A NOTE ON APATITE FROM HUDDERSFIELD TOWNSHIP, QUEBEC

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Reprinted from

THE CANADIAN MINERALOGIST, VOL. 12, PART 4, PAGE 289 (1974)

Canadian Mineralogist,
Vol. 12, pp. 289-291 (1974)

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Introduction

Apatite crystals from Huddersfield Township, Quebec, have been the quest of numerous amateur, as well as professional, mineralogists (Sabina 1964). The crystals are well-formed and are up to 30 cm or more in length. To date, however, there have been few quantitative data on their mineralogy.

The best crystals are found in a skarn zone on the Yates Uranium Mines property, lot 20, range 4 in Huddersfield Township where they are commonly associated with fluorite, pyroxene and pink-coloured calcite. This locality is also listed as Otter Lake, in many mineral dealer catalogues. The area has recently been investigated for radioactive minerals known to occur in the skarn zone (Kretz 1957; Shaw 1958). For the present study a 7 cm long apatite crystal from the Yates property was selected from the mineralogy collection at École Polytechnique.

Physical and optical properties

The apatite crystals from the Yates property are well-formed prisms {10$\bar{1}$0} that are doubly terminated {10$\bar{1}$1}. They vary in colour from the most commonly found deep green to red and brown. The length ranges from 2 to more than 30 cm while the widths range from a fraction to several centimeters. A polished thin section cut perpendicular to the long dimension shows trace quantities of calcite inclusions and a few small red stains assumed to be of iron oxide. In transmitted light the apatite is colourless. The indices of refraction measured in sodium light ($\lambda = 589$ mμ) are $\omega = 1.638$ and $\varepsilon = 1.633$. The indices of the oils where checked with an Abbé refractometer immediately after each determination. The specific gravities of four different apatite grains, measured with a Berman balance and toluene at 28°C, were found to be 3.30, 3.36, 3.21, and 3.23, an average of 3.28. The density and the indices of refraction correspond closely to those listed for fluorapatite in Deer, Howie & Zussman (1962).

Chemistry

To check the homogeneity of the crystal two perpendicular microprobe traverses, parallel to the long and short axes of the crystal, were made on the polished thin section. Using the homogeneity index of Boyd *et al.* (1969) the four elements (P, Ca, Ce, and Si) present as more than 1 wt. % oxide have *H*-values significantly less than 3 (table 1), indicating homogeneity within the crystal.

A complete chemical analysis (table 1) of a portion of the crystal was carried out in the Laboratoire de Géochimie analytique at École Polytechnique. To eliminate the calcite inclusions the original material was gently washed in dilute acetic acid. The remaining CO_2 in the analysis is regarded as structural CO_2. Fe_2O_3 found by the chemical analysis is assumed to account for the red staining and thus has been subtracted from the recalculated analysis (table 1).

TABLE 1. CHEMICAL ANALYSIS OF HUDDERSFIELD APATITE

Foot-note	Wt. %	As Analyzed	Recalc. free of Fe_2O_3	No. of ions on basis of 26(O,OH,F)		
1	P_2O_5	38.26	38.08	P	5.55	6.16
2	CO_2	0.88	0.88	C	0.21	
3	SiO_2	1.76	1.75	Si	0.30	
2	SO_3	0.72	0.72	S	0.09	
6	CaO	53.91	53.66	Ca	9.35	9.59
3	SrO	0.28	0.28	Sr	0.03	
3	Y_2O_3	0.15	0.15	Y	0.01	
3	Ce_2O_3	1.23	1.22	Ce	0.08	
3	La_2O_3	0.44	0.44	La	0.03	
4	Na_2O	0.28	0.28	Na	0.09	
	Fe_2O_3	0.13	--			
5	F	3.92	3.90	F	2.12	2.45
2	H_2O^+	0.29	0.29	OH	0.33	
	Total	102.25	101.65			
	F = O	1.65	1.64			
		100.50	100.01			

HOMOGENEITY INDICES

Element:	P	Ca	Si	Ce
H:	1.22	1.67	1.14	1.84

1. gravimetric methods 2. firing in induction furnace and then by volumetry of evolved gases 3. x-ray fluorescence 4. atomic absorption 5. specific electrodes 6. see text

The complex nature of the Huddersfield apatite made it necessary to use a combination of gravimétric, volumetric and instrumental techniques. Minor elements and rare earths were measured by *x*-ray fluorescence. CaO was precipitated as an oxalate in a weak acidic solution. Because some rare earths and phosphorus came down with the calcium it was necessary to redissolve the oxalate and reprecipitate the last vestiges of the rare earths and phosphorus (Hildebrand *et al.* 1953). Determinative methods for the other elements are given in table 1.

On the basis of 26(O,OH,F), phosphorus is less than the ideal 6 anions. The difference is more than compensated for by the addition of C, Si, and S, which give a total of 6.152 in the *P* structural site. In the *C* structural site the sum of cations is 9.588, less than the ideal 10. This inverse occupancy relationship was also found by McClellan & Lehr (1969) in their general study of apatites.

X-ray data

Approximately 5 grams of the crystal and 2 grams of quartz were thoroughly ground together under acetone in an agate mortar to produce a homogeneous powder for *x*-ray diffraction studies. The seven quartz lines observed on the diffractometer trace served as an internal standard and showed that the 2θ measurements are valid to a standard deviation of 0.01° 2θ. Cu$K\alpha$ radiation and a graphite monochrometer were used to produce the diffractometer trace. Twenty-two lines between $20° - 55°$ 2θ were used to refine *a* and *c* using the computer program PARAM of Stewart *et al.* (1972). The refinement procedure gave final values of : $a = 9.3796(2)$ and $c = 6.8924(2)$ where the numbers in parentheses are the standard deviation in units for the last given digit. Table 2 shows that the data for the Huddersfield apatite are nearly identical to those of synthetic fluorapatite.

From the chemical and *x*-ray data the most important substitutions are Si^{4+} and C^{4+} for P^{5+}. Substitution of Si^{4+} for P^{5+} commonly leads to vacancies in the F^{1-} and Ca^{2+} positions (McClellan & Lehr 1969) as well as an increase in the *a* and *c* cell dimensions. Substitution of C^{4+} for P^{5+} decreases *a* without significantly affecting *c*.

Relationship of chemistry, density and refractive indices

As a check of the internal consistency of chemical, optical and density data, one may use the rule of Gladstone and Dale (Jaffe 1956) : $n - 1 = dK$ (Table 3). The density calculated from the *x*-ray data and chemical composition is 3.17 assuming 26(O,OH,F) in the unit cell From the chemical composition and refractiv indices the density calculated by the rule o Gladstone and Dale is 3.13 (Table 3). This valu is lower than the average measured density 3.28 The discrepancy may be reduced if we us $K(P_2O_5) = 0.170$, which is the value for syn thetic fluorapatite (Jaffe 1956). P_2O_5 was choser as having too high a *K*-value (Larsen & Bermar 1934) because the other major component ir apatite, CaO, has a *K*-value that is consisten for other major CaO-bearing minerals (Jaff 1956). It was also found that the calculatec densities for apatites in Deer, Howie & Zussmar (1962) are lower than measured densities. Usin

TABLE 2. *X*-RAY POWDER PATTERNS OF FLUORAPATITE

Huddersfield Township, P.Q.				Synthetic $Ca_5(PO_4)_3F$ **	
I/I_1	*d*(meas.)	*d*(calc.)	*hkl*	*d*	I/I_1
			100	8.12	8
			101	5.25	4
			110	4.684	<1
8	4.053	4.061	200	4.055	8
6	3.880	3.878	111	3.872	8
			201	3.494	<1
53	3.452	3.446	002	3.442	40
11	3.170	3.172	102	3.167	14
18	3.069	3.070	210	3.067	18
100	2.803	2.804	211	2.800	100
41	2.777	2.777	112	2.772	55
42	2.707	2.708	300	2.702	60
21	2.629	2.628	202	2.624	30
4	2.520	2.520	301	2.517	6
5	2.294	2.292	212	2.289	8
16	2.252	2.253	310	2.250	20
2	2.222	2.220	221	2.218	4
7	2.142	2.141	311	2.140	6
			302	2.128	4
4	2.059	2.063	113	2.061	6
			400	2.028	2
3	2.001	2.000	203	1.997	4
20	1.943	1.939	222	1.937	25
11	1.887	1.886	312	1.884	14
4	1.864	1.864	320	1.862	4
24	1.849	1.840	213	1.837	30
12	1.800	1.799	321	1.797	16
12	1.773	1.773	410	1.771	14
12	1.750	1.750	402	1.748	14
35	1.724	1.723	004	1.722	16
a=9.3796(2), c=6.8924(2)Å				a=9.3684, c=6.8841Å	

**JCPDS 15-876

TABLE 3. COMPARISON OF THE MEASURED DENSITY WITH THAT COMPUTED FROM THE RULE OF GLADSTONE AND DALE*

Weight %		$K^{\dagger}$	$\phi K/100$	Weight %		$K^{\dagger}$	$\phi K/100$
P_2O_5	38.08	0.190(0.170)	.0724(.0647)	Ce_2O_3	1.22	0.149	.0018
CO_2	0.88	0.217	.0019	La_2O_3	0.44	0.142	.0006
SiO_2	1.75	0.207	.0036	Na_2O	0.28	0.181	.0005
SO_3	0.72	0.177	.0013	F	3.90	0.043	.0017
CaO	53.66	0.225	.1207	H_2O^+	0.29	0.335	.0010
SrO	0.28	0.143	.0004	O ≡ F	1.64	0.203	-.0033
Y_2O_3	0.15	0.170	.0003			K=.2029(.1952)	

$(2\omega+\varepsilon)/3=[2(1.638)+1.633]\ /\ 3=1.636$

$(n-1)/K=d \quad (1.636-1)/(0.029)=3.13(K_{P_2O_5}=0.19)$

$(1.636-1)1.953=3.26(K_{P_2O_5}=0.17) \qquad d(\text{measured})=3.28$

* $n-1=dK$ where $n=(2\omega+\varepsilon)/3$, d=density, $K=\Sigma[(\phi_iK_i)/100]$; ϕ_i=oxide wt. of each component and K_i=specific refractive energy of oxide component i (Larsen & Berman 1934; Jaffe 1956).

† K values taken from Larsen & Berman (1934) except for Y_2O_3, Ce_2O_3, and La_2O_3 which are from Jaffe (1956).

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7	.0036	Na_2O 0.28	0.181	.0005
7	.0013	F 3.90	0.043	.0017
5	.1237	H_2O^* 0.29	0.335	.0010
3	.0004	O = F 1.64	0.203	-.0033
3	.0033		K=.2009(.1962)	

=1.633] / 3=1.636

6-1)/(0.029)=3.13($K_{P_2O_5}$=0.19)

26($K_{P_2O_5}$ = 0.17) d(measured)=3.28

Kn=1/3, d=density, $K=\Sigma[(a_iK_i)/100]$; a_i=oxide wt. % and K_i=specific refractive energy of oxide com- & Berman 1934; Jaffe 1956).

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$K(P_2O_5)$ = 0.170 gives a density of 3.26 for the Huddersfield apatite, and it gives a better agreement between the measured and calculated densities in Deer, Howie & Zussman. It is therefore suggested that $K(P_2O_5)$ = 0.170 be used when applying the rule of Gladstone and Dale. Young & Munson (1966) also suggested that the *K*-value for P_2O_5 in Larsen & Berman (1934) is too high.

Initially the work on the Huddersfield apatite was done to establish a phosphate standard for our microprobe laboratory. As a result about 15 grams of the analyzed crystal are available for exchange with interested laboratories for other standards.

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