

SODIUM CHLORIDE HYDRATES WITH HIGH HYDRATION NUMBERS, STABLE AT ICY OCEAN WORLD SURFACE AND INTERIOR CONDITIONS. B. Journaux¹, A. Pakhomova^{2,3}, I. E. Collings^{3,4}, S. Petitgirard⁵, T. Boffa Balaban⁶, J. M. Brown¹, S. D. Vance⁷, S. Chariton⁸, V. .B. Prakapenka⁸, D. Huang⁵, J. Ott¹, K. Glazyrin², G. Garbarino³, D. Comboni³, M. Hanfland³ ¹Department of Earth and Space Sciences, University of Washington; Seattle, WA 98195, USA. ²Deutsches Elektronen-Synchrotron, D-22607 Hamburg, Germany, ³European Synchrotron Radiation Facility; 38000 Grenoble, France., ⁴Center for X-ray Analytics, Empa - Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland., ⁵Institute of Geochemistry and Petrology, ETH Zürich, 8092 Zürich, Switzerland., ⁶Bayerisches Geoinstitut, University of Bayreuth, 95440 Bayreuth, Germany., ⁷Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA., ⁸Center for Advanced Radiation Sources, University of Chicago, Chicago, IL, USA.

Introduction: Sodium chloride, the main solute in Earth's oceans, has been long predicted in the oceans of icy worlds—Europa, Ganymede, and Enceladus—by geochemical models, cryogeysir plumes composition and observed surface features [1–3]. Yet, no known solid NaCl or hydrated form can match the observed near-IR spectral features [4,5]. The H₂O-NaCl system has only one hydrate phase known to date, the hydrohalite mineral, or sodium chloride dihydrate, NaCl·2H₂O (SC2), space group *P2₁/c* [6]. Surprisingly, the H₂O-NaCl system has been poorly studied at the conditions of the surface and interior of icy worlds (up to 2000 MPa and 150-300 K).

Based on state-of-the-art experimental techniques at high pressures and low temperature, we report the discovery of 3 new hydrates. We performed in-situ experiments in the H₂O-NaCl systems over a large range of pressures (from near vacuum up to 2500 MPa) using a cryogenically cooled diamond anvil cell, coupled with single crystal X-ray diffraction (SCXRD), and Raman spectroscopy. We also studied the thermodynamic stability of those hydrates over the entire range of conditions expected in the hydrospheres of icy worlds in the Solar System [7].

Experimental Method: We performed *in situ* X-Ray diffraction experiments at ID15B beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France), and at the P02.2 beamline of Deutsches Elektronen Synchrotron (DESY, Hamburg, Germany). A mixture of ultrapure MiliQ™ water with NaCl (4 mol/kg solution) was loaded in the sample chambers, along with a ruby sphere used as a pressure calibrant. Temperature was regulated using in-house He-cryostats available at respective beamlines. Powder- and single-crystal X-ray diffraction data were collected. The crystal structure, unit-cell lattice parameters and the integrated intensities of the Bragg reflections were obtained from the measured images using the program CrysAlisPro™. Raman spectra were collected on the DAC optimized confocal Raman system at GSECARS equipped with ultralow frequency (<10 cm⁻¹) Raman

edge filters and a deep-depleted back illuminated CCD detector (PIXIS100 from Princeton Instruments™).

Results: We identified three new hydrate phases in the H₂O-NaCl systems in the 150-300 K temperature range and up to 2500 MPa (25 kbar). We refined the crystal structures of two new sodium chloride hydrates at high pressure: the disodium chloride decaheptahydrate, 2NaCl·17H₂O (SC8.5), and the sodium chloride decatriahydrate, NaCl·13H₂O (SC13). We also report the symmetry and lattice parameters of a third phase. These phases stand out for their unique structures: Sodium and Chloride are fully dissociated (hyper-hydrated) and Sodium is in a full solvation shell configuration within a Na⁺(H₂O)₆ octahedron as shown in fig. 1a. They are also the only 8.5 and 13 hydrates known to date, providing evidence for a greater diversity of hydrates and hydrogen-bonded crystal structures than previously recognized. Having many waters of hydration (stoichiometric number of H₂O molecules per salt ions pair) is surprising. Other alkali halides have a small number of waters of hydration, less than 5 in most cases. This unexpected level of hydration suggests that many other hydrates with hyper-hydrated structure might be found at higher pressure for many planetary relevant systems.

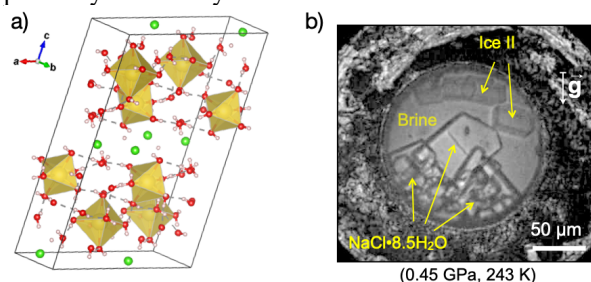


Figure 1: a) Refined structure of disodium chloride decaheptahydrate (SC8.5). Na in yellow, Cl in green, O in red, H in white. b) Microphotograph of the diamond anvil cell pressure chamber showing SC8.5 crystal habits.

We studied the stability of these hydrates and determined that SC8.5 and SC13 should be the main

NaCl hydrates present inside the high-pressure mantles of large icy worlds like Ganymede, Titan or Callisto. To determine the stability of SC8.5 up to icy moon surface conditions, we performed a quenching experiment and recovered SC8.5 at near vacuum condition at 150K. Upon heating, SC8.5 remained stable up to 235 K, where it transformed into a hydrohalite + ice Ih assemblage. Measurements of SC8.5 liquidus at higher pressures and temperatures allows us to predict the transition around 235K as well. This low-pressure stability supports a revision of the H₂O-NaCl phase diagram with a solid-solid phase transition SC2+ice Ih <-> SC8.5+ice Ih at 235K.

Conclusion: The discovery that SC8.5 is stable at low pressures supports its possible presence on icy worlds surface conditions; we predict that it should be the most common NaCl hydrates found on icy surfaces of the outer solar system. Previous work on the surface compositions of Europa and Ganymede did not identify any NaCl hydrates. Absent adequate spectral information for NaCl hydrate phases, several studies tried to fit Galileo near-IR spectra from Europa's surface with various other hydrates and found that species with high water of hydration and often hyper-hydrated structures—including sulfates, or the chlorinated species: chlorates (ClO₃⁻) or perchlorates (ClO₄⁻) hydrates [4,8]—most closely fit the observed spectral features. SC8.5, with its hyper-hydrated structure could resolve the discrepancy between clues pointing toward the presence of NaCl at the surface and the cryptic near-IR observations.

These discoveries also suggest that many other phases of common and planetary relevant hydrate species are waiting to be unveiled, and call for a community effort studying aqueous systems at conditions relevant to planned and future planetary exploration missions—Europa Clipper [9], JUICE[10], NASA DragonFly [11], Uranus Orbiter and Probe.

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