

# Prediction of Structure Topology from Chemical Composition in Ti Silicates

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In a group of minerals of fixed structure topology, the relation between structure and chemical composition is usually straightforward: the sum of the sites in the structure gives the stoichiometry of all minerals in that group. However, in a group of minerals of reasonable complexity in which the structure topology is related but not identical, the general relation between structure topology and chemical composition is not known. This problem is of major theoretical significance in terms of the relation between structure and chemical composition. It is simple to go from structure topology to chemical composition. However, what one wants to do is to go in the inverse direction: from chemical composition to structure topology. Here, I consider structural hierarchy and stereochemistry for titanium disilicate minerals containing the TS (titanium-silicate) block, describe general structural principles and the relation between structure topology and chemical composition which I have developed for those minerals.

There are thirty titanium disilicate minerals that contain the TS block, a central trioctahedral (O) sheet and two adjacent heteropolyhedral (H) sheets of [5]- and [6]-coordinated polyhedra and (Si<sub>2</sub>O<sub>7</sub>) groups. The TS block is characterized by a planar cell based on translation vectors, **t**<sub>1</sub> and **t**<sub>2</sub>, with *t*<sub>1</sub> ~ 5.5 and *t*<sub>2</sub> ~ 7 Å and **t**<sub>1</sub> ^ **t**<sub>2</sub> close to 90°. The general formula of the TS block is A<sup>P</sup><sub>2</sub> B<sup>P</sup><sub>2</sub> M<sup>H</sup><sub>2</sub> M<sup>O</sup><sub>4</sub> (Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub> X<sub>4+n</sub>, where M<sup>H</sup><sub>2</sub> and M<sup>O</sup><sub>4</sub> are cations of the H and O sheets; M<sup>H</sup> = Ti, Nb, Zr, Mn<sup>2+</sup>, Ca; M<sup>O</sup> = Ti, Zr, Mn<sup>2+</sup>, Ca, Na; A<sup>P</sup> and B<sup>P</sup> = cations at the peripheral (P) sites = Na, Ca, Ba; X = anions = O, OH, F; n = 0, 2, 4. There are three topologically distinct TS blocks, depending on the type of linkage of two H sheets and the central O sheet. All structures consist of a TS block and an I (intermediate) block that comprises atoms between two TS blocks. Usually, the I block consists of alkali and alkaline-earth cations, (H<sub>2</sub>O) groups and oxyanions (PO<sub>4</sub>)<sup>3-</sup>, (SO<sub>4</sub>)<sup>2-</sup> and (CO<sub>3</sub>)<sup>2-</sup>. These structures naturally fall into four groups, based on the content of Ti and differences in topology and stereochemistry of the TS block. In Group I, Ti = 1 *apfu*, and (Si<sub>2</sub>O<sub>7</sub>) groups link to a Na polyhedron of the O sheet (linkage 1). In Group II, Ti = 2 *apfu*, and (Si<sub>2</sub>O<sub>7</sub>) groups link to two M<sup>2+</sup> octahedra of the O sheet adjacent along **t**<sub>2</sub> (linkage 2). In Group III, Ti = 3 *apfu*, and (Si<sub>2</sub>O<sub>7</sub>) groups link to the Ti octahedron of the O sheet (linkage 1). In Group IV, Ti = 4 *apfu* and (Si<sub>2</sub>O<sub>7</sub>) groups link to two Ti octahedra of the O sheet adjacent along **t**<sub>1</sub> (linkage 3).

These structural principles allow prediction of structural arrangements and possible chemical compositions. Here, I show how these principles work and review results of recent single-crystal X-ray structure work for three Ti disilicate minerals: delindeite, bornemanite and nechelyustovite. In these three minerals, Ti = 3 *apfu* and they must exhibit the stereochemistry of Group III. However, structure models for bornemanite and nechelyustovite built using polysomatic approach report TS blocks with the stereochemistry of Groups IV (Ti = 4 *apfu*) and II (Ti = 2 *apfu*), respectively. The direct determination of the crystal structures of bornemanite and nechelyustovite showed that previous models were wrong and both minerals have the TS block with the stereochemistry of Group III (Ti = 3 *apfu*) in accord with our general structural principles. In delindeite, the TS block has the stereochemistry of Group I (Ti = 1 *apfu*) and the stereochemistry of Group III (Ti = 3 *apfu*, and (Si<sub>2</sub>O<sub>7</sub>) groups link to the Ti octahedron of the O sheet) does not occur due to a partial occupancy of the cation and anion sites in the O sheet.

## References

Sokolova, E., 2006, From structure topology to chemical composition. I. Structural hierarchy and stereochemistry in titanium disilicate minerals: Canadian Mineralogist, 44, 1273-1330.