

## The effect of Al and water on the compressibility of diopside

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### ABSTRACT

The equation of state of four clinopyroxenes was measured at room temperature by single-crystal X-ray diffraction in a diamond anvil cell up to 10 GPa. The bulk modulus of pure diopside is  $K_0 = 106(1)$  GPa,  $K' = 6.1(5)$ . The bulk modulus of a pure diopside containing 600 ppm by weight of water is  $K_0 = 108(1)$  GPa,  $K' = 6.3(4)$ . The effect of water on the elastic properties of pure diopside is therefore small. In addition, we studied two hydrous samples containing 9.6 wt%  $\text{Al}_2\text{O}_3$  that were synthesized on the join between diopside and Ca-Tschermak component ( $\text{CaAlAlSiO}_6$ ). The sample containing 976 ppm of water yielded  $K_0 = 120(1)$  GPa and  $K' = 4.4(4)$ , while the sample containing 2510 ppm of water yielded  $K_0 = 114(1)$  GPa and  $K' = 5.8(5)$ . Aluminum therefore clearly makes the clinopyroxene stiffer. A direct comparison of the two aluminous samples, however, is difficult, since the sample containing the lower amount of water appears also to contain some  $M2$  vacancies, indicating some solid solution with Ca-Eskola component. This is consistent with a different substitution mechanism for water in the two samples, as indicated by differences in the infrared spectra. Our results suggest that detecting upper mantle water contents from variations in P wave velocities is probably impossible. Increasing water fugacity will increase the Al content in pyroxenes and hence their stiffness. The resulting increase in bulk modulus is opposite to the effect of water on olivine. The different response of olivine and pyroxenes to water is due to a different dissolution mechanism. Under conditions of low silica activity, water in clinopyroxenes is mostly dissolved by the coupled substitution of  $\text{Al}^{3+} + \text{H}^+$  for  $\text{Si}^{4+}$ , which does not create any vacancies. This dissolution mechanism is consistent with polarized infrared data (one single band at  $3650\text{ cm}^{-1}$ ), with an excess of tetrahedral Al in the microprobe analyses of hydrous samples and with the results of structure refinements. Infrared bands at  $3450$  and  $3500\text{ cm}^{-1}$ , which are seen in the Al-rich diopside with lower water content of this study, probably indicate Al on  $M1$  charge compensated by a  $M2$  vacancy and a proton.

**Keywords:** Equation of state, water substitution, Al substitution, high-pressure single-crystal diffraction, diopside