Model pyroxenes I: Ideal pyroxene topologies

RICHARD M. THOMPSON* AND ROBERT T. DOWNS

Department of Geosciences, University of Arizona, Tucson, Arizona 85721-0077, U.S.A.

ABSTRACT

Ideal pyroxenes are hypothetical structures based on ideal closest-packed arrangements of O anions. They are modeled after observed pyroxene structures and have the general formula M2M1T2O6, where M2 and M1 represent octahedrally coordinated cations, and T represents tetrahedrally coordinated cations. An algorithm has been created to construct all possible ideal pyroxenes based on closest-packed stacking sequences of length 12 or less. These structures are reported.

The only significant structural parameters that vary between different ideal pyroxenes are the M1-T and M2-T distances. We show that the repulsive forces between these pairs of cations distinguishes the energetics of the ideal pyroxenes and may be important in determining the topologies of observed pyroxenes.

INTRODUCTION

The term pyroxene refers to a group of crystal structures that include important components of the Earth’s crust and mantle, lunar and Martian rocks, and meteorites (Deer et al. 1978). Many pyroxene phases not found in nature have been synthesized. There are several naturally occurring polymorphs. These commonly display P2\textsubscript{1}/c, C2\textsubscript{1}/c, Pbcn, or Pbca symmetry. More rarely, cation ordering at a given site results in stacking sequences of closest-packed monolayers with identical letters reversed, e.g., ABAB versus BA. It will also be important to distinguish between the non-unique sequence of letters representing that structure.

We establish a working definition of “ideal pyroxene” by describing and illustrating the structural features and relationships that can be used as building blocks to derive crystal structures for these hypothetical constructs. Two of the defining structural elements in ideal pyroxenes are chains of edge-sharing octahedra and corner-sharing tetrahedra that run parallel to c. These chains can be constructed by placing cations in the interstitial voids between closest-packed monolayers of anions stacked along a*. The cation sites in a given chain are related to each other by a c-glide perpendicular to b. This is the only symmetry element common to all possible ideal pyroxene structures. In many ideal pyroxenes, it is the only symmetry element.

The arrangements of anions in these ideal structures can be described as stacking sequences of closest-packed monolayers, denoted A, B, and C in the traditional way (Patterson and Kasper 1959). For example, the anion arrangement in ideal P2\textsubscript{1}/cn protopyroxene can be described by the stacking sequence ABAC. Since all of the cations between a given pair of monolayers are exclusively tetrahedral or octahedral, we can modify the stacking sequence to include superscripted Ts or Os to indicate tetrahedral or octahedral ion layers, respectively. The complete ideal P2\textsubscript{1}/cn protopyroxene can be described as A\textsuperscript{0}B\textsuperscript{1}A\textsuperscript{0}C\textsuperscript{1}, with octahedrally coordinated cations between AB and AC and tetrahedrally coordinated cations between BA and CA.

It will be important to our discussion to distinguish between monolayer sandwiches with identical labels reversed, e.g., AB and BA. We define AB to mean that the atoms in the A-layer have smaller x-coordinates than those in the B-layer, and vice versa for BA. It will also be important to distinguish between the stacking sequence ABAC and the stacking sequence label ABAC. The former refers to the physical structure, a unique closest-packed arrangement of O anions; the latter refers to the four letters that represent the structure. The label can be manipulated using certain rules that represent changes of basis to derive equivalent labels representing the same stacking sequence or structure (Thompson and Downs 2001b). In this example, BABC, CBCA, ACAB, etc. all represent the same structure. Similarly, “pyroxene A\textsuperscript{0}B\textsuperscript{1}A\textsuperscript{0}C\textsuperscript{1}” refers to the unique physical structure, while “pyroxene label A\textsuperscript{0}B\textsuperscript{1}A\textsuperscript{0}C\textsuperscript{1}” refers to the non-unique sequence of letters representing that structure.

In an ideal pyroxene, we define the basal faces of the tetrahedra as the faces parallel to (010). The two anions that are shared with other tetrahedra at the corners of these basal faces are referred to as the bridging O3 anions (Fig. 1). The non-bridging basal anions are referred to as O2 and the apical anions as O1. This nomenclature is consistent with the traditional labeling of atoms in observed structures.

The chain-forming symmetrically equivalent edge-sharing octahedral sites are called M1 and are related to each other by...