

## Apatite - An Adaptive Framework Structure

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### Historical Perspective

Apatite, the most common phosphate mineral, is generally described by the formula  $\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$  or, more completely with regard to its usual description in  $P6_3/m$  symmetry, by the unit cell contents  $[\text{Ca}_4][\text{Ca}_6][(\text{PO}_4)_6][\text{OH},\text{F},\text{Cl}]_2$ . The notion of apatite as an industrially significant microporous mineral is not new. In 1944, V.M. Goldschmidt who had studied apatite deposits in Scandinavia and at that time had found refuge from war-ravaged Europe at the Macaulay Institute of Soil Research, Aberdeen (Kauffman 1997; McIntyre 2004) persuaded C.A. Beevers to undertake a new refinement of fluorapatite. The results collected in the seminal paper of Beevers and McIntyre (1946), lead not only to the most accurate crystallographic data available at that time, but also provided the first overview of  $[\text{Ca}_4][\text{Ca}_6][(\text{PO}_4)_6][\text{F}]_2$ , noting that it was composed of  $\text{CaO}_6$  columns linked together with  $\text{PO}_4$  groups to form 'a hexagonal network like a honeycomb with channels extending right through the structure in the  $c$  direction' (Fig. 1). More generally, it was recognized that the one-dimensional tunnel structure was determined primarily by 'the calcium and phosphate arrangement, which is likely to be a strong and stable one'. Into these tunnels were inserted the remaining calcium and fluorine. In comparing the hydroxyl and fluorapatites it was observed that  $\text{OH}^-$ , being slightly larger than  $\text{F}^-$ , leads to the former structure being expanded compared to the latter. Thus, Beevers and McIntyre identified the three critical elements of the microporous description of apatites namely: (1) the structure can be considered a tunnel structure with walls composed of corner-connected  $\text{CaO}_6$  and  $\text{PO}_4$  polyhedra as relatively invariant units; (2) filling of these tunnels by Ca and anions ( $\text{OH}^-$ ,  $\text{F}^-$ ) leads to characteristic adjustments that best satisfy bond-length requirements; and (3) even slight changes in the ionic radii of the tunnel atoms lead to expansion or contraction of the tunnel. On this basis, it was surmised that the 'very critical fit' of the fluorine and hydroxyl ions was responsible for the greater stability of fluorapatite, consistent with the observation that bone could take up fluorine selectively even from dilute solutions. The possibility of reducing dental caries by increasing fluorine content was thus established and provided the fundamental underpinning for water fluorination technology.

### Exploiting Microporosity

While the microporous description of apatites pioneered by Beevers and McIntyre was largely overlooked for many years, it has become increasingly significant as apatites of various chemistries are investigated for assorted applications in chemical synthesis, clean energy and environmental remediation. For example, the so-called 'lacunary' apatites are prospective fuel cell electrolytes, while lead apatites are potential photocatalysts, and radiation resistant phosphate apatites may be useful for retaining nuclear wastes. Although apatites have one-dimensional channels, as distinct from the three-dimensional channels in classic zeolites, they do display several zeolitic features including: a framework which can be tuned to accommodate different tunnel contents; an ability to accept large cations of different valance through the introduction of framework counter ions; and reversible ion exchange for some anions and cations. Unlike zeolites however, completely empty channels have not yet been reported. Most recently, it has been recognised, in both natural and synthetic materials, that intergrowth of tunnels of different size at the nanoscale is possible, a feature with important technology performance implications.

