seven hours, with an abundance of platinum utensils and continuous use of air and

water or steam baths through the night, as to finish every three days, after the completion of the first analysis, barring accidents and delays, one of a series of rocks of generally similar character, each containing from eighteen to twenty quantitatively determinable constituents, excluding, for instance, fluorine, carbon as such, nitrogen, metals of the hydrogen sulphide group, and cobalt."[2]

Geologists are probably getting all they are paying for and perhaps more. Would it not be wiser for us to have fewer analyses, to pay a little more for them, and to insist on a higher quality?

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[2] Hillebrand, W. F.: The analyses of silicate and carbonate rocks. U. S. Geol. Surv. Bull. 700, p. 32, 1919.

HARVARD UNIVERSITY,
CAMBRIDGE, MASS.