**Thermal expansion of minerals in the amphibole supergroup**

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**ABSTRACT**

We have investigated the thermal expansion of 15 naturally occurring chemically diverse amphiboles utilizing high-temperature X-ray powder diffraction. As done in the first paper of this series on pyroxenes, volume-temperature data were analyzed using the physical Kroll and empirical Fei thermal expansion models. As in pyroxenes, orthorhombic amphibole end-members expand more than monoclinic ones, which is related to the greater kinking of the chains of tetrahedra permitted by the Pnma symmetry. In the case of chemically similar phases, increased Al in octahedral cation sites decreases expansion. Although the ranges of thermal expansion coefficients for amphiboles and pyroxenes are similar, expansion patterns are not the same. Amphiboles exhibit higher expansion along $a^*$, but lower along $b$, just the reverse of that observed in pyroxenes. An exception to this is the data for pargasite, which shows higher expansion along the $b$ axis due to the presence of Al in tetrahedral sites. Current data will be useful in modeling reactions involving amphiboles in both metamorphic and igneous environments.

**Keywords:** Amphiboles, thermal expansion, X-ray diffraction, modeling

**INTRODUCTION**

In a recent paper, Hovis et al. (2021) reported thermal expansion results for a chemically diverse group of pyroxene minerals based on high-temperature X-ray powder diffraction data. In addition to thermal expansion comparisons within the pyroxene group, the new data, along with previously published results of other investigators, were utilized to examine a wide variety of thermal expansion models based on volumes ranging upward from temperatures ($T$) near absolute zero (and pressure of 1 bar) to those extending into metamorphic and igneous regimes. As a follow-on to our previous work on the pyroxene system, we now present data on the thermal expansion of 15 chemically diverse amphiboles.

The overall goal of our research has been to determine how chemical composition within various mineral groups affects thermal expansion. To do so, we have studied compositionally diverse groups of minerals in the garnet, olivine, pyroxene, amphibole, and tourmaline supergroups.

The fundamental structural element of an amphibole, shown in Figure 1, is a double tetrahedral chain that parallels the $c$ crystallographic axis. The latter is in essence a pyroxene single chain bonded to a second chain that is a mirror reflection of the first. Chain orientation and repetition within a single unit cell is like that of pyroxenes, but chain-width doubling results in a doubled $b$ axis. In a structure hierarchical approach (Day and Hawthorne 2020) the amphibole double chain is defined as a ribbon, as it is not possible to break the chain by removing a single tetrahedron. The basic unit of the ribbon is made by four tetrahedra, two of which are connected with two tetrahedra and the other two with three [$T_1^\prime$, $T_2^\prime$ in Day and Hawthorne (2020) notation]. A strip of octahedrally coordinated M(1), M(2), and M(3) sites (the C sites) that collectively correspond to the M1 octahedra of pyroxenes links to $T_1^\prime$$T_2^\prime$ ribbons in the $a$- and $b$-directions. The M(4) sites (also known as B sites) are located along the flanks of the octahedral band, surrounded by 8 O atoms, not all of which are coordinated to the central atom. The A site is located between the back-to-back (as opposed to apical) sixfold tetrahedral rings of the ribbon unit; this typically is occupied by large cations such as Na or K and associated with hydroxyl groups of the so-called W site.

Overall, then, the greater structural complexity of amphiboles relative to pyroxenes correlates with wider chemical variation, as reflected by the general formula $A_{a_{°}}B_{b_{°}}C_{c_{°}}T'_1T'_2W_2$, where $A = \square, Na, K, Ca, Li; B = Ca, Na, Mn^{2+}, Fe^{3+}, Mg, Li; C = Mg, Fe^{3+}, Mn^{2+}, Al, Mn^{2+}, Fe^{3+}, Ti^{4+}, Li; T = Si, Al, Ti, Be^{2+};$ and $W = OH^-, F, Cl, O^2-$ (Hawthorne et al. 2012). Together, the structural complexity and extensive chemical substitution (including potential order-disorder phenomena at elevated $T$) make the modeling of thermal expansion for amphiboles difficult. This is even more exacerbated by the difficulties involved in synthesizing some amphibole end-members (Maresch and Czank 2007).

The above factors help explain why the comparison of pyroxene and amphibole thermal expansion behavior has been limited. Indeed, in the Holland and Powell (2011) database, thermal expansion coefficients for 8 of 11 amphibole end-members were estimated. Prior to the investigation of synthetic glaucophane by Jenkins and Corona (2006), the lone amphibole studies were those on tremolite (Sueno et al. 1973) and synthetic K and Na richterite (Cameron et al. 1983). Since 2006, high-temperature studies have been conducted on additional natural and synthetic amphibole specimens [synthetic richterite (Tribaudino et al. 2008a); anthophyllite (Welch et al. 2011a); gedrite (Zema et al. 2012); riebeckite (Oberti et al. 2018); pargasite (Comboni et al. 2018); Fe-holmquistite (Oberti et al. 2019)]. Related studies also have been carried out on the high-temperature $P_{2_1}$/m–$C2/m$