

*The unit-cell contents of anthophyllite.*

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*Summary.* Conclusions concerning the unit-cell contents and chemical formula of a mineral are all too often drawn from a small part of the available data. A procedure is outlined by which any chemical analysis for which a density is available can be utilized, provided X-ray data are available for a reasonable range of analysed specimens. The effects of possible errors in the determination of water, and in the assessment of essential and non-essential water, are discussed both qualitatively and quantitatively.

A survey of all available data for anthophyllite has not disclosed any specimens in which the number of oxygen atoms per unit cell is significantly in excess of 96 with the possible exception of the Glen Urquhart gedrite and the Edwards (New York) material. But it is certain that the number of cations per unit cell is normally well in excess of 60 (partial occupation of the *A* lattice positions), and that, although 'excess' water in some fibrous anthophyllites may be adsorbed impurity, the number of hydroxyl groups in others is well in excess of 8 per unit cell; it is also fairly clear that the number of hydroxyl groups may fall below 8 per unit cell.

It has generally been assumed that the total number of large anions per unit cell in anthophyllite, and indeed in silicates generally, is always an exact integer (96 in anthophyllite) within the limits of experimental error. It is true that in a number of hydroxyl-bearing minerals partial dehydration without lattice breakdown is possible,<sup>1</sup> a process ( $2\text{OH}' \rightarrow \text{O}'' + \text{H}_2\text{O}$ ) that must produce vacancies in the oxygen lattice; that a few examples of oxygen lattice deficiencies are known among oxide minerals;<sup>2</sup> and that interstitial substitution of large anions is not unknown.<sup>3</sup> But the Glen Urquhart gedrite described by one of the authors<sup>4</sup> may be the first example of a non-integral oxygen content in a silicate (apart, of course, from the water of the zeolites). A critical

<sup>1</sup> See, for example, R. E. Grim and W. F. Bradley, *Journ. Amer. Ceram. Soc.*, 1940, vol. 23, p. 242 [M.A. 8-295]; S. Z. Ali and G. W. Brindley, *Proc. Leeds Phil. Soc.*, 1948, vol. 5, p. 109 [M.A. 11 104]; G. W. Brindley and S. Z. Ali, *Acta Cryst.*, 1950, vol. 3, p. 25 [M.A. 11-104]; W. F. Bradley and R. E. Grim, *Amer. Min.*, 1951, vol. 36, p. 182 [M.A. 11-345]; W. P. Johns, *Min. Mag.*, 1953, vol. 30, p. 186.

<sup>2</sup> L. G. Sillén and B. Aurivillius, *Zeits. Krist.*, 1939, vol. 101, p. 483 [M.A. 7-491]; L. G. Sillén, *Inaug. Diss.*, Stockholm, 1940 [M.A. 9 98]; B. Aurivillius, *Arkiv Kemi, Min. Geol.*, 1943, vol. 16A, no. 17 [M.A. 9 44].

<sup>3</sup> E. Zintl and A. Udgard, *Zeits. anorg. Chem.*, 1939, vol. 240, p. 150 [M.A. 8 117].

<sup>4</sup> G. H. Francis, *Min. Mag.*, 1955, vol. 30, p. 709.

review of the unit-cell contents of anthophyllite appeared desirable, and is presented here.

We feel that all too often conclusions concerning the unit-cell contents and chemical formula of a mineral are drawn from a small part of the available data, and represent only a portion of the field of variation. Chemical analyses are often rejected for no other reason than their age, whereas there is adequate evidence that the standard of accuracy of analyses of many, though by no means all, classes of minerals has changed very little in the last hundred years,<sup>1</sup> and many of Berzelius's analyses, made 130 years ago, appear to be perfectly satisfactory. Particular analyses are often rejected solely because they fall outside the general field defined by the bulk of analyses of the same species; but it seems to us that, while the unusual analysis may well be in error, it should never be rejected out of hand but examined critically, since it may represent some unusual and unexpected isomorphous substitution, and will at least suggest where useful new data should be sought. For quite a number of minerals, a critical review of existing data is at least as important as the accumulation of additional data.

While true empirical unit-cell contents, based on chemical analyses of specimens for which X-ray and specific-gravity data are available, form the most satisfactory evidence for a suggested chemical formula, it is often possible, as will be shown below, to make good use of any analysis for which the specific gravity is available; when the specific gravity is not known, interpretation is more difficult and uncertain.

A major difficulty in the interpretation of many chemical analyses, including some of minerals generally accepted as anhydrous, is to define the role of water shown in the analysis. Apart from difficulties in the accurate determination of the total water content, there is no known method by which a reliable discrimination between adsorbed and essential water can always be made.<sup>2</sup>

<sup>1</sup> For many elements modern analytical methods are more rapid, more convenient, and more adaptable to microchemical procedures, but do not appear to be inherently more accurate. On the other hand, many old analyses are demonstrably incomplete, and for some elements (e.g. B, Cb, and Ta) satisfactory methods of analysis have only recently been developed.

<sup>2</sup> Even if a complete dehydration curve is prepared, it is often impossible to fix with any certainty the point at which loss of adsorbed water ends and loss of essential water begins; often the two stages overlap inextricably. And, as has been pointed out by G. D. Nicholls and J. Zussman (*Min. Mag.*, 1955, vol. 30, p. 717), the amount of adsorbed water may vary sufficiently with the state of subdivision to call for caution in derivation of empirical unit-cell contents, owing to uncertainties in the correction of the observed density for adsorbed water.

In many cases the only satisfactory procedure is to calculate empirical unit-cell contents on two or more different assumptions concerning the distribution of the water; even then the interpretation of the results may remain in doubt.<sup>1</sup> Fortunately, certain generalizations are possible.

*The effect of errors in the determination of water on the empirical unit-cell contents.*

If the reported  $H_2O(+)$  does not truly represent the hydroxyl or other essential water of the mineral there are four possibilities to consider: either the reported  $H_2O(+)$  is too high, in that it includes non-essential adsorbed water, that is, impurity; or it is too low, in that some of the essential water was included in the reported  $H_2O(-)$  and incorrectly regarded as an impurity; or it is too low, in that part of the essential water escaped determination altogether; or too high, in that the analysis shows more water than was actually present.

Further, even if the non-essential  $H_2O(-)$  is correctly distinguished from the essential  $H_2O(+)$ , it may be in error by excess or defect, and this error will affect the empirical unit-cell contents. The treatments appropriate to these several possibilities may now be considered (obviously the water determination may be in error in more than one respect in the same analysis, so more than one correction may be needed).

If a mineral, of observed density  $D_o$ , gives on analysis  $a$  % of an oxide  $A_m O_n$ , of molecular weight  $M$ , an unknown part of which is present as an impurity of density  $d$ ; if the conversion factor<sup>2</sup> is  $F_o = VD_o/1.6603 S$ , calculated on the assumption that the oxide is all essential; and if it may be assumed that the element  $A$  fills  $\alpha$  lattice positions in the mineral, and that the rest,  $x$  %, of the oxide  $A_m O_n$  is impurity, then it can be shown that  $x = Sd(\alpha - aF_o m/M)/(D_o \alpha - SdF_o m/M)$ . The modifications necessary when the  $\alpha$  lattice positions include elements other than  $A$ , or when the impurity is a compound including other oxides than  $A_m O_n$ , will not now be considered.

This relation is obviously applicable to the first possibility mentioned above, the inclusion of adsorbed water in the  $H_2O(+)$ , and in the present instance, with  $M/m = 9.0078$ ,  $d = 1$ , and  $\alpha = 8$ , it simplifies to  $x = S(aF_o - 72)/(SF_o - 72D_o)$ ; but it is also applicable where essential water has been wrongly included with the  $H_2O(-)$ , and the same equation will then give a negative value of  $x$ , indicating the amount of water that

<sup>1</sup> M. H. Hey, *Min. Mag.*, 1954, vol. 30, p. 493.

<sup>2</sup> Here  $V$  is the volume of the unit cell in Å.<sup>3</sup>, and  $S$  the summation of the analysis.

must be transferred from 'H<sub>2</sub>O(-)', accounted as impurity, to 'H<sub>2</sub>O(+)', accounted as essential. In either case the density must be corrected for the amount of adsorbed water now found (if any), before the unit-cell contents are recalculated, a recalculation based on the assumption that there are exactly 8(OH) per unit cell. It will be found that a recalculation in which part of the water formerly regarded as essential is now taken as an impurity will almost always increase both the oxygen atoms per unit cell and the total cations.<sup>1</sup>

The position is different if essential water has escaped determination altogether. In this case the density does not need correction, and the factor  $F_o$  is only affected by the underestimation of the total analytical sum (excluding impurities),  $S$ . If  $y$  % of essential water had escaped determination, all the constituents except oxygen, and their sums, will be high in the uncorrected calculation by a factor  $(S+y)/S$ , that is, by approximately  $y$  % of their value, while the oxygen atoms per unit cell will invariably be low; the corrected value of  $\sum(O, OH, F)$  will be obtained by adding  $F_o y/18$  to the uncorrected value and multiplying the sum by  $S/(S+y)$ , while the corrected value of  $\sum(OH, F)$  is obtained by adding  $F_o y/9$  to the uncorrected value and multiplying by  $S/(S+y)$ . An overestimation of the essential water is obviously the converse of this.

If the adsorbed water, H<sub>2</sub>O(-), is in error by simple underestimation the net sum  $S$  will be unaffected, but the corrected density  $D_{\text{corr}}$  will be low; accordingly, all the empirical unit-cell contents, including oxygen, will be low by the same factor.

The qualitative effects on the observed  $\sum(O, OH, F)$  and  $\sum(\text{cations})$  of various possible errors in the water determinations are summarized in table I. Even in their qualitative form these general relations will be found very useful in deciding on the possible interpretation of an analysis; and when combined with a rough estimate of the probable accuracy of the physical data they provide a useful device for the critical appraisal of analyses.

#### *The unit-cell contents of anthophyllite.*

*The available data.* J. C. Rabbitt<sup>2</sup> lists 84 chemical analyses of anthophyllite, together with a further nine that can<sup>3</sup> be rejected on the grounds

<sup>1</sup> G. H. Francis, *Min. Mag.*, 1955, vol. 30, p. 713 (footnote).

<sup>2</sup> J. C. Rabbitt, *Amer. Min.*, 1948, vol. 33, p. 263 [M.A. 10-416].

<sup>3</sup> He actually lists 11 analyses as 'doubtful or discredited'. Of these, nine can certainly be excluded on the grounds he assigns; but no. 88, while indeed very doubtful on many grounds, including the high value for  $b_{\text{calc}}$ , cannot be unequivocally rejected; and no. 85 is also doubtful, but cannot be definitely excluded.

TABLE I. Summary of the effect of errors in the water determination on the empirical unit-cell contents of a mineral (provided the atomic ratio of oxygen, derived from the percentage composition and molecular weights, is greater than  $5.51/(D+1)$  where  $D$  is the density of the mineral).

| If:   | $\Sigma$ (O,OH,F) observed will be: | $\Sigma$ (cations) observed will be: |
|---|-------------------------------------|--------------------------------------|
| Part of the H <sub>2</sub> O, taken as essential, is really adsorbed:   | Low                                 | Low*                                 |
| Part of the H <sub>2</sub> O, rejected as adsorbed, is really essential:  | High                                | High*                                |
| Part of the essential H <sub>2</sub> O has escaped determination, but the estimate of adsorbed H <sub>2</sub> O is correct: | Low                                 | High                                 |
| The essential H <sub>2</sub> O is overestimated; adsorbed H <sub>2</sub> O absent or correctly estimated:                   | High                                | Low                                  |
| Essential H <sub>2</sub> O absent or correctly estimated; adsorbed H <sub>2</sub> O underestimated:                         | Low                                 | Low†                                 |
| Essential H <sub>2</sub> O absent or correctly estimated; adsorbed H <sub>2</sub> O overestimated:                          | High                                | High†                                |

\* In these cases the observed  $\Sigma$  (cations) will be low (or high) by a larger factor than is the observed  $\Sigma$  (O,OH,F).

† In these cases the observed  $\Sigma$  (cations) and the observed  $\Sigma$  (O,OH,F) will be low (or high) by the same factor.

of gross incompleteness or inaccuracy, or demonstrable impurity or misidentification of the material analysed; in the following discussion, all analyses included in Rabbitt's review will be referred to by his numbers. To these we add a further seven analyses, distinguished below by the letters *A* to *G*.

This collection of analyses can be divided into three classes, of decreasing value in assessing the unit-cell contents: Analyses for which X-ray measurements and density determinations are available; for these the empirical unit-cell contents can be determined. Analyses for which densities are available but not X-ray data; for such analyses it may be possible in favourable circumstances (and is possible in the case of anthophyllite) to form an estimate of the probable cell dimensions, and using this we can calculate what we may perhaps call semi-empirical unit-cell contents. And analyses for which neither X-ray measurements

nor densities are available; for these, only atomic ratios to an assumed basis can be calculated. We consider each class separately.

*Empirical unit-cell contents.* There are only 11 analyses for which all the data necessary to calculate the empirical unit-cell contents are available. J. C. Rabbitt (loc. cit.) studied seven gedrites and anthophyllites from Montana and a gedrite ('bidalotite') from Mysore; K. Johansson<sup>1</sup> examined anthophyllite from Falun, Sweden; and B. E. Warren and D. I. Modell<sup>2</sup> obtained X-ray measurements and a density on material from Edwards, New York, for which the chemical data by E. T. Allen and J. K. Clement<sup>3</sup> may reasonably be accepted. The empirical unit-cell contents for these 10 analyses have been calculated on the assumption that the water is all essential, and are included in table II, together with the unit-cell contents for the Glen Urquhart gedrite (G. H. Francis, loc. cit.).

The resulting figures are of considerable interest; analyses 1, 8, 9, 14, 26, 29, and 30 yield values for the sum (O+OH+F) within the probable experimental error<sup>4</sup> of the accepted 96, but all of these, except nos. 26 and perhaps 30, show a distinct excess of cations over the repeat formula  $4[(\text{Mg}, \text{Fe}^{\prime\prime}, \text{Al})_7(\text{Si}, \text{Al})_8\text{O}_{22}(\text{OH}, \text{F})_2]$ , and it is clear that an appreciable proportion of the so-called A-positions, commonly assumed to be vacant in anthophyllite, are in fact occupied, probably mainly by (Na+Ca).

For analysis 17, the (O+OH) figure, 97.6, is high, but we note that there is a considerable discrepancy between the density as measured by the pycnometer and by the suspension method (J. C. Rabbitt, loc. cit., p. 298), and that if the latter value is accepted instead of the former, an (O+OH) content much nearer the normal 96 results; clearly the evidence of abnormality in this anthophyllite is not conclusive. For completeness, the (O+OH) contents deduced for the other six Montana specimens using the suspension value for the density instead of the pycnometric have also been included in table II, and it will be seen that for analyses 1, 8, and 14, as well as analysis 17, a value nearer 96 results, while for analyses 9, 29, and 30 the departure from 96 is increased.

<sup>1</sup> K. Johansson, *Zeits. Krist.*, 1930, vol. 73, p. 31 [M.A. 4-356].

<sup>2</sup> B. E. Warren and D. I. Modell, *ibid.*, 1930, vol. 75, p. 161 [M.A. 4-463].

<sup>3</sup> E. T. Allen and J. K. Clement, *Amer. Journ. Sci.*, 1908, ser. 4, vol. 26, p. 111.

<sup>4</sup> J. C. Rabbitt did not assess the probable accuracy of his chemical data, but it may probably be assumed that the errors are of the same order as those for the Glen Urquhart gedrite (column G, table II). It is possible that some of his water determinations may be a little low, in view of his experience with no. 30; if they are, the true values for  $\Sigma(\text{O}, \text{OH}, \text{F})$  would be higher, and those for  $\Sigma(\text{cations})$  lower than the values in table II.

TABLE II. Empirical unit-cell contents of anthophyllite occurrences for which full physical and chemical data are available.

|                   | 1.    | 8.    | 9.    | 14.   | 17.   | 20.   | 26.   | 29.   | 30.   | 43.   | 43a.   | 43b.               | G.            |
|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|--------------------|---------------|
| Si                | 24.97 | 26.10 | 26.27 | 27.61 | 29.47 | 30.06 | 31.33 | 31.40 | 31.51 | 30.63 | 32.02  | 31.41              | 23.97 ± 0.25  |
| Al                | 12.23 | 10.73 | 10.05 | 8.70  | 5.56  | 7.02  | 0.39  | 0.91  | 1.26  | 0.36  | 0.38   | 0.37               | 17.50 ± 0.22  |
| Ti                | 0.21  | 0.19  | 0.23  | 0.18  | 0.19  | 0.48  | —     | —     | —     | 0.01  | 0.01   | 0.01               | 0.30 ± 0.02   |
| Fe <sup>m</sup>   | 0.45  | 1.27  | 0.27  | 0.55  | 0.96  | 1.86  | 0.61  | —     | —     | 0.11  | 0.12   | 0.12               | 0.28 ± 0.06   |
| Fe <sup>n</sup>   | 8.94  | 7.36  | 8.32  | 6.95  | 8.99  | 8.24  | 7.20  | 4.01  | 5.12  | 0.03  | 0.03   | 0.03               | 5.44 ± 0.06   |
| Mn                | 0.07  | 0.04  | 0.02  | —     | —     | —     | 0.23  | 0.05  | 0.06  | 1.20  | 1.27   | 1.23               | 0.06 ± 0.003  |
| Mg                | 13.51 | 15.08 | 15.56 | 17.45 | 15.33 | 8.53  | 19.23 | 23.65 | 22.05 | 23.86 | 24.95  | 24.47              | 7.96 ± 0.14   |
| Ca                | —     | 0.09  | 0.04  | 0.02  | 0.47  | —     | 0.22  | 0.88  | 0.38  | 0.69  | 0.73   | 0.71               | 0.76 ± 0.04   |
| Na                | 1.72  | 0.31  | 0.52  | 0.12  | 0.79  | —     | 0.12  | 0.70  | 0.29  | 0.37  | 0.39   | 0.38               | 0.52 ± 0.10   |
| K                 | 0.02  | —     | —     | —     | —     | —     | 0.02  | —     | 0.04  | 0.12  | 0.13   | 0.12               | 0.15 ± 0.04   |
| OH                | 7.55  | 7.05  | 5.75  | 5.62  | 6.60  | 7.67  | 8.70  | 5.84  | 7.58  | 13.10 | [7.66] | 13.42              | 12.43         |
| F                 | 0.57  | —     | —     | —     | —     | —     | 0.80  | —     | —     | 0.32  | 0.34   | 0.33               | —             |
| O                 | 88.71 | 89.79 | 89.78 | 90.95 | 90.99 | 87.34 | 86.36 | 90.18 | 88.89 | 81.40 | 88.05  | 83.34              | 83.57         |
| Σ (cations)       | 62.12 | 61.17 | 61.28 | 61.58 | 61.76 | 56.19 | 59.35 | 61.60 | 60.71 | 57.38 | 60.03  | 58.85              | 56.95 ± 0.54  |
| Σ (O,OH,F)        | 96.83 | 96.84 | 95.53 | 96.57 | 97.59 | 95.01 | 95.86 | 96.02 | 96.47 | 94.82 | 96.05  | 97.15 <sup>†</sup> | 98.55 ± 0.81  |
| D <sub>corr</sub> | 3.277 | 3.261 | 3.245 | 3.259 | 3.279 | 3.22  | 3.157 | 3.106 | 3.102 | 2.91  | 3.01   | [2.984]            | 3.150 ± 0.010 |
| D <sub>sup</sub>  | 3.25  | 3.25  | 3.25  | 3.25  | 3.23  | —     | —     | 3.09  | 3.04  | —     | —      | —                  | —             |
| Σ (O,OH,F)*       | 96.04 | 96.51 | 95.09 | 96.30 | 96.13 | —     | —     | 95.53 | 94.54 | —     | —      | —                  | —             |
| b <sub>obs</sub>  | 17.96 | 17.86 | 17.84 | 17.70 | 17.99 | 18.14 | 18.08 | 17.94 | 18.02 | 17.94 | —      | —                  | 17.79         |
| b <sub>calc</sub> | 17.90 | 17.80 | 17.82 | 17.79 | 18.03 | 18.17 | 18.03 | 18.00 | 17.98 | 17.95 | —      | —                  | 17.95         |

For the localities, percentage compositions, &c., of analyses 1 to 43, see J. C. Rabbitt, *Amer. Min.*, 1948, vol. 33, p. 263 [M.A. 10-416], and for analysis G, see G. H. Francis, *Min. Mag.*, 1955, vol. 30, p. 709. Analyses 43a and 43b are analysis 43 recalculated on two different assumptions.

\* The density determined pycnometrically was used for all the empirical cell contents except this sum, which was derived using the density as found by the suspension method, D<sub>sup</sub>.  
 † Including 1.15 and 2.55 mols. H<sub>2</sub>O respectively.

Analysis 20 shows a rather low figure for (O+OH), combined with a very low figure for the total cations (normally 60), and a normal water content; there must be an appreciable proportion of vacancies in the lattice positions normally occupied by Mg, Fe<sup>2+</sup>, with a replacement  $3\text{Mg} \rightleftharpoons 2\text{Al}$ . There is no evidence here of the presence of interstitial water molecules, indeed, there is a shortage of (O+OH); but the analysis has a rather low summation (99.68), and the water determination may be too low. The optical data also show some peculiarities, and a new study of this material ('bidalotite') would be of considerable interest; if the water content and density prove to be in error on the low side, we may, indeed, have here an example of interstitial water.

Analysis 26 shows normal values for (O+OH+F) and total cations, but (OH+F) is high, at 9.50 instead of the accepted 8; the excess is not great and could be accounted for by reckoning some of the H<sub>2</sub>O(+) as adsorbed water, without bringing  $\Sigma(\text{O,OH,F})$  too high to be explained by the probable error of the physical data; accepting the water as all essential, the analysis can be formally expressed in many ways—for instance, as a substitution of AlOH for SiO.

Analysis 43, from Edwards, New York, is of particular interest in that it is the only hydrous anthophyllite for which complete data are available. Unfortunately, the density was not determined on the analysed material but on the specimen used by B. E. Warren and D. I. Modell for their X-ray work. Accepting this density, and assuming the water is all essential, we derive the low total (O+OH+F) = 94.8, along with a low value of total cations; if it is assumed that the water in excess of 8(OH+F) per unit cell is adsorbed impurity, we calculate, using the formula given above (p. 175), that this impurity amounts to 1.67 %, leaving 2.13 % of essential water, and yielding the corrected density and empirical unit-cell contents shown in table II under 43a. Clearly this assumption of adsorbed water is a plausible one so far as the analysis and physical data go, but E. T. Allen and J. K. Clement found that at 600° C. only 0.6 % of water was lost in 60 hours, while at 820° C. 2.05 % of water was lost in 37 hours without any marked change of optical properties.

A third interpretation is to assume that the water is all essential; that the material has an integral total of anions, cations, and water molecules (156), but some water molecules in cation positions; and that the density determined by Warren and Modell is low. If a density of 2.984 is assumed, we derive the cell contents shown in table II

under 43*b*, with 1.2 molecules of water per unit cell in cation positions. This interpretation is supported by the dehydration experiments of Allen and Clement and appears to us the most probable one. The Edwards anthophyllite is practically free from FeO, so that their loss in weight figures can be taken as a true value for the loss of water. The water lost at 600°C. is 0.6 % = 1.2 molecules of H<sub>2</sub>O per unit cell; this is almost exactly the amount of interstitial water shown under 43*b* (table II), whilst at 820° C. nearly half the remaining water has been lost. The Edwards anthophyllite was originally described by G. Cesàro as a new species and named *valléite*; it is particularly low in iron, and higher in manganese than most anthophyllites though its manganese content is only about 3 %. It has been analysed by G. Cesàro (anal. 79*a*) and by W. Kunitz (anal. 41), with results appreciably different from those of Allen and Clement. Kunitz did not give X-ray data, but it will be shown below (table III) that his analysis corresponds to a normal anthophyllite; on the other hand, his refractive indices are noticeably low compared with the values calculated from the regression equations<sup>1</sup> we have obtained. Cesàro found a density of 2.88, even lower than Warren and Modell's figure, and this, taken with his analysis, leads to a very low value for both (O+OH) and total cations; if we assume that the true value for (O+OH) should be 96, the density calculated for Cesàro's analysis, 2.96, agrees reasonably with the value of 3.006 observed by Kunitz (see table III). On the other hand, the dehydration work of Allen and Clement and the distinctly low refractive indices observed by Kunitz suggest some abnormality, and a new study of the Edwards anthophyllite is clearly desirable.

*Semi-empirical unit-cell contents.* In order to determine the empirical unit-cell contents of any substance it is necessary to know the cell dimensions, density, and chemical composition. If the density is not known, no estimate of the unit-cell contents is possible, but if only the cell dimensions are lacking it may still be possible to determine the cell contents, though not with the same degree of confidence as when density, cell dimensions, and chemical analysis are made on the same materials. For example, it may be known that the cell dimensions do not vary appreciably with composition, or only vary within fairly narrow, known limits; or it may be possible to predict the approximate cell dimensions from the composition, through a regression equation derived from X-ray work on analysed material. Both these possibilities are exemplified by anthophyllite; the variation in the *a*- and *c*-dimensions is small and we

<sup>1</sup> M. H. Hey, *Min. Mag.*, 1956, vol. 31, p. 69.

TABLE III. Semi-empirical unit-cell contents of anthophyllite (summarized), taking  $a = 18.58 \text{ \AA}$ ,  $c = 5.30 \text{ \AA}$ , and  $b$  values calculated from the composition, using the above regression equation.

|                    |       |       |       |       |       |       |       |       |       |       |        |
|--------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|
| $b$ (Å)            | 2.    | 3.    | 4.    | 6.    | 7.    | 13.   | 16.   | 21.   | 22.   | 24.   | 34.    |
| $D_{\text{corr}}$  | 18.16 | 17.89 | 17.62 | 18.02 | 18.01 | 18.29 | 18.22 | 17.81 | 18.10 | 18.05 | 17.93  |
| (OH+F)             | 3.371 | 3.281 | 3.178 | 3.26  | 3.176 | 3.23  | 3.27  | 3.068 | 3.241 | 3.157 | 3.134  |
| $\Sigma$ (O,OH,F)  | 4.9   | 7.9   | 5.4   | 8.8   | 10.5  | 4.3   | 4.4   | 7.6   | 9.0   | 8.8   | 8.7    |
| $\Sigma$ (cations) | 95.9  | 98.6  | 96.5  | 97.2  | 96.2  | 93.5  | 92.8  | 93.2  | 97.6  | 98.7  | 96.4   |
|                    | 62.9  | 62.1  | 61.7  | 62.0  | 60.8  | 60.8  | 59.5  | 58.0  | 61.0  | 62.4  | 61.3   |
| $b$ (Å)            | 35.   | 38.   | 39.   | 40.   | 41.   | 49.   | 50.   | 62a.  | 76.   | 79a.  | 85.    |
| $D_{\text{corr}}$  | 17.91 | 17.84 | 17.83 | 17.85 | 18.04 | 18.18 | 17.80 | 18.14 | 17.96 | 18.25 | 17.77  |
| (OH+F)             | 3.101 | 2.98  | 2.86  | 2.96  | 3.006 | 3.225 | 2.98  | 3.26  | 3.068 | 2.88  | 3.100  |
| $\Sigma$ (O,OH,F)  | 6.1   | 13.2  | 15.4  | 5.9   | 9.9   | 7.4   | 10.4  | 8.9   | 12.1  | 10.9  | 5.0    |
| $\Sigma$ (cations) | 97.0  | 95.6  | 92.5  | 92.4  | 96.7  | 93.3  | 94.9  | 83.6  | 97.4  | 93.2  | 96.8   |
|                    | 62.0  | 57.9  | 55.0  | 58.7  | 59.9  | 58.0  | 59.4  | 54.2  | 59.2  | 57.4  | 63.3   |
| $b$ (Å)            | 88.   | A.    | B.    | C.    | D.    | E.    | F.    | 38X.  | 39X.  | 76X.  | 79aX.  |
| $D_{\text{corr}}$  | 18.62 | 17.63 | 18.27 | 17.85 | 17.93 | 18.02 | 17.97 | 17.90 | 17.89 | 17.99 | 18.30  |
| (OH+F)             | 3.243 | 3.21  | 3.15  | 3.05  | 3.07  | 3.06  | 3.08  | 3.08  | 3.00  | 3.15  | [2.96] |
| $\Sigma$ (O,OH,F)  | 7.8   | 6.4   | 7.9   | 8.4   | 8.8   | 8.2   | 3.0   | [8.0] | [8.0] | [8.0] | 11.2   |
| $\Sigma$ (cations) | 94.3  | 99.2  | 95.4  | 100.0 | 102.6 | 101.5 | 95.0  | 97.7  | 95.3  | 99.3  | [96.0] |
|                    | 59.9  | 64.0  | 59.7  | 62.5  | 64.9  | 64.1  | 61.8  | 61.0  | 59.2  | 60.6  | 58.7   |

For the localities, references, and other details of analyses 2 to 88, see J. C. Rabbitt, Amer. Min., 1948, vol. 33, p. 263 [M.A. 10-416].

A. Fiskeris, Greenland. - Lorenzen [Undersøelse Min. Grønland, Kjøbenhavn, 1884]; quoted in C. F. Rammelsberg, Handb. Mineralchemie, 2nd edn, 1875, p. 398.  
 B. Greenland. - Lechartier, in C. F. Rammelsberg, Handb. Mineralchemie, 2nd edn, 1875, p. 398.  
 C. Val di Bressino, Italy. R. Pirani, Atti (Rend.) Accad. Naz. Lincei, Cl. fis. mat. nat., 1952, ser. 8, vol. 13, sem. 2, p. 83 [M.A. 12-30].  
 D. Alpe di Brez, Italy. R. Pirani, ibid., p. 170 [M.A. 12-140].  
 E. Vedrette, Alta-Hochwart, Italy. R. Pirani, ibid., 1953, vol. 15, sem. 2, p. 422 [M.A. 12-374].  
 F. Ilmen Mts., Russia. (Kupfferite.) R. Hermann, Bull. Soc. Nat. Moscou, 1862, vol. 35, p. 243.

38X, 39X, and 76X. Analyses 38, 39, and 76 recalculated on the assumption that all water in excess of 8 (OH) per unit cell is impurity. This involves the rejection of 1.59% of the  $\text{H}_2\text{O}(\pm)$  in analysis 38, 2.38% in analysis 39, and 1.25% in analysis 76.  
 79aX. Analysis 78a recalculated on the assumption that the observed density is in error, and that  $\Sigma(\text{O,OH}) = 96$ .

can write  $a = 18.58 \text{ \AA.} \pm 0.06$ , and  $c = 5.30 \text{ \AA.} \pm 0.03$  for any anthophyllite with fair confidence; and the  $b$ -dimension is related to the composition by the approximate regression equation:<sup>1</sup>

$$b \text{ (\AA.)} = 16.44 + 0.28\text{Si} - 0.13\text{Mg} + 0.40(\text{Ca} + \text{Na} + \text{K}) \pm 0.04,$$

where the composition is expressed in atoms per  $24(\text{O,OH,F})$ . Using the cell dimensions thus derived, a considerable number of analyses for which densities are available yield the results collected in table III. If we take the  $b$ -dimensions as liable to an error of  $\pm 0.09$ , not independent of the errors in  $a$  and  $c$ , and assume an accuracy of  $\pm 0.02$  in the density, we calculate that the probable error in  $\Sigma(\text{O,OH,F})$  should be about 1.6, and in  $\Sigma(\text{cations})$  about 1.0. In view of the fact that the regression equation is being used outside the range of composition for which it was established, and that it neglects the effect of variations in  $\text{OH}'$ ,  $\text{F}'$ , and  $\Sigma(\text{cations})$ , this error is probably on the low side, and we may reasonably extend it to about 2.0 in  $\Sigma(\text{O,OH,F})$  and 1.5 in  $\Sigma(\text{cations})$ .

Of the 29 analyses included in table III,  $\Sigma(\text{O,OH,F})$  for 15 falls within  $\pm 2.0$  of the normal 96, but only five of these have  $\Sigma(\text{cations})$  within 1.0 of 60, while seven have markedly high values for  $\Sigma(\text{cations})$ ; this is in agreement with the result found above for the 11 analyses for which direct cell dimensions are available and it is clear that an appreciable proportion of the  $A$ -positions is normally occupied in anthophyllite. Six analyses give high values for both  $\Sigma(\text{O,OH,F})$  and  $\Sigma(\text{cations})$ ; these analyses (nos. 3, 24, *A*, *C*, *D*, and *E*) show low or normal water contents and good summations, and it appears probable that the densities are in error, from 2 to 7% (0.06 to 0.2) too high. The remaining eight analyses (nos. 13, 16, 21, 39, 40, 41, 50, and 79*a*) have low values for  $\Sigma(\text{O,OH,F})$  and low or normal values for  $\Sigma(\text{cations})$ . Of these no. 39 is very high in water, and, as will be shown below, it is possible that much of this water is adsorbed impurity and that the composition is normal; no. 79*a* is an analysis of the Edwards mineral, and is discussed above; the other 6 are probably to be explained by low density determinations, from 2 to 4% low (0.06 to 0.12).

It will be noted that the high  $b$ -dimensions calculated for analyses 13, 88, and *B*, falling well outside the range observed by J. C. Rabbitt, do not lead to high cell contents, while of the analyses yielding low values for  $\Sigma(\text{O,OH,F})$ , not one has a calculated  $b$ -axis outside the range observed by Rabbitt; this tends to support the validity of the proposed regression equation for  $b$ .

<sup>1</sup> M. H. Hey, *Min. Mag.*, 1956, vol. 31, p. 69.

*Atomic ratios to 96 (O,OH,F).* There remain five analyses for which no densities are available, and for these we cannot calculate the cell contents; the best we can do is to calculate atomic ratios to an assumed basis, preferably 96(O,OH,F), since the evidence so far goes to show that this is the normal unit-cell content of anthophyllite (with the possible exceptions of the Glen Urquhart gedrite and the Edwards anthophyllite). As J. C. Rabbitt has already made such a calculation to the basis 24(O,OH,F) new calculations are needless. From Rabbitt's tables it is clear that of these analyses only no. 66, a highly hydrous anthophyllite from the Lizard, Cornwall, analysed by J. J. H. Teall,<sup>1</sup> falls outside the field of compositions defined by the first 40 analyses. This specimen may perhaps contain interstitial water, but it is more likely that an analysis has been made on impure material. In other respects these analyses confirm the conclusions reached on the evidence of the first 40 analyses in that there is a marked tendency for  $\Sigma$  (cations) to be high ( $> 15.2$  in 21 of the 51 analyses); and more than a third of the analyses, irrespective of date, show water contents differing substantially from 2(OH,F) per 24(O,OH,F).

*Other possible interpretations of the anthophyllite analyses notably high or low in water.* Before summarizing the results of this survey of the unit-cell contents of anthophyllite, we must consider a number of analyses that appear to be notably high or low in water. Of the 40 available analyses of anthophyllite for which densities, or densities and X-ray data are available (tables III and II respectively), six show a notable excess of water (nos. 38, 39, 43, 76, 79a, and the Glen Urquhart gedrite, *G*) and 10 show less than three-quarters of the usually accepted figure of 8(OH) per unit cell (nos. 2, 4, 9, 13, 14, 16, 29, 40, 85, and *F*); and there are 18 analyses showing substantially abnormal water contents (nine low, nine high) among the group for which density data are not available.

Some of these apparently abnormal water contents may be explicable as adsorbed water, or by errors in the water determination. To test this possibility, we must consider the effect of assuming that an apparent excess of hydroxyl groups is due to adsorbed water, or that an apparent deficit of hydroxyl groups is due to analytical error; if in either case the effect is to increase the departure of  $\Sigma$  (O,OH,F) from the normal 96, we can reasonably reject the assumption.<sup>2</sup> If the qualitative effect (see

<sup>1</sup> J. J. H. Teall, *Min. Mag.*, 1888, vol. 8, p. 116.

<sup>2</sup> To prove that  $\Sigma$  (O,OH,F) for any particular analysis really differs from the normal, it is essential to show that the departure from normality exceeds the probable experimental error, however we assess the distribution of the water.

table I) favours a proposed explanation of any apparently abnormal analysis, we can then consider it quantitatively. Clearly such tests are not possible for those analyses for which density data are not available; such analyses can only serve as secondary confirmation to conclusions based on empirical and semi-empirical unit-cell contents, or as pointers to occurrences for which new data would be of particular interest.

If it is assumed that an amount of water sufficient to bring the hydroxyl groups to 8 per unit cell has escaped determination in analyses 2, 4, 9, 13, 14, 16, 29, 40, and 85, the amount involved will be from 0.6 to 0.7 % and this will involve a decrease of  $\Sigma$ (cations) by about 0.4 to 0.5, and an increase in  $\Sigma$ (O,OH,F) by about 0.5 to 0.7; for analysis *F*, 1.4 % H<sub>2</sub>O would have to have escaped determination, reducing  $\Sigma$ (cations) by 0.9 and increasing  $\Sigma$ (O,OH,F) by 1.2. This improves the approach of  $\Sigma$ (cations) to 60 in every case except nos. 16 and 40, and improves the approach of  $\Sigma$ (O,OH,F) to 96 in analyses 9, 13, 16, 40, and *F*, but makes it less satisfactory in the other five. Clearly we have a strong suggestion, though no definite proof, that the hydroxyl content may fall quite appreciably below 8 per unit cell.<sup>1</sup>

Turning to the hydrous anthophyllites, analyses 38, 39, 43, 76, and 79*a*, the oxygen content is low<sup>2</sup> (39, 43, 79*a*) or normal (38, 76). Of the five analyses, no. 43 (Edwards, New York), for which unit-cell measurements are available, has already been discussed above, together with no. 79*a*, also from Edwards; of the other three, nos. 38 and 39 are asbestiform minerals from Paakila, Finland, in which much of the excess water might well be adsorbed; calculations made by the above methods<sup>3</sup> on the assumption that all water in excess of 8(OH) per unit cell is adsorbed yield the results included in table III under 38*X* and 39*X*, and it will be seen that this interpretation is quite possible. Similar calculations for analysis no. 76, a coarsely crystallized anthophyllite from Mainland, Shetland (table III, 76*X*), indicate that the water in this specimen was probably all essential; this analysis was rejected by J. C. Rabbitt (*loc. cit.*) on the grounds of date (1879) and a high summation (100.68), but it would have to be very badly in error to conform

<sup>1</sup> Another possible explanation of some of these low water contents is that the mineral might contain fluorine, which passed undetermined; this would have very nearly the same effect as an underestimation of the water.

<sup>2</sup> The additional evidence of a dehydration curve suggests that the observed densities for nos. 43 and 79*a* may be in error, and that this material may have  $\Sigma$ (O,OH,F) a little in excess of 96 (see above).

<sup>3</sup> Since the *b*-dimension of the unit cell was calculated from the composition by means of the above regression equation, a revision of this dimension was also made.

to the 'normal' 8(OH) per unit cell, and it appears probable that we have here another truly hydrous anthophyllite, with a low cation total and high hydroxyl content; a new and complete study of this material is clearly desirable.

*Conclusions.* The results of our survey of all available data for the unit-cell contents of anthophyllite are: The total anions per unit cell,  $\Sigma(O,OH,F)$ , cannot be shown to depart significantly from 96 except possibly in the Glen Urquhart gedrite and the anthophyllite from Edwards, New York. The total cations per unit cell are normally significantly in excess of 60. And the hydroxyl (+fluorine) content may depart considerably from 8 per unit cell, either by excess or by defect.

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*Addendum.* Since this paper was submitted doubt has been cast on the purity of the powdered gedrite from Glen Urquhart, owing to the presence of un-indexed lines in the X-ray powder pattern. The traces of impurity mentioned in the original study (Min. Mag., 1955, vol. 30, p. 710) are colourless and may have been underestimated owing to their parallel growth on the gedrite prisms. A re-investigation of the mineral is being undertaken.

G. H. F.