

The crystal chemistry and elastic properties of clinopyroxenes with 6-coordinated silicon

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Introduction

It has long been assumed that clinopyroxene - in spite of its pressure stability to approximately 18 GPa – contains silicon exclusively in tetrahedral coordination. This assumption was disproved by a study of Angel et al. (1988) presenting a pyroxene with a stoichiometry $\text{Na}(\text{Mg}_{0.5}\text{Si}_{0.5})\text{Si}_2\text{O}_6$ (NaPx) that contains both tetrahedrally and octahedrally coordinated silicon. This pyroxene was synthesized at 10 and 15 GPa and a temperature of 1600 °C. Its major structural feature is the presence of Si on *M1*-sites. Due to the large difference in size and charge between Mg and Si the two cations are completely ordered, resulting in a symmetry reduction from *C2/c* to *P2/n* even at the very high temperatures of formation and rapid quenching after the experiment that would stabilize the *C2/c* symmetry in omphacitic clinopyroxenes.

The discovery that clinopyroxene can accommodate 6-coordinated silicon is of fundamental importance for an understanding of the crystal chemistry of chain silicates at high P and T in particular and high-P minerals in general. This is because phase transitions involving a change in coordination of silicon from fourfold to sixfold have significant effects on material properties such as density, bulk modulus and elastic moduli and, consequently, on the P-(T) stability fields of these phases. Thus, in order to gain insight into the crystal chemical effects of [6]Si-substitution in clinopyroxene, we initiated a study of the crystal structures and elastic properties of NaPx and its solid solutions with common clinopyroxene endmembers..

The relevance of pyroxenes with 6-coordinated silicon to the Earth's interior

A key requirement for the stability of silica-rich sodium pyroxenes at high P and T is an excess of sodium with respect to aluminum in the bulk, a situation not known to prevail in peridotitic portions of the upper mantle regularly sampled by xenoliths. In spite of this restriction, the existence in nature of NaPx-solid solutions was demonstrated by Wang & Sueno (1996). These authors reported an inclusion in diamond from a Chinese kimberlite

with a composition 62.7 wt % SiO₂, 0.15 wt % Al₂O₃, 0.46 wt % FeO, 33.3 wt % MgO, 1.19 wt % CaO, 2.34 wt % Na₂O, 0.28 wt % K₂O, which can be recalculated to a NaP_x₁₆En₈₄ pyroxene solid-solution. Based on the phase diagram for the system NaP_x-enstatite presented by Gasparik (1989), Wang & Sueno (1996) concluded that this NaP_x-enstatite solid-solution must have formed at P in excess of 16 GPa.

First results

Multi-anvil experiments were performed at 15 GPa and 1500–1600 °C to synthesize clinopyroxene solid-solutions with 6-coordinated silicon in the systems NaP_x [Na(Mg_{0.5}Si_{0.5}Si₂O₆) (Angel et al. 1988) -jadeite, NaP_x-diopside, NaP_x-kosmochlor and NaP_x-Ca-Eskola pyroxene and to study their crystal chemistry and elastic properties. The systems NaP_x-jad and NaP_x-di produced a continuous range of solid solutions NaP_x₉₀₋₂₄jad₁₀₋₇₄ and NaP_x₈₉₋₀₅di₁₀₋₈₇ respectively for nominal compositions NaP_x₉₀₋₃₀jad₁₀₋₇₀ and NaP_x₉₀₋₃₀di₁₀₋₇₀. First results of single crystal structure determinations for NaP_x-jad_{ss} and NaP_x-di_{ss} show a C2/c symmetry as compared to a P2/n symmetry for pure NaP_x. The elastic properties of a NaP_x_{66.9}jad_{29.9}en_{3.2} composition were determined with the following results: a₀=9.4195(2) Å, b₀=8.5867(3) Å, c₀=5.2414(1) Å, β₀=107.82(6)°. Weighted volume and pressure data fit to a second-order Birch-Murnaghan equation of state with V₀=403.60(2) Å³ and K₀=137.7(5) GPa, with K' fixed to 4.0. The linear compressibilities of the a, b, and c dimensions at room pressure are as follows: β_a=0.00258, β_b=0.00224 and β_c=0.00233 GPa⁻¹, respectively, yielding axial compression ratios of 1.15:1.00:1.04, very similar to those of jadeite with 1.17:1.00:0.98. Most C2/c-pyroxenes show β_b > β_a while the NaP_x-jad_{ss} as well as jadeite itself shows β_b < β_a. This suggests that an introduction of Si/Al into the M1-site not only increases the bulk modulus of C2/c-pyroxenes but also alters their compression mechanisms. Furthermore, our preliminary high-P data for pure NaP_x yield K₀>200 GPa, the highest bulk modulus of all pyroxenes measured so far.

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