

9.2. LAYER STACKING

groups (subfamilies). For more details, see also Evans & Guggenheim (1988).

The chlorite-vermiculite group: There are two kinds of octahedral sheets in these structures: the *Oc* sandwiched between two *Tet* and the *interlayer* (Fig. 9.2.2.14). The structures belong to category IV. Any *Oc* can be independently homo-, meso-, or hetero-octahedral, and thus, theoretically, there are nine families here. Although vermiculites have a crystal chemistry different from chlorites, they can be, from the symmetry point of view, treated together. There are 20 (24) homo-homo-octahedral, 44 (60) homo-meso-octahedral and 164 (256) meso-meso-octahedral MDO polytypes (the first prefix refers to the 2:1 layer, the second to the interlayer); the other families have not yet been treated. Some of these polytypes have also been derived by other authors (for references, see Bailey, 1980; Zvyagin *et al.*, 1979).

In order to preserve a unitary system, some monoclinic polytypes necessitate a 'third' setting, with the *a* axis unique. These should not be transformed into the standard second setting.

9.2.2.3.1.2. Diffraction pattern and identification of individual polytypes

Owing to the trigonal symmetry of the basic structural units and their stacking mode, the single-crystal diffraction pattern of hydrous phyllosilicates has a hexagonal geometry and it can be referred to hexagonal or orthohexagonal reciprocal vectors \mathbf{a}_1^* , \mathbf{a}_2^* or \mathbf{a}^* , \mathbf{b}^* , respectively (Figs. 9.2.2.15 and 9.2.2.16). It contains three types of diffractions:

(1) Diffractions $00l$ (or $000l$), always sharp and common to all polytypes of a family including all its subfamilies. They are indicative of the mineral group, but useless for the identification of polytypes.

(2) The remaining diffractions with $k_{\text{ort}} \equiv 0 \pmod{3}$, always sharp and common to all polytypes of the same subfamily.

(3) All other diffractions: sharp only for periodic polytypes, otherwise present on diffuse rods parallel to \mathbf{c}^* . These are characteristic of individual polytypes. Diffractions $0kl$ – if sharp – are common to all polytypes of the family with the same *bc* projection.

From descriptive geometry, it is known that two orthogonal projections suffice to characterize unambiguously any structure and, therefore, the superposition structure (which implicitly contains the *ac* projection) together with the *bc* projection suffice for an unambiguous characterization of any polytype. It also follows that the diffractions with $k \equiv 0 \pmod{3}$ together with the $0kl$ diffractions with $k \not\equiv 0 \pmod{3}$ suffice for its determination (except for homometric structures) (Đurovič, 1981).

From the trigonal or hexagonal symmetry of any superposition structure and from Friedel's law, it follows that the reciprocal

rows $20l$, $13l$, $\bar{1}3l$, $\bar{2}0l$, $\bar{1}\bar{3}l$, and $\bar{1}\bar{3}l$ (Fig. 9.2.2.16) carry the same information. Therefore, for identification purposes, it suffices to calculate the distribution of intensities along the reciprocal rows $20l$ (superposition structure – subfamily) and $02l$ (*bc* projection) for all MDO polytypes. Experience shows (Weiss & Đurovič, 1980) that a mere visual comparison of calculated and observed intensities along these two rows suffices for an unambiguous identification of a MDO polytype. A similar scheme has been presented by Bailey (1988b).

The above considerations are based on the ideal Radoslovich model. Diffraction patterns of real structures may exhibit deviations owing to the distortion of the ideal lattice geometry and/or symmetry of the structure.

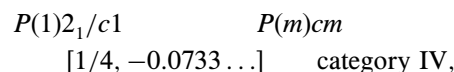
9.2.2.3.2. Stibivanite Sb_2VO_5

The crystal structure of this mineral has been determined by Szymański (1980). It turned out to be identical with that of the compound of the same composition synthesized earlier (Darriet, Bovin & Galy, 1976). The structure is monoclinic with space group $C12/c1$, lattice parameters $a = 17.989$ (6), $b = 4.7924$ (7), $c = 5.500$ (2) Å, $\beta = 95.13$ (3)°.

Structural units are formed of $\text{SbO}_2\text{--O--VO--O--SbO}_2$ extended along *a*, with adjacent units bonded along *c* through Sb--O--Sb and V--O--V bonds. Ribbons are thus formed with no bonding along *b*, and only the Sb--O interactions [2.561 (4) Å] along *a* (Fig. 9.2.2.17). This accounts for the excellent acicular cleavage.

Merlino *et al.* (1989) recognized in this structure sheets of VO_5 square pyramids (*Pyr*) parallel to *bc*, with layer symmetry $P(2/m)2/c2_1/m$ alternating with sheets containing chains of distorted SbO_3 tetrahedron-like pyramids (*Tet*) with layer symmetry $P(1)2_1/c1$ (Fig. 9.2.2.18). Owing to the higher symmetry of *Pyr*, they concluded that there may also exist an alternative attachment of *Tet* to *Pyr*, such that the triples (*Tet*; *Pyr*; *Tet*) will exhibit the layer symmetry $Pmc2_1$, and they will be arranged so that another polytype $2O$ with symmetry $P2_1/m2_1/c2_1/n$ (Fig. 9.2.2.19) is formed [in the original $2M$ polytype, the triples (*Tet*; *Pyr*; *Tet*) have the layer symmetry $P(1)2/c1$]. A mineral with such a structure, with lattice parameters $a = 17.916$ (3), $b = 4.700$ (1), $c = 5.509$ (1) Å, has actually been found.

The polytypism of stibivanite is reflected in its OD character: the two kinds of sheets *Pyr* and *Tet* correspond to two kinds of non-polar layers: their relative position is given by the family symbol:



the NFZ relations being

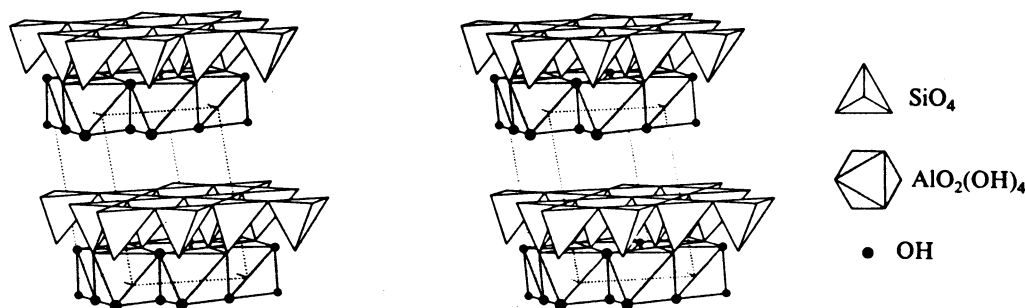


Fig. 9.2.2.11. Stereopair showing the sequence of sheets in the structures of the serpentine-kaolin group (kaolinite-1A, courtesy Zoltai & Stout, 1985).