The effect of pressure upon hydrogen bonding in chlorite: A Raman spectroscopic study of clinochlore to 26.5 GPa

ANNETTE K. KLEPPE,1,* ANDREW P. JEPHCOAT,1 AND MARK D. WELCH2

1Department of Earth Sciences University of Oxford, Parks Road, Oxford, OX1 3PR, U.K.
2Department of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, U.K.

ABSTRACT

The effect of pressure upon hydrogen bonding in synthetic end-member clinochlore, (Mg,Al)(Si3Al)O10(OH)8, has been studied in situ by high-pressure micro-Raman spectroscopy in a moissanite-anvil cell to 26.5 GPa at 300 K. The ambient spectrum consists of three OH-stretching bands between 3400 and 3650 cm⁻¹, attributed to the hydrogen-bonded interlayer OH, and a narrow band at 3679 cm⁻¹ that is assigned to the non-hydrogen-bonded OH groups of the talc-like 2:1 layer. The pressure dependence of the OH modes is linear up to 6 GPa. Near 9 GPa a major discontinuity occurs in the pressure dependence of the interlayer OH-stretching modes. It involves frequency increases >100 cm⁻¹ that indicate major changes in hydrogen bonding. The OH mode of the 2:1 layer does not show discontinuous behavior at 9 GPa. A further discontinuity occurs at ~16 GPa. This discontinuity affects both interlayer and 2:1 OH, and is likely to be associated with a change in the overall compression mechanism of clinochlore. The spectroscopic behavior is a completely reversible function of pressure. Predictions based upon recent high-pressure diffraction studies of hydrogen bonding and compression of clinochlore suggest that the 9 GPa transition is associated with attainment of an O²⁻–O²⁻-contact distance of 2.7 Å.

INTRODUCTION

The range of minerals in the Earth capable of hosting water in the form of H₂O and/or OH ranges from ice to nominally anhydrous silicate phases. Chlorite, one of the most OH-rich silicates, is a major constituent of hydrated oceanic crust and may have a significant role as a water carrier in cold, old subduction zones (Peacock 1990). The Mg end-member chlorite, clinochlore (Mg₅Al)(Si₃Al)O₁₀(OH)₈, is expected to be the major aluminous phase in low-alkali hydrous peridotites below 800 °C (Jenkins 1981).

The crystal structure of chlorite is characterized by an alternation of a talc-like 2:1 layer (two opposing tetrahedral sheets with an octahedral sheet between them) and a brucite-like layer (Fig. 1). Bonding between these layers involves only hydrogen bonds. In the case of end-member clinochlore, the octahedra of the 2:1 layer are fully occupied by Mg, and those of the brucite-like layer have the following occupancies: M₃ = Mg, M₄ = Al (M₃:M₄ = 2:1). Increasing Al substitution in clinochlore via the Mg-Tschermak’s exchange, ⁶Mg + ⁴Si ↔ ⁶Al + ⁴Al, involves only compositional changes in the 2:1 layer; the cation composition of the brucite-like layer remains fixed at Mg₄Al. Brown and Bailey (1962) derived the twelve regular one-layer chlorite polytypes that arise from different ways of stacking the 2:1 and brucite-like layers with stacking vectors defining translations within the plane of the polyhedral sheets and also reversals of the “slant direction” of the octahedral sheets of the two layers (parallel, anti-parallel). The one-layer monoclinic IIb-2 (C2/m) and triclinic IIb-4 polytypes (C-T) are common in nature. The triclinic IIb-4 polytype is metrically monoclinic (β ~ 97°), and only slight differences exist between the X-ray powder diffraction patterns of these two polytypes. Both polytypes have the reversed slant orientation of the octahedra of the 2:1 and brucite-like layers (both are class II polytypes). The main structural difference between IIb-2 and IIb-4 polytypes is that in the latter the two tetrahedral sheets are staggered relative to each other, thus breaking mirror and diad symmetry. This offset also results in a different configuration for the OH groups of the 2:1 layer. The consensus of studies on end-member clinochlore synthesized at high-pressure favors, albeit marginally, the IIb-2 polytype (Jenkins and Chernowsky 1986; Bailey 1988; Welch et al. 1995; Baker and Holland 1996). This opinion was confirmed in the neutron diffraction study of synthetic clinochlore by Welch and Marshall (2001). Hereafter, we refer to IIb-2 as “C2/m” and IIb-4 as “C-T.”

The hydrogen bonds of H₂ and H₃ in synthetic C2/m clinochlore are 1.9 and 2.1 Å long (Welch and Marshall 2001), and are of moderate strength. In C2/m clinochlore, Al and Si mix statistically at just one tetrahedral site, but there is a high degree of short-range Al-Si order at tetrahedral sites and Al-O-Al avoidance operates (Welch et al. 1995). Such ordering leads to only two different configurations for bridging O atoms, Si-O-Si and Si-O-Al. The NMR study of Welch et al. (1995) did not see any evidence for long-range ordering at two non-equivalent tetrahedral sites.

Our motivation to investigate clinochlore was stimulated...