In-situ infrared spectroscopic studies of hydroxyl in amphiboles at high pressure

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ABSTRACT

Oceanic plates contain numerous hydrous phases including amphiboles, which are important carriers of water into subduction zones. The hydroxyl bound within the crystalline structure of hydrous minerals, as well as changes in hydrogen bond symmetry, can impact the bulk properties of these minerals. In this study, 12 natural amphibole samples spanning a range of 10 compositions were probed with synchrotron infrared spectroscopy at room temperature and pressures up to 60 GPa. Infrared spectra were collected at atmospheric pressure and at regular intervals during compression, allowing for the collection of spectra centered on the typical O-H stretching region at 3600–3700 cm⁻¹ as they evolved with pressure for each composition. The number of O-H bands within each sample was found to vary with composition, but the pressure dependence of O-H frequency shifting more closely correlated with mode frequency at ambient pressure than with composition. Combined with earlier results, these data reveal a linear relationship between mode frequency at ambient pressure and the pressure dependence of O-H stretching modes in amphiboles and sheet silicates.

Two sample preparation methods utilized in this study allowed for direct comparison between quasi-hydrostatic neon-loaded sample conditions and the conditions achieved with a KBr pressure medium. Samples loaded in neon preserved sharper peaks, allowing greater spectral resolution, especially at higher pressures when peaks are most likely to broaden or disappear due to crystalline disorder and pressure gradients across the sample. This new quasi-hydrostatic loading method proved valuable to tracing O-H stretching behavior in amphiboles to higher pressures than previously obtained and will lend itself to future study of O-H stretching pressure dependence in a wide range of hydrous minerals.

Keywords: Infrared, high pressure, diamond-anvil cell, hydroxyl, amphiboles

INTRODUCTION

Oceanic plates contain numerous hydrous phases, and since amphiboles contain ~2 wt% H₂O they are important carriers of water into subduction zones (Stern 2002). As amphiboles within the oceanic slab are subjected to increasing temperatures and pressures as the slab subducts along the cold slab geotherm, a dehydration reaction is initiated. The dehydration of amphiboles may extend to depths of 100 km, depending on local variations in the subducting slab’s geotherm (Stern 2002). This reaction influences island arc volcanism, as 5–20% of the water released from subducting basaltic slabs into overlying mantle may originate from amphibole dehydration (Schmidt and Poli 1998). The accommodation and subsequent loss of this hydroxyl at elevated pressure has been predicted to vary with composition in response to the repulsive interactions between cations, as well as the influence on hydrogen bonding by next-to-nearest neighbors, in a chemically complex system, which merits further study (Hawthorne and Della Ventura 2007). Hydrogen cycling in the Earth’s interior is critical due to the influence of hydroxyl on melting temperatures, rheology, electrical conductivity, and atomic diffusivity, as well as macro-scale phenomena including plate tectonics and volcanism (Hofmeister 2004; Hirschmann 2006). Hydrogen bond symmetrization in hydrous minerals may influence the response of bulk properties to pressure, for example increasing bulk modulus by as much as ~20% (Tsuchiya et al. 2005; Sano-Furukawa et al. 2009; Hushur et al. 2011).

Amphiboles are a group of inosilicates that accommodate an extensive range of both cation and anion substitutions (AB₂C₅OH₂W₂), resulting in classification into eight sub-groups (Hawthorne et al. 2012). In this generalized formula the large A site may contain a cation (e.g., Na, Ca, etc.) but is often vacant, the B represents the cations of the M4 site that may be six- or eightfold coordinated, and the C represents the cations of the octahedral M1, M2, and M3 sites. Structurally, amphiboles are comprised of corner-linked double chains of silicate tetrahedra (T sites) that extend along the c-axis and bookend a single octahedral strip. O atoms occupy two distinct planes; basal or bridging oxygen link adjacent (SiO₄)⁴⁻ tetrahedra along the c-axis and apical or non-bridging oxygen are coordinated to single tetrahedra. The A site between the octahedral and tetrahedral strips (also A in the generalized formula above) can host large alkali ions such as Na⁺ and K⁺ but often remains vacant. Three sites within the inner octahedral strip accommodate divalent and trivalent cations including Al, Ca, Fe, Mg, and Ti, and are represented by B and C in the generalized formula. The W site hosts OH⁻ or halogens. The amphibole family is divided into two symmetries (monoclinic and orthorhombic) and five structures (C2/m, P2₁/m, P2/a,

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