

1 REVISION 1

2 Technical Note: Calculation of stoichiometry from EMP data for apatite and other phases with
3 mixing on monovalent anion sites

4 Richard A. Ketcham¹

5 ¹Jackson School of Geosciences, The University of Texas at Austin, Austin, TX, USA

6 **Abstract**

7 A new method is presented for calculating the chemical formula for apatite, and any other
8 mineral that features mixing between halogens and hydroxyl ions on monovalent anion sites,
9 from electron microprobe data that omit H₂O determination. It removes errors of up to 4% in
10 stoichiometric calculations that occur for apatite when an incorrect normalization is used. The
11 method also provides an estimate of OH content and uncertainty that can be included in chemical
12 analysis totals.

13 **Introduction**

14 Apatite (Ca₁₀(PO₄)₆(F,Cl,OH)₂) is a challenging mineral for electron microprobe analysis
15 (EMPA), both due to fluorine migration under the electron beam (Goldoff et al., 2012; Stormer
16 et al., 1993) and the necessity to compensate for the presence of halogens when calculating
17 stoichiometry. EMPA analysis does not provide H₂O measurements, and some degree of mixing
18 on the monovalent anion site is common, and thus OH content must be estimated based on F and
19 Cl results. However, in the presence of this mixing, the correct normalization method for
20 calculating stoichiometry is not straightforward.

21 In most geochemical major-element analyses, cations are determined and reported as
22 charge-neutral oxides, while halogens are reported simply as negative ions. The oxygen
23 attributed to the oxides is not determined directly, but rather is inferred from the presence of the
24 cations. This leads to an implicit charge imbalance for minerals with monovalent anion sites (i.e.
25 containing F, Cl, OH, etc.), which in turn leads to a mass imbalance: some of the negative charge
26 attributed to oxygen in the cation oxides is really in the halogens. To compensate, the surplus of
27 oxygen in the cation determinations must be removed for evaluation of total weight per cents and
28 stoichiometric calculation of chemical formula.

29 A standard reference for calculating mineral formulas from chemical analyses is
30 Appendix 1 of the textbook by Deer, Howie and Zussman (1966; 1992; 2013). Their method is
31 briefly summarized here, referring to the columns of the tables in that Appendix; an example is
32 also provided in the Microsoft Excel spreadsheet supplement to this article, and the reader is
33 encouraged to consult that Deer et al. (2013) directly for a more thorough explanation.

34 Each oxide and halogen measurement (wt. %; column 1) is divided by the molecular
35 mass to determine its molecular proportion (column 2). Oxides are then multiplied by their
36 respective number of oxygen atoms determine the proportion of oxygen from each molecule;
37 halogens are multiplied by one (column 3). These proportions are then summed. Then, if
38 halogens are present, this sum is corrected by subtracting half of the contribution from the
39 halogens, corresponding to the surplus oxygen. A normalization factor is then calculated by
40 dividing the total number of anions (O, OH, F, Cl) in the mineral formula by this corrected sum,
41 and the column 3 values are multiplied by this factor, giving the number of oxygens attributable
42 to each oxide (column 4). Finally, these values are multiplied by the number of cations per
43 oxygen (e.g., 1/2 for SiO₂, 2/3 for Al₂O₃) to provide the number of each cation (column 5).

44 The method presented in Deer et al. (2013) is correct if H₂O content is measured. If H₂O
45 is not measured or the measurement is considered unreliable, Deer et al. (2013) advise that
46 stoichiometry can be calculated “on an anhydrous basis assuming the [OH] content to be ideal.”
47 In this case, the hydroxyl ions in the mineral formula are converted to oxygen equivalents based
48 on charge (two [OH] per one [O]), and stoichiometry is normalized based on oxygen equivalents.

49 The common practice for calculating stoichiometry from EMPA apatite analyses today is
50 to correct the oxygen totals for the halogen content, and then normalize using 26 or 25 anions.
51 The 26-anion value corresponds to the total number of anions in the apatite formula, while the
52 assumption of ideal [OH] content leads to 25 oxygen equivalents. Both of these methods are
53 incorrect, except in ideal circumstances. Table 1 shows example stoichiometry calculation
54 results for end-member F-apatite and OH apatite, 50:50 F-OH-apatite, and 33:33:33 F-Cl-OH
55 apatite. The stoichiometry for the non-hydrous apatite is correctly recovered when the
56 normalization uses 26 anions, and OH-apatite is recovered using 25, but if the apatite being
57 analyzed does not satisfy the chosen condition the stoichiometry will be incorrect by up to 4%.
58 It is important to point out that the cation errors can be large even if the anion errors are small.
59 Below is presented a method that works for apatite with any mixture of F, Cl and OH.

60 **Method**

61 There are two approaches which are mathematically equivalent; both are presented for
62 illustrative purposes. The starting point for both is the stoichiometry calculation method
63 described in Appendix 1 of Deer et al. (1966; 1992; 2013), as outlined above.

64 *Approach 1*

65 The number of anions for normalizing can be adapted based on an estimate of the [OH]
66 content. We start with the definitions:

$$S_{PO} = \sum P_{O,i}, \quad S_{POc} = S_{PO} - \frac{1}{2}(P_{O,F} + P_{O,Cl})$$

67 where P_O refers to the atomic proportion of oxygen or, more generally, negative ions in the
68 apatite from each chemical species analyzed (i) (Deer et al. 2003, Appendix 1 tables, column 3).
69 The terms S_{PO} and S_{POc} correspond to the uncorrected and corrected sum of all measured
70 components. In the case of an apatite with no OH, the ratio S_{PO}/S_{POc} is 27/26: there are 26 anions
71 in apatite, but the surplus oxygen in the oxides results in a total of 27 before the correction for F
72 and Cl. For an end-member OH-apatite, the correction is zero, and $S_{PO}/S_{POc} = 1$. In this case, the
73 method of calculating on an anhydrous basis assuming ideal OH content entails assuming that
74 there are 25 oxygen equivalents, and so we can say that $S_{PO}/S_{POc} = 25/25$. Combining these two
75 cases, it becomes evident that:

$$\frac{S_{PO}}{S_{POc}} = \frac{27 - [OH]}{26 - \frac{1}{2}[OH]}$$

76 where [OH] refers to molecules of OH in the final formula. This can be solved to estimate [OH]:

$$R = \frac{S_{PO}}{S_{POc}}; [OH] = \frac{27 - 26R}{1 - \frac{1}{2}R}$$

77 The number of anions to normalize by then becomes $26 - [OH]/2$, and the normalization factor is
78 thus $(26 - [OH]/2)/S_{POc}$.

79 *Approach 2*

80 A simpler alternative is to extend the advice of Deer et al. (2013) and assume that the
81 monovalent anion site is behaving in an ideal fashion, without making any assumptions

82 concerning how the site is occupied. In this case the sum S_{PO} is calculated omitting the F and Cl
83 analyses, there is no S_{POc} calculation, and normalization is done using 25 oxygen equivalents.

84 It may seem counterintuitive to omit the halogens entirely from the normalization factor,
85 but the mathematical equivalence with Approach 1 can be recognized by the relation:

$$\frac{S_{PO,oxides}}{S_{PO,oxides} + S_{PO,halogens}} = \frac{25}{25 + \frac{1}{2}[F + Cl]} = \frac{25}{26 - \frac{1}{2}[OH]},$$

86 where $S_{PO,oxides}$ and $S_{PO,halogens}$ refer to sums for oxides and halogens, respectively. The
87 respective normalization factors for approaches 1 and 2 are thus equal:

$$\frac{26 - \frac{1}{2}[OH]}{S_{PO,oxides} + S_{PO,halogens}} = \frac{25}{S_{PO,oxides}}.$$

88 **Implementation**

89 Both approaches are implemented in a Microsoft Excel spreadsheet (supplement) that
90 allows both for entry of a synthetic stoichiometry, to demonstrate that the stoichiometry is indeed
91 recovered, and for entry of EMPA data. Recovery of synthetic stoichiometry is perfect with the
92 new method, so long as unbalanced cation charges that result in too many or too few oxygens are
93 avoided. Conversely, stoichiometry is not recovered with one of the static normalizations except
94 in the ideal cases discussed previously.

95 Table 2 shows results of calculating mineral formulas from various apatite analyses
96 reported by Carlson et al. (1999, Table A1), including near-end-member F (RN), Cl (B3) and
97 OH (HS) apatites, as well as three featuring various amounts of mixing (FC, B3, TI). In all cases
98 the occupancy calculated using the new method for the Ca and P sites are either similar or closer
99 to expected values (10 and 6, respectively) than obtained by correcting for F and Cl content and

100 using 26 or 25 anions, particularly if there is mixing among anions. Again, the differences in
101 cation stoichiometry are larger than for anions. In most cases the errors in stoichiometry are
102 small, and the maximum possible inaccuracy is about 4%, or 1/25. After correct calculation, all
103 cation totals are within 1% of the expected values, implying good data quality that would
104 otherwise be obscured by poor stoichiometry calculations.

105 Also included in the supplemental spreadsheet is an example of uncertainty calculations
106 based on multiple spot analyses. The uncertainty in each weight percent determination can be
107 straightforwardly propagated to the uncertainty in each component of the chemical formula. The
108 uncertainty in hydroxyl content, σ_{OH} , is estimated from the halogen uncertainties using standard
109 error propagation as:

$$\sigma_{OH} = \sqrt{\sigma_F^2 + \sigma_{Cl}^2}$$

110 This should be taken as a minimal estimate, as it presumes ideal site occupancy.

111 Although this method eliminates the need to adjust oxygen totals for halogen content, it
112 remains valid and appropriate to correct weight percent totals (Deer et al. 2013, Appendix 1
113 tables, column 1). These totals may be further improved by calculating and including the
114 estimated weight percent of OH, using the mass proportions of the chemical components in the
115 final derived formula, as shown in the supplemental spreadsheet.

116 **Discussion**

117 The stoichiometric calculation method presented in this contribution is valid for apatites
118 with any degree of mixing between F, Cl, and OH. However, it should also be noted that this
119 method presumes that all stoichiometrically significant components are measured, which can be

120 evaluated based on the revised weight percent totals. A related assumption is that there is an
121 insignificant number of vacancies, as the method presumes full occupancy on the monovalent
122 anion site. To the extent that this site is occupied by vacancies, the [OH] content will be
123 overestimated by a like amount. Although exotic synthetic apatite varieties can host a large
124 number of vacancies on this site (e.g., Wilson et al., 1977), and ternary apatites accommodate
125 packing constraints partially through vacancies (Hughes et al., 1990), in most practical
126 applications this approximation is reasonable, especially to within the uncertainties of the
127 chemical analyses.

128 The principles and calculations in this contribution apply similarly to any mineral that
129 features significant mixing among halogens and hydroxyl ions. As a demonstration, the
130 supplemental spreadsheet also includes worksheets corresponding to the fluor-phlogopite
131 $(K_2Mg_6[Al_2Si_6O_{20}](F,OH)_4)$ example from Deer et al. (2013, Appendix 1). Even though H₂O
132 analysis is omitted, the result of the stoichiometry calculation is almost identical to that given by
133 Deer et al. (2013); all cation site occupancies match to within the data precision.

134 These improved calculations allow EMPA analyses of these phases to be evaluated more
135 rigorously and held to a higher standard.

136 **Acknowledgements**

137 This research was supported by National Science Foundation grant EAR-0948636, and
138 the Jackson School of Geosciences. The spreadsheet in the supplement is based on a file
139 originally created by W. Carlson, who is also thanked for an early conversation on this topic.
140 Reviews by Alan Treiman and an anonymous reviewer helped improve this contribution.

141 **References**

- 142 Carlson, W.D., Donelick, R.A., and Ketcham, R.A. (1999) Variability of apatite fission-track annealing
143 kinetics I: Experimental results. *American Mineralogist*, 84, 1213-1223.
- 144 Deer, W.A., Howie, R.A., and Zussman, J. (1966) *An Introduction to the Rock-Forming Minerals* (1st
145 Edition). 528 p. Longman, Essex.
- 146 Deer, W.A., Howie, R.A., and Zussman, J. (1992) *An Introduction to the Rock-Forming Minerals* (2nd
147 Edition). 696 p. Longman, Essex.
- 148 Deer, W.A., Howie, R.A., and Zussman, J. (2013) *An Introduction to the Rock-Forming Minerals* (3rd
149 Edition). 498 p. The Mineralogical Society, London.
- 150 Goldoff, B., Webster, J.D., and Harlov, D.E. (2012) Characterization of fluor-chlorapatites by electron
151 probe microanalysis with a focus on time-dependent intensity variation of halogens. *American*
152 *Mineralogist*, 97, 1103-1115.
- 153 Hughes, J.M., Cameron, M., and Crowley, K.D. (1990) Crystal structures of natural ternary apatite: Solid
154 solution in the $\text{Ca}_5(\text{PO}_4)_3\text{X}$ (X = F, PH, Cl) system. *American Mineralogist*, 75, 295-304.
- 155 Stormer, J.C.J., Pierson, M.L., and Tacker, R.C. (1993) Variation of F and Cl X-ray intensity due to
156 anisotropic diffusion in apatite during electron microprobe analysis. *American Mineralogist*, 78,
157 641-648.
- 158 Wilson, A.J.C., Sudarsanan, K., and Young, R.A. (1977) The structures of some cadmium 'apatites'
159 $\text{Cd}_5(\text{MO}_4)_3\text{X}$. II. The distributions of the halogen atoms in $\text{Cd}_5(\text{VO}_4)_3$ I, $\text{Cd}_5(\text{PO}_4)_3\text{Br}$, $\text{Cd}_5(\text{AsO}_4)_3\text{Br}$,
160 $\text{Cd}_5(\text{VO}_4)_3\text{Br}$ and $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$. *Acta Crystallographica*, B33, 3142-3154.
- 161
- 162

Table 1: Ideal apatite compositions and stoichiometric calculation results.

F-apatite						OH-apatite					
	wt%		Atoms pfu				wt%		Atoms pfu		
			26	25	this			26	25	this	
			anions	anions	study			anions	anions	study	
CaO	55.60	Ca	10.00	9.62	10.00	CaO	54.94	Ca	10.40	10.00	
SrO	0.00	Sr	0.00	0.00	0.00	SrO	0.00	Sr	0.00	0.00	
Na ₂ O	0.00	Na	0.00	0.00	0.00	Na ₂ O	0.00	Na	0.00	0.00	
Ce ₂ O ₃	0.00	Ce	0.00	0.00	0.00	Ce ₂ O ₃	0.00	Ce	0.00	0.00	
La ₂ O ₃	0.00	La	0.00	0.00	0.00	La ₂ O ₃	0.00	La	0.00	0.00	
MnO	0.00	Mn	0.00	0.00	0.00	MnO	0.00	Mn	0.00	0.00	
FeO	0.00	Fe	0.00	0.00	0.00	FeO	0.00	Fe	0.00	0.00	
		Σ	10.00	9.62	10.00			Σ	10.40	10.00	
P ₂ O ₅	42.22	P	6.00	5.77	6.00	P ₂ O ₅	41.72	P	6.24	6.00	
SiO ₂	0.00	Si	0.00	0.00	0.00	SiO ₂	0.00	Si	0.00	0.00	
		Σ	6.00	5.77	6.00			Σ	6.24	6.00	
F	3.77	F	2.00	1.92	2.00	F	0.00	F	0.00	0.00	
Cl	0.00	Cl	0.00	0.00	0.00	Cl	0.00	Cl	0.00	0.00	
		OH	0.00	0.08	0.00			OH	2.00	2.00	

F-OH apatite						F-Cl-OH apatite					
	wt%		Atoms pfu				wt%		Atoms pfu		
			26	25	this			26	25	this	
			anions	anions	study			anions	anions	study	
CaO	55.27	Ca	10.20	9.80	10.00	CaO	54.79	Ca	10.13	9.74	
SrO	0.00	Sr	0.00	0.00	0.00	SrO	0.00	Sr	0.00	0.00	
Na ₂ O	0.00	Na	0.00	0.00	0.00	Na ₂ O	0.00	Na	0.00	0.00	
Ce ₂ O ₃	0.00	Ce	0.00	0.00	0.00	Ce ₂ O ₃	0.00	Ce	0.00	0.00	
La ₂ O ₃	0.00	La	0.00	0.00	0.00	La ₂ O ₃	0.00	La	0.00	0.00	
MnO	0.00	Mn	0.00	0.00	0.00	MnO	0.00	Mn	0.00	0.00	
FeO	0.00	Fe	0.00	0.00	0.00	FeO	0.00	Fe	0.00	0.00	
		Σ	10.20	9.80	10.00			Σ	10.13	9.74	
P ₂ O ₅	41.97	P	6.12	5.88	6.00	P ₂ O ₅	41.60	P	6.08	5.84	
SiO ₂	0.00	Si	0.00	0.00	0.00	SiO ₂	0.00	Si	0.00	0.00	
		Σ	6.12	5.88	6.00			Σ	6.08	5.84	
F	1.87	F	1.02	0.98	1.00	F	1.24	F	0.68	0.65	
Cl	0.00	Cl	0.00	0.00	0.00	Cl	2.31	Cl	0.68	0.65	
		OH	0.98	1.02	1.00			OH	0.65	0.70	

Atoms pfu – 26 anions and 25 anions refer to using method of Deer et al. (2013) and normalizing with 26 or 25 anions.

Table 2: Example EMPA analyses and stoichiometry calculations for six apatites from Carlson et al. (1999).

RN						B3					
EMPA			Atoms pfu			EMPA			Atoms pfu		
wt%		26	25	this	wt%		26	25	this		
		anions	anions	study			anions	anions	study		
CaO	54.33	Ca	9.93	9.55	9.92	CaO	52.73	Ca	9.79	9.41	9.77
SrO	0.10	Sr	0.01	0.01	0.01	SrO	0.06	Sr	0.01	0.01	0.01
Na ₂ O	0.18	Na	0.06	0.06	0.06	Na ₂ O	0.40	Na	0.13	0.13	0.13
Ce ₂ O ₃	0.38	Ce	0.02	0.02	0.02	Ce ₂ O ₃	0.32	Ce	0.02	0.02	0.02
La ₂ O ₃	0.11	La	0.01	0.01	0.01	La ₂ O ₃	0.06	La	0.00	0.00	0.00
MnO	0.06	Mn	0.01	0.01	0.01	MnO	0.01	Mn	0.00	0.00	0.00
FeO	0.00	Fe	0.00	0.00	0.00	FeO	0.08	Fe	0.01	0.01	0.01
		Σ	10.04	9.65	10.03			Σ	9.96	9.58	9.95
P ₂ O ₅	41.38	P	5.98	5.75	5.97	P ₂ O ₅	41.23	P	6.05	5.81	6.04
SiO ₂	0.17	Si	0.03	0.03	0.03	SiO ₂	0.05	Si	0.01	0.01	0.01
		Σ	6.00	5.77	6.00			Σ	6.06	5.82	6.04
F	3.62	F	1.95	1.88	1.95	F	0.08	F	0.04	0.04	0.04
Cl	0.03	Cl	0.01	0.01	0.01	Cl	6.37	Cl	1.87	1.80	1.87
		OH	0.04	0.11	0.04			OH	0.09	0.16	0.09
HS						FC					
EMPA			Atoms pfu			EMPA			Atoms pfu		
wt%		26	25	this	wt%		26	25	this		
		anions	anions	study			anions	anions	study		
CaO	55.13	Ca	10.26	9.87	9.90	CaO	54.19	Ca	9.97	9.58	9.84
SrO	0.03	Sr	0.00	0.00	0.00	SrO	0.05	Sr	0.00	0.00	0.00
Na ₂ O	0.03	Na	0.01	0.01	0.01	Na ₂ O	0.09	Na	0.03	0.03	0.03
Ce ₂ O ₃	0.05	Ce	0.00	0.00	0.00	Ce ₂ O ₃	0.65	Ce	0.04	0.04	0.04
La ₂ O ₃	0.00	La	0.00	0.00	0.00	La ₂ O ₃	0.23	La	0.01	0.01	0.01
MnO	0.05	Mn	0.01	0.01	0.01	MnO	0.18	Mn	0.03	0.03	0.03
FeO	0.02	Fe	0.00	0.00	0.00	FeO	0.07	Fe	0.01	0.01	0.01
		Σ	10.29	9.89	9.92			Σ	10.09	9.70	9.97
P ₂ O ₅	42.49	P	6.25	6.01	6.03	P ₂ O ₅	41.53	P	6.03	5.80	5.96
SiO ₂	0.03	Si	0.01	0.01	0.01	SiO ₂	0.36	Si	0.06	0.06	0.06
		Σ	6.25	6.01	6.03			Σ	6.10	5.86	6.02
F	0.12	F	0.07	0.06	0.06	F	2.09	F	1.13	1.09	1.12
Cl	0.35	Cl	0.10	0.10	0.10	Cl	0.81	Cl	0.24	0.23	0.23
		OH	1.83	1.84	1.84			OH	0.63	0.68	0.65
B2						TI					
EMPA			Atoms pfu			EMPA			Atoms pfu		
wt%		26	25	this	wt%		26	25	this		
		anions	anions	study			anions	anions	study		
CaO	53.63	Ca	9.99	9.60	9.79	CaO	53.32	Ca	9.86	9.48	9.68
SrO	0.07	Sr	0.01	0.01	0.01	SrO	0.00	Sr	0.00	0.00	0.00
Na ₂ O	0.31	Na	0.10	0.10	0.10	Na ₂ O	0.17	Na	0.06	0.05	0.06
Ce ₂ O ₃	0.34	Ce	0.02	0.02	0.02	Ce ₂ O ₃	0.18	Ce	0.01	0.01	0.01
La ₂ O ₃	0.11	La	0.01	0.01	0.01	La ₂ O ₃	0.04	La	0.00	0.00	0.00
MnO	0.06	Mn	0.01	0.01	0.01	MnO	0.47	Mn	0.07	0.07	0.07
FeO	0.15	Fe	0.02	0.02	0.02	FeO	0.82	Fe	0.12	0.11	0.12
		Σ	10.16	9.77	9.96			Σ	10.12	9.73	9.93
P ₂ O ₅	41.79	P	6.15	5.91	6.03	P ₂ O ₅	42.03	P	6.14	5.90	6.03
SiO ₂	0.00	Si	0.00	0.00	0.00	SiO ₂	0.08	Si	0.01	0.01	0.01
		Σ	6.15	5.91	6.03			Σ	6.15	5.92	6.04
F	0.28	F	0.15	0.15	0.15	F	1.63	F	0.89	0.86	0.87
Cl	2.95	Cl	0.87	0.84	0.85	Cl	0.58	Cl	0.17	0.16	0.17
		OH	0.98	1.02	1.00			OH	0.94	0.98	0.96

Atoms pfu – 26 anions and 25 anions refer to using method of Deer et al. (2013) and normalizing with 26 or 25 anions.