The 10 Å phase: Crystal structure from single-crystal X-ray data

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ABSTRACT

Here we report the results of the first three-dimensional refinement of the 10 Å phase performed with single-crystal X-ray data.

The 10 Å phase, Mg₃Si₄O₁₀(OH)₂H₂O, is monoclinic, space group C2/m, a = 5.323(1) Å, b = 9.203(1) Å, c = 10.216(1) Å, β = 99.98(1)°, V = 492.9(2) Å³; the calculated density, assuming Z = 2, is 2.676 g cm⁻³. The structure has been solved by direct methods and refined by least-squares method with anisotropic displacement parameters. The final agreement index (R) was 0.088 for 54 refined parameters and 499 unique observed reflections collected with a diffractometer with a CCD detector.

The structure of the 10 Å phase is very similar to that of a homo-octahedral, 1 M trioctahedral mica: it is a silicate consisting of 2:1 tetrahedral-octahedral layers parallel to (001). The mean Si-O, Mg1-O, and Mg2-O bond lengths are 1.626, 2.082, and 2.081 Å, respectively. The ditrigonal rotation angle α is 0.53°. The interlayer of the 10 Å phase is occupied by water molecules. According to the oxygen occupancy, 1 H₂O p.f.u. is assumed in the investigated sample. Although the average water oxygen position is in the mid-plane, structural refinement suggests disorder along c*. Twelve hydrogen bonds are located between the water molecule and the 6 + 6 oxygen atoms of the basal rings of adjacent tetrahedral sheets (water-oxygen distances averaging 3.19 Å). Therefore there are six possible orientations for the water molecule, with six hydrogen bonds pointing toward the upper basal ring and six pointing toward the lower ring of tetrahedral sheets. The orientational disorder of water, in agreement with previous Raman spectroscopy data, is a feature relevant to the evaluation of thermodynamic functions and thermal stability of the 10 Å phase, which is a possible water carrier (9.1 wt%) in subducting slabs at high pressure.

INTRODUCTION

The 10 Å phase, Mg₃Si₄O₁₀(OH)₂H₂O, is a dense hydrous magnesium silicate that forms from talc at pressures between 3–5 GPa (Yamamoto and Akimoto 1977; Pawley and Wood 1995). Recently Perrillat et al. (2004), with real-time X-ray diffraction data, followed the mineralogical reactions of antigorite breakdown. They showed that, in the range 1.5–5 GPa, the data, followed the mineralogical reactions of antigorite breakdown. They showed that, in the range 1.5–5 GPa, the breakdown of antigorite is temperature-dependent and above 550 °C forsterite and a phyllosilicate close to the talc structure form at the expense of chlorite starting from 4.8 GPa, 680 °C, contributing significantly to the water budget in subduction zones (Fumagalli et al. 2001). Micro-Raman spectra give an indication of partial static disorder in the orientation of the water molecules. Moreover, none of the three peaks in the OH stretching region agrees with the occurrence of hydronium (H₃O⁺) is not supported by Raman spectroscopy. On the contrary, the occurrence of water molecules in the interlayer is strongly suggested by the H₂O bending mode at 1593 cm⁻¹ and two OH stretching modes at 3593 cm⁻¹ and 3668 cm⁻¹ in addition to the OH stretching of structural hydroxyl groups at 3622 cm⁻¹ (Fumagalli et al. 2001). Micro-Raman spectra give an indication of partial static disorder in the orientation of the water molecules. Moreover, none of the three peaks in the OH stretching region agrees with the stretching mode frequency of hydronium in micas (White and Burns 1963).

Miller et al. (1991) hypothesised, from thermogravimetric data and calculation of dehydration enthalpies, that O²⁻ occupies the interlayer site and is stabilised by two resonating protons leading to momentary formation of OH, H₂O, and H₃O⁺, without direct interaction with neighbouring OH groups.

The structure of the 10 Å phase has recently been studied from neutron powder diffraction data (Pawley et al. 2004); the results from a deuterated 10 Å phase further confirm that a phlogopite-like model fits the measured spectra better than a...