**Ca-Zn solid solutions in C2/c pyroxenes: Synthesis, crystal structure, and implications for Zn geochemistry**

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**ABSTRACT**

The effect of Zn substitution on a series of clinopyroxenes along the join CaZnSi₂O₆-Zn₂Si₂O₆ was studied. The pyroxenes were synthesized at \( P = 4–5 \) GPa and \( T = 1000–1200 \) °C by a multi-anvil apparatus. SEM-EDS and XRD analysis showed complete solid solution; all of the samples have the C2/c space group. No miscibility gap between clinopyroxene and melt. The volume of Ca-Zn pyroxenes decreases less than expected from the decrease of the average cation size for the substitution of Zn for Ca.

The crystal structures of three synthetic pyroxenes of composition (Ca₀.₅Zn₀.₅)ZnSi₂O₆, (Ca₀.₃Zn₀.₇)ZnSi₂O₆, and (Ca₀.₂Zn₀.₈)ZnSi₂O₆ were refined by single-crystal X-ray diffraction (\( R\_o\_s\_b\) between 3 and 4.5%). It was observed that the Ca-Zn substitution occurs in the M2 polyhedron, with a sub-site splitting of Zn in a position at approximately 0.7 Å from Ca. In this position, Zn retains a highly distorted fourfold coordination; moreover, the tetrahedral chain configuration is little changed along the series, and the M1 polyhedral size increases with Zn substitution in M2.

An implication of the present work is the interpretation of the partitioning of Zn between clinopyroxene and melt. The distribution coefficients of Zn and Co are quite different in rocks of the same composition, despite their very similar ionic radius, and the difference is related to the preference of Zn for the M2 site, where Zn may find a suitable atomic coordination.

**Keywords:** Clinopyroxene, high pressure, X-ray diffraction, trace elements, Zn

**INTRODUCTION**

The crystal structure of pyroxene, due to its inherent flexibility, provides an effective playground for obtaining models relating the atomic structure to composition and \( P-T \) conditions and for interpreting phase equilibria and solid solutions in minerals.

The formula unit of pyroxenes is \( \text{M}_2\text{M}_1\text{T}_2\text{O}_6 \) (Fig. 1). In natural pyroxenes, the M2 site is occupied by larger cations, such as Ca, Na, Mg, Fe\(^{2+}\), and Li, the M1 site is occupied by Mg, Fe\(^{2+}\), Fe\(^{3+}\), Al, and Cr, whereas the T site is occupied by only Si and Al. Further substitutions are possible in synthetic pyroxenes: the M2 site can also be filled by Sr, Co, Ni, Mn, and Zn; the M1 site can be filled by Co, Ni, Cr, Mn, Ni, Zn, Sc, Ti, Cu, Ga, and V; and Ge can fully exchange with Si in the tetrahedral site (Ohashi et al. 1990; Redhammer and Roth 2004; Redhammer et al. 2012; Redhammer and Tippelt 2014; Tribaudino et al. 2005a, 2005b; Arlt and Angel 2000; Tribaudino et al. 2002, 2009; Heuer et al. 2005; Thompson et al. 2005; Hugh-Jones et al. 1994).

The above synthetic pyroxenes are a counterpart to natural ones. For instance, in a recent investigation on the crystal structure, phase equilibria, and phase transitions in synthetic pyroxenes along the series CaCoSi₂O₆-Co₂Si₂O₆ (Mantovani et al. 2013, 2014), Co-pyroxyenes were compared with natural Ca-Mg and Ca-Fe pyroxenes to study the effect of cation substitutions in the M2 site. It was observed that in Ca-richer pyroxenes with C2/c structure, the solid solution is ideal and volume changes simply due to the different cation radii of the substituting cations; the apparent deviation from the ideal behavior in Ca-poorer compositions is due to the negative excess volume for the transition from the C2/c to the P2₁/c space group.

Moreover, it was observed that the C2/c-P2₁/c phase transition occurs at an average M2 cation radius between 0.86 and 0.88 Å.

A different behavior can be expected in Ca-Zn pyroxenes. Zn has a ionic radius very similar to that of Co and Mg, i.e., 0.74 vs. 0.745 and 0.72 Å, respectively, but it enters differently in the M2 site. Co, Mg, and Fe in the M2 site show a 4+2 sixfold coordination, whereas Zn exhibits a fourfold coordination (Morimoto et al. 1975). Moreover, at room pressure and temperature, monoclinic ZnSi₂O₆ has a C2/c structure, whereas monoclinic CoSi₂O₆, Mg₂Si₂O₆, and Fe₂Si₂O₆ show a P2₁/c space group (Morimoto et al. 1960, 1975; Ohashi et al. 1975; Sasaki and Takéuchi 1981; Ohashi 1984). The fourfold coordination of Zn in the M2 cavity was explained by the preference of Zn for covalent bonding and an sp³ tetrahedral hybrid electronic configuration (Morimoto et al. 1975).

Experimental data on Zn substitution in pyroxenes are scarce.