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Nano- to micro-meter scale characterization of pore networks in fine-grained rocks using electron microscopy and small angle neutron scattering

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Introduction

Rock pore networks carry reactive fluids to surfaces of minerals. The pore network is a dynamic interface between minerals and pores that, through geochemical reactions, changes the physical properties of the rock. As the surface advances or retreats with mineral precipitation or dissolution, the volume of pores (or porosity), connectivity of pores, surface area, and surface roughness may change [1, 2]. Understanding these changes is important for prediction of pore-scale processes that control transport and mineral-weathering rates, as well as reaction mechanisms. Despite the importance of the pore network on many fundamental transport phenomena, the physical characteristics of pore networks in rocks are poorly understood, in part due to their dynamic nature and features at different length scales.

Characterization of pore networks in fine-grained rocks, such as shales and mudstones, is especially difficult. These rocks have numerous pores in the micron to nm length scales that require advanced techniques for quantification and characterization [3]. Increasingly, these rocks are of interest because they are sources of hydrocarbon energy and play an important role in the containment of waste fluids in the subsurface. Small angle neutron scattering (SANS) provides statistical data on the topology and architecture of pore networks [4-6]. Combined with high-resolution imaging, gas sorption (N_2-BET), and other techniques, a full characterization of the multiscale and often irregular pore system is possible. Here we characterize pore networks of five fine-grained rock samples using neutron scattering and electron microscopy techniques. This information is compared to data from Heath et al. [3] who previously reported on these samples, which represent continental to marine mudstone caprocks at CO_2 sequestration sites.

Methods

SANS - Shale chips, ranging in size from 0.2 to 2 mm, were packed in quartz cuvettes to randomly orient the pores. Scattering intensity (I(Q)) was measured as a function of pore size from ~ 5 Å to 700 nm at the High Flux Ionization Rector at Oak Ridge National Laboratory (Figure 1). Similar to many rock systems, these data were interpreted with a two-phase model [6, 7] that allows the calculation of porosity, pore size distribution, and surface area from the scattering data [8].

Scanning Electron Microscopy - SEM images were collected on a JEOL JSM-7000F field emission scanning electron microscope at Colorado School of Mines at 5 to 10 keV accelerating voltage and magnification from 10 to 40,000 x. Energy dispersive x-ray data were collected with a Genesis X-ray spectrometer on the same instrument. Chips of the shale were mounted on aluminium stubs and gold sputter coated.

Results and Discussion

Pores were observed in the SEM images at length scales from microns to < 100 nm (Figure

2). Larger pores typically exist at silt-sized grain boundaries or between sheets of clay particles. Smaller pores (< 100nm) exist at grain boundaries and within mineral grains (i.e., intragranular porosity). Much of the nm scale structure is related to surface roughness of the pore-mineral interfaces. This surface roughness gives rise to a fractal distribution that is observed in the scattering data as a power-law relationship between intensity and scattering vector (Figure 1). A power-law relationship is observed for features > 100 nm in all samples. For small length scales this power-law relationship is masked by a distinct population of scatter at ~ 15 nm that in some samples create an intensity peak (Figure 1). Unfortunately, the resolution of FESEM and FIB-SEM images of these samples is ~ 15 nm and we are unable to conclusively identify these distinct features.

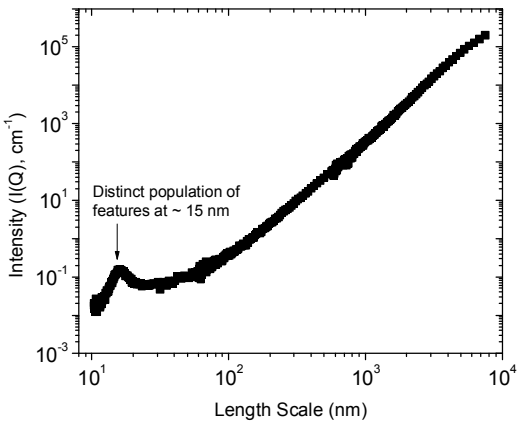

Figure 1. Scattering diagram for one sample.

The SANS data demonstrate the importance of small pores in the pore network. Pores < 10 nm radius contribute 20-50% of the total porosity and > 80% of the total surface area of these mudstones. The porosity determined from SANS is higher than porosity determined from FIB-SEM reconstruction and mercury intrusion porosimetry [3] for most of the samples. The discrepancy between the SANS-measured porosities and MIP may be related to low pore connectivity, or the inability of MIP to fully access the pore network due to pressure limitations of the method. Differences in SANS and FIB-SEM porosity may be related to heterogeneity in the samples, or to the presence of numerous pores in the size range less than the FIB-SEM resolution (~16 nm). A comparison of cumulative pore fractions determined from SANS and MIP suggests that < 30% of the total porosity is accessible through pore throats < 1 nm radius. At these length scales, Fickian diffusion of solutes and Knudsen diffusion of gas become the dominant transport mechanisms.

Future work will include TEM imaging to identify features at length scales < 15 nm, and creation of digital pore networks from FIB-SEM data that honour the small-scale topology of the pore network determined from SANS. Fluid-flow simulations will be performed on these digital pore networks to better understand transport mechanisms in tight rocks.

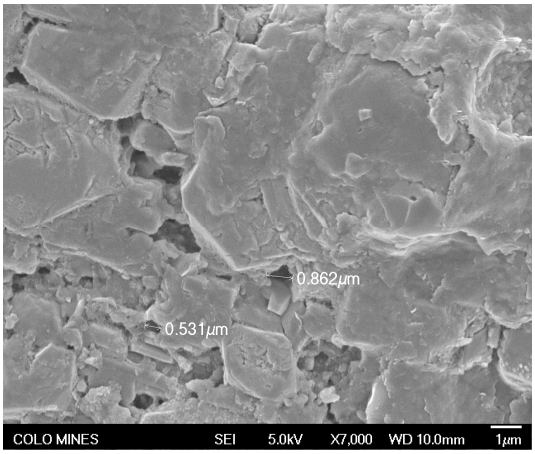

Figure 2. FESEM image of one of the rock samples showing pores in the 10's to 100's of nm length scale.

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