Introduction: Humites are a polysomatic series of hydrous magnesium silicates consisting of olivine-like and brucite-like layers. The close structural similarity to olivine accounts for the fact that minor amounts of water in some hydrated olivines result from the intergrowth of olivine and humite-like monolayers. Therefore, studies of the hydrogen atom environment in humites provide useful insights into the local environment of OH defects in olivine. Humites may also be important phases involved in the storage, transport and recycling of water in the mantle. The O-H1 and O-H2 bond lengths in OH-chondrodite and OH-clinohumite are two of the longest O-H distances reported in mineral structures. In the case of OH-clinohumite, these long distances may be due to the extensive network of hydrogen bonds formed with oxygen atoms in the olivine-like and brucite-like layers. There is also evidence from atomic displacement parameters that the lengths of the O-H distances in OH-chondrodite are an artifact of the disorder of the oxygen atom. Recent Raman studies at pressure using water as the pressure-transmitting medium have shown that the frequency of all OH bands in both OH-clinohumite and OH-chondrodite increase with pressure. In addition, a mode softening (splitting) of one of the OH bands in OH-clinohumite was observed at ~18 GPa. In this study, we performed high-pressure synchrotron infrared absorption investigations on OH-chondrodite and OH-clinohumite up to 38 GPa at ambient temperature. One objective of these experiments was to re-examine the results from the Raman studies using a more hydrostatic pressure medium (argon).

Methods and Materials: OH-clinohumite and OH-chondrodite single crystals were synthesized at 7 GPa and 1000°C and 3 GPa and 910°C, respectively. In-situ high-pressure FTIR absorption experiments were performed at the U2A beamline of NSLS. To avoid any saturated absorption, a thin pellet with thickness less than 1 µm and ~50 µm in diameter was created from a single crystal grain using a diamond anvil cell. A stainless gasket with a 150 µm hole was placed between the two anvils and several ruby grains were loaded into the gasket hole for pressure calibration. Argon gas was liquefied with liquid nitrogen and loaded into the sample chamber as a pressure-transmitting medium. All spectra were recorded from 4000 to 550 cm⁻¹ on a Bruker IFS 66s/V FTIR spectrometer with a MCT detector.

Results: Fig. 1 represents typical IR absorption spectra of OH-clinohumite at different pressures and room temperature and similar spectra have been obtained for OH-chondrodite as well. These absorption bands are related to symmetric and asymmetric stretching modes of the silicate tetrahedron and to OH stretching vibrational modes. Our results indicate that the crystal structures of both clinohumite and chondrodite are preserved up to 38 GPa at room temperature. However, dis ordering of the silicate framework appears to become more pronounced at high pressure based on the significant broadening of the IR bands with increasing pressure. All three OH bands in both structures shift linearly to higher frequency with pressure up to 18 GPa. Above 18 GPa, the variation of OH frequency with pressure remains linear; however, the slopes for the three OH bands are significantly different as a result of different degrees of hydrogen bonding. The results are compared with the behavior of other hydrous magnesium silicates, where the OH vibrational frequency decreases with pressure, implying an increase in hydrogen bond strength as O-H…O distances shorten at high pressure.