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In-situ high-temperature vibrational spectra for synthetic and natural clinohumite: Implications for dense hydrous magnesium silicates in subduction zones

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Abstract

Clinohumite is a potentially abundant silicate mineral with high water concentration (2~3 wt% H_2O) that is generated from dehydration of serpentine-group minerals in subduction zones. Previous studies show that fluorine substitution ($OH^- = F^-$) can stabilize clinohumite to significantly higher temperature in subduction zones, although temperatures within the slabs are thought to be well within the stability field of both F-bearing and OH-clinohumite. We collected in-situ high-temperature Raman and Fourier transform infrared (FTIR) spectra for both the synthetic [$Mg_9Si_4O_{16}(OH)_2$] and natural [$Mg_{7.84}Fe_{0.58}Mn_{0.01}Ti_{0.25}(SiO_4)_4O_{0.5}(OH)_{1.30}F_{0.20}$] clinohumite samples up to 1243 K. Three OH bands above 3450 cm^{-1} are detected for both the natural and synthetic samples with negative temperature dependence, due to neighboring H-H repulsion in the crystal structure. Additional OH peaks are detected for the natural sample below 3450 cm^{-1} with positive temperature dependence, which could be explained by non-polar F^- substitution in the OH site. Hence, F^- substitution significantly changes the high-temperature behavior of hydrogen bonds in the humite-group minerals. On the other hand, we evaluated the mode Grüneisen parameters (γ_{iP}, γ_{iT}), as well as the intrinsic anharmonic parameters (a_i) for clinohumite, chondrodite, and phase A, the dense hydrous magnesium silicate (DHMS) phases along the brucite–forsterite join. The estimated averaged anharmonic parameters (a_{i_avg}) for these DHMS phases are systematically smaller than those of olivine. To model the thermodynamic properties of minerals (such as heat capacity) at the high-temperature conditions of the mantle, the DeBye model, which simply approximates the lattice vibrations as harmonic oscillators, is commonly used. In contrast to forsterite, such quasi-harmonic approximations are valid for clinohumite at subduction zone temperatures, as the anharmonic contribution is no more than 2% when extrapolated to 2000 K. Hence, the classic DeBye model can reasonably simulate the thermodynamic properties of these DHMS phases in subduction zones.

Keywords: Clinohumite, F substitution, Grüneisen parameter, anharmonicity, subduction slab, DHMS phases