

Nanoscale Structure and Dynamics in Geochemical Systems

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ABSTRACT

Neutron scattering is a powerful tool to elucidate the structure and dynamics of systems that are important to geochemists, including ion association in complex aqueous solutions, solvent-exchange reactions at mineral–water interfaces, and reaction and transport of fluids in nanoporous materials. This article focusses on three techniques: neutron diffraction, which can reveal the atomic-level structure of aqueous solutions; quasi-elastic neutron scattering, which measures the diffusional dynamics at mineral–water interfaces; and small-angle neutron scattering, which can show how pore structures change during gas, liquid, and solute imbibition and reaction. The usefulness and applicability of the experimental results are extended by rigorous comparison to computational simulations.

KEYWORDS: neutron scattering; complex aqueous solutions; mineral–water interface; nanopores

INTRODUCTION

The structure and dynamics of water, aqueous species, and the interaction of these substances with Earth materials, all play essential roles in geochemical processes. Understanding the interaction between a solute and its solvent is critical for predicting solid solubilities, the kinetics of mineral and amorphous phase growth and dissolution, the weathering or alteration of geological materials, and many other properties or processes. Neutron scattering methods described by Ross and Cole (2021 this issue) provide the opportunity to quantify these processes. We begin by showing how the nature and extent of ion pairing and chemical complex formation can be revealed in aqueous solutions. Next, we offer examples of how mineral surface reactivity is interrogated, demonstrating how the nanoscale structure of the mineral–water interface modifies reactivity compared to bulk phases. Finally, we show how neutron scattering provides a unique window on fluid

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structure and dynamics within nanoporous media, where the reactivity of the mineral–water interface is inextricably coupled to the rate of transport. The information learned from neutron scattering is dramatically enhanced by a rigorous comparison to atomic-level simulations, allowing unambiguous interpretation of atomic structure and validation of the molecular model. This can then be used to predict other geochemical processes with a greater degree of confidence.

This article is focused on three methods: neutron diffraction, quasi-elastic neutron scattering, and small-angle neutron scattering. Neutron diffraction permits the direct determination of pair distribution functions of solutions and materials, which provides molecular-level structural information about the distribution of distances between atoms in the sample. Neutron diffraction with isotopic substitution (NDIS), a technique unique to neutron scattering, yields increased chemical specificity of the signal by eliminating contributions from certain elements by substituting a different isotope of one element in the sample, changing its scattering. Quasi-elastic neutron scattering (QENS) yields diffusional motions of hydrogen-bearing solvent molecules (such as water) on the picosecond-to-nanosecond timescale. Applying a validated computational model allows for the extraction of surface site-specific solvent exchange rates, a key parameter for understanding mineral reactivity (Casey 2015). Small-angle neutron scattering is a method analogous to diffraction, but the scattering is from phase boundaries instead of atoms, and yields the characteristics of pore structures from the nanometer-to-micrometer scales: larger scales can be achieved by combining with the related technique of ultra-small neutron scattering. Performing small-angle neutron scattering in situ permits quantification of poorly constrained rates of crystal growth. The dynamical behavior of fluids and gases contained within porous solids can also be observed using QENS. The richness and complexity of fluid behavior (e.g., phase transitions, molecular orientation and relaxation, diffusion, adsorption, wetting, capillary condensation) in confined geometries continues to be the focus of numerous applications of neutron scattering.

COMPLEX ION ASSOCIATION IN AQUEOUS SALT SOLUTIONS

The study of aqueous solution structures by total scattering (diffraction) methods has been well-established since the early 1900s. Modern high-flux neutron sources, combined with rigorous comparison to atomic-scale simulations, are beginning to reveal the rich structural and chemical complexity of these systems that has hitherto been understood only in the most general terms. It is long-known that contact and solvent-separated ion pairs, or monomeric and dimeric ion complexes, may exist in a given solution, and one can find a multitude of measurements of the extent and nature of ion-pair and complex formation in the literature.

Although numerous quantitative estimates of the thermodynamics of ion association exist, they are often derived from macroscopic solution properties (e.g., conductivity measurements). This approach is simple and more-or-less robust, but it is not an actual measurement of the extent of ion-pair formation. It does not include the molecular-scale information necessary to predict reaction mechanisms, nor does it allow us to move beyond classical concepts of the nonideality of solutions. More recent evidence argues for higher-order extended networks of ions (Gebauer et al. 2018); however, quantitative estimates of the thermodynamics of their formation are difficult to make.

This situation may be rectified by neutron total-scattering data, used to derive the pair distribution function (PDF) (Ross and Cole 2021 this issue). A PDF shows atomic-level structure in terms of a series of peaks (and valleys), with positions determined by the distances between atoms and with intensities controlled by the concentration of each element and their propensity to scatter neutrons (or X-rays). Integration of the PDF peaks yields coordination numbers. Whereas X-ray PDF analysis tends to exhibit a much stronger signal than neutron PDF, X-ray PDF is weighted towards heavier elements and is typically used for distances <1 nm for solutions. Neutron total scattering/PDF techniques, on the other hand, are uniquely capable of capturing the extent of ion association due to their sensitivity to both light elements (H and O) and heavier elements (solute cations, anions) with the added ability to observe longer-range structures (e.g., several nanometers using the Nanoscale Ordered Materials Diffractometer instrument, part of the Spallation Neutron Source at Oak Ridge National Laboratory in Tennessee, USA). Because the neutron scattering contrast between elements varies with the isotope, one can further utilize isotopic substitution (e.g., D for H) to manipulate scattering from a sample.

In NDIS, isotopic substitution is taken to the extreme by observing two solutions that are identical, except in the composition of the isotope of one the elements (e.g., ^{35}Cl vs. ^{37}Cl). The difference in scattering between the two solutions is then taken, which yields the PDF with respect to just the labeled element (as opposed to all the atoms in the sample). This procedure removes the vast majority of peaks in the PDF (e.g., those from bulk water), immensely simplifying the interpretation. However, it also has the potential to introduce error because any contaminant present in one sample and not in the other will show up as a peak (or valley). Similarly, concentration differences will also cause peak intensity to vary, interfering with the calculation of the coordination number during integration of the PDF. And because protium (i.e., ^1H) is highly effective at scattering neutrons incoherently (see Ross and Cole 2021 this issue), any additional hydrogen, such as from ambient water vapor

in the air, will increase the background noise. Thus, extreme care is needed in the preparation of samples for making robust NDIS measurements.

As an example of this method, Wang et al. (2018) conducted a benchmark study of oxyanion solvation structure for saturated potassium nitrate solution (3.4 mol $\text{KNO}_3/\text{kg D}_2\text{O}$), using nitrogen and oxygen isotopes on the nitrate-N or nitrate-O sites (FIG. 1 TOP LEFT). Historically, NDIS measurements with oxygen isotopes (^{18}O vs. ^{16}O) were not thought to be possible because the difference in scattering would be too small. Recent work has shown that it is possible, just not easy (Fischer et al. 2012). The total scattering data from both the nitrogen-label and the oxygen-label is shown in FIGURE 1 BOTTOM LEFT, as are the PDFs with respect to these elements (FIG. 1 BOTTOM RIGHT). The attraction of doing such a difficult experiment is that, by focusing on the coordination oxygen on the oxyanion rather than its central atom, one can obtain a much less ambiguous coordination number, because one is measuring nearest neighbors and not next-nearest neighbors. Wang et al. (2018) revealed a coordination number of 1.3 ± 0.4 D(H)-bonded water molecules per oxygen on the anion (3.9 ± 1.2 for the whole nitrate), a smaller number than typically observed, but also a much higher precision measurement than was previously possible. The low water coordination number suggests that contact ion pairing in that solution is significant: classical molecular dynamics simulations calibrated to the NDIS data gave $\sim 1\text{--}2$ K^+ per NO_3^- oxyanion (FIG. 1 TOP RIGHT). The extent of ion association in KNO_3 solution, which is at saturation (3.4 mol $\text{KNO}_3/\text{kg D}_2\text{O}$), was found to be limited to simple contact ion pairs. No evidence for complex ion networks, clusters of solute species, or even solvent-separated ion pairs was found in this particular system. However, clustering of solute species has been observed using total scattering in more highly concentrated solutions than those found in typical geochemical systems (e.g., ~ 18 mol $\text{NaOH}/\text{kg D}_2\text{O}$) (Semrouni et al. 2018). While there is still work to do to improve the computational models, a rigorous comparison to PDF data is opening a new path to molecular-based arguments for macroscopic thermodynamic properties, such as activity coefficients and an improved understanding of the relationship between concentration and activity.

Moving beyond average structures of complex aqueous solutions, QENS probes the diffusional motions of hydrogen-bearing species that have characteristic times from ~ 1 ps (e.g., self-diffusion of bulk water at room temperature) (Teixera et al. 1985) up to several nanoseconds (diffusion of viscous solutions and some solvent exchange reaction rates on ions and surfaces). Diffusional characteristics are quantified either by fitting the data to an empirical model or by comparing the data to the predictions of computational simulations. To put this dynamic range into perspective, QENS measures slower motions than bond

vibrations, but faster than those observable by nuclear magnetic resonance methods. Both QENS and nuclear magnetic resonance are also sensitive to different types of motions: QENS can differentiate between the rotational and translational motions of protons (often on water molecules), depending on how the signal changes as a function of the scattering angle, whereas nuclear magnetic resonance is sensitive to the motions of a specific isotope (e.g., ^{17}O).

The dynamics of aqueous solution components observed by QENS are connected to their reactivity. For example, Wang et al. (2019) were able to use QENS to relate ion–water diffusive mobilities and dynamic properties of water to induction times for nucleation and phase selection in highly concentrated aluminate solutions containing sodium (Na^+) or potassium (K^+) as counter ions. In the presence of sodium, the diffusional motions of water were up to an order of magnitude smaller than those within the potassium-containing solution. Additionally, more local or confined motions were observed in sodium-containing solutions, which was interpreted as sodium promoting locally ordered structure of the aluminate and solvent species that, in turn, frustrates diffusion. In potassium-containing solutions, less confined motions and faster diffusion were observed. These microscopic dynamics correlate with the induction times for aluminum (oxy)hydroxide crystallization and mechanisms, where potassium-bearing solutions crystallized within a few hours to a day, but the equivalent sodium-bearing solution did not crystallize at all, instead forming a gel after 3–6 months. Although the specifics of how a counterion might control nucleation mechanisms are not known, it is clear that solvent exchange dynamics play a role (e.g., Casey 2015). More generally, this conclusion is also true for other geochemical processes, such as mineral dissolution (Casey 2015). By quantifying the rates of solvent exchange in aqueous solution using QENS, coupled to the improving of our understanding of the structure of aqueous solutions measured by total scattering/PDF, it is hoped that these techniques will allow us to discover the specific reaction mechanisms for geochemical processes. In turn, these discoveries will allow us to develop robust quantitative predictive models for the rates of geochemical processes occurring under a variety of circumstances: weathering, carbon sequestration, mineral replacement reactions, leaching, contaminant remediation, and so on.

REACTIVITY AND SOLVENT EXCHANGE AT MINERAL–FLUID INTERFACES

When bulk fluids come in contact with a mineral surface, a nanoscale interfacial region is created with structural and dynamic properties that may affect, or even control, diffusive transport and reactivity of the dissolved species and the solvent molecules within it. Surface sites of a mineral interact with solvent molecules to change their local density and, sometimes, the rates of solvent exchange reactions (e.g., Wang et al. 2007). Although not

unequivocal, these interactions may also drive changes in the rates of diffusion and even reaction mechanisms relative to the bulk species. Because mineral–fluid surface area can be extremely high in the subsurface, many geochemical reactions are strongly affected by the properties of this nanoscale region, and mineral–fluid interfaces have correspondingly been recognized as an important area of research. And because of its ability to measure atomic and nanoscale structure and dynamics, neutron scattering is an ideal method to better our understanding of geochemistry in these unique nanoscale environments.

To determine the atomic structure of interfaces, X-ray scattering in a reflection mode (X-ray reflectivity) is the method of choice (Fenter 2002). The equivalent method for neutrons is only available for a small number of substrates because neutrons have a much lower flux and typically have a larger beam size. For example, the beam footprint at the Spallation Neutron Source liquid reflectometer is $\sim 1 \text{ cm}^2$, so a sample needs to have a more or less atomically flat substrate over that range (contrast to $< 1 \text{ mm}^2$ sample sizes required for X-ray reflectivity). A key limiting factor is obtaining natural materials with a sufficiently low roughness to obtain coherent scattering from the surface: silicon and alumina wafers are the most common substrates. However, it has been successfully shown that a silicon wafer can be coated using thin-film deposition to create an analog of a mineral surface (Mayes et al. 2013). From these studies one can probe the thickness of layers of sorbed materials under varying solution conditions to determine e.g., the effects of hydrophobic versus hydrophilic adsorbates on interface structure.

If the mineral can be obtained as nanoparticles with a fairly monodisperse size distribution, one can obtain surface structure information from a PDF measurement. For example, Wang et al. (2013) examined the role of interfacial water in driving aggregation of cassiterite (SnO_2) nanoparticles. They were able to observe that Ostwald ripening of the nanoparticles occurs only after the samples are heated sufficiently to drive off sorbed water, indicating that water stabilizes the nanoparticle phase. This work is significant because, thermodynamically, one would expect these nanoparticles to have high surface energies and so make them unstable (Navrotsky 2009). Due to the ability of neutrons to probe the atomic structure of light elements, however, it was determined that the adsorbed water, in the form of surface hydroxyls, dampens surface energy sufficiently such that recrystallization is suppressed. In another study, structural information was gained about swelling of clay particles that had reacted with supercritical CO_2 (Rother et al. 2013). From this it was concluded that the CO_2 has a limited capacity to adsorb within the interlayers of montmorillonite clays, leading to expansion of the distance between clay particles. This piece of information is critical to understanding how CO_2 moves in the subsurface and suggests

that there is a tendency for self-sealing of caprocks above a reservoir which, in turn, could enhance the storage security of CO₂.

As above, dynamical information for interfacial water and solvents is a key piece of information that can be observed by neutron scattering. For interfacial solvents, one typically employs either QENS or inelastic neutron scattering. As above, QENS tends to help determine dynamical motions of species in the picosecond-to-nanosecond timescale, such as diffusional and solvent exchange motions at the interface, whereas inelastic neutron scattering is sensitive to faster, vibrational motions of various bond types. Commonly with QENS one might probe the timescale of diffusive motions of water adsorbed to a nanoparticulate mineral that has a high surface area. By necessity, only a few monolayers of adsorbed water are possible to measure, such as those that form when a mineral is exposed to humid air. Otherwise, the spectra will be dominated by the contribution from the bulk fluid. By comparing the timescales of these motions to those of self-diffusion of water, one can determine the extent to which the kinetics of diffusion are slowed at the interface (Teixera et al. 1985). Comparison to molecular models allows one to interrogate different types of water at the interface, depending on their bonding environments (Mamontov et al. 2008). However, some surprising behavior has been observed in low-water environments, such as very dry surfaces or the molecular-level channels within some hydrated minerals. This includes quantum tunneling of hydrogen atoms during rotational motions of water in beryl (Kolesnikov et al. 2016) and a loss in the ability to freeze (Mamontov et al. 2009).

One challenge with this method is that the large number of different surface sites will have varying solvent exchange rates (FIG. 2). Such a large array of motions with different timescales creates the danger that the empirical fits to, say, a jump diffusion model respond more to the dynamic range of the spectrometer rather than anything intrinsic about the system. In Stack et al. (2016), this issue was partially addressed by running a series of classical molecular dynamics simulations of the interface (FIG. 2B). The water trajectories of the simulations were Fourier transformed and convoluted with the measurement of the background scattering from the experiment (i.e., the resolution function) (FIG. 2A). This allowed Stack and colleagues to make a direct comparison of what the model predicted the QENS data should look like. From there, the researchers interrogated the model for the solvent exchange rates of as many surface sites as possible (FIG. 2C). An outstanding issue, however, is that only the interface from a single crystallographic surface was considered in that study. Dealing with complex particle morphologies is an as-yet unsolved problem.

FLUIDS IN NANOPOROUS MEDIA

Geological fluids containing inorganic and organic solutes (including hydrocarbons) and gaseous species (e.g., CO₂, CH₄) can occupy nanopores, grain boundaries, and fractures in complex heterogeneous Earth materials. The collective structure and properties of bulk fluids are altered by solid substrates, with the effects of confinement between two mineral surfaces or in narrow pores dependent on the interplay of the intrinsic length scale of the fluid and the length scale of confinement (Cole and Striolo 2019). The combined effect of intermolecular forces and fluid confinement results in unique (but poorly constrained) perturbations to a wide range of thermodynamic, thermophysical, and transport parameters, different from those observed in the bulk phase (Gubbins et al. 2014). Because the interfacial areas (fluid–fluid and mineral–fluid) in Earth materials may be relatively large, confinement effects may control transport behavior and chemical reactivity. However, direct observations and modeling of the physical (transport) and chemical (reactivity) properties are challenging when considering the smaller length scales typical of pore and fracture features and their extended three-dimensional network structures.

In this context, neutron scattering, in concert with molecular-level (or larger) simulations, plays a vital role in examining the behavior of fluid–solid interactions in nanopores. The properties of neutrons make them an ideal probe for comparing the properties of bulk fluids with those of fluids in confined geometries. Thus far, neutron scattering measurements of Earth materials containing fluid-filled pores has centered primarily on clays and other layered silicates (e.g., serpentine), zeolites, coal, and certain rock types such as shale, limestone, and sandstone. As one might expect, much more neutron scattering research has been performed on engineered materials, such as micro- and mesoporous silica and carbon with relevance to controlling adsorption, chemical separation, nanofluidics, catalysis, batteries, and supercapacitors (Gautam et al. 2017). However, in many cases these systems can be used as proxies for structural and dynamical behavior of natural fluids in Earth materials.

The unique structural properties of confined liquids can be assessed using coherent scattering techniques: neutron diffraction, and small-angle neutron scattering. There has been considerable attention focused on determining the structure of water confined in hydrophilic systems, such as mesoporous silica and clays, using neutron diffraction complemented by a classical molecular dynamics simulation, which is an approximate simulation method commonly used to probe structure, dynamics, and energies at the atomic scale. Neutron diffraction studies indicate that confined water molecules form hydrogen bonds to each other and to the silicate surface such that their local environment relaxes to

being close to that of a bulk water structure beyond roughly two molecular layers of the surface (Findenegg et al. 2008).

Neutron diffraction has allowed an exploration of the structure of the double layer that forms in swelling clays (e.g., vermiculite and smectite) and how interlayer cations can progress from nonsolvated inner-sphere complexes to solvated outer-sphere complexes (Skipper et al 2006). The neutron diffraction difference methods described above allow the determination of the radial distribution functions that characterize the interlayer structure: in particular, D–H isotope substitution experiments have been conducted to interrogate the environment of the interlayer protons or interlayer cations. Neutron diffraction and complementary classical molecular dynamics simulations indicate that the coordination of the interlayer cations with water and clay surface oxygens is controlled largely by cation size and charge, in a manner similar to that observed for ions in concentrated aqueous solutions. There is a tendency for the clay mineral structure to exert more of an influence on the larger cations, such as K^+ , leading to nonsolvated inner-sphere complexes. Conversely, smaller monovalent and divalent cations, such as Li^+ , Ca^{2+} , and Ni^{2+} , tend to form highly solvated outer-sphere complexes.

Our ability to extract hydrocarbon gases (methane, ethane, propane) and oil from shales has significantly altered the global energy landscape and has led to economic growth and environmental impacts due to water use and subsequent disposal. Recent developments involving the recovery of methane, ethane, and propane from gas shale have sparked great interest in the geo-neutron science community to explore the behavior of these fluids, as well as CO_2 in nanoporous regimes (Ruppert et al. 2013; Xu 2020). Interest in the behavior of supercritical CO_2 in nanoporous regimes has also increased due to supercritical CO_2 being used to enhance hydrocarbon recovery. There is also the need to understand the behavior of supercritical CO_2 as part of subsurface storage projects to mitigate atmospheric emissions.

Rother et al. (2014) combined small angle neutron scattering (SANS), gravimetric adsorption, and molecular simulations to probe sorption of supercritical CO_2 as a function of temperature and pressure using nanoporous silica as a model substance (Fig. 3). The sorption phase is significantly denser than the bulk fluid at low density (low pressures), but of equal or lower density than the bulk fluid at high pressures. At the sorption maximum, which corresponds approximately with the bulk critical density, the sorption phase is up to ~ 3 times denser than the corresponding bulk fluid. The silica pore walls with mesh-like nanometer structure provide a random network of adsorption sites, acting as anchor points for a continuous sorption phase. This pattern of fluid enrichment and then depletion has been measured for other weakly wetting fluids like methane, ethane, and propane.

The dynamical behavior of water and other geo-fluids in subsurface porous matrices impacts a variety of geochemical phenomena, including ion adsorption and exchange, mobility of contaminants, weathering, hydrothermal alteration, and fluid flow, to name but a few. The type of diffusive motion exhibited by hydrogenous fluids most affected by nanoconfinement includes both translation and rotation typically probed by QENS (picoseconds to nanoseconds) and neutron spin echo (another spectroscopic technique which probes motions on the timescale of tens of nanoseconds). Fundamentally, as the pore size decreases so does the mobility of water, as demonstrated, for example, by Osti et al. (2016) who used QENS to constrain the translational diffusivity of water in mesoporous silica (4–8 nm) with varying levels of surface hydration. This motion can be isotropic, as is commonly the case in cylindrical-pore materials such as silica. Conversely, water diffusion can be anisotropic, as in clays such as vermiculite, where QENS studies have revealed no significant water motion in the direction perpendicular to the clay platelets. This implies a 2-D motion of water along the planes of the platelets. The diffusion of this confined water tends to be slightly reduced compared to the bulk. Furthermore, order-of-magnitude decreases in water mobility compared to bulk water can occur in nanopores containing aqueous solutions comprised of structure-making ions (XCl_2 with $X = Ba^{2+}, Ca^{2+}, Mg^{2+}$) (Baum et al. 2019).

The fact that hydrogen has a much larger neutron scattering cross section compared to deuterium also provides the opportunity to interrogate the behavior of one hydrogenous fluid in the presence of another that is deuterated. Gautam et al. (2019) used QENS to probe the interaction and dynamics of propane (C_3H_8) mixed with “invisible” D_2O in 4 nm silica pores and so demonstrated the presence of two types of propane behavior: a slow diffusion component with longer residence times and jump lengths associated with fluid close to the pore wall, and a faster component with shorter residence times and shorter jump lengths located in the center of the pore.

OUTLOOK

The advances that neutron scattering are providing rely on its sensitivity to light elements, especially hydrogen, and that scattering intensity varies with the isotopic composition of the sample. Many current neutron scattering methods are not themselves new, but modern experiments are being made more powerful by rigorous coupling to computational simulations and by having more intense neutron sources. This allows for a much-improved interpretation and deconvolution of the experimental data, as well as serving to improve the confidence and extensibility of the simulation. Moving forward, neutron scattering will remain a key to understanding geochemical phenomena, especially as more advanced techniques are developed. These include more accurate and large-scale simulation

capabilities (e.g., machine-learning parameterized atomic-scale simulations), as well as more advanced sample environments that will allow researchers to observe geochemical processes in situ as they happen (Chakoumakos and Parise 2021 this issue). Lastly, new neutron sources, such as the Second Target Station at Oak Ridge National Laboratory and the European Spallation Source (Lund, Sweden), will improve the intensity of signal through improved peak or average brightness. Moreover, they will provide new beamline geometries and detector configurations, which will open up exciting new types of experiments that are not currently possible, including the simultaneous collection of both wide- and small-angle scattering, which could yield atomic structure and nanopore geometries in the same measurement. Thus, the future is bright for neutron scattering to help improve our understanding of geochemistry at the nanoscale.

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FIGURE CAPTIONS

FIGURE 1 Determination of an atomic-scale solution structure using neutrons. (TOP) Schematic of an experiment using neutron diffraction with isotopic substitution (NDIS). The difference in scattering of two solutions, which only vary in the isotope of one element, is taken, yielding the structure of the solution surrounding that element. Symbols: H = hydrogen; D = deuterium; T = tritium; nat = natural; O_n = oxygen on a nitrate molecule; m =

mol KNO₃/kg D₂O; inter. = intermolecular PDF (excluding structure from within the nitrate molecule); intra. = intramolecular PDF (including structure from within the nitrate molecule); ΔF^{norm} = **normalized structure factor that shows the difference in scattering as a function of wave vector (q)**; ΔG^{norm} = **PDF, showing probability of finding atoms at distance r from each other in the sample**. (BOTTOM LEFT) Data from an NDIS experiment on a 3.4 mol KNO₃/kg D₂O solution using the two different labels of ¹⁵N and ¹⁸O. (BOTTOM RIGHT) Normalization and a Fourier transform yield the pair distribution function. Because the contribution to the PDF from the nitrate molecule is known, it can be subtracted out (intermolecular only), yielding the solvation structure. ADAPTED WITH PERMISSION FROM WANG ET AL. (2018). COPYRIGHT (2018) AMERICAN CHEMICAL SOCIETY.

Note on Figure 1 itself:

- 1) Change m to mol/kg.

FIGURE 2 Solvent exchange from quasi-elastic neutron scattering (QENS) experiments. (A) A barite (BaSO₄) nanoparticle powder with only a few monolayers of water adsorbed is measured using QENS at six different temperatures (K). Data is intensity of scattering as a function of energy transfer. Larger values of energy transferred often indicate faster motions. Solid lines are the classical molecular dynamics fit; points are the experimental data. (B) A computational molecular dynamics model is run at the same adsorbed water concentration as in the experiment and is fit to the data in FIGURE 2A. Water is color-coded by the type of surface site it is bound to: purple = barium; brown = sulfate; white = water bound to other interfacial water. “High” refers to **barium surface site in a high position relative to the interface**; “low” refers to **barium surface site in a low position relative to the interface**; “residence time” is the average time a water molecule is bound to a specific surface site. (C) Once validated, the solvent exchange rates for the four types of surface site are interrogated (high and low; barium and sulfate sites). REPRODUCED FROM STACK ET AL. (2016) WITH PERMISSION FROM THE *PHYSICAL CHEMISTRY CHEMICAL PHYSICS* OWNER SOCIETIES.

Note on Figure 2 itself:

- 1) Change subpart labels ‘a, b, c’ to capitals ‘A, B, C’.

FIGURE 3 (LOWER LEFT) Adsorbed pore fluid density of CO₂ in high porosity silica aerogel (0.1g/cm³) at 35°C and variable pressure derived from small angle neutron scattering (SANS) versus bulk fluid density (g/cm³). The dashed line identifies the condition where adsorbed fluid density equals bulk fluid density – i.e., absence of fluid densification in the pores. **(UPPER INSET)** Transmission electron microscope image of the silica aerogel (medium gray regions are the pores, average pore size ~14 nm, scale bar = 16 nm). **(MIDDLE INSET)** The mathematical 3-D rendering of this aerogel material based on SANS and TEM results, revealing it to have a fractal character. **(LOWER INSET)** The high *P-T* experimental small-angle neutron scattering (SANS) cell. To gain more detailed insight into supercritical fluid sorption, lattice gas grand canonical Monte Carlo (GCMC) simulations utilized the mathematically rendered silica and tuned the fluid-aerogel system to emulate the experimental neutron data. The labels A, B, and C on the graph are the distinctive points of evolution of the simulated fluid density and correspond to the labeled 2-D density maps (slices through the 3-D volume) in the three surrounding color images. **(A)** At low bulk fluid density, the fluid adsorbs on the pore surface in a monolayer. **(B)** As the CO₂ density approaches the bulk critical value of 0.4676, the fluid condenses in an increasingly larger volume near the pore walls. **(C)** For higher pressures with more loading of CO₂ into the pores, the pore fluid density decreases as the CO₂ fills the pore more evenly due to stronger attractive fluid-fluid interactions compared to solid-fluid interaction. SANS provides a unique “window” into quantifying the density and volume (data not shown, see Rother et al., 2014) of pore fluids such as CO₂ and methane in nanoporous matrices. REPRINTED WITH PERMISSION FROM ROTHER ET AL. (2014); COPYRIGHT (2014) AMERICAN CHEMICAL SOCIETY.

Note on Figure 3 itself:

- 1) Please change title to “CO₂ Adsorption in SiO₂ Aerogel Mesopores” [to make immediately clear what the substance is]
- 2) (ADDED BY AGS): Please note that we replaced the data in Figure 3 because of the issues that Jodi noted, but also because we realized that the data in it was not the SANS data, but a gravimetric data instead. We replaced the data with the SANS measurement of the same properties.