A TEST OF THE ACCURACY OF CHEMICAL ANALYSIS OF SILICATE ROCKS

H. W. Fairbairn, *Massachusetts Institute of Technology, Cambridge, Mass.*

AND

J. F. Schairer, *Geophysical Laboratory, Carnegie Institution of Washington*

Abstract

A six-component silicate glass of the proportions found in granite was prepared and its composition controlled so that significant errors were eliminated except for SiO_2 (.02%) and Al_2O_3 (.01%). Analysis of this glass by eleven chemical laboratories gave mean values which showed satisfactory agreement ($<.1\%$) for MgO, CaO, Na_2O, K_2O. For SiO_2 and Al_2O_3 a reciprocal systematic error appeared whereby SiO_2 was .4% low and Al_2O_3 was .6% high; total SiO_2 and Al_2O_3 agreed almost exactly ($<.1\%$) with the glass standard. The practical problem of evaluating error in a single analysis is discussed briefly in its relation to these results.

Introduction

The need for reliable standards in spectrochemical analysis of the major elements of silicate rocks led recently to a chemical study of the composition of two provisional standards (*G-1*, a granite from Westerly, R. I.; *W-1*, a diabase from Centerville, Va.). With the co-operation of twenty-four laboratories from various parts of the world, data on these two rocks were assembled and means computed for all the major elements. This work, together with an investigation of the minor elements and a study of the modal composition of the granite, has been recently published (1).

Although a majority of the chemical determinations were closely grouped about a central consensus value, the over-all dispersion for a number of elements was disturbingly large and it was suggested (1) that, if a synthetic silicate mixture could be obtained, a second round of analyses on this new material of *known* composition might be illuminating. In other words, whereas the original investigation was a test of analytical precision, the second one would test accuracy as well. So far as we are aware, no check of this kind has ever been carried out to test the various procedures used in silicate analysis. Through the co-operation of a number of organizations and individuals, acknowledged elsewhere in this paper, we are now able to report on this matter and to comment on its relation to the previous work.

Preparation of the Standard

A composition for the standard was selected which would closely approximate the granite *G-1* already analyzed. This would tend to maintain precision of analysis at the same level as for *G-1* and thus simplify interpretation of the results. The following composition was decided on:

Norm		*Composition (Wt. %)*	
Q	27.0	SiO_2	72.64
Cor	1.0	Al_2O_3	15.78
Or	34.0	CaO	1.82
Ab	27.0	MgO	0.80
An	9.0	K_2O	5.76
En	2.0	Na_2O	3.19
Sum	100.0	Sum	99.99

A silicate mixture of this kind may be termed a haplogranite, following Bowen's nomenclature.* No iron was deliberately added, although a small amount is present (as Fe_2O_3) in the final product through contamination from steel mortars. Similarly, a small amount of platinum is present because of preparation in platinum crucibles. The MgO content is slightly higher than in many granites but no higher than in some biotite or pyroxene granites. The value for MgO was deliberately selected to lower viscosity of the melt and thereby reduce the labor of preparation.

The sample was prepared at the Geophysical Laboratory† using materials and procedures which have been standard there for many years. As a source of potash, potassium tetrasilicate glass ($K_2O \cdot 4SiO_2$) was prepared in a platinum crucible from purified quartz (residue after treatment with HF and H_2SO_4, 0.03%) and chemically pure $KHCO_3$ (Baker & Adamson, lot No. 3772). If these materials are first sintered at 700° C., and the temperature is then raised very gradually over a period of several days, the K_2O loss after complete fusion at 1200° C. is negligible. The loss of K_2O from 20.0000 gms. of $K_2O \cdot 4SiO_2$ glass was 0.0013 gm. This small loss was replaced and the glass fused three times at 1200°, with intermediate crushing, to yield a homogeneous glass which was crystallized completely at 700° C. to pure crystalline $K_2O \cdot 4SiO_2$. This remained dry in a desiccator over fused KOH sticks and could easily be weighed on a watch glass. Similarly, as a source of Na_2O, sodium disilicate glass ($Na_2O \cdot 2SiO_2$) was prepared from the same purified quartz and from chemically pure anhydrous Na_2CO_3 (prepared by heating $NaHCO_3$, Merck & Co., lot No. 42584, at 350° C.). During the preparation of $Na_2O \cdot 2SiO_2$ the loss before correction on a 20.0000 gm. batch after the

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* The term haplobasaltic was used by N. L. Bowen (*Am. Jour. Sci.*, **40**, 161–185, 1915) for compositions approaching the composition of basalt, *i.e.*, a simplified basalt. In an analogous way we use the term haplogranite.

† J. F. Schairer prepared the sample, assisted by Robert D. Thwaite.

complete fusion at 1200° C. was only 0.0019 gm. Crystalline $Na_2O \cdot 2SiO_2$ remains dry in a desiccator over fused KOH sticks and can easily be weighed on a watch glass.

To provide the proper amounts of SiO_2, Al_2O_3, CaO, and MgO to yield the desired haplogranite composition when mixed with the appropriate amounts of $K_2O \cdot 4SiO_2$ and $Na_2O \cdot 2SiO_2$, a "haploresidue" glass was prepared. This had the composition SiO_2 73.778%, Al_2O_3 22.489%, CaO 2.594%, and MgO 1.140%. Three 25-gram batches of the "haploresidue" glass were prepared from the purified quartz, tabular Al_2O_3 (T61, Aluminum Company of America), C. P. MgO (J. P. Baker & Co., lot. No. 82735), C. P. $CaCO_3$ (Baker & Adamson, C. P. Special). Each batch was fused six times at 1600° C. with intermediate crushing in a steel mortar and removal of steel particles magnetically. Although the resulting glass was uniform in composition (as shown by refractive index tests), small, evenly distributed laths of mullite were present because of the very high liquidus temperature of this composition. After drying for eighteen hours at 900° C., the powdered glass remained dry in a desiccator over fused KOH sticks and could be weighed readily into a platinum crucible.

Four 25-gram batches of haplogranite were prepared in platinum crucibles from the three ingredients whose preparation has just been described. Each batch was fused six times at 1520° C. with intermediate crushing in a steel mortar and removal of steel magnetically. Finally, the four batches were combined in one large platinum crucible and fused at 1200° C. four times with intermediate rough crushing (without use of a steel mortar) to insure thorough mixing of the four batches. Optical examination of the final glass showed a uniform index of refraction 1.491.

The final glass was crushed in a large steel mortar to pass 80-mesh bolting cloth; no metallic sieves were used. Great care was taken to avoid any rotation of the pestle during crushing which might produce a smear of steel on the glass powder. A small amount that would not crush fine in this mortar was rejected. To avoid excessive platinum contamination no attempt was made to remove all glass from the large crucible. Despite these losses and others inherent in each crushing operation, a 92-gram sample of the haplogranite was obtained.

As stated above, no iron was deliberately added in the preparation of the haplogranite. Small amounts, however, are unavoidably introduced by the numerous crushings in a steel mortar even though great care was taken to remove as many as possible of the tiny steel fragments with a magnet after each crushing. The residual iron was oxidized to Fe_2O_3 and dissolved in the melt. On the basis of past experience it might be expected that at least 0.1%, and possibly (though not likely) as much as 0.3% of Fe_2O_3 is present because of this unavoidable contamination during crushing operations.

RELIABILITY OF THE COMPOSITION

It is obviously important to list and assess all possible sources of error in preparation of the haplogranite glass. These are of two kinds: (1) errors arising from impurities in the original ingredients and of the intermediate products, and (2) errors arising from processing of the ingredients. Tables 1 and 2 summarize and evaluate these types of error.

Ingredients

Errors arising from impurities in the ingredients are significant only for SiO_2 and Al_2O_3, quantitatively the two principal constituents of the glass. The quartz used as a source of the SiO_2 is a very pure vein material obtained a number of years ago from Lisbon, Maryland. Several hundred pounds of selected fragments were crushed in a ball mill (using steel balls), treated with hot dilute HCl, then washed and dried. A 10-gram sample of this material treated with H_2SO_4 and HF left an insoluble residue of only .03%.

TABLE 1. ERRORS IN THE GLASS COMPOSITION ARISING FROM IMPURITIES IN THE ORIGINAL INGREDIENTS

Ingredient	Impurity		Estimated Resultant Error		
	Amount	Nature of Impurity	Constituent	Amount	Remarks
Quartz	.03%	Insoluble residue	SiO_2	.02%	Deficiency
Alumina	.075%	(SiO_2 .02, Na_2O .02, Fe_2O_3 .03, TiO_2 .005)	Al_2O_3	.01%	Deficiency
Magnesia	.02%	Alkalis, mostly Na_2O	MgO	.00×%	Negligible
Calcium carbonate	.03%	Alkalis	CaO	.000×%	Negligible
Sodium bicarbonate	.037%	Insoluble .015 CaO+MgO .002 Fe .020	Na_2O	.00×%	Negligible
Potassium bicarbonate	.005%	SiO_2 .003, Al_2O_3+Fe_2O_3 .001, CaO .001	K_2O	.000×%	Negligible
			Total	.03%	Deficiency

The alumina (Tabular Alumina T-61, Aluminum Company of America) has impurities as listed in the table. The SiO_2 impurity in the alumina will replace a small part of the SiO_2 deficiency of the quartz, but not by a significant amount (only .003% proportionately). Likewise the amount of Na_2O is too small (~.003% proportionately) to make any significant change in the over-all amount of Na_2O in the haplogranite glass. The Fe_2O_3 and TiO_2 impurities (.006% proportionately) will appear as a minor part of the total Fe_2O_3 unavoidably added to the glass by grinding in steel mortars (Table 3).

The magnesia has a much greater proportion of impurity than the other ingredients (.20% alkalis, mostly Na_2O,) but because of the small amount required in preparation of the haglogranite glass the proportion of alkalis added is negligible.

Calcium carbonate, the source of CaO, is a highly purified compound (Baker & Adamson, C. P. Special). A careful alkali determination made at the Geophysical Laboratory showed .03% total alkalis in a 5-gram sample.* The net impurity added to the haplogranite from this source is obviously negligible. The sodium and potassium bicarbonates used to prepare the intermediate products $K_2O \cdot 4SiO_2$ and $Na_2O \cdot 2SiO_2$ were C. P. grade and contained the impurities noted in the table. No significant contribution to the total error in the haplogranite composition was made by either of these two ingredients.

Processing of Ingredients

Table 2 subdivides errors arising from preparation of the haplogranite glass into three groups. The first of these is considered negligible for the reason noted in the table. The second concerns volatilization losses in synthesizing $K_2O \cdot 4SiO_2$ and $Na_2O \cdot 2SiO_2$. The precautions taken to avoid these losses have already been stated. The losses, .0013 gm. K_2O and .0019 gm. Na_2O, are in themselves negligible, but were nevertheless replaced.†

The next source of error stems from crushing and grinding operations. Loss of fines, at any stage of preparation where the glass is still inhomogeneous, could be a serious source of error. As indicated in the table and already mentioned in the preceding section, precautions were taken which it is believed have avoided any significant error from this source.

Contamination of the glass by fusion in platinum crucibles and grinding in steel mortars is a significant and unavoidable source of error. Table 3 gives the available data for Fe_2O_3. The laboratories not listed made no separate determination of Fe_2O_3 from their R_2O_3 precipitates. Omitting the result from Laboratory 8, which statistically as well as by later admission of the analyst is improbable, a mean of .15% Fe_2O_3 is the best

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* $CaSiO_3$ made from this $CaCO_3$ provides a standard for calibration of thermocouples at the Geophysical Laboratory, since its freedom from significant impurities gives it an unusually small melting interval of .75° C.

† Further evidence that loss of alkalis can be controlled and eliminated comes from crystallization studies of glasses of feldspar composition. New hydrothermal techniques now make possible rapid crystallization and it is found that such glasses crystallize completely to feldspar, with no evidence of residual glass or additional crystal phases.

TABLE 2. ERRORS IN THE GLASS COMPOSITION ARISING FROM PROCESSING OF ORIGINAL INGREDIENTS AND OF INTERMEDIATE PRODUCTS

Source of Error	Evaluation
Weighing	*Negligible,* in view of .000× uncertainty in individual weighings and relatively large sample size. (The smallest weighing was 0.2850.)
Volatilization of Alkalis	.0013 gm. loss in K_2O from preparation of 20.0000 gm. sample of $K_2O \cdot 4SiO_2$. .0019 gm. loss in Na_2O from preparation of 20.0000 gm. sample of $Na_2O \cdot 2SiO_2$. These losses were replaced and error from volatilization is believed to be *negligible.*
Crushing and Grinding	
1. Loss of Fines	Unknown losses, but could lead to significant error only after the *first* fusion when glass is relatively inhomogeneous. Fine grinding was avoided at this stage and error is believed to be *negligible.*
2. Contamination by Containers	.15% Fe_2O_3 is the estimate of contamination by steel mortars .10% *Pt* is the estimate of contamination by platinum crucibles.
Adsorption of Water by Glass Powder	.08% H_2O is the preferred estimate of error arising from adsorption.

TABLE 3. DATA ON Fe_2O_3 IN THE HAPLOGRANITE GLASS

Laboratory	Wt. %	Remarks
3	.20	
4	.16	Analyst made careful determination with an independent sample.
6	.12	
8	.32	Analyst later reported that this value was probably too high.
10	.16	Average of .16 and .17.
11	.07	Reported as .05 Fe.
12	.17	Average of .14, .16, .20 by three analysts. Each analyst made triplicate determinations.
Average (omitting Laboratory 8)	.15	

available estimate of iron contamination and is entirely in line with the past experience at the Geophysical Laboratory.

A platinum content of .10% was determined by Laboratory 10, which would appear to be a reasonable estimate of view in the repeated fusions carried out in platinum crucibles.

Adsorption of water by the finely ground glass is to be expected and the available data are summarized in Table 4. Because of the low concentration of adsorbed water, agreement is poor and one result (Laboratory 1) may be considered improbable. However, as the correction for water is small relative to that for Fe_2O_3, it makes little difference whether or not the estimate of .08 is off by one or more digits.

TABLE 4. DATA ON H_2O+ IN THE HAPLOGRANITE GLASS

Laboratory	Wt. %	Remarks
1	.00	Improbable
2	.08	
3	.01	
4	.14	
6	.14	
7	.08	Analyst reported two determinations, each .08%.
8	.08	
9	.05	
11	.12	
12	.05	Average of .05, .03, .06 by three analysts, each making triplicate determinations.
Average (omitting Laboratory 1)	.08	

In summary, the composition of the glass as given shows a deficiency of .02% SiO_2, .01% Al_2O_3; in addition it contains .15% Fe_2O_3, .10% Pt., .08% H_2O. Considering also possible "handling" errors, loss of fines by grinding before homogenization of the glass, etc., it is nevertheless believed that at worst each value given for the synthetic rock is correct in the first decimal place, with small uncertainties in the second.

SELECTION OF ANALYSTS

As only a limited amount of the synthetic standard was available, the test had to be on a smaller scale than its predecessor. It was desirable in general to have the same laboratories, and, if possible, the same analysts, carry out the work. With one or two exceptions this was done. The selection of the laboratories and analysts listed under "Acknowledgments" was based on the nearness of their determinations in *G-1* and *W-1* to the mean values. The selection was somewhat arbitrary, for two reasons:

(1) the mean value is assumed to be an unbiased estimate of the correct value, which may or may not be true; and (2) certain analysts approached the mean very closely for some constituents and were wide of this mark for others. Real uncertainty arose, therefore, in several instances as to which would probably have given essentially the same data. Each analyst was provided with 3 grams of the standard; small additional quantities were supplied if requested.

RESULTS OF THE TEST

Table 5 shows the analyses of the glass as reported by twelve laboratories. Table 6 shows the analyses after alterations have been made as follows:

(1) .15% Fe_2O_3 is deducted from Al_2O_3 if no Fe_2O_3 was reported by the analyst (see Table 3 for data on Fe_2O_3).

(2) .08% H_2O+ is added to the analysis if none was reported (see Table 4 for data on H_2O).

TABLE 5. DATA ON GLASS AS REPORTED BY ANALYSTS

Laboratory*	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	H_2O+	H_2O-	Total
1	72.06	16.30		.88	2.04	3.81	5.38	.00		100.47
2	72.08	15.93		.87	1.83	3.34	5.70	.08	.10	99.93
3	71.69	16.71	.20	.75	1.91	3.14	5.74	<.01	.12	100.27
4	72.06	16.32	.16	.90	1.66	3.24	5.55	.14	.02	100.05
5	72.18	16.22		.82	1.88	3.07	5.68			99.85
6	72.49	16.06	.12	.81	1.84	3.12	5.63	.14†		100.21
7	72.02	16.36		.82	1.99	3.06	5.74	.08		100.06
8	72.00	16.27	.32	.88	1.99	3.10	5.60	.08	.01	100.25
9	71.90	16.01	tr.	.89	2.34	3.26	5.73	.05	.00	100.28
10	72.06	15.92	.19	.86	1.89	3.26	5.77			99.95
11	71.11	16.15	.07‡	.86	1.89	3.13	5.82	.12	.08	99.16
12	72.47	15.59	.14	.84	1.79	3.22	5.60	.05		99.70
	72.51	15.70	.20	.88	1.80	3.04	5.62	.03		99.78
	72.28	15.92	.16	.87	1.84	3.15	5.64	.06		99.92

* In the same order, these laboratories are numbered 17, 19, 25, 8, 13, 12, 10, 34, 20 7, 23, in the earlier test (1).

† Reported as ignition loss.

‡ Analyst reported .05 Fe.

TABLE 6. DATA ON SYNTHETIC GRANITE GLASS—Recalculated for Comparison with the Standard Composition

Laboratory	SiO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O	$SiO_2+Al_2O_3$	Total
1	72.30	16.20	.88	2.05	3.82*	5.40*	88.50	100.65
2	72.40	15.85	.87	1.84	3.35	5.72	88.25	100.03
3	72.01	16.78*	.75*	1.92	3.15	5.76	88.79	100.37
4	72.37	16.39	.90	1.67	3.25	5.57	88.76	100.15
5	72.42	16.12	.82	1.89	3.08	5.70	88.54	100.03
6	72.75	16.12	.81	1.85	3.13	5.65	88.87	100.31
7	72.25	16.27	.82	1.99	3.07	5.76	88.52	100.16
8	72.24	16.34	.88	2.00	3.11	5.62	88.58	100.19
9	72.11	15.91	.89	2.35	3.27	5.75	88.02	100.28
10	72.35	15.98	.86	1.90	3.27	5.79	88.33	100.15
11	71.38*	16.14	.86	1.90	3.14	5.84	87.52	99.26
$\bar{x}$	*72.23*	*16.19*	*.85*	*1.94*	*3.24*	*5.69*	*88.42*	*1100.15*
$s_{\bar{x}}$	.10	.08	.01	.05	.06	.04	.11	.09
E	.1	.5	1.6	2.6	2.0	.7	.1	.9
s	.34	.26	.05	.17	.21	.12	.36	.31
C	.5	1.6	5.4	8.7	6.5	2.2	.4	.3
12	72.69	15.64	.84	1.79	3.23	5.61	88.33	99.80
(Not included	72.75	15.75	.88	1.81	3.05	5.64	88.50	99.88
in above	72.51	15.97	.87	1.85	3.16	5.66	88.48	100.02
average)								
Mean for Lab. 12	*72.65*	*15.79*	*.86*	*1.82*	*3.15*	*5.64*	*88.44*	*99.91*
Standard Composition	*72.64*	*15.78*	*.80*	*1.82*	*3.19*	*5.76*	*88.42*	*99.99*

Symbols: $\bar{x}$ arith. mean
s standard deviation } for single
C % relative deviation } determinations
$s_{\bar{x}}$ standard error } for the mean
E % relative error } for the mean

Analyses based on Fe_2O_3 = .15
H_2O+ = .08
Pt = .10
as the best estimate of unavoidable impurities. Each analysis recalculated in terms of SiO_2, Al_2O_3, MgO, CaO, Na_2O, K_2O only.

* Values which differ from the mean $\bar{x}$ by more than $2s$.

(3) .10% Pt is added to each analysis.

(4) A new summation is made which includes Fe_2O_3, Pt, H_2O+.

(5) Using this revised summation the glass composition is then recalculated omitting Fe_2O_3, H_2O+, H_2O-, and Pt.

The above alterations permit direct comparison of the analyses with the standard composition. In compiling the table Laboratory 12 is not included in the calculation of mean values as it did not participate in the original tests on *G-1* and *W-1.*

At the outset it need hardly be said that all the analytical work was done without foreknowledge of the composition of the glass. The nature of the test was, however, made known to each laboratory and presumably better-than-routine work was accomplished.

Precision

Data on precision of the test are included in Table 6. The standard deviation s, standard error $s_{\bar{x}}$, and their per cent equivalents, C and E respectively, are of the same order of magnitude as calculated for these laboratories in the previous test on the two rock samples *G-1* and *W-1.* Table 7 is a comparison with *G-1.* With one exception relative precision increases regularly with concentration of constituent. The exception, MgO, shows higher precision than might be expected. This stems at least in part from its higher concentration in the glass than in *G-1* and in any case need cause no concern.

TABLE 7. COMPARISON OF PRECISION OF ANALYSIS OBTAINED FOR HAPLOGRANITE GLASS AND G-1

	SiO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O
Glass $\bar{x}$	72.23	16.19	.85	1.94	3.24	5.69
$s_{\bar{x}}$	.10	.08	.01	.05	.06	.04
E	.1	.5	1.6	2.6	2.0	.7
G-1 $\bar{x}$	72.42	14.42	.39	1.38	3.30	5.52
$s_{\bar{x}}$	.08	.06	.02	.03	.04	.05
E	.1	.4	6.1	2.5	1.5	1.0

Accuracy

Since the level of precision is closely comparable with the previous test on *G-1,* the quite different matter of accuracy can now be fairly assessed. Inspection of Table 6 shows differences between standard and analytical (mean) values of somewhat less than 0.1% for MgO, CaO, Na_2O, and K_2O. Lacking evidence to the contrary, these differences may be attributed either to experimental error, or to the relatively small number of determinations made. For SiO_2 and Al_2O_3, however, a systematic discrepancy appears in the data for Laboratories 1 to 11, whereby the analytical means for SiO_2 and Al_2O_3 are 0.4% low and 0.6% high, respectively. The sum, $SiO_2+Al_2O_3$, however, agrees with the known composition almost exactly. If values for each constituent which differ from the mean by more than 2*s* are discarded, the revised means for Na_2O, CaO, K_2O change in the direction of the standard value; the new mean alters the difference from the standard from .4 to .5 for SiO_2 and for Al_2O_3 from .6 to .5. The changes for CaO, Na_2O, K_2O are all in a direction which indicates that the discarded values are erroneous; as will be indicated in the next paragraph, this also holds for SiO_2 and Al_2O_3.

The reciprocal low and high values for SiO_2 and Al_2O_3, respectively, form an aspect of the investigation which was quite unforeseen. Since the trend of these discrepancies corresponds with a recognized direction of analytical error, the test indicates that this type of systematic error still remains and has been inadequately investigated by the majority of silicate rock analysts. The discrepancies cannot stem from imperfections in the standard,* since the $Al_2O_3+SiO_2$ totals agree too closely. Laboratory 12 obtained excellent agreement with each of SiO_2 and Al_2O_3, as well as with the total. Since individual analyses in Table 6 vary between 0.1% and 0.9% low for SiO_2 and between 0% and 1% high for Al_2O_3, it becomes an important matter to review the procedures which have led to these aberrations. Several laboratories are now engaged with this and may report on it at a later time.

If it is assumed that the systematic error in SiO_2 and Al_2O_3 can be removed and that these values can be made to match as closely as for the other constituents, it may then be said that the test of accuracy has been squarely met by the analysts and the specter of systematic error laid low. A qualifying statement must follow, however, that the test compares *mean* values only. As a practical matter, for reasons both of time and expense, few rock samples are ever subjected to more than *one* chemical analysis, and, whatever the problem, the matter of accuracy usually stands or falls on the merits of the single analysis. This is, of course, the same problem which arose in the more comprehensive test on the provisional standards *G-1* and *W-1* (1) except for the fact that no standard of accuracy could there be applied. In the present test where an accuracy standard is available, and there is satisfactory agreement between the analytic mean and the standard values, the purely statistical approach would point to the standard deviation as a measure of the error of a single analysis. That is, based on a mean of 11 determinations, only one out of three determinations is likely to deviate from the mean by more than the number representing *s*. Since for MgO, Na_2O, K_2O the difference between the composition of the standard and the analytic means is much

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* Even if one applies to the glass standard the estimated errors in SiO_2 (.02) and Al_2O_3 (.01) (Table 1), the maximum range in values for these constituents will not significantly alter this conclusion.

TABLE 8. NORMS FOR SYNTHETIC GRANITE GLASS

Laboratory	Quartz	Corundum	Orthoclase	Albite	Anorthite	Enstatite
1	23.4*	.3	31.9*	32.2*	10.1	2.2
2	25.5	.8	33.8	28.3	9.1	2.2
3	26.1	1.8	34.0	26.6	9.5	1.9*
4	27.0	2.0	32.9	27.4	8.3	2.2
5	27.1	1.4	33.7	26.0	9.4	2.0
6	27.4	1.5	33.4	26.5	9.2	2.0
7	26.6	1.3	34.0	25.9	9.9	2.0
8	26.7	1.5	33.3	26.3	9.9	2.2
9	24.5	0*	34.0	27.6	11.6*	2.2
10	25.5	.9	34.2	27.6	9.4	2.1
11	25.1	1.2	34.5	26.5	9.4	2.1
$\bar{x}$	*25.9*	*1.2*	*33.6*	*27.4*	*9.6*	*2.1*
$s_{\bar{x}}$	.4	.2	.2	.5	.2	.03
E	1.4	15.4	.6	2.0	2.6	1.6
s	1.2	.6	.7	1.8	.8	.1
C	4.8	50.8	2.2	6.6	8.5	5.2
Lab. 12 Norm	*27.3*	*1.2*	*33.4*	*26.6*	*9.0*	*2.1*
Standard Norm	*27.0*	*1.0*	*34.0*	*27.0*	*9.0*	*2.0*

Symbols: $\bar{x}$ arith. mean
s standard deviation } for single determinations
C % relative deviation } for single determinations
$s_{\bar{x}}$ standard error } for the mean
E % relative error } for the mean
* Values which differ from the mean by more than 2s.

Classification of Glass
Class I
Order 4
Rang 2
Sub-rang 3

less than the standard deviation (CaO excepted), a reasonable estimate of the true value is given by the majority of the individual determinations where s is known. This is not true of the values with an asterisk in Table 6, each of which differs from its mean by more than $2s$. Unfortunately, even with a selected group of laboratories aware of the nature of the test, one determination in each column has an asterisk and so fails to measure up to the statistical standard. That is, about 10% of the determinations are of doubtful value. Routine work and less experienced analysts would undoubtedly have produced a larger percentage of improbable results. It should also be noted that the analysts responsible for the $>2s$ determinations in Table 6 were well within the $2s$ limit for these same constituents in *G-1* and *W-1*. There is thus no unique way to evaluate error in the components of a single analysis. The best compromise would be frequent checking by the analyst on his ability to approach the mean values obtained for *G-1* and *W-1* (1). A revised set of means for these standards* will be available shortly; these will be based on the later results of this investigation and on additional analyses of *G-1* and *W-1*.

Summarizing these results, the accuracy obtainable with present analytical procedures for MgO, CaO, Na_2O, K_2O is satisfactory; additional research is needed for SiO_2 and Al_2O_3. Evaluation of error in a *single* analysis, even without the SiO_2–Al_2O_3 complication, is a difficult matter and the present study offers no final solution.

APPENDIX

For those petrologists accustomed to the *C.I.P.W.* norms as a basis for evaluating chemical data, Table 8 will serve as the analogue of Table 6. Unlike the more comprehensive test, the norms here all have the same classification (Table 8, lower right). Individual values of doubtful significance are starred, as in Table 6. Quartz is definitely low relative to the standard norm; corundum is slightly higher. These trends are similar to those for SiO_2 and Al_2O_3 in Table 6. Orthoclase, albite, and enstatite are in satisfactory agreement with the standard norm; anorthite is notably higher than the standard.

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* These two standards are available in small quantities to responsible persons working in silicate chemistry. Inquiries should be directed to Dr. Michael Fleischer, Geological Survey, Department of the Interior, Washington, D. C.

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