On conventional calculations of amphibole formulae from chemical analyses with inaccurate $H_2O(+)$ *and* F *determinations*

By I. Y. Borg

Lawrence Radiation Laboratory, University of California,
Livermore, California

[Taken as read 2 November 1967]

Summary. For chemical analyses with inaccurately reported $H_2O(+)$ or F, calculation of an amphibole formula on the basis of 23(O) after discarding the reported $H_2O(+)$ is in most cases as unsatisfactory as a standard calculation including $H_2O(+)$ based on 24(O, OH, F). The sum of the cations in X, Y, and Z groups most closely approaches theoretical values in a 23(O) calculation, but only by virtue of compensating and compounded errors of opposite sign. Realization of the ideal formula by either method without additional data is not an infallible criterion of accuracy of the analysis or the correct site occupation. These conclusions stem from the observation that although $H_2O(+)$ may be incorrect, most analyses add up to 100·00 or greater; thus compensating errors in metallic oxides are implicit.

THE practice of calculating formulae of amphiboles from chemical analysis in which reported $H_2O(+)$ and F have been discarded has become more common in recent years. Miyashiro (1957) and others have reasoned as follows: poorly determined $H_2O(+)$ and F are endemic to chemical analyses of amphiboles; furthermore, many were performed before presence of (OH) in the structure was firmly established by Coblentz (1911) and Schaller (1916); therefore, calculation of the formula is best based on the remaining reported oxides which contain 23 of the 24 oxygen atoms per half unit cell (henceforth called the 23(O) calculation); (OH, F) = 2·00 per half unit cell is usually tacitly assumed.

It is clear that the results obtained by this method are identical with those from the more conventional calculation, which includes $H_2O(+)$ and F, in the case of a normal amphibole with 2(OH, F). However, especially in those instances in which Σ(OH, F) is not ideal, the 23(O) method has gained favour because of the resultant better fit of ΣX, ΣY, and ΣZ to values in the ideal formula, $AX_2Y_5Z_8O_{22}(OH, F)_2$

(Binns, 1965, p. 317). The purpose of the present note is to show that the closer approximation to the ideal by the 23(O) calculation is in fact generally true for analyses in which total (OH, F) departs more than ±0·30 units from 2·00 per half unit cell, and to demonstrate that the closer approach is by virtue of compensating and compounded errors of the opposite sign. A few important exceptions will be noted later, but in most cases the realization of the ideal formula by 23(O) calculations is not a reliable guide to the accuracy of either implied site occupancy or chemical analysis.

Evidence of apparent good fit of 23(O) *calculation to ideal* ΣX, XY *and* XZ

The seeming superiority of 23(O) calculations is borne out by the data in table I, which is a tabulation of results of both calculations of 516 amphibole analyses (163 alkali and 353 calcic and sub-calcic amphiboles chosen without design from a group of 936 analyses compiled by Leake (in press)). The analyses were programmed and calculated on an IBM 7094 computer.

The only suitable criterion of close approach to ideal formula is ΣY, which includes Al, Ti, Fe‴, Fe″, Mn, Mg, and Cr‴. The ΣZ by convention is forced to a 8·00 value by adding Al^{iv} when necessary to the reported Si. The ΣX is uncertain because of the possible occupation of the A site by cations normally included in X; e.g., Ca, Na, and K. The ΣX of those amphiboles in which A is almost certainly empty, e.g., the glaucophanes, are included in table I. In addition, ΣX is less useful than ΣY because of its relative insensitivity to the method of calculation. Nevertheless, with either ΣX or ΣY used as a criterion, there is little difference in the results of the two methods of calculation when (OH, F) approaches the ideal 2·00.

Assumptions. The argument that follows concerns the relative merits of the two methods of calculation and is based on two premises: that there are 24(O, OH, F) in half the actual unit cell; and that errors in $H_2O(+)$ and F are compensated by errors in weight % of reported metal oxides.

Most analyses, irrespective of whether (OH+F) is greater or less than 2·00, add to totals *greater than* 100·00 (fig. 1). Neither low nor high Σ(OH, F) is reflected in correspondingly low or high total reported oxides. However, it is in those analyses where there is a clear relation between the total oxide and high or low $H_2O(+)$ and F that a 23(O) calculation is demonstrably superior to the 24(O, OH, F). In these instances, additional compensating errors are not implicit.

Result of analytical errors on calculated atomic ratios

Errors in calculated density and atomic ratios that are contingent on incorrectly reported H_2O and F have been discussed in detail by Hey (1939, 1954). The following remarks incorporate his conclusions and extend the argument to 23(O) calculations.

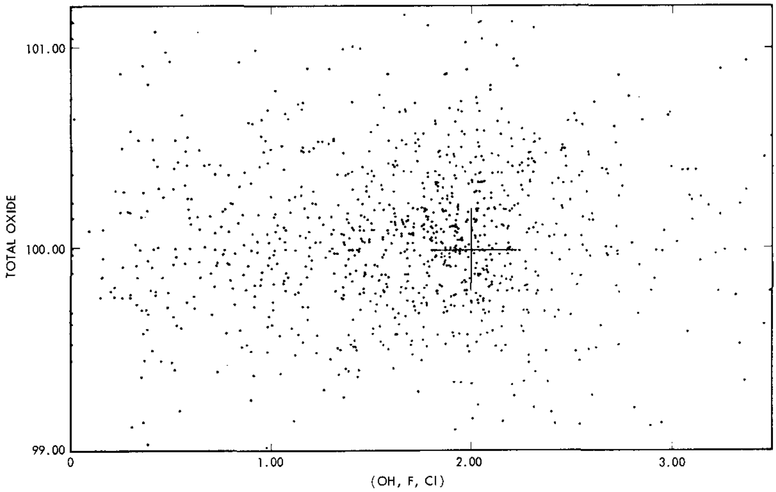

FIG. 1. Relation of (OH, F) based on 24(O, OH, F) calculation to total reported oxides in 1059 amphiboles (924 calcic and subcalcic and 135 alkali). Forty-six amphiboles plot outside the confines of the diagram.

To illustrate the result of analytical errors in $H_2O(+)$ on formula calculation by the two methods, in table II a chemical analysis of a normal, hypothetical amphibole is juxtaposed with the same analysis altered so as to have excess $H_2O(+)$ (Cases 2 and 3) and deficient $H_2O(+)$ (Cases 4, 5, and 6). All five analyses contain compensating errors in a reported oxide (starred) so that the total remains 99·88. An erroneously high Al_2O_3 content (Case 4) is fairly common (Filby and Leininger, 1960, p. 71), whereas high SiO_2 and FeO (Cases 5 and 6) are contrary to the usual bias (Stevens and Chodas, 1960, p. 46; Stevens and Niles, 1960, p. 21). The assumed error of 1 % is perhaps large relative to the likely error in $H_2O(+)$, but it is convenient for illustrative purposes.

All atomic ratios in Cases 2 to 6 are subject to an error contingent on incorrect total for the moles of oxygen present. Certain of them (starred in table II) are also subject to the introduced error. In the cases of $H_2O(+)$ deficiency, the error affecting all atomic ratios is the result of

Table I. Comparative results of formula calculation on the basis of 23(O) and 24(O, OH, F) for 516 amphiboles

	Calculation most closely approaching ideal formula								Calculation yielding highest atomic ratios			
	Criterion: $\Sigma Y = 5{\cdot}00$				Criterion: $\Sigma X = 2{\cdot}00$							
(OH, F) on basis of (O, OH, F)	Total no. of analyses	23(O)	24(O, OH, F)	Same*	Total No. of analyses	23(O)	24(O, OH, F)	Same*	Total no. of analyses	23(O)	24(O, OH, F)	Same*
< 1·70	218	165	49	4	129	61	29	39	218	1	216	1
> 2·30	126	58	64	4	100	22	29	49	126	114	9	3
≃ 2·00 (1.70–2.30)	172	44	51	77	137	1	1	135	172	26	68	78

* Methods yield values within 0·02 of each other.

Table II. Effect of 1 % $H_2O(+)$ error on atomic ratios and ΣX, Y, and Z in 23(O) and 24(O, OH, F) calculation

	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
SiO_2	56·31	56·31	56·31	56·31	*57·31	56·31
Al_2O_3	9·45	*8·45	9·45	*10·45	9·45	9·45
TiO_2	0·08	0·08	0·08	0·08	0·08	0·08
Fe_2O_3	4·14	4·14	4·14	4·14	4·14	4·14
FeO	8·55	8·55	*7·55	8·55	8·55	*9·55
MnO	0·19	0·19	0·19	0·19	0·19	0·19
MgO	10·49	10·49	10·49	10·49	10·49	10·49
CaO	1·88	1·88	1·88	1·88	1·88	1·88
Na_2O	6·50	6·50	6·50	6·50	6·50	6·50
K_2O	0·06	0·06	0·06	0·06	0·06	0·06
$H_2O(+)$	2·17	*3·17	*3·17	*1·17	*1·17	*1·17
$H_2O(-)$	0·03	0·03	0·03	0·03	0·03	0·03
F	0·03	0·03	0·03	0·03	0·03	0·03
Cl	0·02	0·02	0·02	0·02	0·02	0·02
Total	99·90	99·90	99·90	99·90	99·90	99·90
−O = F+Cl	0·02	0·02	0·02	0·02	0·02	0·02
	99·88	99·88	99·88	99·88	99·88	99·88

	1*a*	2*a*	2*b*	3*a*	3*b*	4*a*	4*b*	5*a*	5*b*	6*a*	6*b*
Si	7·82	7·75	7·91	7·71	7·87	7·90	7·74	*8·03	*7·87	7·94	7·79
Al	1·55	*1·37	*1·40	1·53	1·56	*1·73	*1·69	1·56	1·53	1·57	1·54
Ti	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01
Fe‴	0·43	0·43	0·44	0·43	0·44	0·44	0·43	0·44	0·43	0·44	0·43
Fe″	0·99	0·99	1·00	*0·86	*0·88	1·00	0·99	1·00	0·98	*1·13	*1·11
Mn	0·02	0·02	0·02	0·02	0·02	0·02	0·02	0·02	0·02	0·02	0·02
Mg	2·17	2·15	2·20	2·14	2·18	2·19	2·15	2·19	2·15	2·20	2·16
Ca	0·28	0·28	0·28	0·28	0·28	0·28	0·28	0·28	0·28	0·28	0·28
Na	1·75	1·73	1·77	1·72	1·76	1·77	1·73	1·77	1·73	1·78	1·74
K	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01
(OH)	2·01	*2·91	(1·98)	*2·90	(1·98)	*1·09	(1·98)	*1·09	(1·98)	*1·10	(1·98)
F	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01
Cl	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01
Error in atomic ratios	0 %	−0·92 %	+1·08 %	−1·42 %	+0·50 %	+0·92 %	−1·08 %	+0·75 %	−1·25 %	+1·42 %	−0·50 %
ΣZ	8·00	8·00	8·00	8·00	8·00	8·00	8·00	8·02	8·00	8·00	8·00
ΣY	4·99	4·72	4·98	4·70	4·95	5·29	5·03	5·22	4·99	5·31	5·06
ΣX	2·04	2·02	2·06	2·01	2·05	2·06	2·02	2·06	2·02	2·07	2·03
(OH, F)	2·03	2·93	(2·00)	2·91	(2·00)	1·11	(2·00)	1·11	(2·00)	1·12	(2·00)
O	21·97	21·07	(22·00)	21·09	(22·00)	22·89	(22·00)	22·89	(22·00)	22·88	(22·00)

a. Calculation based on 24(O, OH, F); *b.* Calculation based on 23(O).

Case 1. Hypothetical amphibole analysis with no error (glaucophane).
Case 2. Excess compensated by deficiency in oxygen-rich oxide (Al_2O_3).
Case 3. Excess compensated by deficiency in oxygen-poor oxide (FeO).
Case 4. Deficiency compensated by excess of oxygen-rich oxide (Al_2O_3).
Case 5. Deficiency compensated by excess of oxygen-rich oxide (SiO_2).
Case 6. Deficiency compensated by excess of oxygen-poor oxide (FeO).

* Oxides affected by hypothetical errors; parentheses indicate assumed values.

erroneously reporting the weight of a relatively oxygen-poor metal oxide instead of oxygen-rich water.[1] All atomic ratios are too high in a 24(O, OH, F) calculation (Cases 4, 5, and 6) and too low in a 23(O) calculation, with the exception of the one or more oxides that are high by virtue of the initial error. Thus, ΣY as well as calculated densities (see Binns, 1965, p. 318) are too high in 24(O, OH, F) calculations. They are more nearly correct in the 23(O) method because the erroneously low atomic ratios of cations making up the total are compensated by the initially high values of one or more of them.

Failure to report appreciable amounts of fluorine when present makes the calculated number of moles of oxygen in both calculations too low, thereby worsening the 24(O, OH, F) and improving (apparently) the 23(O) by the criterion of approach to ideal ΣX, ΣY, and ΣZ.

If water is reported in excess, the converse situation holds (Cases 2 and 3); namely, the atomic ratios and ΣY are too low in 24(O, OH, F) calculations and cancelling errors of opposite sign in 23(O) calculations give rise to a reasonable ΣY. The tabulation of calculations of real analyses (table I) bears out these conclusions. The fact that not all 23(O) calculations appear superior to 24(O, OH, F) points to the existence of additional random errors in the analyses or, alternatively, departures from the ideal amphibole formula.

The effect of spreading the compensating analytical errors among all twelve components rather than concentrating it in one oxide as in examples in table II does not affect the over-all result in the case of the 24(O, OH, F) method because the critical error is in the total moles of oxygen, irrespective of the oxide(s) in which it resides. However, in the case of a 23(O) calculation, because the two sources of error are of the opposite sign and are cancelling, it is possible to calculate nearly correct atomic ratios and formula in the case where compensating errors are in fact spread out over all oxides. Unfortunately, it is not possible to recognize this situation.

As Phillips (1963) points out, a 23(O) is also unsatisfactory in the case of oxyhornblendes in which a deficiency in hydrogen and hence (OH) is compensated for by oxidation of Fe‴. In such cases a 24(O, OH, F) calculation should give satisfactory values for ΣX, ΣY, and ΣZ in combination with low Σ(OH, F).

---

[1] The magnitude of the error in either calculation depends on the size of the error in $H_2O(+)$ and F, and on which of the metal oxides has been reported in excess of its true value. In the 23(O) calculation, errors in oxygen-poor oxides (Case 6, table II) lead to smaller errors than similar errors in oxygen-rich oxides (Cases 4 and 5). The converse holds for the 24(O, OH, F) method.

Discussion and conclusions

It has been shown that a formula derived from a 23(O) calculation is not necessarily a better approximation of the true atomic ratios than that derived from the 24(O, OH, F) calculation even if reported $H_2O(+)$ and F are demonstrably inaccurate, with the exceptions cited below. In general, in such cases 23(O) calculation produces values of ΣX, ΣY, and ΣZ closer to the ideal because of compounding and cancellation of errors. These conclusions derive from the fact that the total reported constituents almost always add up to approximately 100·00.

The 23(O) calculation is to be preferred to a 24(O, OH, F) in those instances in which it is reasonable to assume either that an error in $H_2O(+)$ accounts for the high (common) or low (uncommon) reported total oxide content (e.g., weight % of $H_2O(+)$ and F are not reported and the total is near to 98·00), or that errors in reported $H_2O(+)$ and F are accompanied by equal compensating errors of the opposite sign in the remaining ten components such that the total oxide content remains close to 100·00.

In general, without additional information there is little to recommend one method over the other. Atomic ratios of the accurately reported cation oxides lie on either side of their 'true' value in analyses containing errors in $H_2O(+)$ and F when calculated by both methods.

Clearly, additional criteria must be invoked in order to test the reliability of an amphibole analysis. Leake (1965*b*, p. 849) has shown that the diagnostic features of a bad analysis are not always ΣX, ΣY, or ΣZ but, rather, some particular cation fraction within them.

By ignoring water or likely site distribution or both, it is possible to fit chemical analyses of amphibolites (Leake, 1965*a*, p. 314) and most basalts to an amphibole formula. For example, from Nocholds's compilation (1954) the following formulae can be obtained:

Average tholeiitic olivine basalt, $(AX)_{1\cdot96}\,Y_{5\cdot28}\,Z_{8\cdot00}\,\mathrm{O}_{22\cdot00}\,(\mathrm{OH, F})_{(2\cdot00)}$;
Average subsilicic igneous rock excluding nepheline types, $(AX)_{2\cdot43}\,Y_{4\cdot97}\,Z_{8\cdot00}\,\mathrm{O}_{23\cdot30}\,(\mathrm{OH, F})_{0\cdot67}$;
Average olivine gabbro, $(AX)_{2\cdot32}\,Y_{4\cdot80}\,Z_{8\cdot00}\,\mathrm{O}_{22\cdot00}\,(\mathrm{OH, F})_{(2\cdot00)}$;
Average gabbro, $(AX)_{2\cdot44}\,Y_{4\cdot94}\,Z_{8\cdot00}\,\mathrm{O}_{23\cdot38}\,(\mathrm{OH, F})_{0\cdot62}$;
Average tholeiitic andesite, $(AX)_{2\cdot45}\,Y_{4\cdot66}\,Z_{8\cdot00}\,\mathrm{O}_{23\cdot16}\,(\mathrm{OH, F})_{0\cdot84}$.

These calculated rock analyses are closer to the ideal amphibole formula than are analyses of many amphiboles.

Lacking additional data, the writer's preference is for the 24(O, OH, F) calculation with the exceptions previously noted. Analytical errors when present are not disguised by a fortuitous fit to the ideal formula, such as is characteristic of the 23(O) calculation.

Acknowledgements. The author is grateful to B. Leake for making his collection of analyses available before publication, and for profitable discussion and criticism. This work was performed under the auspices of the U.S. Atomic Energy Commission.

References

BINNS (R. A.), 1965. The mineralogy of metamorphosed basic rocks from the Willyama Complex, Broken Hill District, New South Wales. Part I. Hornblendes. Min. Mag., vol. 35, pp. 306–325.

COBLENTZ (W.), 1911. The role of water in minerals. Franklin Inst. Journ., vol. 172, p. 334.

FILBY (R. H.) and LEININGER (R. K.), 1960. Spectrographic determinations of the major constituents of granite G-1 and diabase W-1. U.S. Geol. Surv. Bull. 113, pp. 57–82.

HEY (M. H.), 1939. On the presentation of chemical analyses. Min. Mag., vol. 25, pp. 407–411.

—— 1954. A further note on the presentation of chemical analyses of minerals. *Ibid.*, vol. 30, pp. 481–497.

LEAKE (B. E.), 1965*a*. The relationship between composition of calciferous amphiboles and grade of metamorphism. Chap. 17 in Controls of Metamorphism by PITCHER (W. S.) and FLINN (G.). Boyd and Oliver, pp. 299–318.

—— 1965*b*. The relationship between tetrahedral aluminum and the maximum possible octahedral aluminum in natural calciferous and subcalciferous amphiboles. Amer. Min., vol. 50, pp. 843–851.

MIYASHIRO (A.), 1957. The chemistry, optics and genesis of alkali-amphiboles. Journ. Fac. Sci. Univ. Tokyo Ser. 2, vol. 11, pp. 57–83.

NOCKOLDS (S. R.), 1954. Average chemical compositions of some igneous rocks. Bull. Geol. Soc. Amer., vol. 65, pp. 1007–1032.

PHILLIPS (R.), 1963. The recalculation of amphibole analyses. Min. Mag., vol. 33, pp. 701–711.

SCHALLER (W. T.), 1916. The chemical composition of tremolite *in* Mineralogic notes, Series 3, U.S. Geol. Serv. Bull. 610, pp. 133–136.

STEVENS (R. E.) and NILES (W. W.), 1960. Part I: Chemical analyses of the granite and the diabase. *Ibid.*, no. 1113, pp. 3–44.

—— and CHODOS (A. A.), 1960. Part II: Special study of the silica content of G-1 and diabase W-1. *Ibid.*, pp. 45–56.

[*Manuscript received 11 April 1967*]