INTRODUCTION

The hydroxyl humite minerals have the general formula $n\text{Mg}_2\text{SiO}_4\cdot\text{Mg(OH)}_2$ where $n = 1$ (norbergite), 2 (chondrodite), 3 (humite), or 4 (clinohumite). They may be viewed as hydrated forms of forsterite and can be described simplistically as comprising forsterite-like blocks and intervening layers of brucite. The presence of titanian chondrodite and titanian clinohumite in kimberlites (McGetchin et al. 1970; Aoki et al. 1976) and the experimentally determined stability fields of the corresponding hydroxyl compounds (Yamamoto and Akimoto 1977; Burnley and Navrotsky 1996; Wunder 1998) indicate that these phases could exist in the upper mantle. Although the importance of these minerals as a repository of mantle water is likely to be limited, it is possible that water may be accommodated as a clinohumite-type defect in olivine (Kitamura et al. 1987). Nominally anhydrous minerals such as olivine may contain the entire water budget of the upper mantle at defect sites (Bell and Rossman 1992; Kohlstedt et al. 1996). The position of the hydrogen atoms in clinohumite is integral to understanding the stability of the hydrated layer. Although the humite structures are otherwise well defined, the hydrogen positions have only been determined approximately from X-ray diffraction studies (Yamamoto 1977; Fujino and Takeuchi 1978; Cámara 1997; Ferraris et al. 2000) and structure energy calculations (Abbott et al. 1989). The orientation and strength of the O-H bond is also important for understanding the infrared hydroxyl stretching bands, which are commonly used to quantify the water content of mantle olivines. This paper reports the first precise determination of hydrogen locations in a humite mineral.

ABSTRACT

The structure of synthetic hydroxyl-clinohumite $[\text{Mg}_7\text{Si}_4\text{O}_{14}\cdot2\text{Mg(OH)}_2]$ was refined for a deuterated sample using powder neutron diffraction data and the Rietveld technique ([$P2_1/b$; $Z = 2$; $a = 4.7488(1)$ Å; $b = 10.2875(2)$ Å; $c = 13.6967(3)$ Å; $\alpha = 100.63(1)^\circ$; $V = 657.65(2)$ Å$^3$]). The H atoms of the hydroxyl groups are disordered over two positions with an occupancy of approximately 0.5. This removes the possibility of a strong H-H interaction that was thought to destabilize the structure. The limited occurrence of hydroxyl-clinohumite in nature is the result of compositional rather than crystal chemical constraints.

EXPERIMENTAL METHODS

Synthesis

Clinohumite was synthesised at 29 kbar and 830 °C from a 5:2 molar mixture of Mg(OH)$_2$ or Mg(OD)$_2$ and SiO$_2$. Mg(OD)$_2$ was prepared by the addition of D$_2$O to Mg$_3$N$_2$. The OD content was determined to be 87 ± 1% from a comparison of the oscillator strength corrected OD and OH stretching bands in the infrared spectrum. The clinohumite reaction conditions were achieved using a 30 mm piston cylinder apparatus with end-load supplied by a 500 ton press. The sample was contained in a capsule (35 × 15 mm) machined from Ag rod with a press-on lid that forms a water-tight seal under pressure (Woodland and O’Neill 1997). A graphite heater, pressure medium of NaCl/pyrex/boron nitride, and pyrophyllite end-pieces were used. Around 2.5 g of clinohumite could be produced in each run and 5 g of both the hydrate and deuterate were synthesized. Run times were approximately four hours.

Powder neutron diffraction

Powder neutron diffraction measurements were made on the high-resolution powder diffractometer (HRPD) using thermal neutrons ($\lambda = 1.4930$ Å) from the HIFAR nuclear reactor at the Australian Nuclear Science and Technology Organisation (ANSTO). The minimum instrumental resolution (FWHM) for HRPD is 0.27°. Data were collected using a bank of 24 $^3$He detectors over the range 0° < 2θ < 153° in 0.05° steps. Structural refinements were carried out for the deuterated sample by the Rietveld method (Rietveld 1969) using the LHPM program (Howard and Hunter 1997), with Voigt peak shapes and a refined background.

RESULTS

The initial model used for refinement of the hydroxyl-clinohumite structure was that proposed for clinohumite by Robinson et al. (1973). The initial positions of the hydrogen