Technical Note: Calculation of stoichiometry from EMP data for apatite and other phases with mixing on monoanion sites†

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ABSTRACT

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

Keywords: Apatite, stoichiometry, electron microprobe analysis, site mixing

INTRODUCTION

Apatite \([\text{Ca}_x(\text{PO}_4)_y(\text{F,Cl,OH})_z] \) is a challenging mineral for electron microprobe analysis (EMPA), both due to fluorine migration under the electron beam (Goldoff et al. 2012; Stormer et al. 1993) and the necessity to compensate for the presence of halogens when calculating stoichiometry. EMPA analysis does not provide H₂O measurements, and some degree of mixing on the monoanion site is common, and thus OH content must be estimated based on F and Cl results. However, in the presence of this mixing, the correct normalization method for calculating stoichiometry is not straightforward.

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

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

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

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

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

① Deposit item AM-15-75171, Supplemental spreadsheet. Deposit items are stored on the MSA web site and available via the American Mineralogist Table of Contents. Find the article in the table of contents at GSW (ammin.geoscienceworld.org) or MSA (www.minsocam.org), and then click on the deposit link.

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