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 CO_3^{2-}, 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 O^{18} 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 NH_4NO_3 solution (prepared from distilled and demineralized water, distilled NH_4OH and reagent grade HNO_3). 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 CaF_2 band head.

Unit-cell dimensions. X-ray powder diffraction films were obtained with a Nonius Guinier-deWolff focusing camera. The $K_{\alpha 2}$ 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 $\pm 0.005°$ 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 $C6_3/m$ 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 CO_2 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 CO_2 obtained. However they were reproducible to ± 2 percent.

The CO_2 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

	a (Å)		C (Å)		V (Å³)		ϵ^a	ω
M83	9.3434	± 0.0006	6.8938	± 0.0006	520.20	± 0.07		1.607
M84	9.3960	± 0.0011	6.8800	± 0.0012	526.03	± 0.12	1.636	1.638
M85(1)	9.3825	± 0.0006	6.8902	± 0.0009	525.33	± 0.075	1.633	1.638
M85(2)	9.3812	± 0.0005	6.8900	± 0.0006	525.13	± 0.06	1.633	1.638
M86	9.6148	± 0.0018	6.7896	± 0.0019	543.57	± 0.19		1.663
M87	9.3767	± 0.0004	6.8880	± 0.0006	524.48	± 0.04	1.633	1.636
M90	9.3704	± 0.0004	6.8888	± 0.0005	523.82	± 0.05	1.629	1.633
M91	9.3705	± 0.0004	6.8900	± 0.0005	523.93	± 0.05	1.631	1.635

[a] Refractive indices on Na_D at $25 \pm 2°C$.

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:

$$Ca_5[(PO_4)_{1-x}(CO_3)_x]_3(F, Cl, OH)_{1+3x}.$$
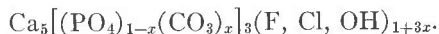
2. The formula weight is 508 ± 15. This average was determined using the extremes $Ca_5(PO_4)_3$ $Cl = 523$ and $Ca_5[(PO_4)_{0.8}(CO_3)_{0.2}]_3(OH)_{1.6} =$

TABLE 2. CHEMICAL DATA AND CALCULATED FORMULAE

	M83	M84	M85	M86	M87	M90	M91
F ppm	39000	24000	25000	1100	34000	30000	31000
Cl ppm	19	2700	390	39000	350		420
Br ppm	1	0.1	3	3	2	0.3	0.7
I ppm	25						
CO_2 %	3.34	0.76	0.35	0.0036	1.30	0.54	0.52
δC^{13} %[a]	-6.5	-1.9	-2.8		-1.9	-3.7	-4.4
δO^{18} %[b]	34.5	24.4	16.6		27.5	15.0	16.1

Calculated Formulas[c] (mole numbers)

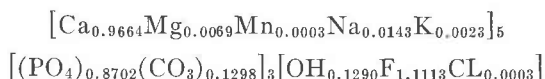|							
CO_3	0.39	0.089	0.040	0.00042	0.15	0.062	0.060
Cl	.00027	.039	.0056	.56	.0050		.0060
F	1.04	.64	.67	.029	.91	.80	.83
OH	.34	.41	.37	.41	.24	.26	.23
F+OH	1.39	1.05	1.03	.71	1.15	1.06	1.05

[a] δ values relative to the Chicago PDB-1 Belemnite.

[b] δ values relative to SMOW where δ SMOW $= 1.03837 \times PDB + 38.37$, 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 $Ca_5(PO_4)_3F$ 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):

$$[Ca_{0.9664}Mg_{0.0069}Mn_{0.0003}Na_{0.0143}K_{0.0023}]_5$$
$$[(PO_4)_{0.8702}(CO_3)_{0.1298}]_3[OH_{0.1290}F_{1.1113}CL_{0.0003}]$$

In this case there are 0.3894 moles CO_3, and 0.0830 moles of $Na^+ + K^+$ or 21 percent of the CO_3^{2-} charge deficiency is neutralized by $Na^+ + K^+$. Substitutions of SO_4^{2-}, Si^{4+} or Ti^{4+} 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 CO_3^{2-} and Cl^-, as shown in Figure 1. The six samples for which complete halogen-carbonate
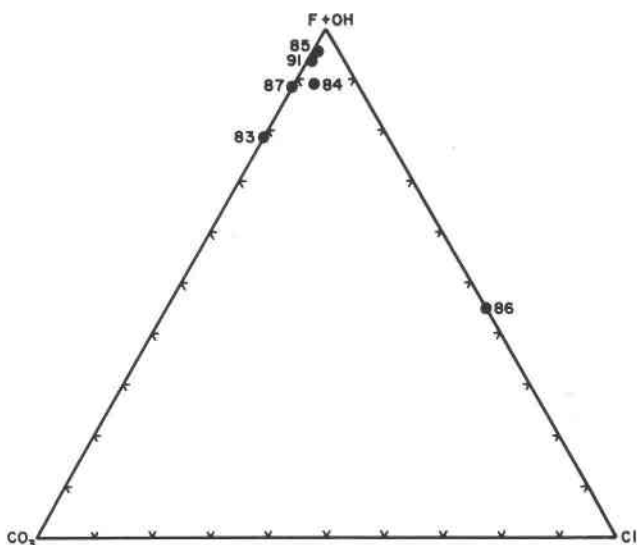

FIG. 1. Compositional variation in apatites studied. Variation expressed in terms of the molecular numbers of CO_3^{2-}, Cl, and $F + OH^-$ as discussed in the text.

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 CO_3 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 ϵ.

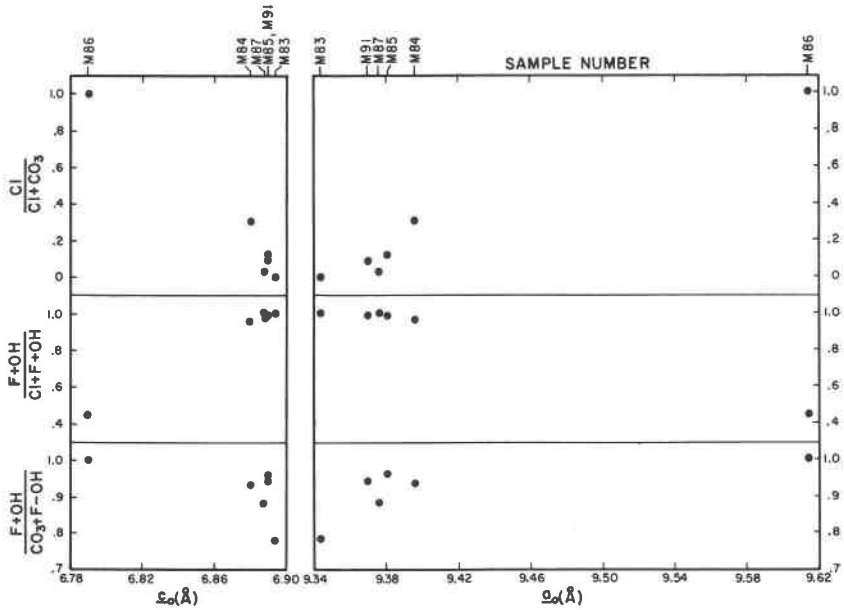The variation in Cl/Br ratio has little effect on the unit-cell dimensions

FIG. 2. Unit-cell dimensions and chemical variations data from Tables
1 and 2. Chemical variation expressed in molecular ratios.

of the fluorapatites, as might be predicted. This ratio varies from 2.7×10^4 (M84) to 1.3×10^2 (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 δO_{18} for sample M83 (34.5 *vs* SMOW) is similar to those reported for marine limestone. The δO_{18} 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 δC_{13} 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 $Ca_3(PO_4)_2$, 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

Beevers, C. A., and D. B. McIntyre (1946) The atomic structure of fluorapatite and its relation to that of tooth and bone material. *Mineral Mag.* **27**, 254–257.

Duce, R. A., and J. W. Winchester (1965) Determination of iodine, bromine, and chlorine in atmospheric samples by neutron activation. *Radiochem. Acta*, **4**, 100–104.

ENGEL, A. E. J., R. N. CLAYTON, AND S. EPSTEIN (1958) Variations in isotopic composition of oxygen and carbon in Leadville limestone (Mississippian, Colorado) and in its hydrothermal and metamorphic phases. *J. Geol.*, **66**, 374–393.

EVANS, W. A., JR., D. E. APPLEMAN, AND D. S. HANDWERKER (1963) The least-squares refinement of crystal unit cells with powder diffraction data by an automatic computer indexing method (abstr.). *Prog. Ann. Meet. Amer. Crystallogr., Ass., March 28, 1963, Cambridge, Mass.*, p. 42–43.

GARLICK, G. D., AND S. EPSTEIN (1967) Oxygen isotope ratios in co-existing minerals of regionally metamorphosed rocks. *Geochim. Cosmochim. Acta*, **31**, 181–214.

HENDRICKS, S. B., M. E. JEFFERSON, AND V. M. MOSLEY (1932) The crystal structures of some natural and synthetic apatite-like substances. *Z. Kristallogr.*, **81**, 352–369.

HOFFMAN, J. (1938) Über Ionen- und atomfarbungen künstlich hergestellter und natürlicher Apatite. *Chemie Erde*, **11**, 552 (M.A. 7–136).

HOGARTH, D. D. (1957) The apatite-bearing veins of Nisikkatch Lake, Saskatchewan. *Can. Mineral.*, **6**, 140.

MCDONNELL, D. S. (1938) A structural investigation of the isomorphism of the apatite group. *Amer. Mineral.*, **23**, 1–19.

NACKEN, R. (1912) Ueber die Bildung des Apatits: I. *Centralb. Mineral.* **1912**, 545–559.

PEHRMAN, G. (1925) Om en Apatitföre-komst i Åbo. *Fennia*, **54**, 1–13.

PRENER, J. S. (1967) The growth and crystallographic properties of calcium fluor- and chlorapatite crystals. *J. Electrochem. Soc.*, **114**, 77–83.

TAYLOR, H. P., JR., AND S. EPSTEIN (1962) Relationship between O^{18}/O^{16} ratios in coexisting minerals of igneous and metamorphic rocks, Part I: principles and experimental results. *Bull. Geol. Soc. Amer.*, **73**, 461–480.

VASILIEVA, Z. V. (1958) On the role of manganese in apatites. *Zap. Vses. Mineral. Obshch.*, **87**, 455–468.

WALLAEYS, R., AND G. CHAUDRON (1950) Sur la préparation de certaines apatites mixtes. *C. R. Acad. Sci. Paris*, **231**, 355–357.

WALTERS, L. J., JR., (1967) *Bound halogens in sediments*. Ph.D. Diss. Dept. Geol., Mass. Inst. Tech.

YOUNG, R. A., AND J. C. ELLIOTT (1966) Atomic-scale bases for several properties of apatites. *Arch. Oral Biol.*, **11**, 699–707.