

# Crystal Chemistry of Sheet Silicates

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## Summary

There are nearly 200 sheet-silicate minerals of sheet silicates. Their crystal structures are based on two-dimensional infinite sheets of Si tetrahedra. Each Si tetrahedron shares three basal oxygens with neighboring tetrahedra. Apical oxygens in tetrahedra can point in the same or in a different direction, giving rise to a variety of structure topologies. According to the classification of Liebau (1985), silicate sheets may be single or double. Double sheets occur as a product of the condensation of two single sheets, and there is a mirror plane or pseudo-mirror plane between two single sheets.

The more common minerals are those that correspond to simple sheets. Thus the structures of the mica-group minerals, chlorite-group minerals, serpentine-group minerals, smectite-group minerals, talc, amesite, petalite, antigorite, sepiolite, sanbornite, makatite, kanemite, palygorskite, etc., are based on the  $6_3$  net, and different topologies arise from the attitude of adjacent tetrahedral apices. The structures of natroapophyllite, ekanite, apophyllite, cavansite, ekanite, gillespite and cuprorivaite are based on the  $4.8_2$  net. The structures of sazhinite, dalyite and armstrongite are based on the  $4.6.8$  net. More complicated nets tend to occur only in rarer minerals. Thus the  $4.5.6.12$  net is found only in parsettensite, and the  $5.6.8$  net occurs only in intersilite. In these structures, six-membered rings are by far the most common, followed by four- and eight-membered rings. Five-, ten- and twelve-membered rings are less common, three- and seven-membered rings are rare, and nine- and eleven-membered rings have not yet been found in sheet-silicate minerals. Tetrahedral sheets in phyllosilicates are connected to various structural units, giving rise to five groups of different topology.

## Introduction

Crystal structures of sheet silicates are based on two-dimensional infinite sheets of Si tetrahedra. Each Si tetrahedron shares three basal oxygens with neighboring tetrahedra. Different topologies arise from the attitude of adjacent tetrahedral apical oxygens. To date, there are nearly 200 sheet-silicate minerals. Tetrahedral sheets in these minerals can be single or double. Double sheets occur as a product of the condensation of two single sheets where there is a mirror plane or pseudo-mirror plane between the single sheets. Here, we focus on the crystal chemistry of sheet silicates and the relations among their crystal structures. The coverage is restricted to those minerals for which structural data are available.

## Theory and Examples

There are 34 distinct single sheets and 20 distinct double sheets of  $(\text{SiO}_4)$  tetrahedra in phyllosilicates. The more common minerals are those that contain simple sheets. Thus the structures of the mica-group minerals, chlorite-group minerals, serpentine-group minerals,

smectite-group minerals, talc, amesite, petalite, antigorite, sepiolite, sanbornite, makatite, kanemite, palygorskite, etc. are based on the  $6_3$  net, and different topologies arise from the attitude of adjacent tetrahedral apices. The structures of natroapophyllite, ekanite, apophyllite, cavansite, ekanite, gillespite and cuprorivaite are based on the  $4.8_2$  net. The structures of sazhinite, dalyite and armstrongite are based on the  $4.6.8$  net. More complicated nets tend to occur only in rarer minerals. Thus the  $4.5.6.12$  net is found only in parsettensite, and the  $5.6.8$  net occurs only in intersillite. In these structures, six-membered rings are by far the most common, followed by four- and eight-membered rings. Five-, ten- and twelve-membered rings are less common, three- and seven-membered rings are rare, and nine- and eleven-membered rings have not yet been found in sheet-silicate minerals.

Apical oxygen atoms in tetrahedra can point in the same or in a different direction, and single or double tetrahedral sheets in phyllosilicates are linked to various structural units, giving rise to a variety of structural topologies. The crystal structures of sheet silicates can be divided in five groups based on these various topologies. The first group includes those structures in which one octahedral sheet (*O*) is connected to two tetrahedral sheets (*T*). These three sheets form a *TOT* layer, separated from adjacent layers in the interlayer cations (*I*) as in mica-group minerals (Fig. 1a), or form *TOT* layers with no interlayer cations as in chlorite-group minerals. In this case, apical oxygens of all tetrahedra in a tetrahedral sheet point in the same direction. The second group includes minerals in which tetrahedral sheets alternate with octahedral sheets. In these structures, apical oxygen atoms point in different directions and each tetrahedral sheet is connected to two octahedral sheets, and these sheets form an uninterrupted sequence *TOTOTO...* (Fig. 1b). There are no interlayer cations in between tetrahedral and octahedral sheets. The second group minerals are manganpyrosmalite-group minerals, bementite, ganophyllite-group minerals. The third group includes structures in which tetrahedral sheets are connected to bands or ribbons of octahedra 3 to 5-octahedra wide (Fig. 1c). Examples include the antigorite, sepiolite, kalifersite, and raite structures. The fourth group includes sheet silicates in which there are tetrahedral sheets interlayered with atoms,  $H_2O$  groups and  $(CO_3)$  or  $(SO_4)$  groups (Fig. 1d). For example, such topology is found in gillespite-group minerals, makatite-group minerals, sanbornite, latiumite, cymrite, kampfite. The fifth group includes structures in which tetrahedral sheets are connected to different structural units (chains of polyhedra, clusters of polyhedra, or single polyhedra) and form heteropolyhedral framework (Fig. 1e). The majority of sheet silicates belong to this group.

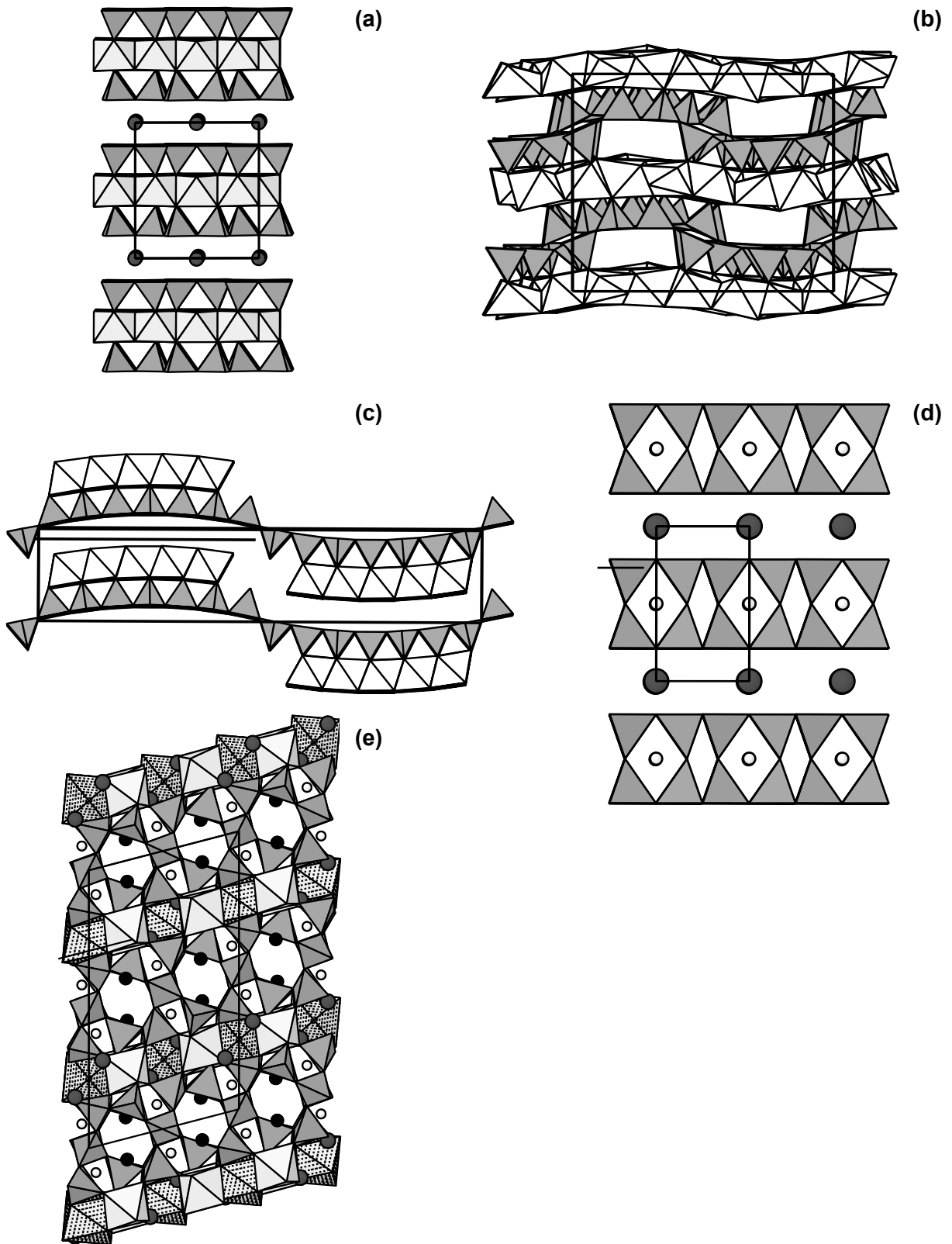


Figure 1: The five different types of linkage between tetrahedral sheets and other structural units: (a) crystal structure of a mica; (b) crystal structure of bementite; (c) crystal structure of antigorite; (d) crystal structure of cymrite; (e) crystal structure of lemoynite.

## Conclusions

There are five groups of structures, each characterized by the topology and stereochemistry of connecting tetrahedral sheets and other structural units (octahedral sheets, bands, chains of clusters of polyhedral or single atoms or groups). There are 34 and 20 different types of single and double sheets, respectively. The more common minerals are those that correspond to the simpler sheets. More complicated nets tend to occur only in rarer minerals. In these structures, six-membered rings are by far the most common, followed by four- and eight-membered rings. Five-, ten- and twelve-membered rings are less common, three- and seven-membered rings are rare, and nine- and eleven-membered rings have not yet been found in sheet-silicate minerals.

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