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Water Signatures and Their Thermal Stability in Bedded Salt for Nuclear Waste Storage: An Incoherent Inelastic Neutron Spectroscopy Study

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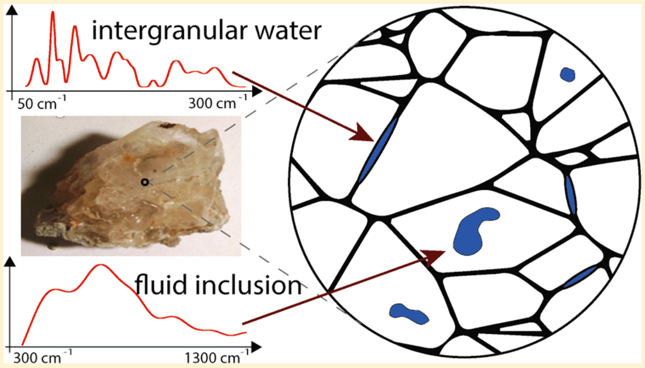

ABSTRACT: The forms of water and their thermal stability in bedded salt are crucial in determining the material's suitability for heat-generating nuclear waste storage. Here we show first-of-its-kind incoherent inelastic neutron scattering (IINS) results of bedded salts to distinguish three water environments: intergranular water molecules confined to grain boundaries, water trapped as brine in fluid inclusions, and structural water in intracrystalline hydrous minerals. Sixteen spectral lines can be distinguished unambiguously in the 0−1100 cm^{-1} multiphonon and librational domain, yielding an unprecedented high resolution for a natural material. The spectral response to temperature illustrates the bimodality of the technique enabling the intergranular water component to be distinguished from that of brine, shedding light on a nearly 30-year-old problem in characterizing different forms of water in rock salt. This pioneering study shows that IINS provides insight into the cause and effect of moisture migration and its coupling to thermomechanical properties in salt formations. Our results are pertinent to subsurface energy exploration and storage, including nuclear waste storage, in salts.

■ INTRODUCTION

Deep geological storage including salt deposits is the ultimate solution in nuclear waste management for long-term safe disposal of nuclear waste.[1−8] Permian salt located near the waste isolation pilot plant (WIPP)[9] in southeast New Mexico is the nation's only licensed deep geologic repository for permanent disposal of defense transuranic (TRC) waste. Its suitability for storage of heat-generating nuclear waste (HGNW) is currently being studied.[10−12]

A homogeneous salt (e.g., Domal salt formations)[13] provides a well-defined, predictable geological barrier. However, bedded Permian salt formations commonly found in the United States are heterogeneous. They contain hydrous minerals, such as gypsum, clay, and polyhalite, providing brine mobility paths not found in Domal salt.[14,15] Thus, research into water content and transport behavior in bedded rock salt is one of the key focus areas, having historically been of concern for performance assessment of nuclear waste storage,[11,16,17] and is essential to justify using Permian salt formations as repositories for the disposal of HGNW.[10,18]

Water in salt and its role in deformation and weakening of rock salt during long-term creep have been studied extensively.[14,15,19−25] In addition, brine migration in salt under thermal gradients has been reported by numerous researchers.[18,26−30]

Previous studies indicate that water occurs in rock salt in three forms: bound water in hydrous minerals (e.g., clays and hydrated salts),[2,17,18,20] intergranular pore water in grain boundaries,[20,29−31] and free water trapped as brine in fluid inclusions.[20,29,30] However, as pointed out three decades ago by Roedder and Bassett,[17] errors and problems persist in assigning these three water forms unambiguously, leading to incompatibilities among published results.

Two major problems impede progress in determining water content and study of its transport behavior in rock salt. One is the experimental lack of a technique to distinguish and quantify the three different water forms, particularly for intergranular water. The second problem is intrusive sample preparation required by analytical techniques, causing changes in brine analysis.[17] However, progress in micrography has made chemical analysis of 30 μm brine inclusions feasible.[32,33] Another important unexplored issue is the effect of water

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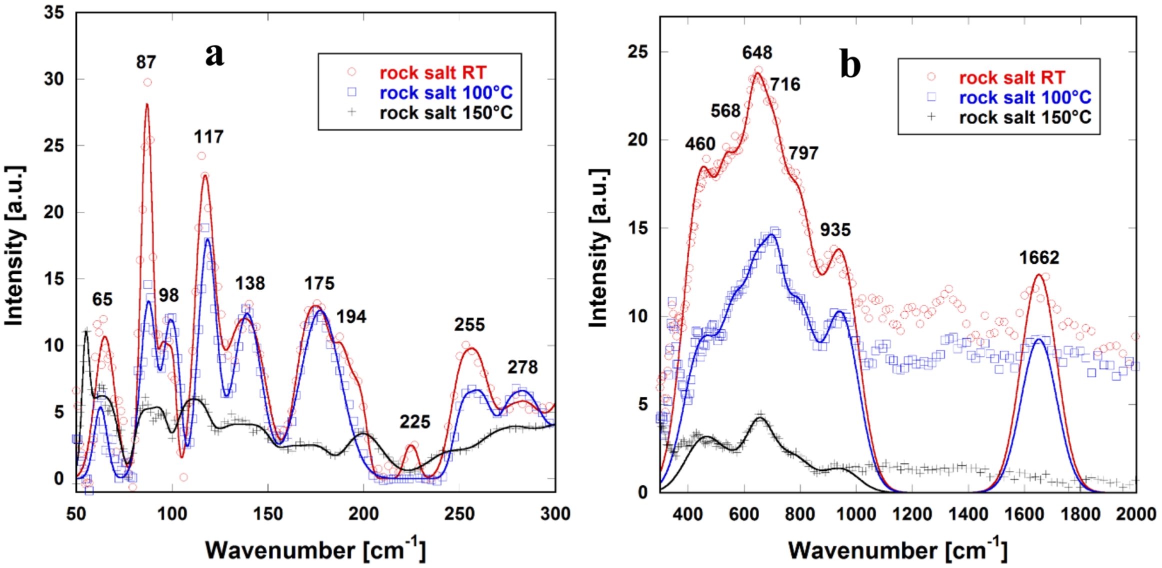

Figure 1. Three IINS spectra of rock salt in (a) the multiphonon domain and (b) librational domain and a small segment of the vibration domain at room temperature (RT, red), dehydrated at 100 °C (blue), and at 150 °C (black). The dots represent the experimental data; the lines are fitted results using Gaussians. Disappearance of the 1662 cm^{-1} bending mode after treatment at 150 °C indicates the absence of water in the sample within the IINS detection limit.

release and movement of nanoscale pore water confined in grain boundaries, as opposed to bulk water, on the coupled thermomechanical behavior of intact and crushed salt.[32,34]

To characterize specific water forms in rock salt and investigate the release of water, including nanoscale pore water, at elevated temperatures, we explored incoherent inelastic neutron scattering (IINS), using the filter difference spectrometer (FDS) at the Los Alamos Neutron Science Center (LANSCE).

IINS, a vibrational spectroscopic method, is an energy loss spectroscopy in which a fraction of the incident neutrons loses energy by exciting vibrational modes of the scatterer.[35] It is selectively sensitive to the dynamics of hydrogen atoms, has no selection rules, and is nondestructive and thus easily penetrates large samples.[36−40] We use this technique in a first exploratory effort to characterize water in rock salt. Our principal result shows that the observed spectral lines discriminate unambiguously among multiphonon, librational, and O−H stretching modes of intergranular pore water, brines, and bound water in hydrous minerals. This capability has profound implications in unveiling the fundamental aspects of moisture migration in rock salt, a prerequisite for safe and robust sequestration of HGNW in bedded salt formations.

■ MATERIALS AND METHODS

Two samples, unadulterated rock salt and its insoluble residue from the Permian salt formations located near Carlsbad, New Mexico, were loaded in the instrument cylinder sample cell (ϕ2 cm, L15 cm), which can hold up to 150 g of intact rock salt. The sample must be carefully selected as it has been well-known since the pioneering studies of Usiglio[41] and van't Hoff[42] that salt deposits are laterally inhomogeneous: calcium−magnesium carbonates as least soluble minerals precipitating first, followed by gypsum, halite, magnesium sulfate, potassium chloride, and magnesium chloride, as most soluble, precipitating last in the center of the basin. The Permian bedded salt in the WIPP area is inhomogeneous, mainly halite (NaCl) and polyhalite [$K_2Ca_2Mg(SO_4)_4 \cdot 2(H_2O)$], with minor amounts of magnesite ($MgCO_3$), clays, gypsum ($CaSO_4 \cdot 2H_2O$), and quartz (SiO_2).[43] This phase assemblage is characteristic of late Precambrian, Permian, and ternary seawater precipitates with high Mg/Ca ratios, polyhalite being one of the characteristic phases.[32] The rock salt sample we selected is nearly pure halite with a small amount of magnesite. The residual (~0.5 wt %) consists primarily of quartz and corrensite (an interlayered smectite/chlorite swelling clay) and kaolinite, with still some halite and magnesite.

Our thermogravimetric analysis (TGA) results resemble those published for halite,[44] modified by the small amount of corrensite.[43] Pristine halite in our sample contains 0.07 wt % moisture (combined intergranular pore water and brine). The insoluble residue (0.5 wt % of the total sample) contains 22.5 wt % moisture (H_2O and OH), 4.1 wt % of which is released as H_2O by 150 °C. The water content due to corrensite in our rock salt sample is 0.02 wt %.

IINS Spectroscopy. The filter difference spectrometer at LANSCE is used for IINS molecular vibrational spectroscopy. Technical details can be found at http://lansce.lanl.gov/lujan/instruments/FDS.shtml. The room-temperature (RT) samples and those heat treated at 100 and 150 °C for rock salt, at 150 and 450 °C for the insoluble residue, were loaded in cylindrical aluminum sample holders, mounted in a closed-cycle refrigerator, and measured at 10 K. A vanadium rod was used as background.

■ RESULTS AND DISCUSSION

IINS Spectra of Rock Salt at Elevated Temperatures. Figure 1 shows the IINS rock salt spectra of the RT sample and those after heat treatment at 100 and 150 °C. The frequency in inverse centimeters (1 meV = 8.065 cm^{-1}) is given above each peak. Three frequency domains occur (1) the multiphonon modes-H_2O between 1 and 300 cm^{-1} (Figure 1a), (2) the water libration modes between 300 and 1100 cm^{-1} (Figure 1b), and (3) the intramolecular vibrations as referenced by the H−O−H bending mode around 1660 cm^{-1} (Figure 1b).

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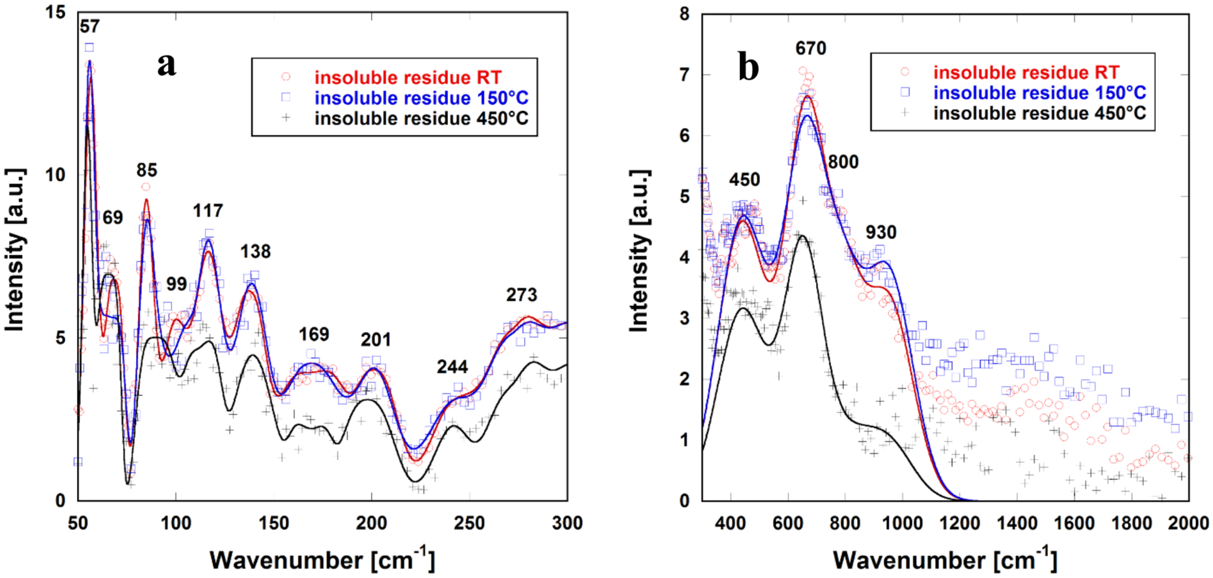

Figure 2. Three IINS spectra of the insoluble residue in (a) the multiphonon domain and (b) the librational domain at room temperature (RT, red), dehydrated at 150 °C (blue), and at 450 °C (black). The dots represent the experimental data; the lines are fitted results using Gaussians.

Our focus is on the first two domains and their scattering intensity variation as a function of temperature. Though detailed assignment of the vibrational modes falls outside the scope of this study, some generalities may be observed. The first domain is characteristic of interaction of water with NaCl lattice vibrational modes. There are six of these modes in NaCl, the highest-energy, optical modes occurring at ~240 cm^{-1}.[45] The domain has exceedingly narrow resonances with a full width at half-maximum (FWHM) approximately half that of the narrowest and most intense translational peak in crystalline ice, [ice$_h$].[39] It represents specific coupling between a water molecule and the halite phonons. They must be associated with grain boundaries for two reasons. First, the halite crystal structure has no sites to accommodate water molecules. Second, the extreme narrowness of the resonances precludes coupling between different water molecules. Such modes are well-known for hydrogen atoms riding on catalyst supports, in which they follow adiabatically the plane motions in so-called riding modes.[35,46,47] They have never been observed for moisture in zeolites[37,39] or clays.[48] We designate these water modes "Chladni modes" to honor the father of acoustics Ernst Chladni (1756−1827). At higher frequencies, the multiphonon domain is followed by three resonances with somewhat broader FWHMs representing hydrogen stretches from intergranular moisture as well as fluid inclusions.[49]

The sudden rise in intensity around 300 cm^{-1} is designated the librational edge (LE). It marks the onset of the second domain representing interactions of water molecules with one another. These interactions are historically assigned to three modes around the center of mass of the water molecule: rock, twist, and wag, their energy sequencing being a matter of continuous debate as recently described by Parker et al.[50] This domain occurs as bands with or without structure in zeolites and clays.[37,39,48] It is characterized in our case by three high-intensity resonances with a number of subsidiary ones with very large FWHMs. Their intensity is a consequence of the large amplitude motion of librations in the brines; their width reflects the multiple interactions of water with the multiple brine constituents and the 0.02 wt % moisture in corrensite.

What marks the utility of IINS is the difference in the response of the two spectral domains to heat treatment of the sample. After heat treatment of the sample at 100 °C, the resonances in the first domain tend to coincide in position and intensity with those of the RT sample, except for the two resonances at 65 and 225 cm^{-1}, which are possibly associated with corrensite dehydration. The librational mode intensity in the second domain, on the other hand, is nearly halved together with a variation in the intensity ratio of the modes. It indicates primarily loss of the 0.02 wt % of moisture associated with corrensite that occurs between 65 and 75 °C. Thus, the spectrum of the sample heat treated at 100 °C shows the proportion of water confined in grain boundaries and that of brines included in fluid inclusions.

TGA results as well as the absence of the 1662 cm^{-1} bending mode in the 150 °C heat-treated sample indicate beyond 150 °C the absence of water in the sample, corrensite hydroxyl release taking off at 450 °C. Accordingly, the IINS spectra show virtually no resonances for the rock salt sample after treatment at this temperature

IINS Spectra of the Insoluble Residue at Elevated Temperatures. Figure 2 shows IINS spectra of the insoluble residue at RT and after heat treatment at 150 and 450 °C. Our results show an almost identical spectrum for the RT and 150 °C samples. On the other hand, the sample heat treated at 450 °C differs significantly, consistent with the onset of dehydroxylation of corrensite at ~450 °C.

Moisture Release in the Multiphonon and Librational Domain. The temperature-dependent release of water in the multiphonon scattering domain depends on the tenacity with which it is attached to the Chladni modes of the lattice. In the librational domain, it depends on the strength of the walls of the fluid inclusions. To analyze these effects more precisely, we assume that at 150 °C, all moisture has been released and the moisture-free 150 °C halite spectrum is the same as the RT spectrum. Thus, the difference spectrum between RT and 150 °C is the total moisture contribution to the sample, i.e., the 0.07 wt % in pristine halite and 0.02 wt % in corrensite. The difference spectrum between 100 and 150 °C on the other hand is the contribution of the remaining moisture in the

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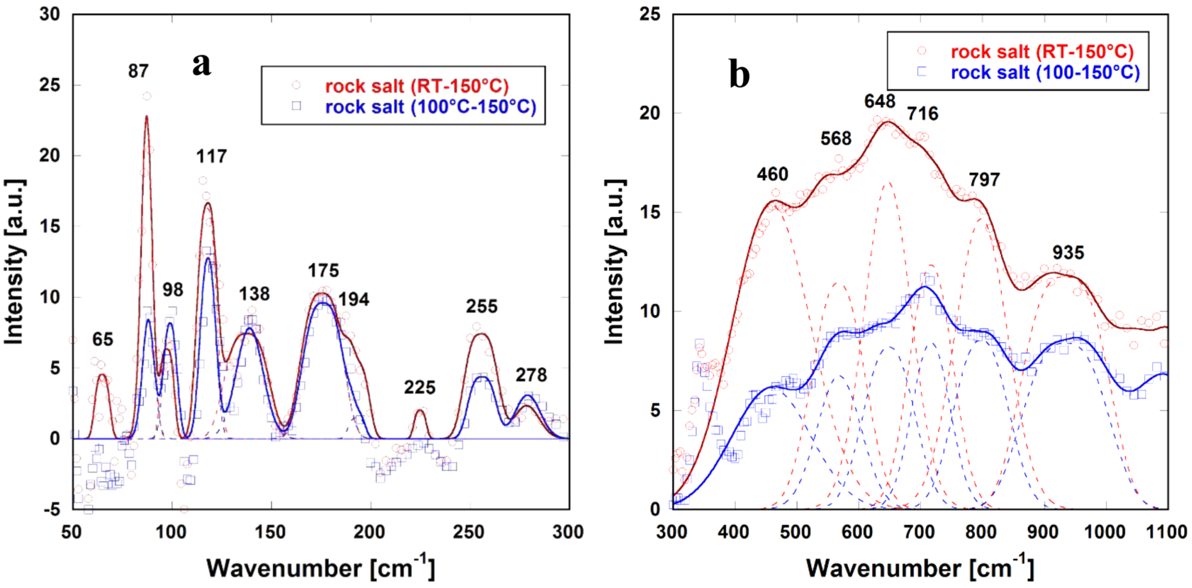

Figure 3. Differences in inelastic incoherent neutron scattering spectra of rock salt in (a) the multiphonon domain and (b) the librational domain. The red curve represents the difference between the 150 °C and RT spectra and the blue curve the difference between the 150 and 100 °C spectra. Symbols represent the experimental data points, and the curve fits are composed of Gaussians centered at the indicated positions.

Table 1. Calculated Peak Areas at Corresponding Frequencies and Moisture Release[a]

frequency (cm^{-1})	peak area (RT – 150 °C)	peak area (100 °C – 150 °C)	% water remaining at 100 °C	form of water
65	36	0	0	intergranular pore water
87	158	63	39.87	
98	48	64	133.33	
117	180	115	63.89	
139	180	133	73.89	
175	236	215	91.10	
194	63	14	22.22	
225	13	0	0.00	
255	135	67	49.63	
278	37	49	132.43	
460	2454	979	39.89	fluid inclusion
568	1163	604	51.94	
648	1574	802	50.95	
716	1058	648	61.25	
797	1563	888	56.81	
935	1778	1278	71.88	

[a] Calculated weight percent loss per formula unit. Corrensite: 13.3 wt % H_2O at 65–75 °C, 13.9 wt % OH at 450 °C. Gypsum: 20.9 wt % H_2O at <100 °C. Polyhalite: 6.0 wt % OH at ~250 °C. Kaolinite: 26.4 wt % OH at >550 °C.

sample treated at 100 °C. Figure 3 illustrates these two derived spectra fitted with an adequate number of Gaussians. Results are given in Table 1, indicating which modes release the most intergranular water or brine. The multiphonon frequency range for NaCl varies between ~80 and ~240 cm^{-1}, with the soft modes being designated the acoustic modes and the most energetic ones the optic modes. Inspection of Table 1 indicates the mode-dependent moisture release. The mode at 172 cm^{-1} represents the most tightly bound moisture. In general, the librational modes tend to release, as anticipated, more moisture over the considered temperature range relative to the multiphonon modes.

Our results show that it is possible with IINS to discriminate two moisture environments in halite due to a difference in the response of the sample to heat treatment at 100 °C. The first one, with very narrow resonances, is indicative of individual water molecules vibrating cooperatively with lattice vibrational modes of halite on grain boundaries. They are not affected by moderate sample heating. The second is the result of fluid motion in brines that become visible once the signal due to corrensite moisture release is eliminated. The ability to partition the 0.07 wt % moisture in pristine halite over these two environments makes it possible to target the proper moisture moiety responsible for hydrolytic weakening of halite. In our open system, this moisture will be released to the surroundings. In a closed system, the communication between brine-released moisture, the source, and intergranular thin film growth, the sink, will show up in spectral intensity variations between the two domains. This spectral capability is a definite significant advance urgently needed to place thermomechanical studies of halite on firm footing and to make pertinent robustness assessments of HNGW storage in bedded salt formations.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) U.S. Nuclear Regulatory Commission. Radioactive Waste: Production, Storage, Disposal. May 2002, NUREG/BR-0216, Rev. 2.

(2) Braitsch, O. *Salt Deposits: Their Origin and Composition*; Springer-Verlag: New York, 1971.

(3) Carter, N. L.; Hansen, F. D. Creep of Rocksalt. *Tectonophysics* **1983**, *92*, 275−333.

(4) Cosenza, Ph.; Ghoreychi, M.; Bazargan-Sabet, B.; de Marsily, G. In situ rock salt permeability measurement for long term safety assessment of storage. *International Journal of Rock Mechanics and Mining Sciences* **1999**, *36*, 509−526.

(5) Wicks, G. G. US Field Testing Programs and Results. *J. Nucl. Mater.* **2001**, *298*, 78−85.

(6) Brewitz, W.; Rothfuchs, T. Concepts and technologies for radioactive waste disposal in rock salt. *Acta Montanistica Ročnik* **2007**, *12*, 67−74.

(7) Final Disposal of High-level Radioactive Waste in Germany-The Gorleben Repository Project, Public Relations/IA8. Federal Ministry of Economics and Technology (BMWi) (October 2008).

(8) Chen, J.; Ren, S.; Yang, C.; Jiang, D.; Li, L. Self-Healing Characteristics of Damaged Rock Salt under Different Healing Conditions. *Materials* **2013**, *6*, 3438−3450.

(9) http://www.wipp.energy.gov.

(10) Hansen, F. D.; Leigh, C. D. Salt Disposal of Heat-Generating Nuclear Waste. Sandia National Laboratories Report SAND2011-0161; Sandia National Laboratories: Albuquerque, NM, 2011.

(11) Robinson, B. A.; Elkins, N. Z.; Carter, J. T. Development of a U.S. Nuclear Waste Repository Research Program in Salt. *Nucl. Technol.* **2012**, *180*, 122−138.

(12) Wald, M. L. Nuclear Waste Solution Seen in Desert Salt Beds. The New York Times, February 9, 2014.

(13) Mönig, J.; Beuth, T.; Wolf, J.; Lommerzheim, A.; Mrugalla, S. Preliminary safety analysis of the Gorleben site: Safety concept of application to scenario development based on a Site-Specific Features, Events, and Processes (FEP) Database-13304. In Proceedings of the WM2013 Conference, Phoenix, AZ, 2013.

(14) Schoenherr, J.; Urai, J. L.; Kukla, P. A.; Littke, R.; Schleder, Z.; Larroque, J. M.; Newall, M. J.; Al-Abry, N.; Al-Siyabi, H. A. S.; Rawahi, Z. Limits to the sealing capacity of rock salt: A case study of the Infra-Cambrian Ara salt from the South Oman salt basin. *AAPG Bull.* **2007**, *91* (11), 1541−1557.

(15) Muhammed, N. Deformation and transport processes in salt rocks: an experimental study exploring effects of pressure and stress relaxation. Utrecht Studies in Earth Sciences, #84, 2015, pp 275.

(16) Roedder, E.; Belkin, H. E. Application of studies of fluid inclusions in Permian Salado Salt, New Mexico, to the problems of siting the Waste Isolation Pilot Plant. In *Scientific Basis for Nuclear Waste Management*; McCarthy, G. J., Ed.; Plenum Press: New York, 1979; Vol. *1*, pp 453−464.

(17) Roedder, E.; Bassett, R. L. Problems in determination of the water content of rock-salt samples and its significance in nuclear-waste storage sitting. *Geology* **1981**, *9*, 525−530.

(18) Jordan, A. B.; Boukhalfa, H.; Caporuscio, F. A.; Robinson, B. A.; Stauffer, P. H. Hydrous mineral dehydration around heat-generating nuclear waste in bedded salt formations. *Environ. Sci. Technol.* **2015**, *49*, 6783−6790.

(19) Knauth, L. P.; Kumar, M. B. Trace water content of salt in Louisiana salt domes. *Science* **1981**, *213*, 1005−1007.

(20) Roedder, E. The fluids in salt. *Am. Mineral.* **1984**, *69*, 413−439.

(21) Urai, J. L. Water assisted dynamic recrystallization and weakening in polycrystalline bischofite. *Tectonophysics* **1983**, *96*, 125−157.

(22) Urai, J. L.; Spiers, C. J.; Zwart, H. J.; Lister, G. S. Weakening of rock salt by water during long-term creep. *Nature* **1986**, *324*, 554−557.

(23) Spiers, C. J.; Urai, J. L.; Lister, G. S. The effect of brine (inherent or added) on rheology and deformation mechanisms in salt rock. In *The Mechanical Behaviour of Salt II*; Hardy, H. R., Jr., Langer, M., Eds.; Trans. Tech.: Clausthal-Zellerfeld, Germany, 1988; pp 89−102.

(24) Peach, C. J.; Spiers, C. J. Influence of crystal plastic deformation on dilatancy and permeability development in synthetic salt rock. *Tectonophysics* **1996**, *256* (1−4), 101−128.

(25) Houben, M. E.; ten Hove, A.; Peach, C. J.; Spiers, C. J. Crack healing in rocksalt via diffusion in adsorbed aqueous films: Microphysical modeling versus experiments. *Phys. Chem. Earth* **2013**, *64*, 95−104.

(26) Bradshaw, R. L.; Sanchez, F. Migration of brine cavities in rock salt. *Journal of Geophysical Research* **1969**, *74* (17), 4209−4212.

(27) Roedder, E.; Belkin, H. E. Thermal gradient migration of fluid inclusions in single crystals of salt from the Waste Isolation Pilot Plant Site (WIPP). In *Scientific Basis for Nuclear Waste Management*; Northrup, J. M., Ed.; Plenum Press: New York, 1980; Vol. *2*, pp 453−464.

(28) Cheung, H.; Fuller, M. E.; Gaffney, E. G. Modeling of brine migration in halite. In *Scientific Basis for Nuclear Waste Management*; Northrup, J. M., Ed.; Plenum Press: New York, 1980; Vol. *2*, pp 471−478.

(29) Pigford, T. H. Migration of brine inclusions in salt. *Nuclear Technology* **1982**, *56*, 93−101.

(30) Hwang, Y.; Chambré; Pigford, T. H.; Lee, W. W. L. Brine migration in a salt repository, Radioactive Waste Management. *Nuclear Technology* **1990**, *90*, 205−214.

(31) Desbois, G.; Urai, J. L.; De Bresser, H. P. Fluid distribution in grain boundaries of natural fine-grained rock salt deformed at low differential stress (Qom Kuh salt formation, central Iran): Implications for rheology and transport properties. *J. Struct. Geol.* **2012**, *43*, 128−143.

(32) Lowenstein, T. K.; Timofeeff, M. N.; Brennan, S. T.; Hardie, L. A.; Demicco, R. V. Oscillations in Phanerozoic Seawater Chemistry: Evidence from Fluid Inclusions. *Science* **2001**, *294*, 1086−1088.

(33) Timofeeff, M. N.; Lowenstein, T. K.; Brennan, S. T.; Demicco, R. V.; Zimmermann, H.; Horita, J.; von Borstel, L. E. Evaluating seawater chemistry from fluid inclusions in halite: Examples from modern marine and nonmarine environments. *Geochim. Cosmochim. Acta* **2001**, *65* (14), 2293−2300.

(34) Fayer, M. D.; Levinger, N. F. Analysis of water in confined geometries and at interfaces. *Annu. Rev. Anal. Chem.* **2010**, *3*, 89−107.

(35) Mitchell, P. C. H.; Ramirez-Cuesta, A. J.; Parker, S. F.; Tomkinson, J. Inelastic neutron scattering in spectroscopic studies of hydrogen on carbon-supported catalysts-experimental spectra and computed spectra of model systems. *J. Mol. Struct.* **2003**, *651−653*, 781−785.

(36) Willis, B. T. M.; Carlile, C. J. *Experimental Neutron Scattering*; Oxford University Press: New York, 2009; pp 325.

(37) Ockwig, N. W.; Cygan, R. T.; Hartl, M. A.; Daemen, L. L.; Nenoff, T. M. Incoherent inelastic neutron scattering studies of nanoconfined water in clinoptilolite and heulandite zeolites. *J. Phys. Chem. C* **2008**, *112*, 13629−13634.

(38) Pechar, F.; Schweiss, P.; Fuess, H. Inelastic neutron scattering study of low frequency vibrations of water molecules in natrolite. *Chemické Zvesti* **1982**, *36* (6), 779−783.

(39) Line, C. M. B.; Kearley, G. J. An inelastic incoherent neutron scattering study of water in small-pored zeolites and other water-bearing minerals. *J. Chem. Phys.* **2000**, *112* (20), 9058−9067.

(40) Li, J. C.; Londono, D. K.; Ross, D. K.; Finney, J. L.; Tomkinson, J.; Sherman, W. F. An inelastic incoherent neutron scattering study of ice II, IX, V, and VI-in the range from 2 to 140 meV. *J. Chem. Phys.* **1991**, *94*, 6770−6775.

(41) Usiglio, J. Analyse de l'eau de la Méditerranée sur les côtes de France. *Ann. Chim. Phys.* **1849**, *XXVII*, 92−107 , 172−191.

(42) Hoff, J. H. V. Zur Bildung der Ozeanischen Salzablagerungen. *Z. Anorg. Chem.* **1905**, *47* (1), 244−280.

(43) Caporuscio, F. A.; Boukhalfa, H.; Cheshire, M. C.; Ding, M. Brine migration experimental studies for salt repositories. Fuel Cycle Research & Development, Los Alamos National Laboratory Report LA-UR-14-26603; Los Alamos National Laboratory: Los Alamos, NM, 2014; pp 67.

(44) Zimmermann, J. L.; Moretto, R. Release of water and gases from halite crystals. *Eur. J. Mineral.* **1996**, *8*, 413−422.

(45) Raunio, G.; Almqvist, L.; Stedman, R. Phonon dispersion relations in NaCl. *Phys. Rev.* **1969**, *178* (3), 1496−1501.

(46) Mitchell, P. C. H.; Ramirez-Cuesta, A. J.; Parker, S. F.; Tomkinson, J.; Thompsett, D. Hydrogen spillover on carbon supported metal catalysts studied by inelastic neutron scattering. Surface vibrational states and hydrogen riding modes. *J. Phys. Chem. B* **2003**, *107*, 6838−6845.

(47) Cavallari, C.; Pontiroli, D.; Jiménez-Ruiz, M.; Ivanov, A.; Mazzani, M.; Gaboardi, M.; Aramini, M.; Brunelli, M.; Ricco, M.; Rols, S. Hydrogen on graphene investigated by inelastic neutron scattering. *J. Phys.: Conf. Ser.* **2014**, *554* (1), 012009.

(48) Neumann, D. A. Quasielastic and inelastic neutron scattering studies of layered silicates. In *Access in Nanoporous Materials*; Pinnavaia, T. J., Thorpe, M. F., Eds.; Plenum Press: New York, 1995; pp 381−404.

(49) Senesi, R.; Flammini, D.; Kolesnikov, A. I.; Murray, E. D.; Galli, G.; Andreani, C. The quantum nature of the OH stretching mode in ice and water probed by neutron scattering experiments. *J. Chem. Phys.* **2013**, *139*, 074504.

(50) Parker, S. F.; Refson, K.; Bewley, R. L.; Dent, G. Assignment of the vibrational spectra of lithium hydroxide monohydrate. *J. Chem. Phys.* **2011**, *134*, 084503.