

CARBONATE-BEARING APATITE FROM FARADAY
TOWNSHIP, ONTARIO, CANADA¹

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ABSTRACT

A new complete chemical analysis of a well-known reference fluorapatite has shown a paired substitution of CO₃ ion and F ion for PO₄ ion, and a balanced pair of Na ion and rare earth ions in substitution for Ca ion.

Apatite from Faraday Township, Ontario, Canada, has long been used as a reference fluorapatite, Ca₁₀(PO₄)₆F₂,—most notably in Dana's System of Mineralogy (Palache, *et al.* 1951, p. 883). The two extant analyses (Dadson, 1933; Walker and Parsons, 1926) of this apatite both show significant amounts of CO₂, which has been attributed to impurities in the sample. On a hunch that the mineral is actually a carbonate-bearing apatite, a sample was obtained from the Royal Ontario Museum for new studies. The new data show not only that the carbonate is indeed in the apatite mineral but also that other substitutions are involved. They also serve to emphasize the need for obtaining accurate and complete data on apatite compositions.

The apatite of this study is from the Basin Property, Lot 31, Concession XV, Faraday Township, the geology of which has been described by Hewitt (1957). It occurs in crystals up to 2 feet in length in a small lenticular carbonate body, 400 feet long by an average of 50 feet thick. The carbonate body lies within a mass of biotite amphibolite in the trough of a syncline formed mainly of syenitic and nepheline syenite gneisses. In addition to apatite and calcite, this body has large crystals of lepidomelane, amphibole, albite, and betafite, and small amounts of zircon, fluorite, sphene, molybdenite and pyrrhotite. As noted by Hewitt, the origin of this carbonate body is in dispute. Many of its characteristics are similar to those of carbonatites, and the deposit is undoubtedly a carbonatite within the definition of Pecora (1956).

The sample for chemical analysis was prepared from clear green crystal fragments which were first ground to minus 200 mesh. In a water mixture the fines of this fraction were decanted and about 25 grams with a grain size range of about 50–74 μ was left for use. This portion was then cleaned of impurities by centrifuging in heavy liquid of specific gravity slightly

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greater than that of the apatite and then in liquid of specific gravity slightly less than that of the apatite. The specific gravity of the apatite is 3.220 ± 0.005 , as determined by a Christian Becker specific gravity balance on a liquid in which the grains of apatite had been evenly distributed after centrifuging. No impurities were observed in the sample by microscopic examination.

TABLE 1. CHEMICAL COMPOSITION OF ONTARIO APATITE AND CALCULATION OF STRUCTURAL FORMULA

	Per cent by weight	Atom ratios		Atoms ^a		Atoms ^b	
CaO	54.7	.9754	Ca	9.88		9.84	
MnO	.15	.0021	Mn	.02		.02	
SrO ^c	.18	.0017	Sr	.02		.02	
Na ₂ O	.18	.0058	Na	.06		.06	
(RE) ₂ O ₃ ^d	.76	.0047	(RE)	.05		.06	
				10.03		10.00	
P ₂ O ₅	40.9	.5763	P	5.84		5.87	
CO ₂	.57	.0130	C	.13		.13	
				5.97		6.00	
		1.5790					
			Total	16.00		16.00	
F	4.0	.2105	F	2.13		2.13	
	101.44						
O=F	1.68						
	99.76						
Structural formula:							
$\text{Ca}_{92.84}\text{Mn}_{.02}\text{Sr}_{.02}\text{Na}_{.06}(\text{RE})_{.06}(\text{P}_{5.87}\text{C}_{.13}\text{O}_{22.87}\text{F}_{.13})\text{F}_2$							
Other constituents (per cent by weight):							
Si ^e	.070	K ₂ O	.03	B ^f	.001	Zr ^g	.0033
Al ^e	.0014	H ₂ O ^{+e}	< .006	Cu ^e	.0006	Cl ^g	< .002
Fe ^e	.036	H ₂ O ⁻	.03	Pb ^e	.003		
Mg ^e	.0040	SO ₃	< .03	Sc ^f	.002		
The following elements were looked for but not found (limit of detectibility in per cent by weight in parentheses) ^f :							
Ag	(.00007)	Cr	(.0001)	Nb	(.001)	Te	(.2)
As	(.02)	Ga	(.0002)	Ni	(.0002)	Th	(.02)
Au	(.002)	Ge	(.0007)	Pd	(.0001)	Ti	(.0003)
Ba	(.0002)	Hf	(.005)	Pt	(.001)	Tl	(.005)
Be	(.0001)	Hg	(.1)	Re	(.002)	U	(.05)
Bi	(.0007)	In	(.0002)	Sb	(.02)	V	(.0002)
Cd	(.005)	Li	(.02)	Sn	(.0007)	W	(.003)
Co	(.0002)	Mo	(.0002)	Ta	(.01)	Zn	(.05)

^a Calculated to total of 16 cations in unit cell.

^b Recalculated to an even 10 cations in Ca positions and 6 cations in P positions. Ca atoms arbitrarily decreased .01 atom and (RE) increased .01 atom to provide for balance of charges.

^c Quantitative spectrographic analyses.

^d Total rare earths including Y and Th. Average atomic weight of 139.11 used in calculations. It is weighted average on the basis of the abundances of the rare earths and Y as shown by semiquantitative determinations.

^e Infrared determination.

^f Semiquantitative spectrographic analyses by Chris Heropoulos.

^g Potentiometric determination using Ag electrode and titrating with AgNO₃.

The sample was analyzed in the laboratories of the U. S. Geological Survey and yielded the results shown in Table 1. The calculated structural formula, shown in the table, includes only those elements present in amounts greater than 0.1 per cent. None of the kinds of indicated substitutions are new (see excellent review of apatite compositions by Deer *et al.* (1962, p. 324), but the acceptance of carbonate substitution in apatite has been slow in coming. The balance of excess F atoms with C atoms, shown in structural formula of Table 1, helps to make the carbonate substitution more plausible. It suggests that the CO₃ ion is accompanied by an F ion in its replacement of a PO₄ ion. Not only is the charge balance maintained by this means, but the tetrahedral coordination for P-position atoms is preserved. This type of substitution does produce, however, a decrease in total charges in the structure. Excess F has been noted by many investigators, but in amount generally less than that required to balance C atoms. Many seemingly low values are possibly due to the difficulty of determining fluorine accurately. Another example of the balance of excess F atoms and C atoms in an apatite, though, is shown by DeVilliers (1942). Presumably OH ions can act in the same fashion in place of, or together with, F ions (Cl substitution is not considered here). If neither of these ions is present in excess, holes will be left in the structure, and a Ca deficiency will result in order to maintain an overall charge balance. Although the results described above preclude the presence of OH ions in the Ontario apatite, a possibly significant amount could not be excluded by regular analytical means. Infrared analysis showed, however, that the amount of OH is less than 0.006 per cent and that OH is effectively absent.

Infrared analysis provides, also, information about the characteristics of the CO₃ ion in the apatite structure. Part of the Ontario apatite spectrum is shown in Fig. 1 along with corresponding spectra of a fluorapatite that contains no carbonate and one that contains 1.44 per cent CO₂. The large absorption maximum in the central part of all three curves is due to the PO₄ ion. The small pair of peaks at 6.88 and 7.00 μ on the Ontario and Phosphoria apatite curves is due to CO₃ ion absorption. Because the absorption curve of calcite (Adler and Kerr, 1963) is characterized by only one peak (7.02–7.03 μ) in this region, the pair of peaks appears unique to carbonate-apatite and indicates that the environment of the CO₃ ion in carbonate-apatite is different from that in calcite. Another absorption peak of CO₃ ion in the carbonate-apatites is barely detected at 11.56 μ , which represents a shift from its correlative position (11.40–11.41 μ) in the calcite spectrum. The third main absorption peak of CO₃ ion (at about 14 μ) found in the calcite spectrum is not detected in these spectra.

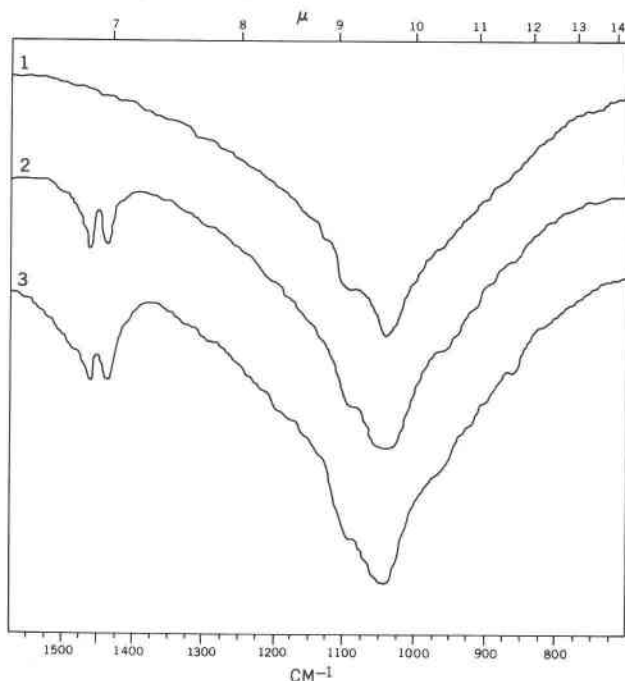


FIG. 1. Tracings of part of infrared absorption curves of apatites in KBr pellets. Apatite 1, Mount Auburn, Maine, no CO_2 ; apatite 2, Ontario, this paper, 0.57 per cent CO_2 ; apatite 3, Phosphoria Formation, Wyoming, 1.44 per cent CO_2 .

The small but significant amount of rare earths found in this apatite has not been recognized previously. Cruft (1965) found that apatites from various metamorphic and igneous environments are all enriched in rare earths relative to the earth's crust. One per cent cerium oxide is reported in an apatite from the Mbeya carbonatite (Fick and van der Heyde, 1959) and large amounts of rare earth oxides, an average of 11.14 per cent, occur in an apatite from magnetite ore (McKeown and Klemic, 1956). It seems likely that rare earths are characteristic of apatite and have been overlooked in past analyses.

Rare earths fit well in the apatite structure due to the close similarity of their ionic sizes with that of calcium. In substitution for calcium, the generally trivalent rare earths require, however, a compensating substitution that preserves the charge balance. In the Ontario apatite this is accomplished by sodium, and the atom balance of the pair that is calculated in Table 1 is well within the range of analytical variation.

A means of checking the chemical composition determined above for the Ontario apatite is provided by comparing calculated and measured

TABLE 2. DENSITY AND CELL DIMENSIONS OF ONTARIO APATITE

Cell dimensions:
$a = 9.368 \pm .002 \text{ \AA}$
$c = 6.890 \pm .002 \text{ \AA}$
Cell volume = 523.59 \AA^3
Density:
Measured = 3.220
Calculated = 3.211

densities or specific gravities (Table 2). The agreement between the two values is good, particularly in view of the possible variations inherent to the calculated density.

Although the goal of obtaining accurate mineral compositions is universal, its attainment for apatites may be more useful to petrology than it would be for many other minerals or mineral groups. Apatite is nearly ubiquitous in its modes of occurrence; it forms in all the major environments—sedimentary, metamorphic and igneous. It is notable for the large number of elements that have been reported as substitutions for its principal components. Characteristically many of the substitutions are in small amount, and extensive solid solution is rare. Whereas the complexity of apatite composition makes complete and accurate analyses a necessity in order not to miss significant constituents, this very complexity may well be turned to advantage by helping to define conditions of apatite formation more completely than can now be done. Carbonate-bearing apatites possibly have more utility for this purpose than most others. They are the only ones which are known to be dependent upon pressure for stability at moderate to high temperatures.

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