UNIT-CELL DIMENSIONS, OPTICAL PROPERTIES, HALOGEN CONCENTRATIONS IN SEVERAL NATURAL APATITES

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ABSTRACT

Unit cell dimensions, optical properties, and halogen and carbonate concentrations were determined for seven samples of natural apatite. The OH− concentrations (determined by difference) were relatively constant for all samples, but CO32−, Cl− and F− varied. The three types of apatite studied were high carbonate-fluor-hydroxy-apatite, high fluor-hydroxy-apatite, and chlor-hydroxy-apatite. The unit cell parameters a and c, as well as the unit-cell volume (V), are sufficient to discriminate among the three types studied. Some carbonate substituted for phosphate in all samples. The isotopic composition of the carbonate reflects the origin of the apatite: the pegmatitic samples (relatively high-temperature origin) being much lighter in 18O than the sedimentary phosphate rock.

This study represents preliminary work on the correlation of physical properties and anion composition in the apatite mineral group. Previous investigators have been primarily concerned with variations in cation composition; minor variations in halogen composition have not been considered. The samples consist of five fluorapatites, one chlorapatite, and the NBS phosphate rock (principally carbonate apatite).

SAMPLES

The samples of apatite were obtained from the MIT research mineral collection, Department of Geology and Geophysics, with the exception of sample M83, the NBS phosphate rock standard 120a. Other than the phosphate rock, all specimens are from pegmatite occurrences. M84 is listed as a Canadian occurrence, M85 is from Rossie, New York; M86 is from Snarum, Norway; M87 is from a pegmatite near Pikes Peak, Colorado; both M90 and M91 are from Burgess, Ontario (M90 is light citrine yellow, and M91 is light red, both in intimate association in a hand specimen).

EXPERIMENTAL PROCEDURE

Halogen concentration. Neutron activation analysis was used to determine the chlorine, bromine, and iodine concentrations. The samples were ground to a size of less than 0.1 mm, and then washed eight times with boiling 0.025 m NH4NO3 solution (prepared from distilled and demineralized water, distilled NH4OH and reagent grade HNO3). After this

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preparation, the samples were irradiated in the MIT reactor, using the pneumatic tube facility. The samples were then fused, and the radioactive chlorine, bromine, and iodine were separated (Duce and Winchester, 1965) and beta-counted. The limit of accuracy was ±10 percent for the chlorine analyses, ±15 percent for the bromine analyses, and ±10 percent for the iodine analysis of sample M83. Contamination of the iodine beta-decay curves by fission product iodine was observed in all of the pegmatite samples. Fluoride analyses were performed by Hoffman Laboratories using an emission spectrographic method; measurement of the CaF₂ band head.

Unit-cell dimensions. X-ray powder diffraction films were obtained with a Nonius Guinier-deWolff focusing camera. The Kα₂ radiation was eliminated by defocusing the camera so that the full optical width of the anode was not used. In general the observations on a given film are found to be reproducible to within less than ±0.005° 2θ. The internal standard method was used to correct the observed 2θ values. The observed diffraction lines were indexed on the basis of an assumed space group C6/m in agreement with the results of Beevers and McIntyre (1946). Least-squares refinement of the unit-cell dimensions was obtained using the IBM 360/65 computer (MIT Computation Center) and the FORTRAN IV program supplied by Dr. D. E. Appleman (Evans, Appleman, and Handwerker, 1965).

Isotope measurements. The carbon and oxygen isotope determinations were made using a Nier-type mass spectrometer. The CO₂ was evolved using 100 percent phosphoric acid and forcing the reaction to completion by heating. The accuracy of these samples was limited because of the small volumes of CO₂ obtained. However they were reproducible to ±2 percent.

The CO₂ content was determined by measuring the volume of gas evolved for isotope determination in a calibrated manometer. The calibration of the manometer is accurate to ±5 percent.

RESULTS AND DISCUSSION

The calculated unit cell dimensions are given in Table 1 for these seven samples. The internal standard method was used to correct the X-ray diffraction films, which were made using a Nonius Guinier-deWolff Quadrupole focusing camera. The spinel internal standard, a = 8.0833 Å

![Table 1. Unit Cell Dimensions and Refractive Indices](image)

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>ε⁸</th>
<th>²/³</th>
</tr>
</thead>
<tbody>
<tr>
<td>M83</td>
<td>9.3434 ± 0.0006</td>
<td>6.8938 ± 0.0006</td>
<td>520.20 ± 0.07</td>
<td>1.636</td>
<td>1.607</td>
</tr>
<tr>
<td>M84</td>
<td>9.3960 ± 0.0011</td>
<td>6.8800 ± 0.0012</td>
<td>526.03 ± 0.12</td>
<td>1.633</td>
<td>1.638</td>
</tr>
<tr>
<td>M85(1)</td>
<td>9.3825 ± 0.0006</td>
<td>6.8902 ± 0.0009</td>
<td>525.33 ± 0.075</td>
<td>1.633</td>
<td>1.638</td>
</tr>
<tr>
<td>M85(2)</td>
<td>9.3812 ± 0.0005</td>
<td>6.8900 ± 0.0006</td>
<td>525.13 ± 0.06</td>
<td>1.633</td>
<td>1.638</td>
</tr>
<tr>
<td>M86</td>
<td>9.6148 ± 0.0018</td>
<td>6.7896 ± 0.0019</td>
<td>543.57 ± 0.19</td>
<td>1.663</td>
<td>1.663</td>
</tr>
<tr>
<td>M87</td>
<td>9.3767 ± 0.0004</td>
<td>6.8800 ± 0.0006</td>
<td>524.48 ± 0.04</td>
<td>1.633</td>
<td>1.636</td>
</tr>
<tr>
<td>M90</td>
<td>9.3704 ± 0.0004</td>
<td>6.8888 ± 0.0005</td>
<td>523.82 ± 0.05</td>
<td>1.629</td>
<td>1.633</td>
</tr>
<tr>
<td>M91</td>
<td>9.3705 ± 0.0004</td>
<td>6.8900 ± 0.0005</td>
<td>523.93 ± 0.05</td>
<td>1.631</td>
<td>1.635</td>
</tr>
</tbody>
</table>

* Refractive indices on NaD at 25 ± 2°C.
was obtained from J. V. Smith and G. V. Gibbs. The chemical data and calculated formulae are given in Table 2.

The following assumptions were made in calculating the chemical formulae given in Table 2.

1. Apatite was represented as having the following general formula:

$$\text{Ca}_5[(\text{PO}_4)_{1-x}(\text{CO}_3)_x]_3(\text{F}, \text{Cl}, \text{OH})_{1+2x}.$$ 

2. The formula weight is 508 ± 15. This average was determined using the extremes Ca$_5$(PO$_4$)$_3$Cl = 523 and Ca$_5$[(PO$_4$)$_{0.6}$(CO$_3$)$_{0.2}$]$_3$(OH)$_{1.6}$.

### Table 2. Chemical Data and Calculated Formulae

<table>
<thead>
<tr>
<th></th>
<th>M83</th>
<th>M84</th>
<th>M85</th>
<th>M86</th>
<th>M87</th>
<th>M90</th>
<th>M91</th>
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<tr>
<td>F ppm</td>
<td>39000</td>
<td>24000</td>
<td>25000</td>
<td>1100</td>
<td>34000</td>
<td>30000</td>
<td>31000</td>
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<tr>
<td>Cl ppm</td>
<td>19</td>
<td>2700</td>
<td>390</td>
<td>39000</td>
<td>350</td>
<td>0.3</td>
<td>0.7</td>
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<td>Br ppm</td>
<td>1</td>
<td>0.1</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>T ppm</td>
<td>25</td>
<td>43000</td>
<td>420</td>
<td>3</td>
<td>0.1</td>
<td></td>
<td></td>
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<tr>
<td>CO$_3$ %</td>
<td>3.34</td>
<td>0.76</td>
<td>0.35</td>
<td>0.0036</td>
<td>1.30</td>
<td>0.54</td>
<td>0.52</td>
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<tr>
<td>$\delta^{18}O$ %$^b$</td>
<td>-6.5</td>
<td>-1.9</td>
<td>-2.8</td>
<td>-1.9</td>
<td>-3.7</td>
<td>-4.4</td>
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<tr>
<td>$\delta^{13}C$ %$^a$</td>
<td>34.5</td>
<td>24.4</td>
<td>16.6</td>
<td>27.5</td>
<td>15.0</td>
<td>16.1</td>
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Calculated Formulas$^c$ (mole numbers)

<table>
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<tr>
<th></th>
<th>CO$_3$</th>
<th>0.39</th>
<th>0.089</th>
<th>0.040</th>
<th>0.00042</th>
<th>0.15</th>
<th>0.062</th>
<th>0.060</th>
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<tr>
<td>Cl</td>
<td>.00027</td>
<td>.039</td>
<td>.0056</td>
<td>.56</td>
<td>.0050</td>
<td>.0050</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>1.04</td>
<td>.64</td>
<td>.67</td>
<td>.029</td>
<td>.91</td>
<td>.80</td>
<td>.83</td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>.34</td>
<td>.41</td>
<td>.37</td>
<td>.41</td>
<td>.24</td>
<td>.26</td>
<td>.23</td>
<td></td>
</tr>
<tr>
<td>F+OH</td>
<td>1.39</td>
<td>1.05</td>
<td>1.03</td>
<td>.71</td>
<td>1.15</td>
<td>1.06</td>
<td>1.05</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $\delta$ values relative to the Chicago PDB-1 Belemnite.

$^b$ $\delta$ values relative to SMOW where $\delta$ SMOW = 1.03837×PDB+38.37, J. O'Neil, pers. comm. 1968.

$^c$ Assuming 1+CO$_3$=OH+F+Cl and molecular weight of apatite=508 grams/mole.

492. A maximum of 20 percent carbonate substitution for phosphate was assumed, likewise OH was used because it was lighter. Fluorapatite Ca$_5$(PO$_4$)$_3$F is intermediate between these two extremes at 507. The OH content was calculated from the charge balance relation, however this could be in error by as much as 25 to 50 percent. The charge deficiency resulting from substitution of CO$_3^{2-}$ for PO$_4^{3-}$ may be neutralized by substitution of Na$^+$ or K$^+$ for Ca$^{2+}$.

The effect of this substitution can be seen in the following formula for M83 (NBS 120a), based on the provisional certificate of analysis (H. C. Allen, Jr., personal communication, July 25, 1961):
In this case there are 0.3894 moles CO₃, and 0.0830 moles of Na⁺+K⁺ or 21 percent of the CO₃²⁻ charge deficiency is neutralized by Na⁺+K⁺. Substitutions of SO₄²⁻, Si⁴⁺ or Ti⁴⁺ within the structure were not considered, but would affect the charge balance within the mineral.

Since the weight and size of OH⁻ and F⁻ are very similar, the sum of these two quantities was compared with the amount of CO₃²⁻ and Cl⁻, as shown in Figure 1. The six samples for which complete halogen-carbonate analyses were obtained can be divided into three groups: M83—high carbonate fluor+hydroxy apatite; M84, M85, M87, and M91—high fluor+hydroxy apatite; and M86—chlorapatite.

The relations between the unit-cell dimensions and variations in chemical composition are shown in Figure 2. The best discriminator between all three groups is $a$. Although $c$ separates the chlorapatite, it does not discriminate between CO₃ and (OH, F). The relation between composition and unit-cell volume ($V$) is similar to that shown for $c$. The ω refractive index is also useful for separating the different types of apatite; however no significant relation was observed for $e$.

The variation in Cl/Br ratio has little effect on the unit-cell dimensions.

\[
[\text{Ca}_{0.9664}\text{Mg}_{0.0062}\text{Mn}_{0.0006}\text{Na}_{0.0142}\text{K}_{0.0028}]_5 \\
[\text{(PO}_4\text{)}_{0.8702}\text{(CO}_2\text{)}_{0.1298}]_5\text{[OH}_{0.1296}\text{F}_{1.1110}\text{Cl}_{0.0008}]
\]
It appears there was a typographical error in the first sentence of the text. The correct sentence should read: "Fluorapatites, as might be predicted. This ratio varies from $2.7 \times 10^4$ (M84) to $1.3 \times 10^8$ (M85); yet the volume change is less than 1 Å$^3$, and this volume change is in the appropriate direction as Cl increases from 390 to 2700 ppm.

Sample M83 (NBS 120a) was the only one in which a significant iodine concentration was observed. Jacob et al. (1933) found the range of iodine concentration in phosphatic rocks to be 0.8–130 ppm. This range correlates well with the iodine and phosphate concentrations in shales (Walters, 1967). Shales have up to 3 ppm I corresponding to 1.5 percent PO$_4^{3-}$, or apatite.

The state of combination of the iodine and bromine in apatite is not known, but may be actually substituted for F or Cl within the crystal structure as suggested by Hendricks et al. (1932).

The oxygen isotope analyses of the CO$_3$ oxygen from these natural apatites compare favorably with those for hydrothermal carbonates (calcite or dolomite) and igneous or metamorphic quartz. The $\delta^{18}O$ for sample M83 (34.5 vs SMOW) is similar to those reported for marine limestone. The $\delta^{18}O$ for pegmatite samples ranges from 15.0 to 27.5 vs. SMOW, a range comparable to that found in the hydrothermally altered Leadville limestone by Engel, Clayton, and Epstein (1958). The very light values
observed for M90, M91, and M85 are similar to those for igneous quartz [9.4 to 12.0, Taylor and Epstein (1962)], and metamorphic quartz [8.4 to 22.3, Garlick and Epstein (1967)]. No significant variation was observed in the $\delta C_{18}$ for these samples.

On the basis of this limited sample we can reach several tentative conclusions. It is commonly reported that a complete crystalline solution series exists between the fluor- and chlor-apatites. Nacken (1912), on the basis of dry fusion synthesis experiments using $\text{Ca}_2(\text{PO}_4)_2$, $\text{CaF}_2$ was among the first to suggest this. Pehrman (1925) suggested that crystalline solution between the Cl-F end members was limited, on the basis of analyses of natural specimens. Hendricks et al. (1932) noted that the structural sites occupied by Cl and F in the two end members were slightly different, and that Cl substitution in the F end member was limited to about 1/2 F in natural materials. McConnel (1938) suggested that a relationship similar to dolomite, an ordered 1:1 compound, might be observed. Wallaeys and Chaudron (1950) suggested the existence of a complete Cl-F series. Prenner (1967) synthesized a “chlorapatite” having a monoclinic structure at low temperatures and hexagonal structure at high temperatures. He noted that an atomic ratio $F/(F+Cl)$ of about 0.16 to 0.36 stabilized the hexagonal structure. Young and Elliott (1966) also noted the stabilizing effect of impurities in the apatite structure.

Although ionic size and structural relations imply that a continuous solution F-Cl may exist at higher temperatures, crystalline solubility may be limited at lower temperatures. It is also possible that the experimental products obtained by Nacken (1912) and Wallaeys and Chaudron (1950) represent metastable high temperature forms. Further studies on the phase relations involving the OH-, F-, and Cl- apatites are under way, and perhaps the answers to these problems, as well as others, will be found.

The two samples from the Burgess, Ontario, locality were separated on the basis of color in an individual hand specimen. Crystals of the two colors yellow and red were in physical contact prior to separation. There is no significant difference in the unit cell dimensions or the refractive indices and composition of these two specimens. This suggests, in agreement with Vasilieva (1958), Hogarth (1957), Hoffman (1938), and others, that the color variation is produced by small changes in minor element concentration, or to disseminated crystals of a second phase.

References


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