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STRUCTURAL PRINCIPLES FOR FLUORITE-RELATED SUPERSTRUCTURES

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The solution of the structure of the mineral tveitite - $Ca_{14}Y_5F_{43}$ (1) led to the recognition of a new structural principle (2) for anion-excess superstructures. As in all fluorite-related structures, the cation array remains as essentially unaltered f.c.c., and it is the anion arrangement which is varied. The fundamental step in this process is the conversion of X_8 anion cubes in fluorite to X_8 anion square antiprisms. More specifically, the fluorite element (M_6X_{32}) of six MX_8 cubes sharing edges to enclose an empty X_8 cube is converted to a cluster of six MX_8 square antiprisms sharing corners to enclose an empty cuboctahedron. This can be represented formally by: $M_6X_{32} + 4X \rightarrow M_6X_{36}$, and if an additional anion is accommodated at the centre of the cuboctahedron, the cluster becomes M_6X_{37}.

This cluster principle has now been used widely in new descriptions of known structures, and in constructing models of unknown structures. This latter enterprise has been outstandingly successful and has led to the experimental determination of previously unknown structures, e.g. Ca_2YbF_7 and (of particular interest) β-U_4O_{9-y}; the latter structure has defied solution for over 30 years. Moreover, the ideal geometrical models closely approximate the real structures where these are known. Models of different cluster arrangements in the structures of the Greis series, R_nF_{2n+5} (R = rare-earth), are shown.

1 '*The structure of tveitite, an ordered yttrofluorite mineral*', D.J.M. Bevan, J. Strähle and O. Greis, *J.Solid State Chem.*, 44 (1982) 75.
2 '*A new structural principle in anion-excess, fluorite-related superstructures*', D.J.M. Bevan, O. Greis and J. Strähle, *Acta Cryst.* A36 (1980) 889.