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Hydroxyl-chlorapatite from the St Austell Granite, Cornwall, England

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CHLORAPATITE, $Ca_5(PO_4)_3Cl$, is a relatively rare member of the apatite group. Most reported occurrences have been in basic igneous rocks such as gabbro, but the species is also reported from calc-silicate marbles and as microgranules in meteorites (e.g. Palache *et al.*, 1951; Roberts *et al.*, 1990). Chlorapatite has not been reported previously in the British Isles. Qualitative analyses of apatite in Welsh metabasites (e.g. at Tal y Fan, Gwynedd) and in Silurian rhyolites from Skomer, west Wales, show the presence of Cl, but analyses are incomplete (R.E. Bevins, pers. comm., 1996). Minor Cl (~0.3 wt.%) was recorded in bulk analyses of rock composed largely of apatite from near Sanquhar, Dumfries, Scotland (Kennedy and Harvey, 1935), and prisms of hydroxylapatite from joint surfaces around the Scrabo Hill explosive volcanic vent, Co Down, Ireland, are sometimes altered to a fibrous apatite, tentatively identified as chlorapatite on the basis of refractive index and birefringence (Preston, 1962), but no analysis is given for the latter specimen.

Chlorapatite has recently been identified on two specimens from Gunheath China Clay Pit, St Austell, Cornwall (NGR SX 005571). EDX analysis (Table 1) shows that the mineral is actually a hydroxyl-chlorapatite. On the basis of 12.5 oxygens, the structural formula is $(Ca_{4.4}Mn_{0.4}Fe_{0.2})_{\Sigma=5.0}(PO_4)_{3.1}(Cl_{0.6}OH_{0.3})_{\Sigma=0.9}$. Oxygen was determined by difference. Additional semi-quantitative analyses were conducted with a windowless detector, but no F could be detected (limit of detection ~0.05 wt.%). FTIR spectroscopy confirmed the presence of OH^-, but showed no significant absorptions due to CO_3^{2-}.

Powder diffraction data were collected over the range 8–55°2θ and corrected for systematic errors using NIST SRM 675 fluorophlogopite as an internal standard. The unit cell (hexagonal setting, $P6_3/m$) was refined from 14 lines yielding $a = 9.537(1)$, $c = 6.799(1)$ Å; vol = 535.5(1) Å^3. Figures of merit were M(14) = 83.1 and F(14) = 55.6 (0.0079, 32), giving high confidence in the refined cell. Synthetic end-member chlorapatite and hydroxylapatite are monoclinic, $P2_1/b$ (see for example Hughes *et al.*, 1989, and references therein), but Schaeken *et al.* (1975) show that hexagonal binary F-OH apatites reasonably obey Vegard's law, and the data of Ekström (1973) suggest that the same is true for the Cl-OH apatite series. Using unit-cell data for end-member chlorapatite and hydoxylapatite quoted by Tacker and Stormer (1989), application of Vegard's law to the refined cell for the Gunheath chlorapatite indicates a fractional Cl content in the range 0.5–0.7, consistent with that determined by EDX. Substitution for Ca^{2+} by Mn^{2+} and Fe^{3+} or Fe^{2+}, as observed in the Gunheath chlorapatite, will reduce the cell volume and the estimate of Cl content from cell dimensions may be an underestimate.

TABLE 1. EDX analysis of Gunheath chlorapatite (wt.% element)

Element	1	2	3
Mn	3.8	–	–
Fe	1.9	–	–
Ca	33.9	38.48	40.22
P	18.2	17.84	18.65
Cl	3.7	6.81	–
F	n.d.	–	–
0	38.5	36.87	40.94
H	–	–	0.19
Total	100.0	100.00	100.00

1. Hydroxyl-chlorapatite from Gunheath China Clay Pit, St Austell, Cornwall. SEM-EDX analysis, 5×10^{-10} A, 25 kV. Average of 8 analyses. O by difference. n.d. = not detected (< 0.05 wt.%)
2. Ideal chlorapatite, $Ca_5(PO_4)_3Cl$.
3. Ideal hydroxylapatite, $Ca_5(PO_4)_3OH$.

The Gunheath chlorapatite occurs as a pale brown-cream horn-like encrustation (to around 1 cm thick) on a complex matrix of mixed phosphates. Black barbosalite forms the bulk of the matrix, but intermediate members of the frondelite–rockbridgeite and chalcosiderite–turquoise series are also present, together with minor leucophosphite. The matrix is veined with chalcocite, and grains of quartz, fluorapatite and cassiterite are scattered throughout. A few grains of fluorapatite and some microscopic blobs of silica or quartz are contained within the chlorapatite, but otherwise the chlorapatite is fairly homogenous, unlike the remainder of the specimen which is composed of complex and small-scale intergrowths of the other species mentioned above. A few minute intergrown crystals of chlorapatite occur in small vugs within the massive chlorapatite.

Gunheath Pit is known for a range of unusual secondary phosphates (e.g. Weiss, 1994). A few species, notably fluorapatite, occur in pegmatite sheets in the northern part of the pit. Most species, however, are found in iron-stained fracture veins within partially kaolinized granite from the same area. The specimens of chlorapatite were collected by the late M.J.E. Grigg from such veins around 1987. The occurrence of chlorapatite in such a geological environment is unusual.

Hydroxlapatite has been reported with triphylite-derived phosphates in the White Elephant pegmatite, Black Hills, Dakota (see under mitridatite, Roberts *et al.*, 1990) and at Gunheath itself as a surface alteration of fluorapatite (Weiss, 1994). Chlorapatite is reported with phosphates in the d'Angarf-Sud pegmatite, Maroc (Fransolet *et al.*, 1985). The phosphate suite at the latter location is also triphylite-derived and chlorapatite was formed at an intermediate stage in the paragenetic sequence before species such as barbosalite, lipscombite and mitridatite. Unfortunately, paragenetic evidence for the Gunheath chlorapatite is equivocal, and it is not possible to locate this species with any certainty in the sequence of secondary phosphate formation.

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