K131-014 Room: 201B Time: May 20 14:00-14:15

Difference of hydrogen bondings in pure water and alkali chloride solutions based on Raman spectroscopy and MD calculation

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We have conducted two series of experiments in order to understand chemical features of aqueous fluids and seawater in the earths interior: (1) Raman scattering spectra of alkali chloride solutions under high pressure conditions at room temperature, and (2) molecular dynamics calculations of pure water and NaCl solutions. Base on these data, we will discuss structural difference beween pure H2O and alkali chloride solutions.

1 Introduction H2O is the most abundant volatile species in the earths interior. H2O have effects on almost all phenomena in the earths interior. Kawamoto and the others (2004) suggested a possible structural change from low-pressure water to high-pressure water based on Raman spectroscopy of pure H2O (Kawamoto, Ochiai, Kagi, Changes in the structure of water deduced from the pressure dependence of the Raman OH frequency. Journal of Chemical Physics 120, 5867-5870, 2004). Sea water can be the aqueous fluid which is introduced into the earths mantle through subduction. Therefore, it is important to know the structural features of alkali chloride solutions under high-pressure conditions. In the present study, we obtained Raman spectra of X12H2O and X72H2O where X is Li, Na, and K under room temperature and high-pressure conditions up to 2 GPa. In addition to this, we carried out molecular dynamics calculations using pure H2O and NaCl solutions.

2.1 High-pressure spectroscopy We put alkali chloride solutions inside of a hole in a rhenium metal located in the middle of a diamond anvil cell w a ruby chip as a pressure marker. High pressure can be attained by approaching two diamonds. Sample can be observed visually under a microscope. At each pressure, Raman spectrum were sampled with Raman microscope (Kaiser Hololab 5000) in the institute of Geothermal Sciences, Kyoto University.

2.2 Molecular dynamics calculation By the use of the MD program developed by Dr. Katsuyuki Kawamura of the Tokyo Institute of Technology (MXDORTO, version 2006), we carried out a series of calculations of pure H2O (512 H2O) and NaCl solutions (8 NaCl in 512 H2O, 16 NaCl in 512 H2O). So far now, the calculations were done at room temperature and room pressure. An effect of pressure will be in progress.

3 Results The Raman data show a increase of Raman frequency with increasing concentration of alkali chloride. This can suggest that the length of hydrogen bonding of H2O increase in the solutions (Nakamoto, K., Margoshes. M., and Rundle, R.E. Stretching frequencies as a function of distances in hydrogen bonds. Journal of the American Chemical Society, 77, 6480-6486 1955). Alternatively, it can be interpreted as a result of decreasing strength of hydrogen bonding. As a function of pressure, the Raman frequencies decrease, suggesting shortening length of hydrogen bonding or strengthening hydrogen bonding. The pressure dependence of Raman frequency seems constant in the X12H2O solutions, while it has a kink at 0.4 GPa in X72H2O solutions, especially NaCl72H2O. Therefore, it is likely to mention that sea water may have a possible structural change as suggested for pure H2O.

MD calculations gave us length of hydrogen bonding, number of hydrogen bonding, and vibration spectrum of pure H2O and the two NaCl solutions. We learned the followings: (1) Increasing NaCl decreases the number of hydrogen bonding between H2O molecules. (2) Increasing NaCl decreases the lengths of hydrogen bonding. This feature was not expected before, because the Raman spectroscopy suggested the opposite. (3) Vibration frequency increase with increasing NaCl. This is consistent with our Raman experimental observation.

4 Conclusion The present MD calculation and the Raman spectroscopy suggest that the number of hydrogen bonding between H2O molecules decrease in NaCl solutions, and this results in decreasing the strength of hydrogen bonding between H2O molecules. The seawater may have a structural change as observed in pure H2O under high PT conditions.