Dielectric properties of hydroxyapatites—a reply

It is, of course, true that Kay, Young, and Posner (1964) showed that the hydroxyl ion is *not* exactly centred in the plane of the calcium ions, and we regret this error. However, our intention was really to contrast the known good properties (low dielectric loss) of the hydroxylapatites where the hydroxyl ion occupies the (2a) site, albeit slightly displaced, with the possibly less favourable situation found in chlorapatites and pyromorphites where halogens (other than F) occupy the (2b) site. By assuming that the Ca ions lie on the *a* plane (i.e. a *y* co-ordinate of 1·000 instead of 0·993) simple calculation using the usual ionic radii shows that the hydroxyl ions must occupy similar situations in both $Ca_{10}(PO_4)_6.(OH)_2$ and $Ca_4La_6(SiO_4)_6(OH)_2$.

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Lead apatite solid-solution series

Recent studies on the crystal chemistry of the apatites (Cockbain, 1968) have shown that apatites with the general formula $A_{10}(XO_4)_6.Z_2$, including the lead apatites or pyromorphites, may be classified into three groups on the basis of the ratio of the size of the A ion to the X ion. Vanadinite has a ratio of 2·21 and belongs to the first group, mimetite has a ratio of 2·82 and belongs to the second group, while pyromorphite itself has a ratio of 3·76 and falls in the third group.

Continuous solid-solution series between these three minerals have frequently been postulated, and experimental studies such as those of Baker (1966) tend to support this view. However, calculations have shown that the discontinuities postulated by Cockbain (1968) cover only restricted composition ranges, and it was thought desirable to re-examine some of the mineral members of the series for evidence of these discontinuities.

A selection of pyromorphite crystals from Roughtengill, Caldbeck Fells, Cumberland (Grid Ref. NY302346) was collected by the author and these comprised the typical 'barrel'-shaped yellow-green or brownish-green crystals, together with some that had an epitaxial growth on one end of tapered hexagonal green prisms (fig. 1). The 'barrel' shape suggested that these were in fact two-phase intergrowths, i.e. they resulted from simultaneous crystallization of two hexagonal apatites that were mutually immiscible, and X-ray diffraction has confirmed this. The two pyromorphite phases have *a* 10·14 Å, *c* 7·42 Å, and *a* 9·97 Å, *c* 7·32 Å, respectively. The tapered hexagonal crystals growing epitaxially have *a* 9·97 Å, *c* 7·32 Å, and are thus identical with one phase of the barrel-shaped crystals, and presumably grew from the ore fluids when they were depleted in the other pyromorphite phase. Although chemical analyses have not been carried out, *a* 9·97, *c* 7·32, corresponds to a pure pyromorphite $Pb_{10}(PO_4)_6.Cl_2$.

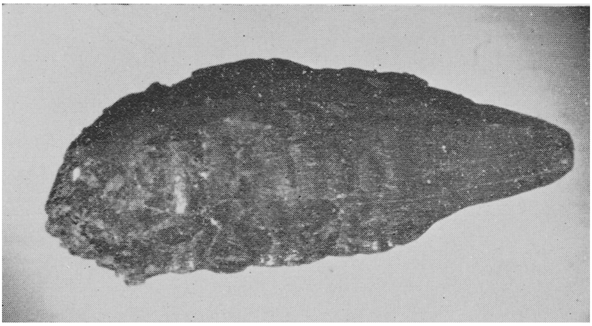

FIG. 1. A crystal from Roughtengill, Cumberland, showing growth of a tapered prism of single-phase pyromorphite on a two-phase base with typical rounded barrel-shaped faces. ×7½.

Assuming that Vegard's Law holds for the system $Pb_{10}\{(P,As)O_4\}_6.Cl_2$ it is possible to calculate that the discontinuity in the series corresponding to $A{:}X$ ratios in the range from 3·25 to 3·35 should correspond to *a* between 10·09 Å and 10·12 Å and *c* between 7·38 Å and 7·395 Å. The two-phase barrel-shaped pyromorphite crystals appear therefore to correspond to a mixed mimetite saturated with the pyromorphite molecule, possibly containing 10% of another apatite molecule, together with another phase that appears to be a pure pyromorphite. These data thus lend support to the view that a discontinuity exists in the range of $A{:}X$ ratios from about 3·25 to 3·35.

Fig. 2 shows the relationships between *a* and *c* assuming Vegard's Law holds for compositions in the series $Pb_{10}(AsO_4)_6.Cl_2$–$Pb_{10}(PO_4)_6.Cl_2$–$Pb_{10}(VO_4)_6.Cl_2$, with data for the Roughtengill samples. Discontinuities

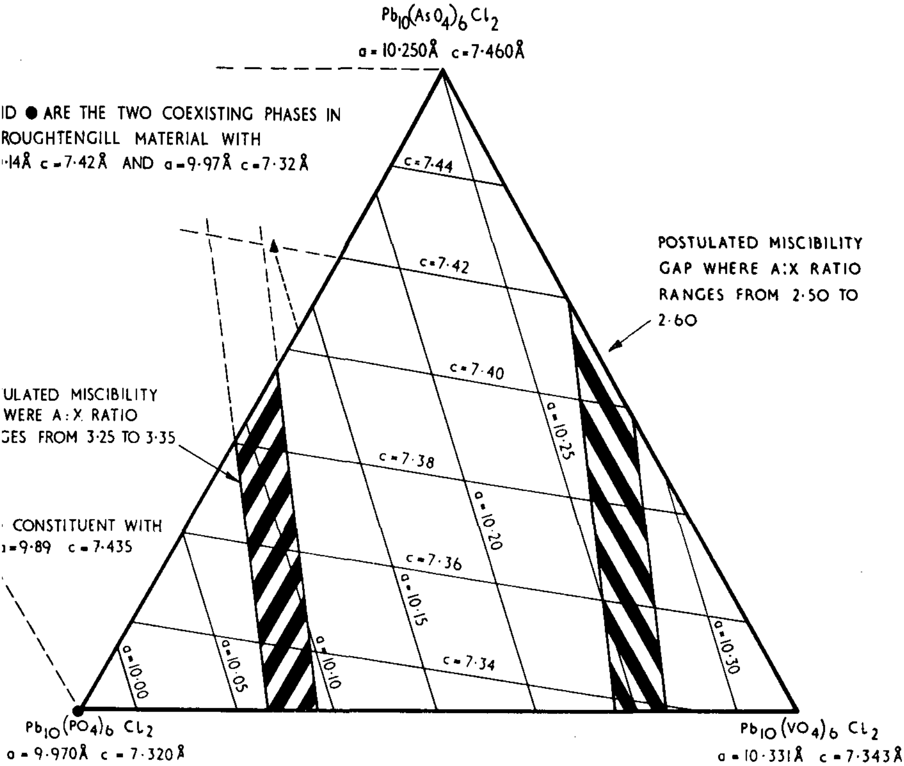

Fig. 2. The ternary system $Pb_{10}(AsO_4)_6Cl_2$–$Pb_{10}(PO_4)_6Cl_2$–$Pb_{10}(VO_4)_6Cl_2$.

corresponding to the $A:X$ ratios in the ranges 2·50–2·60 and 3·25–3·35 have also been plotted on the diagram.

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