CMS WORKSHOP LECTURES

Volume 21

FILLING THE GAPS – FROM MICROSCOPIC PORE STRUCTURES TO TRANSPORT PROPERTIES IN SHALES

THE CLAY MINERALS SOCIETY

Joseph W. Stucki, Series Editor and Editor in Chief
University of Illinois
Urbana, IL 61801-4798, USA

Thorsten Schäfer[1], Reiner Dohrmann[2], and H.C. Greenwell[3], Volume Editors
[1] Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), P.O. Box 3640, D-76021 Karlsruhe, Germany; [2] Federal Institute for Geosciences and Natural Resources (BGR), State Authority of Mining, Energy and Geology (LBEG), Stilleweg 2, D-30655 Hannover, Germany; and [3] Department of Earth Sciences, Durham University, South Road, Durham, DH1 3LE, UK

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Organized By

Thorsten Schäfer
Karlsruhe Institute of Technology, Germany

Reiner Dohrmann
State Authority of Mining, Energy, and Geology (LBEG), Germany
Federal Institute for Geosciences and Natural Resources (BGR), Germany

H.C. Greenwell
Department of Earth Sciences, Durham University, UK

Kevin Murphy
The Clay Minerals Society

Contributors

Guillaume Desbois, Structural Geology, Tectonics and Geomechanics, EMR, RWTH Aachen University, Lochnerstr. 4-20, D-52056 Aachen, Germany

Christopher R. Clarkson, Department of Geoscience, University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4

Andrew Aplin, Department of Earth Sciences, Science Laboratories, South Road, Durham University, Durham, DH1 3LE, UK

Christian Schurig, Chair of Soil Science, Wissenschaftszentrum Weihenstephan, Technische Universität München, 85350 Freising-Weihenstephan, Germany

Tony Lanzirotti, Center for Advanced Radiation Source, The University of Chicago, Chicago, IL 60637, USA

Fred Mosselmans, Science Division, Diamond Light Source, Harwell Campus, Didcot, Oxon OX11 ODE, UK

Marc Fleury, IFP Energies nouvelles, 1, avenue de Bois-Préau, 92852 Rueil-Malmaison, France

Edo Boek, Department of Chemical Engineering, Imperial College, London SW7 2AZ, UK

Daniel Grolimund, Swiss Light Source, Paul Scherrer Institute, CH-5232 Villigen-PSI, Switzerland

Benjamin Rotenberg, Sorbonne Universités, UPMC Univ. Paris 06, UMR 8234 PHENIX, Paris, France

Christophe Tournassat, Water, Environment and Ecotechnology Division, French Geological Survey (BRGM), Orléans, 45060, France

Gioacchino Viggiani, Université Grenoble Alpes and CNRS, Laboratoire 3SR, Saint Martin d'Hères, France

Rosanne Murray, Department of Earth Sciences, Science Laboratories, South Road, Durham University, Durham DH1 3LE, UK

Pieter Bertier, Clay & Interface Mineralogy, RWTH-Aachen University, Bunsenstr. 8, D-52072 Aachen, Germany

Stephan Kaufhold, BGR, Bundesanstalt für Geowissenschaften und Rohstoffe, Stilleweg 2, D-30655 Hannover, Germany

Paul Marschall, National Cooperative for the Disposal of Radioactive Waste, 5430 Wettingen, Switzerland

Frank Friedrich, Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal (INE), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

Katarzyna Górniak, AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, al. Mickiewicza 30, Kraków, 30-059, Poland

Pierre Dick, IRSN - Institut de Radioprotection et de Sûreté Nucléaire, BP 17, F-92262 Fontenay-aux-Roses, France

Nicola Rigonat, The University of Edinburgh, Grant Institute of GeoSciences, James Hutton Road, Edinburgh EH9 3FE, UK

Yukio Tachi, Japan Atomic Energy Agency, 4-33 Muramatsu, Tokai-mura, Ibaraki, 319-1194, Japan

Kenji Yotsuji, Japan Atomic Energy Agency, 4-33, Muramatsu, Tokai-mura, Ibaraki, 319-1194, Japan

Published by
The Clay Minerals Society
3635 Concorde Pkwy Suite 500
Chantilly, VA 20151-1125, USA

Citations of articles in this volume are properly referenced as follows:
CLARKSON, C.R. and SOLANO, N.A. (2016) Combined use of neutron-scattering, fluid-invasion, and image-analysis techniques to assess pore structure, accessibility, and connectivity in tight rock. Pp. 15–31 in: *Filling the Gaps – from Microscopic Pore Structures to Transport Properties in Shales* (T. Schäfer, R. Dohrmann, and H.C. Greenwell, editors). CMS Workshop Lectures, **21**. The Clay Minerals Society, Chantilly, Virginia, USA.

Library of Congress Catalog Number
ISBN - 978-1-881208-46-4

THE CLAY MINERALS SOCIETY

The Clay Minerals Society (CMS) was organized in 1963 to stimulate research and to disseminate information relating to all aspects of the science and technology of clays and other fine-grained minerals. It sponsors an annual Clay Conference where research and invited papers are presented in technical sessions and special symposia. Field trips are organized to important occurrences of clays in regions near the Conference locations and to industrial sites of clay production and application. In conjunction with its annual meetings, workshops are held on technical subjects of interest to clay researchers and technologists. CMS publishes *Clays and Clay Minerals*, which is the leading international journal in the field of clay science. In this journal are presented the latest scientific investigations in all areas of the field and from all parts of the world, along with timely review articles and announcements of new publications on clays and other fine-grained minerals.

CMS also sponsors the Source Clays Repository, which is now well established as the provider of clay samples to a plethora of research groups world wide and to teachers of clay science. It also offers other clay-related publications to its members at a discount over publisher's list prices.

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The Clay Minerals Society
Society Office
3635 Concorde Pkwy Suite 500
Chantilly, VA 20151-1125

Phone: (703) 652-9960
FAX: (703) 652-9951
www.clays.org
E-mail: cms@clays.org

Preface

Thorsten Schäfer[1], Reiner Dohrmann[2], and H. C. Greenwell[3]

[1]*Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), P.O. Box 3640, D-76021 Karlsruhe, Germany*
[2]*Federal Institute for Geosciences and Natural Resources (BGR), State Authority of Mining, Energy and Geology (LBEG), Stilleweg 2, D-30655 Hannover, Germany*
[3]*Department of Earth Sciences, Durham University, South Road, Durham DH1 3LE, UK*

1. Introduction

This CMS Workshop Lecture Series (WLS) volume is intended to give a summary of the current state-of-the-art of different spectroscopy and microscopy methods, as presented during a workshop held in conjunction with the EUROCLAY 2015 conference in Edinburgh, UK, on the 5th of July 2015. This workshop was initiated by the NEA Clay Club, The Clay Minerals Society, and the Euroclay conference series. This EUROCLAY 2015 workshop is a continuation of the very successful workshop *"Clays under Nano- to Microscopic resolution"* which took place from 6th–8th September 2011 in Karlsruhe and documents new developments and the progress made over the past four years concerning research in low-permeability, clay-rich, geological formations (NEA-CLAY-CLUB, 2013). The workshop also provided an excellent opportunity for exchange of knowledge with research communities concerned with the safe long-term management of radioactive waste within argillaceous sediments, and with shale gas and oil exploration.

A wide spectrum of argillaceous media are being considered in Nuclear Energy Agency (NEA) member countries for the purpose of the passive long-term management of radioactive wastes. This includes variously indurated clay-rich bedrock formations to host and enclose a Deep Geologic Repository and clays used as engineered barrier materials to create durable repository seals. In this context, the NEA established in 1990 a Working Group on Argillaceous Media, known informally as the 'Clay Club.' The Clay Club examines those various argillaceous rocks that are being considered for the deep disposal of radioactive waste, ranging from soft clays to indurated shales. These low-permeability rocks exhibit petrophysical, hydrogeologic, and geomechanical properties, among others, which allow them to behave as long-lived passive barriers to the movement of water and solutes on timescales relevant to the safety of a Deep Geologic Repository (*i.e.* 1 Ma) (Dohrmann *et al.*, 2013).

In addition, the shale-gas and oil community is interested in the characterization of sedimentary formations (*i.e.* black shales) from the core- to nano-scale, focusing on clay/brine/organic interfaces and understanding how pore space evolves and affects the transport and production potential of the shale system. Through characterization of fundamental properties such as nanopore/micropore connectivity, all the way up to understanding transport and mechanical fracture properties of whole rock units,

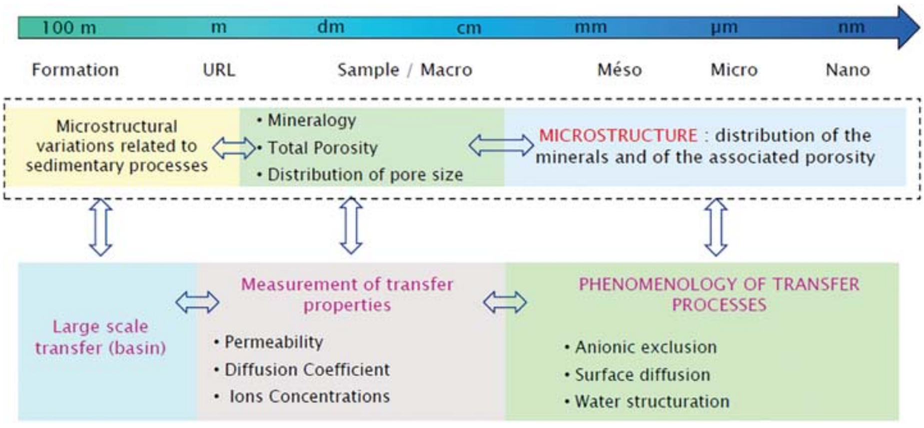

Figure 1. A schematic diagram showing how a multi-scale approach connects mineralogy, porosity, and transport properties in argillaceous media (Figure reproduced from NEA-CLAYCLUB, 2013, with permission).

both communities (radioactive waste disposal, and shale gas and oil) are studying the geological materials with a shared set of tools, from quantum mechanics and molecular dynamics computer simulations, through advanced microscopy and diffraction methods, up to tri-axial mechanical tests and large-scale mass-transport models.

Very generally speaking, these clay rocks are composed of fine-grained minerals showing pore sizes from <2 nm (micropores) up to >50 nm (macropores). Pores of between 2 and 50 nm are mesopores. The fluid migration, solute transport, and mechanical properties are largely determined by this microstructure (Figure 1), the spatial arrangement of the minerals, and the porewater chemical composition. Examples include anion-accessible ('geochemical') porosity and macroscopic membrane effects (chemical osmosis, hyper-filtration), geomechanical properties, and the characteristics of two-phase flow properties (relevant for gas transport).

In shale oil/gas systems, the role of clay minerals in creating porosity and controlling organic-matter distribution is of keen interest, as well as larger-scale phenomena such as how diagenesis affects the mechanical properties of the shale-gas unit. Linking our knowledge to: (1) increased confidence in our understanding of material properties/phenomena used in a typical repository safety case, and (2) how best to up-scale the nano-scale understanding/knowledge are essential.

2. Short summary of research examples presented during the workshop

The one-day workshop was subdivided into five sessions with a two-hour poster session during lunch, which fostered active exchange between students and experts in the field.

The five general topics included:

- Pore structure and connectivity
- Chemical information under high spatial resolution
- Gas/water and ion mobility in tight formations
- Upscaling and implementation in model approaches
- Rock mechanics

The rock formations covered within the workshop included host rocks considered for the deep geological disposal of radioactive waste, such as the Opalinus Clay, the Boom Clay, the Callovo-Oxfordian argillite, and from the generic underground research tunnel within the Toarcian shales. Furthermore, sedimentary formations investigated in the context of oil and gas reservoirs included the Cardium Formation in western Canada, natural siliciclastic mudstones from the London Clay formation, Oligocene Grybów marls, Posidonia shales, and Kimmeridge shales and mine tailings (McLean Lake Tailing Management Facility; TMF). To complete this list, research results also covered bentonite (MX-80) and minerals such as biotite, illite, and boehmite.

2.1. Pore-structure and connectivity (physical imaging)

The Rheinisch-Westfälische Technische Hochschule Aachen University (Germany) group (Jop Klaver) gave an overview of complementary methods working at different scales, providing a conceptual 'toolbox' for the characterization of the clay microstructure. Information about the 3D fracture network, the mineral fabric, and the macroporosity can be obtained by micro-computed tomography (μCT), but is clearly limited in resolution (μm range). Combining μCT with broad ion beam scanning electron microscopy (BIB-SEM), on the other hand, can give information on pore morphology and the identification of elementary islands in 2D at the nm scale. If these methods are further combined with focused ion beam transmission electron microscopy (FIB-TEM), 3D information on pore connectivity and elementary island representative under nm-scale resolution can be achieved. A critical point in this type of investigation is the preservation of the pore structure and connectivity during sample preparation (drying). Several impregnation methods are discussed in the literature (Pret *et al.,* 2004; Robinet *et al.,* 2015) and the Aachen group favors the Woods metal (WM) injection (Woods metal is an alloy of 50.0% bismuth, 26.7% lead, 13.3% tin, and 10.0% cadmium) liquid at elevated temperatures of 70°C (Klaver *et al.*, 2015). The authors encountered unfilled WM regions and interpret them as artefacts during the WM injection process closing accessible pore throats (see Desbois *et al.,* 2016, this volume). With respect to future studies, a comparison with methods such as nuclear magnetic resonance (NMR) or small-angle neutron scattering studies (SANS) should be performed to tackle and quantify the artefacts.

Using a combination of SANS and ultra-small angle neutron scattering (USANS), fluid invasion, and imaging methods, pore structure, accessibility, and connectivity for multiple Cardium Formation tight oil samples have been investigated by Chris

Clarkson and co-workers from the University of Alberta. On the microlithofacies scale down to the μm level, the mapping of permeability, porosity, and microhardness has been performed using computed tomography (CT), μCT, and optical microscopy on core samples. This information is combined with macroscale work (formation scale) on the meter to kilometer scale using seismic surveys, well testing, and well logging (Clarkson and Solano, 2016, this volume).

In a further step, these data are combined with information on the sub-microlithofacies scale using several methods (*e.g.* SEM, TEM, mercury intrusion porosimetry (MIP), low-pressure nitrogen adsorption (LPAN$_2$), or CO_2 adsorption (LPACO$_2$), He pycnometry, Hg intrusion and especially SANS/USANS). The scattering intensity profiles obtained by SANS/USANS measurements revealed a broad pore-size distribution with pore accessibility varying strongly with pore size. The scattering intensity profiles follow a slope of -3 on a log-log scale, which indicates a power-law scattering characteristic of a very rough (fractal) pore-matrix interface.

All images (except for TEM) shown in Figure 2 were taken from reservoir samples obtained from a tight oil reservoir within the Cardium Formation (depth of ~1470 m) (Pembina Field) in western Canada. One surprising result is that the accessibility is smaller for larger pore sizes, a finding consistent with Hg intrusion results. High-resolution SEM imaging has in fact revealed that disconnected pores appear within mineral grains, possibly explaining the SANS/USANS results. The SANS/USANS interpretations may be affected by the assumption of a two-component system (spherical pores + average mineral phase), however. Mineral mapping using energy-dispersive X-ray spectroscopy (EDX) suggests that additional components (strong scattering accessory mineral phases, *e.g.* siderite) may be present which could affect significantly the SANS/USANS-derived porosity, pore-size distribution, and pore-accessibility calculations. A multi-component system will be tried in future work and differences will be quantified using the more conventional two-component model.

The spherical pore-model assumption used to calculate the pore-size distribution from the SANS/USANS scattering profiles was discussed indirectly by Aplin and co-workers, who focused on the permeability estimates from pore size data (see contribution Aplin *et al.,* 2016, this volume) which clearly revealed that a reasonable correlation between the measured and modeled permeability could only be obtained assuming an elongated wedge-shaped geometry (see also Yang and Aplin, 2007).

In the poster session, Bertier *et al.* (2016, this volume) presented a critical discussion about the use of N_2 physisorption for the characterization of the pore structure of shales by addressing some common pitfalls and misconceptions related to the interpretation of physisorption data. Using measurements from a set of nine Opalinus Clay samples, N_2 physisorption values were compared with other methods such as He-pycnometry, MIP, fluid saturation (Archimedes), and USANS. The authors concluded that the results could be used for the analysis of the pore structure of shales and mudrocks, but they should be interpreted with caution.

The pore system of a potential German gas shale (four different Posidonia shales) with different levels of maturity was evaluated critically by Kaufhold *et al.* (2016, this volume). The most important question concerning shale-gas production and

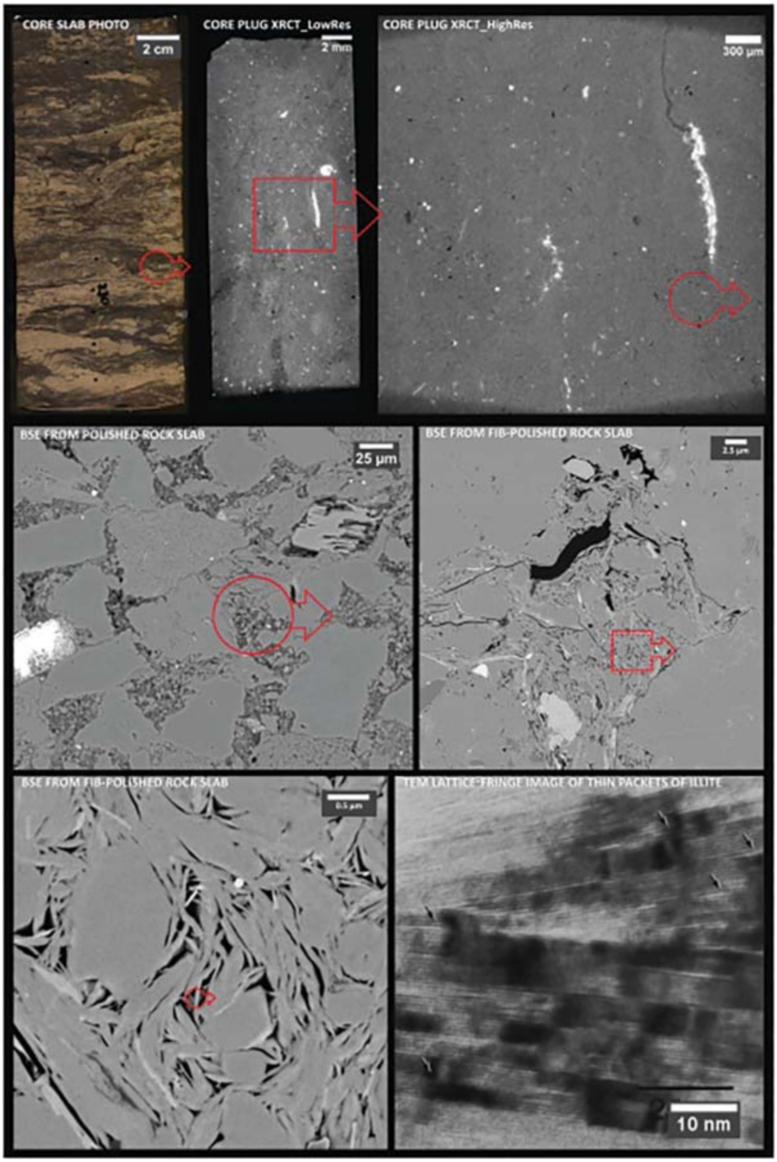

Figure 2. Use of imaging methods to visualize geologic structures controlling flow at the core- and finer-scale (taken from Clarkson and Solano, 2016, this volume). The upper panel illustrates use of core photography (left) for imaging microfacies distribution and X-ray micro-computed tomography (XRμCT, middle and right) for imaging bulk-density contrasts in core plugs (sampled from a large whole-core sample). The middle and lower left panels illustrate the use of backscatter imaging from SEM for imaging micro- to nano-scale pore structures and their associations. The panel on the lower right illustrates use of transmission electron microscopy (TEM) for imaging nano-scale structures (Jiang *et al*., 1997; reproduced with permission). Pores and porous regions in the XRμCT and BSE/SEM images are represented by the darker areas.

porosity relates to the diameter needed to provide gas migration. The authors compared their results with data published on gas shales which are known to be productive. Although both direct microscopical methods and indirect methods based on gas adsorption or MIP were applied, most of the pores within the clays and shales were too small to be detected by any of the direct methods. Natural gas in micropores may be bound too strongly to liberate it without low-pressure/vacuum. For gas production, either meso- or macropores may be important. The authors concluded that the potential of the Posidonia shale for gas production, of course, has to be proven by shale-gas production tests.

Microstructural insights into petrophysical characteristics of indurated clays were given by Marschall *et al.* (2016, this volume), who characterized core samples from the Opalinus Clay using TEM, FIB nanotomography (FIB-nt), and CT with image processing procedures. Results were compared with MIP, nitrogen adsorption/desorption measurements ('BET'), sieving methods, X-ray diffraction (XRD), and triaxial testing. The authors found that the macroscopic (poro-elastic) deformation behavior of the Opalinus Clay was reproduced fairly well by geomechanical modelling on the microscopic scale. In addition, new insight was gained with regard to the role of small mesopores (2–10 nm), which essentially control the macroscopic deformation behavior of the indurated clay.

Apart from clay formations, the development of deep geological repositories for long-term radioactive waste management is also foreseen in crystalline rocks. Multi-barrier repository concepts for crystalline rocks require geotechnical barrier systems based on compacted bentonites (Sellin and Leupin, 2014) which, depending on the compaction efficiency, contain regions of different densities, and were studied using FIB-nT (*e.g.* Keller *et al.*, 2014). In the poster session, hydration experiments with cation-exchanged Febex bentonite samples studied using an environmental SEM (ESEM) were presented by Friedrich *et al.* (2016, this volume). The main finding was that the Sr-exchanged form showed significantly more swelling at low relative humidity.

2.2. Chemical information under high spatial resolution

To obtain chemical information under high spatial resolution to the μm level and even the sub-μm level, the research field clearly benefited from the developments made over the past decade using synchrotron radiation, but not exclusively, as shown in the presentation by Christian Schurig (see Schurig *et al.*, 2016, this volume) from the group of Ingrid Kögel-Knabner at the Technical University Munich (Germany). The authors used nano-scale stable isotope mass spectrometry (NanoSIMS) to characterize the isotopic composition of mineral-associated natural organic matter in complex soil structures. Here, for example, synchrotron-based Scanning Transmission X-ray Microscopy (STXM), with a spatial resolution in the 20 nm range and working on different element absorption edges (Brandt *et al.*, 2012; Kretzschmar and Schäfer, 2005), could give complementary information on the general organic structure or metal oxidation state and isotopic composition. The NanoSIMS presentation also pointed out clearly that for accurate SIMS stable isotope analysis the polishing relief should be less than a few pm, which has to be evaluated by using an optical surface profilometer (Kita *et al.,* 2009).

Two synchrotron beamlines were presented in detail in the oral lectures, the GeoSoil-EnviroCARS (GSECARS) at the Advanced Photon Source (APS, Chicago, Illinois, USA) Sector 13 by Tony Lanzirotti (see Lanzirotti *et al*., 2016, this volume) and the I18 Beamline of the Diamond light source, UK, by Fred Mosselmans (see Mosselmans *et al*., 2016, this volume). The examples given in both presentations were not restricted to clay systems alone, but showed clearly the potential for clay-dominated systems (Lange *et al*., 2010). Improvements included synchronous micro-diffraction capabilities at high spatial resolution and high speed coupled with micro X-ray fluorescence (μXRF) mapping at GSECARS.

2.3. Gas/water and ion mobility in low-permeability formations

Nuclear magnetic resonance studies by the group of Marc Fleury (Institute France Petrol; IFP Energies nouvelles; Rueil-Malmaison, France) demonstrated that water is surprisingly highly mobile, even when strongly confined in nanopores and despite a strong affinity with the solid surface. From these NMR studies, the primary factor governing diffusion in a compacted system seems to be porosity, while the texture or the pore network details play a secondary role. For small pores in the 1–100 nm range, unimodal or multimodal NMR relaxation time distribution can provide simple criteria to characterize connectivity between different compartments of the pore network system at a time scale corresponding to the life-time of the magnetization and for length scales of the order 1 μm or larger. In the interlayer space of smectites, the orientation of water molecules can be observed using specific NMR protocols and show the strong affinity of water with the solid surface (Fleury *et al*., 2016, this volume).

The presentation by Edo Boek (2016, this volume) demonstrated clearly that the segmentation of μCT data for the determination of transport properties in fractured shales using Lattice Boltzmann (LB) and molecular dynamics (MD) simulations must be used with care and the CT resolution must be taken into account. Here, the parallel plate model results corresponded to the LB results, but were much higher (15.3–44.6 Darcy) than the experimental results. For the measured permeability of 1 mDarcy in the example given, the measured aperture would be in the range of ~3.7 μm based on cubic law estimates, which was clearly below the resolution of the CT dataset (here 13.7 μm resolution) and shows the limitations depending on the question to be tackled.

The last presentation in this session, given by Daniel Grolimund from PSI-SLS (Grolimund *et al*., 2016, this volume), focused on the migration behavior of redox-sensitive Se(IV) and monovalent Cs in Opalinus Clay. A multiple-method approach was used including classical tomography for the structural properties, μXRF, μXRD, chemical tomography, and μLA-ICP-MS for the chemical properties, neutron studies for the fluid properties, and macroscopic studies to determine the sorption and diffusion properties. The random-walk simulations of Cs migration were compared with 3D measurements and showed a very good comparability.

Transferring information from high spatial resolution to the large scales of a site (Figure 1) is the goal of these studies. Two posters focused on this scale. Górniak (2016, this volume) studied the pore space in the impure chalk-type source rocks of the Oligocene Grybów Marls (Outer Carpathians, Poland) using SEM. The author concluded that the origin of the clay and the eogenetic overgrowth calcite cementation influenced the pathway of burial diagenesis and, thus, the pore-space evolution in the impure chalk. The internal architecture and permeability structures of faults in shale formations were studied by Dick *et al*. (2016, this volume). The authors showed that microfractures govern the matrix porosity in the damage zone and exert an increasingly dominant role on fluid flow along the boundary between fault core and fault damage zone.

A third poster presented an innovative tool for monitoring of the water chemistry evolution in bentonite buffer materials using magnets (Rigonat *et al*., 2016, this volume). NdFeB magnets were mixed with powdered Na-bentonite, then held at 70°C for 5 months). Results revealed different degrees of corrosion in the magnets but the swelling clay minerals were not degraded.

2.4. Upscaling and implementation in modeling approaches

Detailed sensitivity analysis solving the Poisson-Boltzmann equation for swelling and non-swelling clay materials by the group of Christophe Tournassat and colleagues from BRGM (French Geological Survey) and Lawrence Berkeley National Laboratory (USA) based on the three key parameters that affect model predictions of anion exclusion in clay media, namely the pore-size distribution of clay media, the distance of closest approach of ions to the clay surface, and the accessibility of sub-nanometer-wide clay-mineral interlayer spaces to anions, highlighted the significant impact of pore-size distribution on anion-accessible porosity. The calculations show that all three model assumptions significantly impact values predicted for the anion accessible porosity. As a consequence, macroscopic measurements of anion exclusion in clay media cannot be used to test any of the three model assumptions independently from the other two (Tournassat *et al*., 2016, this volume).

While recent developments in advanced nano-imaging techniques can provide detailed views of the microstructure of non-swelling materials, determination of the microstructure of swelling clays remains a challenge because important additional information must be obtained at the nm to sub-nm scale. In addition, the accuracy of ion-distribution models such as the modified Gouy-Chapman (MGC) model in sub-nanometer-wide interlayer nanopores is not known for compacted clay systems in which overlapping electrical double layers (EDL) are important, particularly with regard to anion accessibility to the interlayer space. Clearly, additional insights from MD simulations are needed to better constrain macroscopic scale models (*cf.* Newton and Sposito, 2015). In natural clay-rocks, where both swelling and non-swelling clay minerals are present (smectite, illite, and interstratified clay minerals), the characterization of the pore-size distribution (from the μm to the nm scale) is a necessary step to accurately predict ion-concentration distributions. Finally, the authors noted that other sources of uncertainty must be better understood, including the domain of validity of the MGC model for complex electrolyte compositions and the fraction of the surface charge that is screened by the Stern layer.

Overall, the characterization of the pore-size distribution and pore shapes is a necessary step to predict accurately the ion distribution and mobility in the pore space. New results on changes in celestine precipitation-induced porosity in compacted illite could demonstrate that anions can be excluded completely from the smallest pores within a compacted illite material, whereas transport of tritium (water) is still observable, clearly showing the absence of full porosity clogging (Chagneau *et al.,* 2015).

Benjamin Rotenberg presented a pore network model for spatial dimensions of >1 μm based on LB or analytical solutions for the pores and channels in the domain range $\sim 1-10$ nm taking into account electro-kinetic effects in charged porous media (see Obliger *et al*., 2016, this issue). Heterogeneity and couplings can be taken into account, but caution is needed concerning “effective single channels” to predict macroscopic properties. The model cannot currently be used to predict desaturation, clogging, or thermal gradients; and the parameterization for natural claystones (Callovo-Oxfordian argillite) is currently in progress in order to constrain the model as much as possible with experimental information.

In the poster session, two posters from the Japan Atomic Energy Agency and Chiba University, Japan, focused on modeling approaches in radwaste-relevant systems. Tachi *et al*. (2016, this issue) studied diffusion and sorption in the argillaceous rock from the Horonobe Underground Research Laboratory, Japan, and compared their modeling results with batch tests. Yotsuji *et al*. (2016, this issue) developed a model taking into account multiple pore structures in compacted bentonite such as inter-layer and inter-particle pores, particularly for anionic species.

2.5. Rock mechanics

The concept of deep geological repositories for the disposal of radioactive waste relies in part on the long-term low permeability of the host and enclosing rock. As the permeability is influenced by mechanical damage, the characterization of damage mechanisms of the host rock (at multiple scales) is important.

A first approach is developed to characterize strain localization at the scale of a laboratory specimen (a few centimeters). The group of Cino Viggiani (University Joseph Fourier, Grenoble, France) presented new results obtained with a new true triaxial apparatus that allows observation of a rock specimen under loading via X-ray CT and 3D digital image correlation (3D-DIC). Here, the development between the previous workshop in 2011, with cell dimensions of 10 mm diameter resulting in a voxel size of 7 μm (laboratory 3SR) and a maximum cell pressure of 10 MPa, could be compared to the current state-of-the-art measurements using an *in situ* tri-axial compression test cell with a specimen diameter of 1.3 mm and a height of 2.5 mm resulting in a voxel size of 0.7 μm (ERSF, beamline ID19).

The strain field in the sample, and its evolution up to and beyond strain localization, can be measured by digital image correlation (DIC) of photographs taken through a hard transparent window. Tests in plane-strain compression have been performed, starting from isotropic stress states at several mean stress levels. Results of the time evolution of the pattern of localization in the specimens are shown. Strain localization appears to start well before the stress peak, sometime at ~50% of the stress peak, by very numerous parallel and conjugated shear bands. This early strain localization, to the authors' knowledge, has never been observed in rocks before. The number of active bands, then, decreases progressively during subsequent loading, down to a very few bands at the peak and during strain softening. It is also possible to demonstrate how localization is influenced by confining pressure. The experimental results are analyzed systematically in terms of fields of shear and volumetric strains.

The second approach focuses on a smaller scale – the scale of mineral inclusions embedded in a clay matrix where the inclusion size is a few microns. Studying the mechanisms of deformation at this scale is a challenge (clay cracking, de-cohesion of inclusions, *etc*...); understanding the mechanisms at a relevant scale for understanding the substantial evolution of some of the physical properties such as fluid permeability is essential, however. The focus of this study was to characterize the mechanisms of deformation at the small scale during loading experiments by combining X-ray micro-tomography and DIC. Where the microstructure of the material is relatively well understood (Robinet *et al.*, 2012), relatively few attempts have been made to

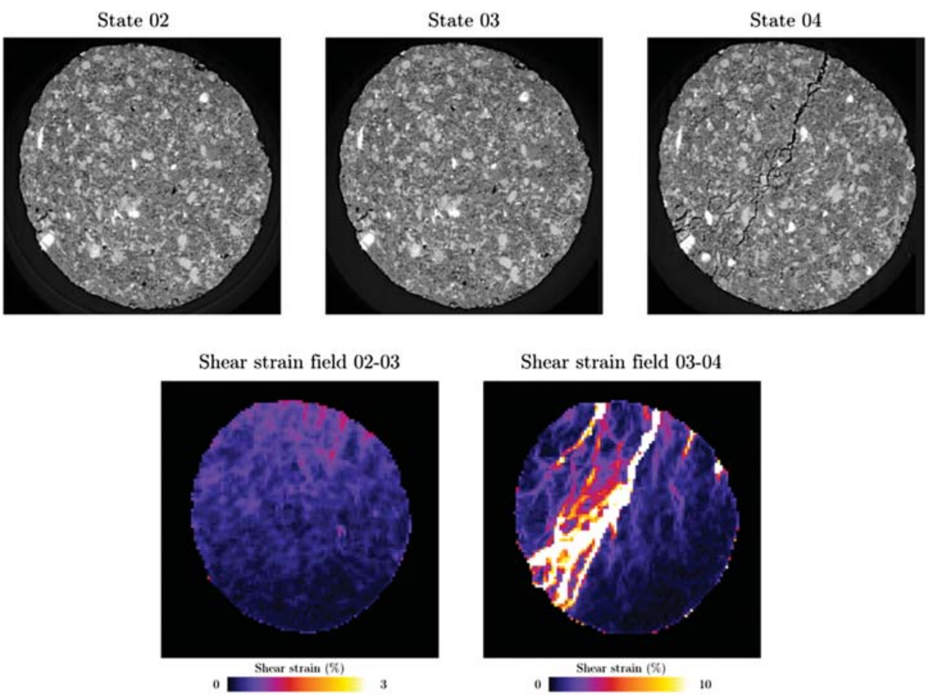

Figure 3. (Upper) Reconstructions (ID19) at different steps of loading of a clay-rock specimen (1 mm diameter). (Lower) Shear-strain fields of the increments of loading, obtained by 3D-DIC. Figure from Viggiani *et al.* (2015), used with permission.

develop new experimental techniques to investigate the micro-scale mechanics of clay rocks in order to feed multi-scale numerical models. Optical microscopy was used recently by Wang *et al*. (2013). Viggiani and coworkers used 3D-DIC to measure the evolution of strain fields at the micro scale from X-ray μCT images (with a spatial resolution of 0.7 μm) of specimens tested at ESRF (ID 19) (Figure 3, Viggiani *et al.*, 2015).

In the second presentation given by Roseanne Murray (Durham University), the focus was on the architecture and frictional properties of faults in shale. The main implications from the data presented were: (1) gouges demonstrate limited ability to nucleate seismic events. Slow fracture/fault propagation will affect the rate at which new fracture areas are created and may limit oil and gas production. (2) Brine-saturated gouges can reduce frictional stability locally and enhance frictional healing, in comparison to wet and dry gouges, which facilitate oil and gas production by the creation of large fracture areas. (3) Fluid composition may vary between basins and, thus, their rate and state properties. Careful analysis must, therefore, be completed prior to reservoir stimulation.

Rock-mechanics studies at high resolution are very important; experimental conditions are challenging and only a few groups have entered this field of research, however.

3. Conclusions

The EUROCLAY 2015 workshop demonstrated the advanced application of experimental techniques such as neutron diffraction and scattering, μ-XAFS, nanoSIMS, TEM, AFM, nano-XCT, BIB-SEM, and NMR, *etc.*, to yield new and fundamental insights into physical/chemical processes acting on the solid phase on a microscopic scale, *i.e.* down to the molecular scale. Despite such continued advances, the lack of standardized procedures for specific approaches to sample preparation and preservation is evident. Further uncertainties exist surrounding 'institutional' codes that are used for post-processing data, such as segmentation and image reprocessing. These very critical steps of sample selection (representation), sample preparation, and sample preservation prior to chemical analysis require increased attention to avoid artefacts and over-interpretation of data. Future improvements could lead to a type of standardized protocol for compacted clay materials, which would reduce uncertainties related to the aspects mentioned above.

In the same manner, guidelines for data segmentation, noise filtering, and post-processing in the form of correlation/distribution, together with a catalog of criteria to rank the techniques available for clay systems, would optimize the scientific output. The workshop has clearly fostered communications between experimentalists and modelers and this needs to continue in order to clarify which kinds of data are needed and which are available at different scales (element distribution, chemical formula, binding environment).

Molecular-modeling techniques will allow elucidation, at an atomic scale, of the mechanisms of radionuclide sorption onto clay minerals, of interfacial water structuring, and of the migration behavior of solutes (anion, cation) through compacted clays. All these new methods will result in an improved understanding of these systems and will help to further identify and reduce conservatism in mass transport models. Furthermore, conceptual approaches were demonstrated throughout this workshop into how these microscopic results may be upscaled to scales in space and time relevant to performance assessments. This is work in progress.

Finally, the use of complementary analytical techniques has been shown to be most successful for most of the applications, bearing in mind the limitations of each analytical method. The interest in chemical evolution over time might, however, constrain the application of techniques to non-destructive methods. The combination of destructive and non-destructive methods is, however, sometimes needed to obtain full quantitative information. It must also be stated clearly that the resolution reached so far is sometimes insufficient to clearly discriminate different processes, but rapid instrumental development is underway, which might overcome this problem in the near future.

Acknowledgments

The NEA Clay Club members from Belgium (FANC, ONDRAF/NIRAS, SCK · CEN), Canada (NWMO/SGDN), France (ANDRA, IRSN), Germany (GRS, BGR, KIT-INE), Hungary (PURAM), Japan (JAEA, NUMO), The Netherlands (COVRA), Spain (ENRESA), Switzerland (ENSI, Nagra, University Bern), the UK (NDA), and the United States of America (LBNL) are gratefully acknowledged for their financial or in-kind contribution to this project. The authors are grateful for the support of the Euroclay organizing team, Stephen Hillier and Kevin Murphy, and the Geological Society (UK) for student support of the workshop poster session. Those who helped by reviewing the chapters which follow are thanked for their work and listed below, after the reference list.

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List of Referees

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Andy Aplin
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Biqiong Chen
Pablo Cubillas
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Katja Emmerich
Eric Ferrage
Mahnaz Firouzi
István Furó
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