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plugs is followed by nondestructive petrophysical testing (NMR, electrical/dielectric properties) with plugs ending up in the rock mechanics laboratory for static and dynamic mechanical testing. Offcuts are sent for mineralogical, geochemical, and physicochemical properties testing, along with characterization of the shale microstructure and pore systems.

Figure 1.2 Example coring plan for subsampling whole cores normal to bedding (top) and parallel to bedding (bottom). Planning from medical CT scan images reduces exposure time to air, preventing further loss of shale pore fluids.

Figure 1.3 Stress-strain curves for Belfast Mudstone under increasing confining pressures with deformation parallel to bedding. The samples seem to become more brittle with increasing confining pressure, with the largest stress drop observed at the highest confining pressure used.

Figure 1.4 The Mohr circles derived from the peak strength takes from the stress-strain curves in Figure 1.3. The failure envelope appears to be linear with low cohesive strength and a friction coefficient lower than the standardly used values for non-shaly rocks.

Figure 1.5 Failure envelopes for Pierre Shale deformed when fully water saturated (grey line) and partially water saturated (black line). S_w is the percentage of water-saturated porosity before samples were confined and axially loaded. The Mohr circles for the upper failure envelope have been omitted for clarity. Pierre Shale becomes substantially stronger as water saturation decreases although the friction coefficient does not change much.

level. (c) Textural segmentation example using ROI 1 of (B) with five principal components.

Figure 3.3 Use of X-ray CT in imaging fracture development in Mancos Shale. (a) Stress-strain curve and CT reconstructions (shown in 2D) including (b) the initial shale at 25 MPa axial stress post-yield and pre-fracture development and at 4.5 MPa post fracture (residual strength) showing conjugate shear bands and interference with strong horizontal laminae at sample center. (c) Raw radiographic images of fracture propagation in Mancos Shale, taken 0.1 s apart. (d) 2D image of Mancos Shale (same as in Figure 3.1, 17 μm resolution) showing lithologic variation as horizontal laminae visible both by changes in layer gray level and in abundance and distribution of bright high-Z pyrite. To the right is seen a 3D X-ray CT reconstruction of fractures seen at left.

Figure 3.4 Dual focused ion beam image and reconstruction of FIB-SEM data of Marine Tuscaloosa Shale. (a) Backscattered electron image of ion-milled surface, 16 μm on the horizontal. Gray-level variations are associated with phases of varying *Z*, with kerogen appearing as dark gray and silicate and carbonate minerals appearing as lighter gray. (b) 2D segmented image of kerogen. (c) 3D rendering of kerogen mass. (d) 3D rendering of pores in kerogen mass which appear as elongate tubules with preferred orientation and CFD simulation of gas flow in one of the tubules.

Figure 3.5 Multi-beam SEM schematic and images. (a) Schematic of multiple beams in parallel [from *Eberle et al.*, 2015]). (b) 3.1 mm × 0.9 mm mosaic of 26,657 images at 4 nm resolution of a siliceous-

the nitrogen adsorption and mercury intrusion data) and the significant differences between results from the four methods.

Figure 4.9 Pore size distribution calculated by the Vonk method from the SANS data obtained from a horizontal cut of a Utah mudstone core taken at a depth of 15,666 ft. Note the bimodal distribution of the pores and the large relative proportion of the smaller pore sizes.

Figure 4.10 Porod plots of the SANS and SAXS data for the Utah mudstone. Units for scattering intensity are not given on the original figure. Note the difference in slope between the SAXS and SANS data on the same sample. The kaolinite data were shown for comparison.

Figure 4.11 Neutron (ρ_{n}) and electron ($I_{\mathrm{e}}\rho_{\mathbf{e}}$) scattering length densities for the five phases present in BMR Urapunga 4 source rocks calculated from the known chemical composition.

Figure 4.12 The variation of SANS intensity at a single q value versus the annealing temperature for an immature hydrocarbon source rock. Data correspond to the average pore size of 300 Å ± 50%. The marked decrease of the scattering intensity constitutes the SANS fingerprint of the hydrocarbon generation and primary migration. The rising trend is caused by increased hydrogen depletion as the annealing temperature increases.

Figure 4.13 Neutron scattering length density for major minerals and OM types present in sedimentary rocks. The solid curve was calculated for saturated hydrocarbons (C_nH_{2n+2}). The scatter reflects the departure from this formula for saturates, polars,

aromatics, asphaltenes, and macerals in whole coals and kerogens.

Figure 4.14 USANS transmission data given as a ratio of the rocking curve and wide transmissions for a series of clay and carbonate-rich samples from the Eagle Ford Shale, TX. While there is significant scatter, it is apparent that transmissions reach values near 0.9 at thicknesses near 150 μm. Smaller values imply significant multiple scattering, suggesting that this is a reasonable maximum thickness for USANS analyses of shales [*Anovitz and Cole*, 2015].

Figure 4.15 Mesopore volumes (top, pore radius = 1–25 nm) and macropore volumes (bottom, pore radius > 25 nm) for the five samples of New Albany Shale, measured using three different methods: N_2 and CO_2 adsorption (green), mercury intrusion porosimetry (blue), and PDSP analysis of SANS/USANS (red).

Figure 4.16 Comparison of the fraction of accessible pores in sample 152 by D_2O and CD_4. D_2O and CD_4 are approximately equally accessible to pores in the USANS range (larger pores), but CD_4 accessibility decreases to about 70% in the SANS range, while any decrease for D_2O is much more minor.

Figure 4.17 (Top) Autocorrelation analysis of the lowest- and (bottom) highest-maturity carbonate-rich samples of the Eagle Ford Shale. The three images for each maturity were calculated from scattering patterns obtained at detector distances of 1, 4, and 13 m (left to right) on NG3-SANS instrument at NIST/NCNR. Focusing on the innermost ring, note the loss of pattern asymmetry with increasing maturity.

Figure 4.18 (Top) Autocorrelation analysis of the lowest- and (bottom) highest-maturity clay-rich samples of the Eagle Ford Shale. The three images for each were calculated from scattering patterns obtained at detector distances of 1, 4, and 13 m on NG3-SANS instrument at NIST/NCNR. As with the carbonate-rich samples (Fig. 4.17), increasing maturity reduces the asymmetry. In this case, however, the effect is incomplete even at the largest scales (13 m) and highest maturities, as can be seen by focusing on the innermost ring, especially of the highest-maturity sample at 13 m.

Figure 4.19 The remaining porosity (scattering porosity minus estimated organic pore volume) as a function of maturity (R_o) for samples from the Eagle Ford Shale was calculated assuming an organic density of 1 g/cm^3. Solid squares, clay rich, parallel to the bedding; open squares, clay rich, perpendicular to the bedding; solid circles, carbonate rich, parallel to the bedding; and open circles, carbonate rich, perpendicular to the bedding. Note that most of the decrease in porosity appears to occur at low R_o values.

Figure 4.20 (a) Schematics showing the shapes of mineral grains in shale samples cut parallel or perpendicular to the bedding. (b) 2D SANS spectra for the BE850 sample cut parallel (left) and perpendicular (right): for the bedding-parallel sample, the scattering pattern is isotropic, and that for the bedding-perpendicular sample is anisotropic. The preferred direction in reciprocal space (the direction of the long axis of the elliptical contours shown in b) is orthogonal to the preferred direction in real space (the direction of grain alignment). (c)

SANS and USANS neutron scattering intensities for a sample cut parallel and perpendicular to the bedding, plotted as functions of the scattering vector Q. Error bars are too small relative to the data symbols to be apparent.

Figure 4.21 Backscattered (left and center panels) and secondary electron (c) SEM images of a carbonate-rich fossiliferous sample (Utica Formation), similar in texture to Utica 19. (center and right panels) are close-up views of the region shown in the white box within the image to its left. Q = quartz, Py = pyrite.

Figure 4.22 Neutron scattering intensity curves and actual detector responses for Pt. Pleasant samples (a (left) calcite rich) and (b (right) clay rich) as a function of scattering vector (q), which can be converted to a characteristic scale of scattering object (d) through Bragg's equation: $d = 2\pi/q$ (note that q is always positive). Therefore, the intensity plotted at a $-q$ value of -0.15 is most sensitive to scattering objects ~40–50 nm in diameter.

Figure 4.23 Comparison of pore volume distribution (PSD) obtained from (U)SANS and nitrogen adsorption data for one example of the Montney Formation.

Figure 4.24 Helium ion microscopy image of organic porosity in the Mowry Formation shale from the Powder River Basin, Wyoming.

Figure 4.25 Neutron-scattering (NS) results on the Eau Claire Formation. Lithofacies and associated depths are: illitic shale (2710.1 ft/826.0 m), carbonate mudstone (2846 ft/867.5 m), and glauconitic mudstone (3102.8 ft/945.7 m). (a) Scattering curves.

(b) Porod plots for the same samples. (c) Cumulative porosity versus pore size for the same samples. (d) Differential pore volume distribution versus pore diameter, defined as change in percent porosity at each pore diameter, divided by the difference in spherical pore diameters, multiplied by the average pore diameter. The letters correspond to SEM images shown in Swift et al (2014a) and indicate the length scales at which each mineral-related pore type contributes to total porosity. (From *Swift et al*. 2014a, Relationship between mineralogy and porosity in seals relevant to geologic CO_2 sequestration. Environ Geosci 21(2): 48; AAPG© [2014], reprinted by permission of the AAPG whose permission is required for further use.)

Figure 4.26 Variations of power law Porod exponent (a), porosity (b), and specific surface area (c) as a function of depth for Rose Hill shales that have been weathered to different extents. The Porod exponent, n, indicates the type of fractal ($2 < n < 3$, mass fractal, $3 < n < 4$, surface fractal) [*Jin et al.*, 2011].

Figure 4.27 Estimates of total and unconnected porosity as a function of depth derived from a comparison of scattering from dry Rose Hill shale versus samples soaked with a D_2O/H_2O mixture [*Jin et al.*, 2011].

Figure 4.28 Comparison of calculated and measured values of the solid SLD for four shale formations and one coal. The vertical extent of the measured values reflects the variation observed over the range in Q, which is greater than other sources of uncertainty. Uncertainties on the calculated values of SLD are calculated from the reported standard deviations for

simulation led to change in fracture aperture, Δb, caused by dissolution of the fracture surfaces. Values of k and $\langle q \rangle$ were varied, but all other parameters including the initial aperture field were identical for each simulation. Each simulation ran until $\langle b \rangle = 2\langle b \rangle_o$. These results show the broad range of plausible dissolution-induced fracture alteration scenarios, which range from very uniform dissolution when reaction kinetics are slow and/or flow rates are high (i.e., large Pe and small $Da \cdot Pe$) to very compact dissolution channels when reaction kinetics are fast and flow rates are low such that local dissolution rates are limited by mass transport rather than local reaction kinetics (i.e., small Pe and large $Da \cdot Pe$). Uniform dissolution may result in fracture closure in fractures subjected to significant normal stress, whereas the formation of dissolution channels is more likely to generate a persistent leakage pathway.

Figure 5.4 A demonstration of the influence of fracture length scale, L, on the formation of dissolution-induced preferential flow paths. Preferential flow paths in the 4 m × 4 m fracture with $k = 0.8 \cdot 10^{-10}$ m/s differ from those in a 1 m × 1 m portion of the same fracture at the same value of $\langle q \rangle$ and k, but are very similar to those in the 1 m × 1 m fracture with $k = 3.2 \cdot 10^{-10}$ m/s. Due to the direct dependence of Da on both k and L, concurrently decreasing L and increasing k leads to no change in Da and very similar dissolution pathways. The scaling behavior of the fracture dissolution process has significant implications when using laboratory-scale observations to infer field-scale fracture alteration.

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original stratigraphy, cores from 1190 to 1225.5 m are classified as the Precipice Sandstone, and 1179 m and above are classified as the Evergreen Formation. Created based on data from the supplementary material of *Horner et al.* [2014].

Figure 7.2 SEM images of core from the Chinchilla 4 well, Surat Basin. Note the variability in grain size and packing between sections of the Precipice Sandstone reservoir, the Evergreen Formation caprock, and the overlying Hutton Sandstone.

Figure 7.3 Mineralogy of core from the Chinchilla 4 well, Surat Basin, created from data in *Farquhar et al.* [2015]. Minerals labeled D dissolved during experimental scCO_2-water reaction. Dissolution of 1% calcite content in the 1138 m core was also observed (not shown), along with dissolution of trace amounts of fine-grained siderite and ankerite from all cores. Minerals labeled D dissolved and C additionally corroded during experimental scCO_2-SO_2-water reaction based on data from *Pearce et al.* [2015b].

Figure 7.4 SEM images of Evergreen Formation 897.9 m (Chinchilla 4 well) caprock. (a and b) Horizontally extruded mixed ankerite and Fe-Mg chlorite (1), 2 = organic matter/coal, 3 = albite, and 4 = K-feldspar. (c) Ankerite and chlorite in the core before and (d) after CO_2-water reaction. (e) Before and (f) after CO_2-SO_2-water reaction.

Figure 7.5 SEM images of (a–c) Evergreen Formation 1138 m (Chinchilla 4 well) core: Fe-Mg-Ti mica (1), K-feldspar (2), Ca-Fe-phosphate containing Ce and La (3), Fe-Mg chlorite (4), kaolin (5), and Ti oxide on chlorite (6). (d) After CO_2-SO_2-water reaction with core disaggregated and Fe leached from chlorite,

bright Ti oxide is still present. (e) Hutton Sandstone 799 m pre and (f) post CO_2-SO_2-water reaction with calcite cement (7) dissolved revealing clays (8) and gypsum precipitated on K-feldspar surface (9); inset magnified view of gypsum with image width 150 µm.

Figure 7.6 Micro-CT images of sub-plugs of caprock core (Chinchilla 4 well) at 2.2 µm resolution: Evergreen Formation 897.9 m (a) before reaction, (b) after CO_2-water reaction, (c) difference image where dark areas indicate loss of material or X-ray density. Evergreen Formation 1138 m (d) before reaction, (e) after CO_2-water reaction (stabilized with KCl), and (f) difference image.

Figure 7.7 Water chemistry during CO_2-water or SO_2-CO_2-water reaction of Chinchilla 4 well Evergreen Formation cores (E = Evergreen) from two depths with concentrations normalized to 1 g of reacted core for comparison. (a) solution pH during reaction, (b) Fe concentration, (c) Ca concentration, and (d) Al concentration. Time zero represents a N_2-water-rock soak prior to CO_2 injection.

Figure 7.8 Mineralogy of sandstone (628 m) and siltstone (626 m top and bottom section) cores from the Stuttgart Formation, North German Basin, Germany. Where chlorite = both chlorite and biotite with an Fe (Mg) composition, plagioclase is albite and albite-anorthite, and illite is illite-muscovite. Minerals labeled D were directly observed to dissolve during experimental CO_2-brine reaction. Mineralogy of caprock cores from the Gryfice Beds, Chabowo anticline, Poland, are also shown.

Figure 7.9 Mineralogy of caprock cores from the Chinle Formation outcrop, Utah, USA; the Tournasin