

COMMENTS ON THE CALCULATION OF THE DENSITY OF MINERALS

J.A. MANDARINO

Department of Mineralogy & Geology, Royal Ontario Museum,
100 Queen's Park, Toronto, Ontario M5S 2C6

ABSTRACT

The densities of minerals are often calculated incorrectly because wrong molecular weights of the formula units are used. If the empirical formula is derived on the basis of a given fixed number of oxygen ions (or other anions), this number divided by the total anionic ratios is equal to a factor F . F is used to multiply the cationic and anionic ratios to obtain formula subscripts; it also provides a simple means of calculating an accurate molecular weight. The analytical sum multiplied by F is the molecular weight of one formula unit.

Keywords: calculated density, molecular weight, empirical formula, anionic ratio method.

SOMMAIRE

On calcule souvent incorrectement la densité des minéraux parce que l'on se sert de poids moléculaires erronés pour les unités formulaires. Où la formule empirique se rapporte à un nombre fixe d'ions oxygène (ou autre anion), ce nombre divisé par le total des rapports anioniques donne le facteur F . En multipliant par F les rapports cationiques et anioniques, on obtient les indices des éléments de la formule; F fournit aussi une façon simple de calculer le poids moléculaire exact. La somme analytique multipliée par F devient le poids moléculaire d'une unité formulaire.

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Mots-clés: densité calculée, poids moléculaire, formule empirique, méthode du rapport anionique.

INTRODUCTION

The calculation of densities from unit-cell parameters and chemical composition is a well-known operation in mineralogy; it is usually done using an equation similar to $D = MZ/VA$, where D is density, M is the molecular weight of one formula unit, Z is the number of formula units per unit cell, V is the unit-cell volume and A is Avogadro's number.

During research on the application of the Gladstone-Dale relationship to the compatibility of chemical composition, mean index of

refraction and density (Mandarino 1979, 1981), it was necessary to calculate densities for numerous compounds. In many cases, densities had already been calculated, but as a routine check they were recalculated, and many significant discrepancies were found. The discrepancies were commonly of such a magnitude that they could not be explained by arithmetic processes such as premature "rounding off" of decimal places. The discrepancies had to arise from one (or more) of the quantities M , Z , V or A used in the foregoing equation. After numerous checks, it became apparent that the main source of the discrepancies was the molecular weight of the formula unit. Furthermore, because the molecular weight of the formula unit is directly related to the derivation of the formula, it is affected by the way in which the formula is derived.

DERIVATION OF THE FORMULA

Throughout the remainder of this paper, derivations of empirical formulae are based on the underlying principle that all minerals can be considered as frameworks of anionic elements, in the interstices of which are found the cations. It follows that for a particular mineral, the number of anions in a given unit-cell volume (or multiple thereof) will be an integer. McConnell (1965) has discussed this principle, and no more need be said here.

Various errors can be introduced during the calculation of the molecular weight of a formula unit. Some are trivial and result from the use by different authors of slightly different atomic weights. In general, this does not result in large errors. The major error in M is produced by the way it is calculated. An example will serve to illustrate the problem.

Table 1 shows the analytical data (average of five analyses) for satterlyite given by Mandarino *et al.* (1978). To illustrate points to be discussed later, the derivation of the empirical formula from these analytical data is given in detail. Column A lists the weight percentage of each constituent. Each weight percentage is

TABLE 1. SATTERLYITE: ANALYTICAL DATA AND DERIVATION OF FORMULA

	A	B	C	D	E
	Wt. %	Molecular Ratios	Anionic Ratios	Cationic Ratios	Number of Ions (Subscripts)
MgO	7.1	0.1762	0.1762	0.1762	Mg 0.36
MnO	1.3	0.0183	0.0183	0.0183	Mn 0.04
FeO	43.1	0.5999	0.5999	0.5999	Fe ²⁺ 1.21
Fe ₂ O ₃	7.5	0.0470	0.1409	0.0939	Fe ³⁺ 0.19
Na ₂ O	1.5	0.0242	0.0242	0.0484	Na 0.10
P ₂ O ₅	34.8	0.2452	1.2259	0.4903	P 0.99
SiO ₂	0.2	0.0033	0.0067	0.0033	Si 0.01
H ₂ O	5.2	0.2886	0.2886	0.5771	H 1.16
Σ	100.7		2.4807		O 5.00

Derivation of factor F: total anionic ratio (2.4807) x F = 5;
 F = 2.0156. Calculation of molecular weight: Σ Wt. % (100.7) x F = 202.97.

ratios by a factor F so that the product is 5. Solving for this factor gave F = 2.0156. Each of the cationic ratios in Column D was multiplied by F to give formula subscripts for those cations. The subscripts are given only to the second decimal place in Column E, but could have been expressed to additional places. If halide or S²⁻ ions are present, an appropriate amount of the oxygen anionic ratio must be subtracted from the sum of the anionic ratios before F can be calculated for a particular number of total anions. An example of this is given later in this paper.

CALCULATION OF MOLECULAR WEIGHT

divided by the molecular weight of the appropriate constituent, and the resulting *molecular ratios* are listed in Column B. Column C contains the *anionic ratios* which, in this case (where the only anionic element is oxygen), are simply the molecular ratios multiplied by the number of oxygens in each constituent. The *cationic ratios* given in Column D are the result of multiplying the molecular ratios by the number of cations in each constituent. Column E lists the number of ions (= subscripts of chemical symbols) in a formula unit of the mineral.

It was decided to calculate the formula subscripts on the basis of five oxygen ions in the formula by multiplying the sum of the anionic

Table 2 lists several ways in which the molecular weight of a formula unit of satterlyite may be derived. The first deals with the empirical formula which, in this case, is (Fe²⁺_{1.21} Mg_{0.36} Fe³⁺_{0.19} H_{0.16} Na_{0.10} Mn_{0.04})_{Σ2.06} (P_{0.99} Si_{0.01})_{Σ1.00} O_{4.00} (OH)_{1.00}. The molecular weight of the mineral represented by this formula can be calculated by multiplying each element's atomic weight by the appropriate subscript from the formula and adding these products together. An alternative method is to use molecular weights of oxide constituents, multiply these by the appropriate factors and add the results. It must be remembered that in the case of R₂O_x consti-

TABLE 2. MOLECULAR WEIGHTS OF FORMULA UNITS DERIVED IN VARIOUS WAYS AND THE RESULTING VALUES OF DENSITY

Method of calculating the molecular weight of one formula unit	Molecular weight of formula unit	Calculated density (g/cm ³)
Empirical formula (Fe ²⁺ _{1.21} Mg _{0.36} Fe ³⁺ _{0.19} H _{0.16} Na _{0.10} Mn _{0.04}) _{Σ2.06} (P _{0.99} Si _{0.01}) _{Σ1.00} O _{4.00} (OH) _{1.00}		
a. subscripts to second decimal place	203.87	3.604
b. subscripts to third decimal place	202.94	3.588
c. subscripts to fourth decimal place	202.96	3.588
Normalized empirical formula (Fe ²⁺ _{1.17} Mg _{0.35} Fe ³⁺ _{0.18} H _{0.16} Na _{0.10} Mn _{0.04}) _{Σ2.00} (P _{0.99} Si _{0.01}) _{Σ1.00} O _{4.00} (OH) _{1.00}		
a. subscripts to second decimal place	199.79	3.532
b. subscripts to third decimal place	200.21	3.540
Normalized ideal formula (Fe ²⁺ _{1.54} Mg _{0.46}) _{Σ2.00} PO ₄ (OH)		
a. subscripts to second decimal place	209.17	3.698
b. subscripts to third decimal place	209.36	3.701
Ideal formula Fe ₂ ²⁺ PO ₄ (OH)	223.68	3.954
Summation x Factor	202.97	3.588

tments, the molecular weights should be multiplied by *half* the subscript in the formula. Thus, for Fe^{3+} the molecular weight of Fe_2O_3 should be multiplied by 0.19/2. In the following discussion of molecular weight calculations, the oxide molecular weights listed by Mandarino (1976) are used.

Let us examine the molecular weight calculated from the empirical formula. Three values of the molecular weight and the corresponding density values are given for the empirical formula. These are based on subscripts expressed to two, three and four decimal places. The density calculated in the first case (3.604 g/cm^3) is significantly different from those calculated in the other two cases (each 3.588 g/cm^3).

The next entries in Table 2 deal with calculations from the "normalized" empirical formula, where each cation (and anion) is recalculated so that the sum of each cationic (and anionic) group is a whole number. Thus, the normalized empirical formula of satterlyite is $(\text{Fe}^{2+}_{1.17} \text{Mg}_{0.35} \text{Fe}^{3+}_{0.18} \text{H}_{0.16} \text{Na}_{0.10} \text{Mn}_{0.04})_{\Sigma 2.00} (\text{P}_{0.99} \text{Si}_{0.01})_{\Sigma 1.00} \text{O}_{4.00}(\text{OH})_{1.00}$. If the subscripts of this formula are carried to two decimal places, the calculated density is 3.532 g/cm^3 ; subscripts to three decimal places give a calculated density of 3.540 g/cm^3 .

Another type of formula that many authors seem to prefer can be called the "normalized" ideal formula, in which only the major constituents are considered. For satterlyite, this formula becomes $(\text{Fe}^{2+}_{1.54} \text{Mg}_{0.46})_{\Sigma 2.00} \text{PO}_4(\text{OH})$. Calculation of the density from this formula using subscripts of two and three decimal places gives, respectively, 3.698 and 3.701 g/cm^3 .

Finally, many authors calculate density on the basis of the theoretical pure mineral and use the "ideal" formula. In the case of satterlyite, this is $\text{Fe}^{2+}_2\text{PO}_4(\text{OH})$, and the calculated density is 3.954 g/cm^3 .

Obviously, the ideal formula should not be used to calculate density, because for a mineral that exhibits significant solid-solution effects the density value would be meaningless. Not only would the calculated density be wrong for the particular mineral studied, but it would also be wrong for the theoretical pure end-member, as it is highly unlikely that the volume of the unit cell would be unaffected by compositional changes. The same argument holds for the calculation of density from the normalized ideal formula. The unit-cell parameters will not be the same for a mineral that does not contain all the constituents reported in a good analysis. Similarly, the normalized empirical formula does not accurately reflect the analytical data and

should not be used to calculate density. In this regard, it should also be remembered that departures from ideal stoichiometry are not at all unusual in minerals.

On the other hand, the unit-cell volume is calculated from cell parameters determined, ideally, from the same material used to determine chemical composition. Therefore, only the empirical formula should be considered in calculating density. Referring back to the first entries in Table 2, it can be seen that the use of subscripts given to two decimal places gave a slightly different density than that derived from subscripts given to three or four decimal places. It would seem necessary, then, to calculate the formula subscripts to at least three decimal places to obtain the proper molecular weight and density. The following section proposes a simple method that enables the molecular weight of a formula unit to be determined without using formula subscripts.

THE ANIONIC RATIO METHOD OF CALCULATING MOLECULAR WEIGHT

Referring to Table 1, we see that the factor F used to determine the formula subscripts of satterlyite is 2.0156. If this factor is multiplied by the analytical sum ($\Sigma = 100.7 \text{ wt. } \%$), the result is the molecular weight of the formula unit. In the example, the molecular weight calculated in this manner is 202.97 and the density is 3.588 g/cm^3 . These compare favorably with 202.96 and 3.588 g/cm^3 calculated from the empirical formula, using subscripts calculated to the fourth decimal place.

MINERALS CONTAINING HALIDE OR SULFIDE IONS

The discussion up to this point has dealt with minerals that contain only oxygen in their

TABLE 3. TRIPLITE: ANALYTICAL DATA AND DERIVATION OF FORMULA

	A	B	C	D	E
	Wt. %	Molecular Ratios	Anionic Ratios	Cationic Ratios	Number of Ions (Subscripts)
CaO	2.17	0.0387	0.0387	0.0387	Ca 0.09
MgO	0.31	0.0077	0.0077	0.0077	Mg 2^{+} 0.02
FeO	6.68	0.0930	0.0930	0.0930	Fe^{2+} 0.21
MnO	53.77	0.7580	0.7580	0.7580	Mn 1.69
Fe_2O_3	0.40	0.0025	0.0075	0.0050	Fe^{3+} 0.01
P_2O_5	32.20	0.2269	1.1343	0.4537	P 1.01
F	7.58	0.3989	0.3989		F 0.89
total	103.11		2.4381		O 4.11
less					
O = F	3.19	0.1994	-0.1994		
Σ	99.92		2.2387		
			$\Sigma O = 1.8398$		

Derivation of factor F: total anionic ratio (2.2387) \times F = 5; F = 2.2334. Calculation of molecular weight: $\Sigma \text{Wt. } \%$ (99.92) \times F = 223.16.

anionic frameworks. If halide or sulfide ions also are present, the procedure for deriving the chemical formula and for calculating the molecular weight must be modified. A triplite from Bagdad, Arizona, described by Hurlbut (1936), has been chosen to illustrate the procedure. Richmond (1940) determined the unit-cell parameters of this analyzed triplite, and his data (converted from kX to Å) give a unit-cell volume of 754.30 Å³.

The analytical data for this mineral are listed in Table 3. Note that in Column A, there is an entry of 3.19 wt. %, which represents the amount of excess oxygen introduced into the analytical data because of the method of reporting the cation contents as oxides. This excess oxygen must be subtracted from the total to give the true analytical sum. In this particular case, the figure of 3.19 is found by multiplying the wt. % of fluorine by the factor 8.00/19.00, where 8.00 is half the atomic weight of oxygen and 19.00 is the atomic weight of fluorine.

In Column B, the excess oxygen (or oxygen-equivalent of fluorine) is divided by the atomic weight of oxygen to give a molecular ratio of 0.1994. This figure is repeated in Column C as an anionic ratio with a negative sign to indicate that it must be subtracted from the total anionic ratio to give the true total. It is this final anionic ratio (2.2387) that is used to determine the factor F. In the case of triplite, the total number of anions (oxygen plus fluorine and possibly hydroxyl) in a formula unit is 5; thus the factor F is 2.2334, and the molecular weight (Σ wt. % \times F) is 223.16. The density calculated from this molecular weight and the unit-cell volume is 3.930 g/cm³; the measured density given by Hurlbut (1936) is 3.84 g/cm³, and the density calculated by Richmond (1940) is 3.94 g/cm³.

Note that the anionic ratio of oxygen is given at the bottom of Column C in Table 3 as $\Sigma O = 1.8398$. This represents the difference between the true total anionic ratio and the anionic ratio of the fluorine (i.e., 2.2387 - 0.3989 = 1.8398). This figure must be used to determine the oxygen subscript.

CONCLUSIONS

In calculating the density of a mineral, only

the empirical formula should be used to calculate the molecular weight of the formula unit. Ideally, the unit-cell parameters and formula should be derived from the same material. An accurate molecular weight can be calculated using the multiplying factor F derived from the sum of the anionic ratios. This factor multiplied by the sum of the analysis gives the molecular weight of one formula unit.

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