The programme is fitted with adequate internal error checks, and has been extensively tested. Card decks are available under the code name APOL, together with a write-up/users' manual in two versions: one suitable for I.B.M. 7090/94 machines, and the other suitable for I.B.M. 360 machines. Both versions are written in Fortran IV language and require about 15 000 words of core storage. Requests for these should be sent to Dr. I. S. Kerr at the following address.

Physical Chemistry Laboratories   J. F. COLE
Imperial College   H. VILLIGER
London, SW. 7

The oxyapatite (voelckerite) problem

THE problem of the existence of an apatitic isotype with the composition $Ca_{10}O(PO_4)_6$ was raised again with the introduction of the name voelckerite (Rogers, 1912); it had first arisen in 1883 (Voelcker). To say that the problem has not been completely resolved during the past half-century, would be an understatement, despite attempts by several highly competent mineralogists.

Today, there seems to be little doubt about the existence of hydroxyl- and/or halogen-deficient apatites ($OH+F+Cl < 2$); the current question is whether there are vacancies in some of the structural sites that are occupied by F in ordinary $Ca_{10}(PO_4)_6F_2$ (these (a) sites are located at $\pm(0, 0, \frac{1}{4})$, according to conventional selection of the origin, whereas Cl is in (b) sites ($0, 0, \frac{1}{2}$)).

As indicated by Merker and Wondratschek (1960) for synthetic $Pb_{10}(PO_4)_6O$, there must be a doubling of c for the unit cell when occupancy of half of the (a) or (b) sites is ordered.[1]

Most recent advocates for vacancies in the (a) sites are Sudarsanan and Young (1968), whereas Ito (1968, pp. 902–3) states: 'The above observations suggest that there is only one oxyapatite . . . in which the loss of hydroxyl ion is compensated by cation replacement, and the stabilized oxyapatite contains 26 oxygens in each unit cell, as originally postulated by . . .'.

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[1] Concerning their 'oxypyromorphite', however, they state: 'Es ist möglich, dass etwas OH in das Gitter des Oxypyromorphits eingebaut wird, vielleicht ist ein solcher Einbau sogar für die Stabilität des Oxypyromorphit-Gitters wesentlich' (p. 29).

Ito's views seem consistent with the premise that stable structures that form in oxygen-containing systems are unlikely to have significant vacancies in sites normally occupied by oxygen or fluorine. Otherwise, large 'holes' must be assumed, interstitially between smaller cations, and such a situation seems highly improbable (in detectable amounts) in oxygenated structures of these types. It has been suggested (McConnell, 1965) that these sites (a and/or b) may be occupied by H_2O, a suggestion adopted by Simpson (1968).

There are only two rational ways of computing a mineral formula from a chemical analysis: either one must bring in the density and unit cell dimensions, calculate the number of atoms of each kind in the unit cell, and group them according to their crystal-chemical affinities; or one must make an explicit assumption regarding the number of some atom or group of atoms in the unit cell. Unfortunately, the importance of making a suitable choice of assumption is not always recognized.

Occasionally the basic assumption is not even mentioned. Thus in Young and Munson's (1966) calculation of an apatite formula, which purports to prove that $\Sigma(O,OH,F,Cl)$ in apatite may be substantially less than 26, it is by no means obvious that their basic assumption is a formula $R_{10}(XO_4)_xZ_y$, and that Ca, Fe^{2+}, Mn, Na, K, Sr, and Ln are allotted to the assumed 10 R positions, and P and S to the X positions. With these assumptions, and ignoring[1] Al and Fe^{3+}, their molecular ratios (table 3, p. 1490) give $\Sigma(O,OH,F,Cl) = 25.659$ (presumably their figure of 25.68, and $\Sigma R = 10.01$ (col. 7) arise from a premature rounding-off in the calculations); the calculated density is[2] 3.188 ± 0.003.

Young and Munson also considered the assumptions $\Sigma(O,OH,F,Cl) = 26$, which leads to high ΣR (10.14) and D_{calc} 3.230 ± 0.003; also $\Sigma(P,S) = 6$, which leads to $\Sigma R = 10.16$, $\Sigma(O,OH,F,Cl) = 26.06$, and D_{calc} 3.238 ± 0.003. They did not, however, consider the assumption $\Sigma(R,X) = 16$, which gives D_{calc} 3.205 ± 0.003 and $\Sigma(O,OH,F,Cl) = 25.80$, but requires the carbon and 0.06 R to be in the X sites.

The observed density, cited as 3.205 ± 0.002, agrees best with the assumption of 16 $(R+X)$ in the unit cell, but in view of the general tendency of density determinations to give low results, $\Sigma(O,OH,F,Cl) = 26$ cannot be ruled out—indeed, all the above four assumptions, and also $\Sigma(R,X,O,OH,F,Cl) = 42$, are well within the bounds of possibility.

Finally, we note that the above calculations are based on the assumption that the analysis is perfectly accurate. Young and Munson state (p. 1486) that two analyses for CaO and two for P_2O_5 were made, each pair matching to 0.1 %, but they say nothing about the analytical methods adopted; with simple duplication, an analysis can involve serious systematic errors and still show reasonable precision and a satisfactory analytical total. If CaO is high and P_2O_5 correspondingly low, not only will Ca appear to be replacing P, but $\Sigma(O,OH,F,Cl)$ will be low, and with some analytical procedures such an error is not impossible.

[1] This really amounts to an assumption that the analysed material included 0.14 % of an aluminian hematite. Inclusion of the Al and Fe^{3+} in the 10 R makes very little difference in any of the values.

[2] The cited standard errors of the X-ray data only have been taken into account.

Accordingly, we must conclude that Young and Munson's data afford no acceptable evidence for the existence of apatites with less than 26 (O,OH,F,Cl) in the unit cell.

Department of Mineralogy   DUNCAN McCONNELL
The Ohio State University
Columbus, Ohio 43210

Department of Mineralogy   M. H. HEY
British Museum (Natural History)
Cromwell Road, London, SW. 7

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