

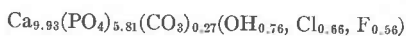
## A CARBONATE-BEARING FLUOR-CHLOR-HYDROXYAPATITE FROM MATALE, CEYLON

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### ABSTRACT

Euhedral to subhedral crystals of blue apatite from 1 to 7 cm long occur in a partly serpentinized marble from a quarry near Matale, north-central Ceylon.

The chemical composition of the apatite is as follows: CaO 55.24, MnO 0.02, P<sub>2</sub>O<sub>5</sub> 40.91, F 1.05, Cl 2.31, H<sub>2</sub>O 0.68, CO<sub>2</sub> 1.18, Fe<sub>2</sub>O<sub>3</sub> 0.03, O=F, Cl 1.17, total 100.25 percent. The calculated cell contents on the basis of 26(O, OH, F, Cl) are



which corresponds to the theoretical formula Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH, F, Cl); the ratio F:Cl:OH is 1.0:1.17:1.36. The composition, as determined, is unusual, and warrants the name carbonate-bearing fluor-chlor-hydroxyapatite. The other properties are  $\epsilon$  1.646,  $\omega$  1.651, density (at 25°C) 3.18.

The apatite crystals are thought to have been formed during regional metamorphism, under granulite facies conditions, of a phosphatic sedimentary limestone.

### INTRODUCTION

Apatite is a common accessory mineral of the marbles of Ceylon and generally occurs as minute pale-blue or sky-blue prismatic crystals with somewhat rounded outlines. In a quarry just outside Matale, north-central Ceylon, however, crystals of blue apatite several centimeters in length occur in a marble which is highly serpentinized in parts. The mode of occurrence, properties, and composition of this apatite are described.

### MODE OF OCCURRENCE OF APATITE

The marble occurs as a wide band running from south to north just east of Matale town, and is being quarried at a spot about 2 miles along the road to Pitakande. The marble is variable in colour and texture and contains numerous patches and bands rich in silicate minerals such as diopside and forsterite. A greenish hue is given to the rock by the presence of green serpentine in streaks and patches.

Pale blue apatite occurs either as euhedral to subhedral prismatic crystals with rounded and pyramidal terminations or as irregularly shaped masses. The crystals vary from 1 to 7 cm in length and up to 3 cm in diameter. The apatite is found mostly in the calcitic portions of the rock though a few crystals occur on the boundaries of or within the grayish-blue forsterite-rich bands and the saccharoidal diopsidic portions; only rarely are they found with the serpentinized portions of the marble. The alignment of some of the smaller prismatic crystals of apatite suggests some degree of plasticity and flowage in the marble after the formation of these crystals.

### PETROGRAPHY OF THE MARBLE

The marble is made up of calcite and dolomite, with forsterite, diopside and apatite; green serpentine is a prominent alteration product of forsterite.

Calcite and dolomite are intimately intergrown in a manner similar to that described by Coomaraswamy (1902) and Adams (1929), and a graphic intergrowth of the two minerals is also present. Many of the crystals of calcite and dolomite are altered to brownish black patches in which are developed stubby, bleb-like crystals of an unidentified mineral, arranged radially. There appears to be some correlation between the amount of alteration of the carbonates and the degree of serpentinization of silicates in the same thin section.

Forsterite occurs as colorless crystals which are variously altered to serpentine, the amount of serpentinization varying from slight alteration along margins and cracks to the formation of complete pseudomorphs. No iron ore has been liberated in the serpentinization, indicating almost pure magnesium olivine. Kelyphitic rims of diopsidic pyroxene are best developed where the forsterite is in contact with dolomite. Serpentinization is absent or nearly so in forsterite crystals completely enclosed by apatite.

Colorless diopside ( $2V = 50^\circ - 60^\circ$ ,  $Z \wedge c$  max.  $45^\circ$ ) is less common in the marble proper, but forms bands and lenses of pure diopsidic rock.

Serpentine, formed by alteration of forsterite, is very pale green to colorless and is both fibrous and lamellar in form. Pseudomorphs of serpentine are made up of a mixture of serphite and antigorite.

Apatite is colorless and clear, and some crystals are traversed by two sets of fractures, inclined at about  $70^\circ$  to each other, one set being parallel to the prism edge. The mineral occurs as scattered grains in the marble or as irregular masses associated with forsterite, sometimes enclosing it completely. It is uniaxial negative and the interference colours shown are shades of gray.

#### PROPERTIES OF APATITE

Crystals of apatite have a prismatic habit of varying length, with the prism  $\{10\bar{1}0\}$  and the pyramid  $\{10\bar{1}1\}$  as the dominant forms. They are pale bluish or bluish green in color, translucent, and with vitreous luster. Basal cleavage is sometimes developed, especially in the larger crystals.

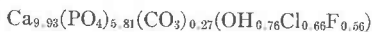
The separation of material for analysis and determination of constants did not present any special problem owing to the relative purity of the idiomorphic crystals. Fragments of these were broken off, hand-picked and crushed, and the admixed calcite and serpentine separated with bromoform. The density was measured on coarse fragments by suspension in methylene iodide diluted with benzene, and the indices of refraction were determined for sodium light using an Abbe refractometer. The chemical composition, cell contents, and optical properties of the apatite are shown in Table 1.

It can be seen from the above analysis that the apatite from Matala conforms to the general formula  $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$  with a slight deficiency of Ca ions as well as an excess of (P+C). This raises the question of substitution in natural apatites which has been commented on by others. In the present instance, excess of  $(\text{CO}_3)^{-2}$  and deficiency in the  $(\text{F}, \text{Cl}, \text{OH})^{-1}$  group is compensated for by deficiency in the divalent  $\text{Ca}^{+2}$  cations. Obviously, the  $(\text{CO}_3)^{-2} + \text{F}^{-1}$  substitution for  $(\text{PO}_4)^{-3}$  on the basis of one-for one  $\text{P} \rightleftharpoons \text{C}$ , as observed by Gulbrandsen *et al.* (1966) is not confirmed by the apatite from Matala. The ratio of F:Cl:OH is 1.0:

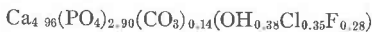
TABLE 1. CALCULATED CELL CONTENTS OF APATITE FROM MATALE ON BASIS OF 26 (O, OH, F, Cl)

Oxide	Wt. %	Atoms
CaO	55.24	9.932
MnO	0.02	.003
Fe <sub>2</sub> O <sub>3</sub>	0.03	.004
		} 9.939
P <sub>2</sub> O <sub>5</sub>	40.91	5.812
CO <sub>2</sub>	1.18	.270
		} 6.082
F	1.05	.558
Cl	2.31	.656
H <sub>2</sub> O	0.68	.761
O = F, Cl	-1.17	
		} 1.975
Total	100.25	

Formula:



or

Optics:  $\epsilon$  1.646  $\omega$  1.651

Density: (at 25°C) 3.18

Analyst: J. P. R. Fonseka, Geological Survey Department, Ceylon, 1958.

1.17:1.36, the corresponding ratio for the calculated composition of apatite for the formula cited being 1:1:1 (Palache, Berman, and Frondel, 1951, p. 883, anal. 1).

The apatites are generally named according to the relative proportions of F, Cl, OH and CO<sub>2</sub> in the unit cell, CO<sub>2</sub> (occurring as CO<sub>3</sub>) now being known to be an essential constituent of the apatite structure. In the present analysis, CO<sub>2</sub> appears to be substituting for PO<sub>4</sub> and the amount of CO<sub>2</sub> present in the unit cell is significant enough for it to be called a carbonate-fluor-chlor-hydroxyapatite, or at least a carbonate-bearing fluor-chlor-hydroxyapatite.

The composition of the apatite from Matale, as determined in this report, thus appears to be rare, if not unique, containing as it does significant amounts of (OH) as well as of Cl and CO<sub>2</sub> in its structure. Such a composition supports the probability that there is "a complete isomorphous series in natural apatites" (Deer, Howie and Zussman, 1966, p. 505).

The density agrees with that for both chlorapatite and fluorapatite (artificial: F = 3.18; Cl = 3.17). The index of refraction  $\omega$  is intermediate

in value between those for pure chlorapatite and fluorapatite (Deer, Howie and Zussman, 1966, Fig. 183) and the birefringence is high for a chlorapatite, due to the relative high values of (OH) and Cl). By comparison, blue apatite occurring as minute crystals disseminated in marble from Digane, Kandy, had  $\omega = 1.636$ ,  $\epsilon = 1.634$ ,  $B = 0.002$ .

Blue apatite is one of the most common accessory minerals in the marbles of Ceylon and the only other full analysis available, made at the beginning of the century, is of a fluorapatite with 15 percent chlorapatite and a calculated formula of  $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl})$  (Schiffer, 1900). Partial analyses are also available, made about the same time, and these also show relatively low contents of Cl e.g. 0.34 and 0.63 percent (Church, 1901). Only in one instance was a high Cl content of 3.21 percent noted.

The origin of the apatite from Matale which is of uncommon composition is not clearly defined. There are no apparent igneous or hydrothermal sources of the constituents OH, F, Cl. On the contrary, nearly all the metasedimentary marbles of Ceylon contain minute crystals of apatite and it is probable that the comparatively large crystals of apatite in the occurrence at Matale were also formed during regional metamorphism, under granulite facies conditions, of the metasedimentary Highland Series (Cooray, 1962) of which this marble is a part. The large size of the crystals may have been due to a local concentration of  $\text{P}_2\text{O}_5$  in a possibly phosphatic sedimentary limestone.

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