Neutrons "101" – A Primer for Earth Scientists

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The fundamental properties of the neutron make it a powerful tool for Earth science investigations because neutrons provide information that cannot be obtained by any other research method. This is because neutrons are magnetically sensitive, nondestructive, and sensitive to the lighter elements, such as hydrogen. They provide a unique, nondestructive method for obtaining information ranging from Ångstrom-scale atomic structures (and related motions) to micron-scale material strain, stress, and texture, and even up to meso-scale porous matrices and defects in materials and functional components. In this article, we introduce neutrons and their unique properties, neutron production and sources, and provide an overview of the different types of neutron methods applicable to the Earth sciences.

KEYWORDS: neutron properties; neutron sources; neutron methods; neutron scattering

INTRODUCTION

The neutron can be used as an amazingly diverse probe by which to investigate Earth materials. The neutron particle was discovered in 1932 by British physicist James Chadwick (Chadwick 1932) and, from that moment, started the development of neutron diffraction and spectroscopic techniques. In the 1940s and 1950s, nuclear reactors, as sources for neutrons, became available to researchers shortly after World War II. Two of the leaders in this emerging field of research, Professor Bertram N. Brockhouse (McMaster University, Canada) and Professor Clifford G. Shull (Massachusetts Institute of Technology, USA), were awarded the 1994 Nobel Prize in Physics for their pioneering contributions to the development of neutron scattering techniques, as well as their studies of condensed matter and developing the neutron diffraction technique. In simple terms, they helped answer the questions of where atoms "are" and what atoms "do". Since then, neutron scattering techniques have played an important role in investigating the atomic-scale origins of a material's structure, as well as its physical, electrical, and magnetic properties. To date, however, relatively few researchers in the Earth sciences are taking advantage of the unique opportunities provided by neutron facilities. As the articles in this issue illustrate, the interaction of neutrons with Earth materials provides unique opportunities for researchers in the fields of mineralogy, geochemistry, and petrology. Neutrons provide a valuable means of exploring such geologic processes as subduction, earthquake generation, and volcanic eruptions, all of which depend on the physical, chemical, and rheological properties of the materials involved. These, in turn, depend on the structure and properties of the constituent minerals and the associated hydrous components, which can be determined using the neutron techniques described in this issue.

Most of us are familiar with the various X-ray methods used for the detailed study of Earth materials. However, X-ray methods are not always adequate to fully characterize a material's structural properties and dynamic processes. Unlike X-rays, which interact strongly with a material's electrons, neutrons scatter from a material's nuclei. The neutron's fundamental attributes make it a unique and complementary probe to X-ray scattering and other techniques.

The purpose of this issue of *Elements* is to provide an introduction for those not familiar with neutrons and their broad-ranging applications. In this article, we introduce neutron science, starting with how the properties of neutrons make them such a unique probe, followed by how we produce neutrons and the major neutron sources where we can do a neutron experiment, followed by an overview of different types of neutron experiments that can be performed and the scientific opportunities, especially for the future. The other articles in this issue provide more in-depth examples of applying neutron scattering methods to the Earth sciences. For additional background, the reader is referred to Liang et al. (2009) and Wenk (2006a, 2012).

WHY NEUTRONS?

The neutron is a subatomic particle: it has zero charge, a mass of 1.0087 atomic mass units, a spin of 1/2, and a magnetic moment. These four properties combine to make neutrons a highly effective probe, providing unique opportunities for research on materials. Similar to X-rays, thermal neutrons have wavelengths comparable to interatomic distances in materials, so neutron diffraction can be used to study the structures of materials. Unlike X-rays, neutrons are scattered from the nuclei of atoms rather than the electron cloud, and neutrons have a strength indicated by a neutron scattering length (*b*) and a corresponding "cross section" (σ, which is the likelihood of the incident neutron interacting with a target nucleus) that varies from

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element to element (and, indeed, isotope to isotope). The unit for *b* is the femtometer (1 fm = 10^{-15} m) and the unit for σ is the barn (b), which is a metric unit of area equal to 10^{-28} m^2, the approximate cross-sectional area represented by a nucleus. FIGURE 1 shows a comparison of scattering lengths of selected elements (and their isotopes) for X-rays and neutrons. In contrast to X-rays, in which scattering is proportional to the number of electrons in the atom, the scattering from neutrons varies in a way that depends on the nuclear structure. The interaction of the spin of the neutron with the spin state of the nucleus of a given atom determines the scattering property of a neutron with that atom. This spin–spin interaction leads both to coherent scattering and to incoherent scattering (Squires 2012). Coherent scattering gives information on long-range properties, such as structure, whereas incoherent scattering can be used as a local probe.

A full list of neutron scattering lengths and thermal cross sections can be found in *Neutron News* (1992), which is easily accessed through the National Institute of Standards and Technology (NIST) website https://www.ncnr.nist.gov/resources/n-lengths/. The widely varying neutron scattering lengths among elements and their isotopes create a number of opportunities in the study of materials:

- Neutrons are particularly sensitive to hydrogen atoms. The pronounced neutron scattering cross section of hydrogen means that neutrons can be used to precisely locate hydrogen atoms and elucidate details of hydrogen bonding (e.g., Gatta et al. 2021 this issue).
- Neutrons can distinguish between different isotopes. Hydrogen (^{1}H) and deuterium (D = ^{2}H), for example, have widely different scattering lengths of −3.739 fm and (+)6.671 fm, respectively. The negative sign means that the scattered neutrons' wave function is out of phase with respect to the incident neutrons.
- Neutrons can locate light atoms in the presence of heavy atoms (compare O and U in FIG. 1) and, in some cases, can distinguish between elements with similar atomic numbers. Redfern et al. (1997), for example, used neutron diffraction to study Fe/Mn order–disorder in olivine at high temperature.

In addition to exploiting the advantages provided by scattering from nuclei, neutrons also offer several other advantages:

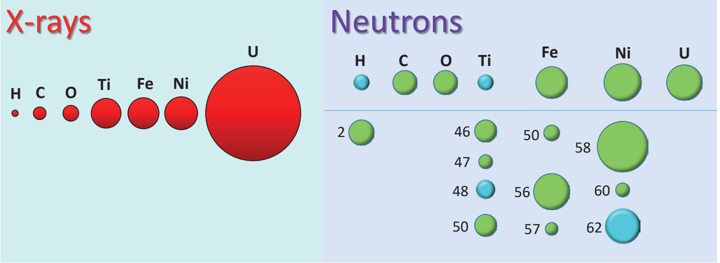


FIGURE 1 Comparison of coherent scattering lengths from X-rays and neutrons. The size of each circle is a measure of the relative cross section; mass numbers identify the different isotopes, with the top row representing an isotopically averaged value. Negative neutron scattering lengths are represented by blue circles. MODIFIED AFTER KARTINI (2007).

- Neutrons have no charge and so interact with atomic nuclei through the very short-range nuclear force (Squires 2012). Consequently, a neutron beam penetrates matter much more deeply than an X-ray or electron beam can. One of the applications of this property is revealing the 3-D mapping of stresses deep inside rocks (e.g., Darling et al. 2004) and the imaging of rocks and cultural heritage artifacts (Artioli and Hussey 2021 this issue).
- Neutrons have a nuclear spin, making them very sensitive to the location and orientation of magnetic moments in materials. Neutrons, thus, are the probe of choice for many studies of magnetism. They can be used to map magnetic structures and phase transitions, as described by Chakoumakos and Parise (2021 this issue).
- Neutrons can transfer momentum and energy to a sample, making it very useful for the study of fundamental vibrations (phonons) within materials which gives information on the strengths of chemical bonds and vibrational density of states. Unlike infrared or Raman spectroscopy, there are no selection rules for inelastic neutron scattering (Parker et al. 2011).
- Nuclei act as pinpoint scatterers compared to X-ray scattering in which the electron cloud has a size comparable to the wavelength of the probing radiation. Thus, the neutron scattering length, b, is independent of the scattering angle, which is in contrast to X-rays where the scattering decreases with increasing scattering angle. Thus, the smaller d-spacing between planes of atoms is better constrained in a neutron experiment as compared to a similar X-ray experiment.

TABLE 1 SELECTION OF CURRENTLY ACTIVE NEUTRON SOURCES AND FUTURE NEUTRON SOURCES UNDER CONSTRUCTION (*).

Reactor Sources		
Opal Pool Australian Lighwater Reactor, Australian Centre for Neutron Scattering	(OPAL) ANSTO	Lucas Heights (NSW, Australia)
Chalk River Laboratories, Canadian Nuclear Laboratories	CRL	Chalk River (Canada)
China Advanced Research Reactor	CARR	Beijing (China)
Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research	FLNP	Dubna (Russia)
Forschungs-Neutronenquelle Heinz Maier-Leibnitz	FRM-II	Munich (Germany)
High Flux Isotope Reactor	HIFR	Oak Ridge (Tennessee, USA)
Institut Laue-Langevin	ILL	Grenoble (France)
Laboratoire Léon Brillouin	LLB	Saclay (France)
Center for Neutron Research, National Institute for Standards and Technology	NIST	Gaithersburg (Maryland, USA)
Spallation Sources		
Chinese Spallation Neutron Source*	CSNS	Dongguan (China)
European Spallation Source*	ESS	Lundt (Sweden)
Rutherford-Appleton Laboratory	ISIS	Harwell (Oxfordshire, UK)
Japan Proton Accelerator Research Complex	J-PARC	Tokai (Japan)
Los Alamos Neutron Science Center	LANSCE	Los Alamos (New Mexico, USA)
Swiss Spallation Neutron Source, Paul Scherrer Institut	SINQ (PSI)	Villigen (Switzerland)
Spallation Neutron Source	SNS	Oak Ridge (Tennessee, USA)

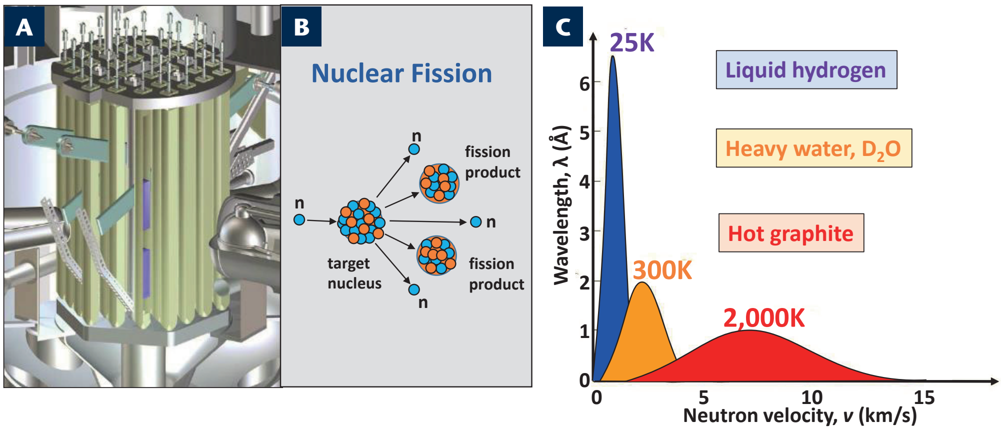


FIGURE 2 (**A**) A 3-D representation of the reactor core at the National Institute of Standards and Technology (Maryland, USA). GRAPHIC IMAGE BY PAUL KOPETKA. (**B**) Schematic diagram showing a fission reaction whereby a neutron (n) collides with a target nucleus such as uranium and splits it, releasing a large amount of energy along with "fast" neutrons traveling with velocities of ~20,000 km/s. (**C**) Moderators are used to slow the neutrons down. The heavy water (D_2O) moderator produces "thermal" neutrons with a wavelength distribution (~1–3 Å) corresponding to the temperature of the coolant (300 K). Hot graphite (2,000 K) is used to produce neutrons at shorter wavelengths. Liquid hydrogen (25 K) is used to produce neutrons at longer wavelengths. MODIFIED FROM GEHRING (2019).

- Neutron scattering provides advantages over other methods because thermal/cold neutrons are a noninvasive probe that interacts only weakly with matter. Neutrons do not change the investigated sample because they do not deposit energy into it.

NEUTRON PRODUCTION AND SOURCES

Neutrons are bound in nuclei. This means that large energies are needed to liberate them. This is achieved either by nuclear fission in a reactor source or by spallation in a spallation source. Reactors deliver a continuous source of neutrons, whereas spallation sources deliver a pulsed beam. The neutrons so-produced have energies of tens or hundreds of MeV, which is far too high for investigations of condensed matter which requires neutrons to have much lower energies. Therefore, neutrons must be cooled to create a beam of "thermal" neutrons with energies around 25 MeV by passing the beam through a moderator (Squires 2012). The spectrum of neutrons emitted by a reactor is dependent on the moderator temperature. This spectrum is Maxwellian in shape and has a maximum that depends on the temperature. For example, for T = 273 K, λ_{max} (the maximum neutron wavelength) is around 1.55 Å; for T = 373 K, λ_{max} is 1.33 Å. Thermal neutrons have wavelengths that can be used to probe excitations across a range of length scales, through elastic and inelastic scattering processes as described below. Using "hot sources," it is possible to move the maximum of the neutron spectrum to short wavelengths and, by cooling the moderator, the maximum of the neutron spectrum can be moved to longer wavelengths (FIG. 2). Because neutrons have no charge and cannot be focused, instruments at a neutron source are arranged around the moderators of the appropriate design.

In a reactor source, the thermal neutron is captured by a fissile heavy isotope, such as ^{235}U, which typically splits into two lighter elements, plus 2 or 3 fast (high energy) neutrons, and a variety of light elementary particles (FIG. 2). This fission reaction is accompanied by a release of energy. A self-sustaining chain reaction requires one neutron per fission event to be scattered back into the fuel element and produce 1 or 2 neutrons per event. There are ~40 operational research reactors for neutron scattering around the world (https://nucleus.iaea.org) that are optimized for basic research experiments in addition to isotope production or fuel development. Examples of reactor sources can be found in TABLE 1. In a spallation source, a pulsed or quasicontinuous neutron beam is produced by accelerating protons to hit a target material of heavy nuclei, such as mercury, tantalum, or lead. Examples of spallation neutron sources are listed in TABLE 1. Generally, the production of neutrons at a spallation source begins with a high-powered proton accelerator: this could be a linear accelerator ("linac") (e.g., SNS), or a combination of linac and synchrotron (e.g., ISIS), or a cyclotron (e.g., PSI). Protons hitting nuclei in the target material trigger an intranuclear cascade, placing individual nuclei into a highly excited state. The nuclei then release energy by evaporating nucleons (mainly neutrons), some of which will leave the target while others go on to trigger further reactions (FIG. 3). These neutrons are then slowed in moderators such as liquid hydrogen, liquid water, liquid methane, or solid methane to the energies that are needed for the scattering instruments. In contrast to the fission of heavy nuclides, one spallation reaction releases about 20–30 neutrons per incident particle, or ~10 times more than nuclear fission. Consequently, spallation has become an established technique for producing high-intensity fluxes of neutrons. However, the design of the targets for high-power spallation sources, having a beam power of several megawatts, presents a formidable technical challenge in terms of heat removal and of taking into account the radiation damage to the target and structural materials.

In comparison with X-ray sources, neutron sources have significantly lower fluxes and, therefore, larger amounts of sample are required for experiments. However, great advances have been made in increasing neutron flux since the days of the earliest neutron sources, which were based on radioactive decay. Their successors, the nuclear fission reactors, produced fluxes whose peak values reached a plateau in the 1950s (FIG. 4). Since then, advances in instrumental energy resolution and detector efficiencies

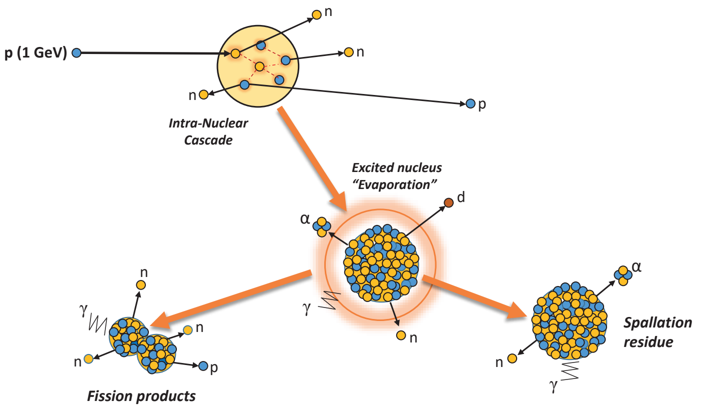


FIGURE 3 Schematic diagram showing the steps involved in a spallation reaction. A high-energy proton hits a heavy-atom target nucleus transferring energy to nucleons inside the nucleus. As the energy is transferred, individual nucleons may be ejected from the nucleus leaving it in a highly excited state. The following stage is nuclear "evaporation" in which energetic particles may leave the nucleus and induce another spallation reaction in a different nucleus. Symbols: p = proton; n = neutron; α = alpha particle; d = deuterium nucleus; γ = gamma radiation. MODIFIED AFTER HTTPS://WWW-NDS.IAEA.ORG/SPALLATIONS/.

have been made to make neutron reactor sources extremely useful for a variety of research applications. Spallation neutron sources have produced the highest intensity fluxes of neutrons to date (Fig. 4). The increased flux has revolutionized the neutron sciences and, as this issue demonstrates, makes neutron analysis viable for a variety of studies of Earth materials, including under extreme conditions of pressure and temperature and even in the presence of a magnetic and/or electric field. The future is bright: currently under construction are the European Spallation Source (ESS) (Sweden) and the China Spallation Neutron Source (CSNS). These facilities, and upgrades to existing facilities, will help to meet the growing research demands of the scientific community and industry and to provide new neutron research capabilities not currently available.

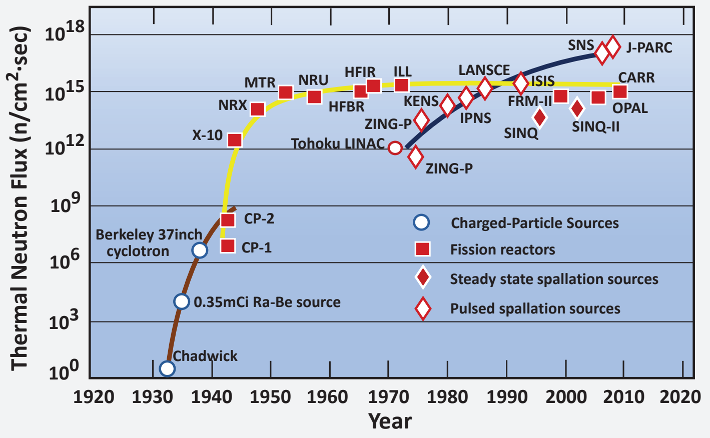


Figure 4 Evolution of neutron sources and neutron fluxes from the discovery of the neutron by Sir James Chadwick in 1932 to the present day. Source acronyms of neutron sources that are operational can be found in Table 1. Historical sources and those no longer in operation include: the Chicago Pile (CP-1 and CP-2) at the University of Chicago (USA); the X-10 Graphite Reactor at Los Alamos National Laboratory (USA); the National Research Experimental (NRX) Reactor and National Research Universal (NRU) Reactor, both at Canadian Chalk River Laboratories (Canada); the Materials Testing Reactor (MTR), Idaho (USA); the High Flux Beam Reactor (HFBR) at Brookhaven National Laboratory (USA); the Zero-gradient synchrotron Intense Neutron Source-Prototype (ZING-P) and Intense Pulsed Neutron Source (IPNS), both at Argonne National Laboratory (USA); the pulsed neutron source (KENS), National Laboratory for High Energy Physics, KEK (Japan). Updated from Carpenter and Yelon (1986).

NEUTRON METHODS AND OPPORTUNITIES

When a neutron beam interacts with a sample, three possible phenomena can take place: (i) transmission, in which neutrons pass through the sample; (ii) absorption, whereby neutrons are taken in by the sample; (iii) scattering, in which the propagation direction of the neutron is deviated with respect to the original direction. Neutron imaging methods, such as neutron radiography and tomography, are based on the detection of the transmission of a neutron beam through an object. Neutron activation analysis (NAA) is used to determine the concentrations of elements in a sample. Neutron scattering enables us to study the crystallographic and/or magnetic structures of Earth materials, as well as the dynamics of atoms and molecules over an enormous range of distances (from micrometers to one-hundred-thousandth of a micrometer) and times (from tens of picoseconds up to a few microseconds).

Neutron Imaging Methods

The neutron imaging methods of neutron radiography and neutron tomography reveal the inner structure of an object. These techniques are based on the transmission and detection of a neutron beam passing through an object. When the beam passes through, the object's different components attenuate the neutron beam differently, depending on their composition. This produces accurate 2-D and 3-D pictures of objects which provide information about the internal structure of an object (Winkler 2006). Large samples can be investigated with little or no radiation damage because of the high penetrating power of neutrons; light elements, such as hydrogen, can be detected in a sample dominated by heavy elements. Hess et al. (2011) describe how neutron computed tomography can be used as a tool for high-contrast imaging of natural glasses (including tektites), hydrothermally altered lavas, and tooth enamel microstructure. With its greatly improved spatial resolution, neutron computed tomography now promises to be a useful tool for a much wider spectrum of research in the Earth sciences. In addition, real-time imaging can also track the movement of material within objects, such as water in porous matrices. Applications of neutron imaging techniques in the Earth sciences are highlighted in the article by Artioli and Hussey (2021 this issue).

Neutron Activation Analysis (NAA)

Neutron activation analysis (NAA) is a mature and established method for determining the concentrations of elements in a material. This method relies on excitation by neutrons so that the treated sample emits gamma-rays that, in turn, allow the precise identification and quantification of the elements in the sample. Neutron activation analysis is a very sensitive method and is, therefore, used to analyze minor and trace elements in a sample. In particular, NAA has been used extensively for the determination of rare earth elements (REEs) in rocks and minerals because REEs have very high thermal neutron cross sections. Researchers are helped by having an online neutron activation analysis database which was developed by Bayrak et al. (2019). A particular advantage of NAA is that it does not destroy the sample, making it ideal to analyze works of art and historical artifacts (Glascock 2014).

Neutron Scattering Methods

Neutron scattering experiments measure the number of neutrons scattered by a sample as a function of the wave vector change (Q) and the energy change (ΔE) of the neutron. The wave vector change is defined as $k_i - k_s$, where k_i and k_s are the wave vectors of the incident and scattered beams, respectively. The scattering process can be either elastic (no exchange of energy between neutrons and sample; $\Delta E = 0$), which is used for neutron diffraction, or inelastic (there is an exchange of energy with the sample; $\Delta E \neq 0$), which is used for neutron spectroscopy.

ELASTIC NEUTRON SCATTERING (NEUTRON DIFFRACTION)

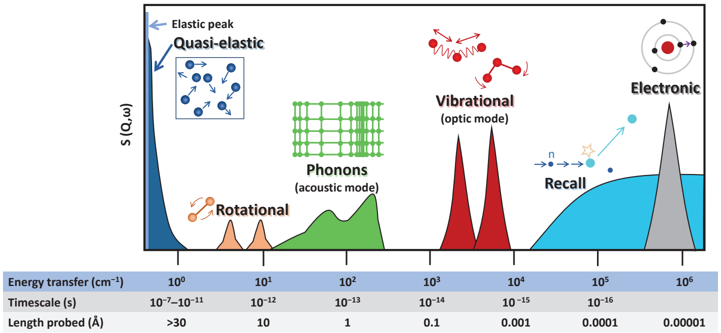
Neutron diffraction, or elastic neutron scattering, is used to determine the atomic and/or magnetic structure of a material. During elastic neutron scattering, there is no energy loss to or from the atoms in the sample studied. The experiment consists of measuring the scattered intensity with varying scattering angles. The technique is similar to X-ray diffraction, due to the different scattering properties of neutrons versus X-rays, but yields complementary information. In particular, neutron diffraction is advantageous for the location of light atoms in a structure and for determining any magnetic ordering. Neutron diffraction is described in detail by Gatta et al. (2021 this issue).

The main types of neutron elastic scattering instruments are diffractometers (either for single-crystal, powder diffraction, or for diffuse scattering from amorphous materials), neutron reflectometers, and small-angle neutron scattering (SANS) instruments. Diffractometers probe the high Q range (Q > 0.5 $Å^{-1}$) and are used to investigate the structures of crystalline systems. Reflectometers and small-angle neutron scattering instruments cover the low-Q range (Q < 0.5 $Å^{-1}$). The small-angle neutron scattering instrument is used to probe a material's structure at the nanometer to micrometer scale and is described in more detail by Stack et al. (2021 this issue). Neutron reflectivity is a technique capable of determining the thickness and the chemical composition of one or several thin layers at a mineral surface. The typical order of magnitude of the thicknesses that can be measured experimentally lies in the range of 5 Å to 5,000 Å. The principle is to measure the coefficient of reflection (R) of a neutron beam sent in at a grazing incidence to the studied surface. Because it is a scattering technique, such a profile will be averaged on the whole surface and the technique and neutron reflectivity will not provide any information on the possible in-plane structure at the surface. Grazing incidence neutron scattering (GINS) is a special configuration of reflectometry used to characterize the "roughness" of surface structures with a length scale from nanometers to several microns. It is usually very valuable to combine neutron reflectivity with a second technique that enables in-plane structure information: this could be a scattering method, such as grazing incidence small-angle scattering (GISAS), or surface diffraction, or off-specular measurements, or a compatible microscopy technique (atomic force microscopy, Brewster microscopy). Example applications include the interrogation of the calcite–liquid interface (Stocker et al. 2012) and probing the substrate effects on biofilm formation on sapphire (Oleson et al. 2012). The general applications of neutron diffraction include

- The determination of crystallographic structures, especially those containing hydrogen (see Gatta et al. 2021 this issue);
- The determination of order/disorder in minerals as a function of pressure and/or temperature (e.g., Redfern et al. 1997);
- The determination of magnetic structures (Harrison 2006; Chakoumakos and Parise 2021 this issue);
- The determination of phase transformations and reaction pathways as a function of external parameters, such as pressure, temperature, and/or magnetic or electric fields (see Chakoumakos and Parise 2021 this issue);
- The analysis of texture and residual strain in rocks and minerals (e.g., Wenk 2006b);
- The investigation of noncrystalline structures, such as liquids or amorphous materials, by using diffuse scattering and pair distribution function analysis (see Benmore and Wilding 2021 this issue);
- The exploration of the internal micro-architecture of rocks (Radlinski 2006). Stack et al. (2021 this issue) describe how small-angle neutron scattering can be used to determine the pore structures of rocks and their change during gas, liquid, and solute imbibition and reaction.

QUASI-ELASTIC NEUTRON SCATTERING AND INELASTIC NEUTRON SCATTERING

Neutrons can lose or gain energy to or from the target atom during inelastic scattering, and this information can be used to describe how atoms move in a structure. Inelastic neutron scattering probes the atomic and molecular movements over a vast range of length scales, ranging from a few Ångstroms to tens of nanometers, and over timescales ranging from tens of picoseconds up to a few microseconds (FIG. 5). However, no single spectrometer can access this full range and, typically, three types are needed: a direct-geometry time-of-flight spectrometer (~10^{-11} s), a backscattering spectrometer (~10^{-9} s), and a neutron spin echo spectrometer (~10^{-7} s). The time-of-flight technique is a general method for determining the kinetic energy of a traveling neutron by measuring the time it takes to fly between two fixed points whose distance is known. It is particularly useful in neutron spectroscopy where the energy of the scattered neutrons has to be determined (Copley and Udovic 1993). Inelastic neutron scattering is used to investigate vibrational properties of a material. Unlike infrared and Raman spectroscopy, there are no selection rules for inelastic neutron scattering. Therefore, the entire frequency distribution of the vibrations of the material (the vibrational density of states) can be determined and the thermodynamic properties of the material can be calculated (Ross 1992; Chaplot et al. 2002).



Energy transfer (cm^{-1})	10^0	10^1	10^2	10^3	10^4	10^5	10^6
Timescale (s)	10^{-7}–10^{-11}	10^{-12}	10^{-13}	10^{-14}	10^{-15}	10^{-16}	
Length probed (Å)	>30	10	1	0.1	0.001	0.0001	0.00001

FIGURE 5 Schematic of the time and energy ranges spanned by neutron scattering phenomena accessible by quasi-elastic and inelastic neutron scattering. MODIFIED FROM PARKER AND COLLIER (2016).

Quasi-elastic neutron scattering is a very low-energy inelastic process which usually manifests itself as a broadening of the elastic line that is most commonly the result of diffusional (translational or rotational) motion of atoms. This method is described in more detail by Stack et al. (2021 this issue).

A quick overview of the types of information provided by neutron spectroscopy (Loong 2006; Parker et al. 2011) includes

- Rotational, acoustic, and vibrational modes in minerals
- Phonon dispersion curves and spectra of minerals
- Vibrational density of states and thermodynamic properties of minerals as a function of pressure and temperature
- Phase transitions
- Diffusional and hopping motions of atoms
- Magnetic and quantum excitations
- Crystal- and electric-field effects.

Thus, neutron spectroscopy provides insights at an atomistic level about phenomena such as the phonon softening associated with structural phase transitions, phase diagrams, melting, reactions at mineral–water interfaces, catalysis, mechanisms of fast-ion diffusion, the origin of negative thermal expansion and low thermal conductivity, to name but a few. There is a symbiotic relationship between theoretical interpretations and the practical analysis of the often-complex neutron data which, in turn, can validate the models used to calculate the phonon, elastic, and thermodynamic properties of a material. The integration of neutron spectroscopy with theoretical methods has been extremely successful in providing important insights about mineral properties relevant to mineralogy, geochemistry, and petrology. These insights will continue to grow as the flux increases at neutron sources.

FUTURE OUTLOOK

For over half a century, neutron-based studies have been used to determine the composition, structural details, and the dynamics of atomic arrangements in materials from measurements of absorption and scattering. Compared to X-rays, the application of neutrons in the Earth sciences are relativity recent, and Earth science users are still in a minority in the neutron community. That said, neutron scattering should be viewed as an essential technology for advancing Earth materials research because it provides information that cannot be obtained from any other research method. This is because neutrons are magnetically sensitive, nondestructive, and sensitive to the light elements. Potential growth of the neutron community is being realized because neutrons provide a unique, nondestructive method to obtain information ranging from the Ångstrom-scale of atomic structures and related motions to the micron-scale of material strain, stress, and texture, as well as the meso-scale of porous matrices and defects in materials and functional components.

The information provided by neutrons can provide a robust understanding of basic geologic processes—crustal subduction, earthquakes, and volcanic eruptions—due to such processes depending on the physical, chemical, and rheological properties of the materials involved (i.e., crustal and mantle rocks, magmas, and fluids). These, in turn, depend on the structure and properties of the constituent minerals and the associated hydrous components, which can be determined using the neutron techniques described in this issue. We envision that important advances will be realized in crystallography (e.g., atomic positions of hydrogen in diverse Earth phases; order/disorder effects in complex silicates; minor element distribution in oxides), mineral magnetic structures, mineral physics at deep Earth and planetary pressures and temperatures, and the interrogation of anisotropy and residual strain relevant to rock mechanics, structural geology, and tectonics. New applications will range from the structure determinations of large crystals, to powder refinements, and to short-range order determination in amorphous materials. The pore features of rock matrices—size, distribution, connectivity, and roughness ("fractality")—can be quantified across over six-orders of magnitude in spatial scale. Additionally, the structure, dynamics, and reactivity of fluids hosted in porous materials, or on mineral surfaces, can yield atomic-to molecular-level details amenable for direct comparison with advanced molecular-level simulations. Finally, as a detailed understanding of more complex Earth materials becomes increasingly important to our economy and national security, neutrons will become ever more essential to answering some of our most challenging science and technology questions.

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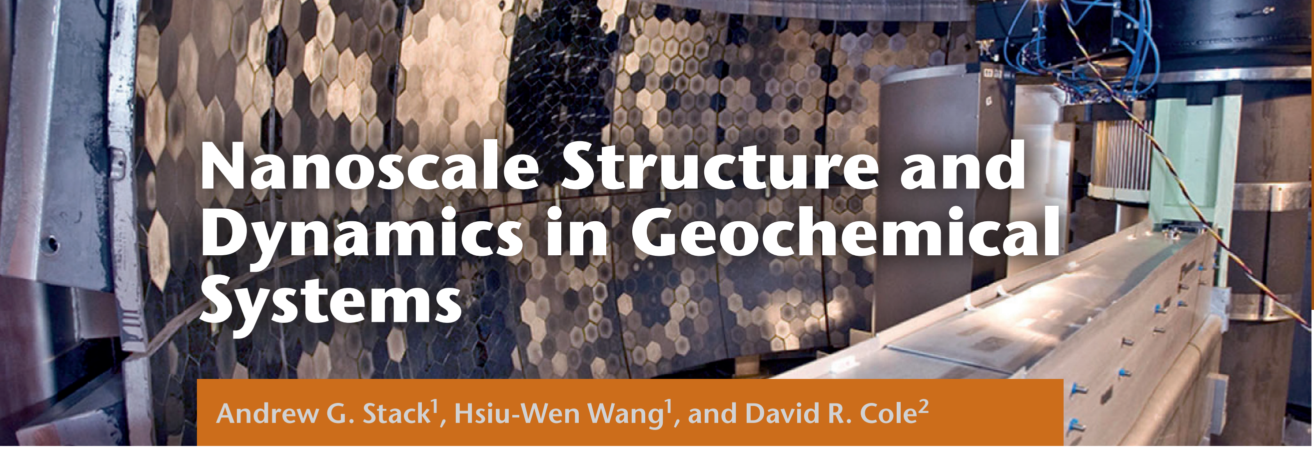

Nanoscale Structure and Dynamics in Geochemical Systems

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The Si(111) crystal analyzer panels inside the ORNL Spallation Neutron Source (SNS) BASIS instrument tank.

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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 and solids; quasi-elastic neutron scattering, which measures the diffusional dynamics at mineral–water interfaces; and small-angle neutron scattering, which can show how properties of nanoporous systems 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 structure and dynamics within nanoporous media, where the reactivity of the mineral–water interface is inextricably coupled to the rate of transport. The information obtained 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 focusses 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. 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

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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., ^{1}H) 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 KNO_3/kg D_2O), 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 ~1–2 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 KNO_3/kg D_2O), 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 NaOH/kg D_2O) (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 molec-

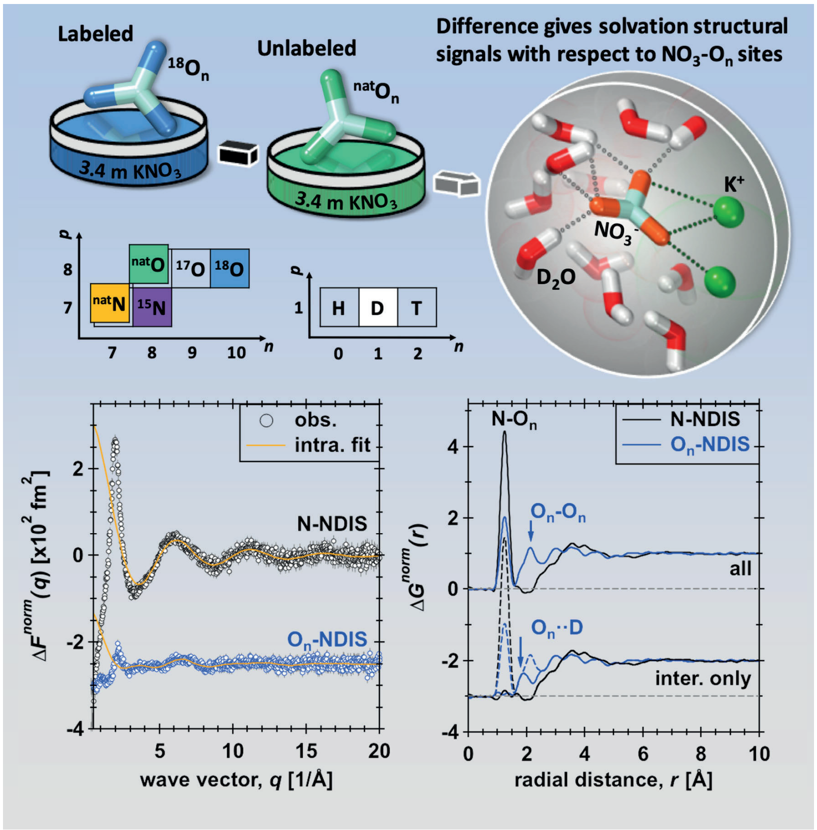

FIGURE 1 Determination of an atomic-scale solution structure using neutrons. (**TOP**) Schematic of an experiment using neutron diffraction with isotopic substitution (NDIS). The difference in scattering of two solutions, which only vary in the isotope of one element, is taken, yielding the structure of the solution surrounding that element. Symbols: H = hydrogen; D = deuterium; T = tritium; nat = natural; O_n = oxygen on a nitrate molecule ; m = mol KNO_3/kg D_2O; 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 KNO_3/kg D_2O solution using the two different labels of ^{15}N and ^{18}O. (**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.

ular-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 ~1 cm^2, so a sample needs to have a more or less atomically flat substrate over that range (contrast to <1 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 CO_2.

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., CO_2, CH_4) 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).

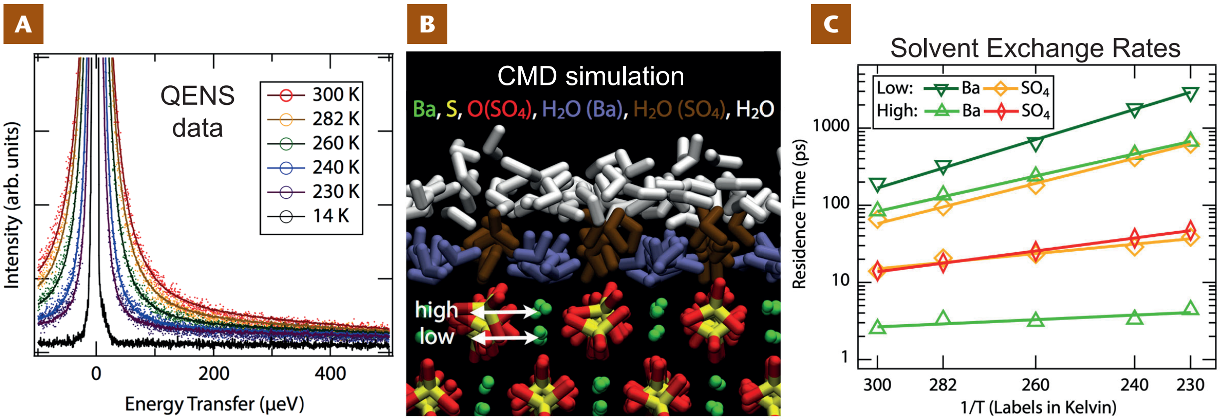

Figure 2 Solvent exchange from quasi-elastic neutron scattering (QENS) experiments. (**A**) A barite ($BaSO_4$) nanoparticle powder with only a few monolayers of water adsorbed is measured using QENS at six different temperatures (K). Data is intensity of scattering as a function of energy transfer. 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.

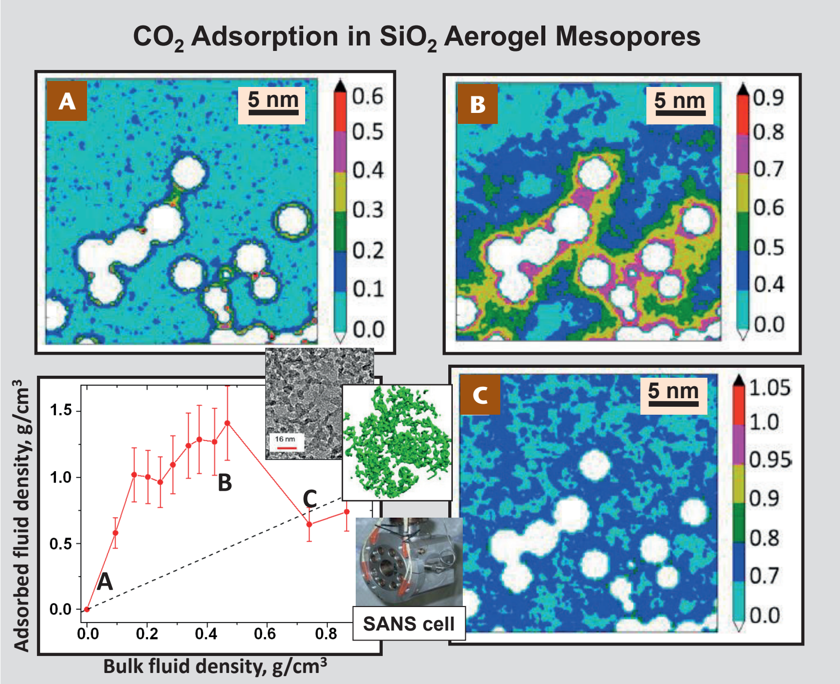

FIGURE 3 (LOWER LEFT) Adsorbed pore fluid density of CO_2 in high porosity silica aerogel (0.1g/cm^3) at 35°C and variable pressure derived from small-angle neutron scattering (SANS) versus bulk fluid density (g/cm^3). The dashed line identifies the condition where adsorbed fluid density equals bulk 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 CO_2 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 CO_2 into the pores, the pore fluid density decreases as the CO_2 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 CO_2 and methane in nanoporous matrices. REPRINTED WITH PERMISSION FROM ROTHER ET AL. (2014); COPYRIGHT (2014) AMERICAN CHEMICAL SOCIETY.

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 exiting 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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