Effect of Quartz Overgrowth Precipitation on the Multiscale Porosity of Sandstone: A (U)SANS and Imaging Analysis

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Abstract

We have performed a series of experiments to understand the effects of quartz overgrowths on nanometer to centimeter scale pore structures of sandstones. Blocks from two samples of St. Peter Sandstone with different initial porosities (5.8 and 18.3 %) were reacted from 3 days to 7.5 months at 100 and 200°C in aqueous solutions supersaturated with respect to quartz by reaction with amorphous silica. Porosity in the resultant samples was analyzed using small and ultrasmall angle neutron scattering and scanning electron microscope/backscattered electron (SEM/BSE) - based image-scale processing techniques.

Significant changes were observed in the multiscale pore structures. By three days much of the overgrowth in the low-porosity sample dissolved away. The reason for this is uncertain, but the overgrowths can be clearly distinguished from the original core grains in the BSE images. At longer times the larger pores are observed to fill with plate-like precipitates. As with the unreacted sandstones, porosity is a step function of size. Grain boundaries are typically fractal, but no evidence of mass fractal or fuzzy interface behavior was observed suggesting a structural difference between chemical and clastic sediments. After the initial loss of the overgrowths, image scale porosity ($> \sim 1$ cm) decreases with time. Submicron porosity (typically ~ 25 % of the total) is relatively constant or slightly decreasing in absolute terms, but the percent change is significant. Fractal dimensions decrease at larger scales, and increase at smaller scales with increased precipitation.

1.0 Introduction

The microstructure and evolution of porosity in time and space play a critical role in many geologic processes, including the migration and retention of water, gas and hydrocarbons, the evolution of hydrothermal systems, weathering, diagenesis and metamorphism, as well as technological processes such as CO₂ sequestration, shale gas and secondary oil recovery. The size, distribution and connectivity of these confined geometries collectively dictate how fluids migrate into and through these micro- and nanoenvironments, wet and react with mineral surfaces. To properly interpret the time-temperature-pressure history of a geological system the physical and chemical “fingerprints” of this evolution in the rock should be interrogated from the nanoscale to the macroscale.

In many sandstones formation of pore-filling overgrowths plays a critical role in the modification of porosity at all scales. However, the effect of pore scale and substrate composition on pore filling processes remains unclear. It has been suggested, on the basis of observations of pore-filling in sandstones (Putnis and Mauthe, 2001, Emmanuel and Berkowitz, 2007, Emmanuel and Ague, 2009, Emmanuel et al., 2010, Cook et al., 2011, Anovitz et al., 2013a), that solubility increases in small pores due to interfacial energy effects, and that larger pores, therefore, fill first. However, preliminary data also suggest that the interaction between precipitate and substrate (e.g. calcite growth in controlled pore glass (CPG), functionalized CPG or limestone, Stack et al., 2014), varying geochemical parameters (pressure, temperature, compositions, etc., Wang et al., 2013) and nonuniformity in the flow field (Noiriel et al., 2012, Molins et al., 2012) can dramatically affect pore filling (Stack et al., 2014). Ising models suggest that the optimum pore size for precipitation may depend on saturation state and pore geometry (Hedges and Whitelam, 2012, 2013). It is apparent that precipitation in porous media is a

complex process that is still poorly understood. In addition, available analysis (Anovitz et al., 2013a) suggests that the surface fractal dimension is pore-size dependent. This, in turn, would suggest a size-dependent variation in the number density of available nucleation sites. In-situ observations of nucleation and precipitation reactions, correlated with their rates, may help identify fundamental principles governing the precipitation process.

Annealing processes during precipitation and recrystallization can also play an important role in the evolution of pore structure. Wong *et al.* (1986) noted that if the fluid is “clean” (i.e. pure water) roughness is controlled by the competition between thermal fluctuations and surface tension. This is analogous to the roughening of domains walls in the pure Ising model which predicts a transition temperature (T_r) above which roughening occurs even under equilibrium conditions (cf. Chui and Weeks, 1981, Barabási and Stanley, 1995). Random contamination of growth sites by impurities in pore fluids can lower T_r , analogous to results obtained from random-field Ising models (Wong, 1985), and the roughening of domain walls by thermal fluctuations in the atomistic nonequilibrium model (Barabási and Stanley, 1995). Similarly, Cohen (1987) noted that sedimentary rocks appear to behave in a manner significantly different from that expected for sintered material, including formation of fractally rough grain boundaries. He suggests this “anti-sintering” behavior is caused by reduction of grain/pore free energy due to interaction with pore waters. A similar effect was observed by Anovitz et al. (2009) in contact metamorphosed Hueco limestone.

The purpose of this paper, therefore, is to investigate the controls on pore-filling processes under experimentally controlled conditions. To do so we have taken samples of the relatively pure St. Peter Sandstone of different initial porosity and exposed them under static, externally buffered conditions, to quartz-oversaturated solutions at 100 and 200°C for periods

ranging from three days to 7.5 months. Although a great deal is known about the factors that control the dissolution and precipitation rates of quartz (cf. Dove and Rimstidt, 1994, Dove, 1999, Dove et al., 2005, 2008), we interrogated how these depend on, and affect the pore structure of, the matrix in which precipitation occurs. We have, therefore, experimentally grown quartz overgrowths in a sandstone matrix, and used a combination of small and ultra-small angle neutron scattering and electron imaging techniques to examine qualitatively and quantitatively the processes by which quartz precipitation occurs.

2.0 Experimental Techniques

2.1 Starting Materials

Starting materials consisted of two samples of St. Peter sandstone from southwestern Wisconsin: 04Wi17b and 05Wi30 (Kelly et al., 2007, Anovitz et al., 2013a). These were chosen for their markedly varied initial porosities, with 04Wi17b containing only about 4.8 % porosity, and 05Wi30 containing 25.8 % initial porosity, the difference being due to the presence of substantial, optically continuous silica overgrowths in the former. Both were otherwise nearly pure quartz arenites, containing only very small amounts of calcite and iron-oxide. In both cases the experimental samples were cut from small samples of the initial rock ($< \sim 1 \text{ in}^3$) with no obvious inhomogeneities to assure that the starting samples for each experiment were as consistent as possible. Further descriptions of the origin and chemistry of these samples are provided by Kelly et al. (2007) and Anovitz et al. (2013).

For these experiments a starting solution was required: 1) that was oversaturated with respect to the solubility of quartz, 2) that contained a significant quantity of dissolved silica, and 3) in which the solubility was relatively independent of temperature. As the solubility of silica in water is essentially independent of pH at low pH values, this meant a high-pH solution was required. The solubility of quartz and amorphous silica over a range of NaOH concentrations was calculated from the data of Wesolowski et al. (2004). At concentrations between about 0.1 and 0.5 molal NaOH the solubilities of both amorphous silica and quartz are nearly temperature-independent. As a higher NaOH concentration increases the silica solubility we selected one near the upper limit of this range for our experiments.

To make the starting solution we placed 3.19 g of Cab-o-Sil fumed silica, 78.0447 g of H_2^{18}O , and 21.9540 g of D_2O (isotopic results will not be presented here) in a quartz-glass liner into a 300 cm^3 , bolt-closure pressure vessel. As both the liner and the Cab-o-Sil were composed of amorphous silica dissolution of the liner during the experiment should have no effect on the solution. The $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixture was sparged with Ar prior to the experiment to remove dissolved CO_2 . The vessel was then placed in the furnace of our high-temperature emf cell (cf. Davis et al., 2011), heated to 150°C and stirred with a glass-magnet stir bar. We then titrated 50 cm^3 of 1.3545 molal (moles/kg solution) NaOH into the solution at temperature using a manually-operated Ruska syringe pump. The resulting solution, with a final NaOH concentration of 0.460 molal was then left to stir at temperature overnight (approximately 18 hours), quenched and stored in a sealed HDPE bottle. For this NaOH concentration the final silica concentration in equilibrium with amorphous silica at 25°C should be approximately 0.45 molal. The measured value, 0.65 molal was slightly high, but may represent either minor contamination of the

analyzed fluid with solid silica, or enhanced solubility due to the fine particle size of the Cab-o-Sil. In either case, however, the concentration remains satisfactory for our experiments.

The measured pH of the solution was 11.88. If we assume that all of the silica is in solution as H_3SiO_4^- , as would be expected at this pH (Busey and Mesmer, 1977, Xiong 2013), and correct for the effect of ionic strength on the dissociation constant of water (Busey and Mesmer, 1978) we can calculate an expected pH of 11.84. These values are in very good agreement, well within the uncertainties of the calculation and the measurement.

2.2 Experimental Approaches

Two slightly different, but essentially similar approaches were used to conduct the quartz precipitation experiments at 100 and 200°C. For the 100°C experiments 5/8" OD, 1/2" ID quartz glass tubes were prepared with one end sealed. Approximately 0.15 grams of Cab-o-Sil were then added, topped by a small plug of silica glass wool. These were followed by blocks of both sandstone starting materials in each tube (weights varied from 0.28 to 1.13 g) and sufficient fluid to more than cover the blocks (exact weights are given in Table 1). These were then frozen, evacuated, thawed, refrozen, repumped to remove air from the sandstone pores and then refrozen to avoid solution loss while the sample was sealed with a torch. The tubes were then bundled together with a thermocouple, wrapped in insulation, and placed in an air furnace. Samples were pulled from this bundle at pre-designated times and allowed to air-cool.

The procedures for the 200°C experiments were similar to those for the 100°C runs, except that samples (blocks of both sandstones plus solution) were placed in Teflon-lined, VCR-based stainless steel vessels that were then placed in a cold vacuum oven to remove air and then inserted into an aluminum block using Pt RTDs (Resistance Temperature Detectors) to monitor

the temperature (cf. Anovitz et al., 2004). For the 200°C experiments the reaction vessels were rapidly quenched in cool water on removal from the oven. In both cases vessels were opened sequentially at times ranging from 3 days to 7.5 months (see Table 1 for times), the fluids were saved for analysis (Table 2), and the sandstone blocks were placed in deionized water overnight before drying to limit silica precipitation during dryout.

2.3 Analytical Approaches

The analytical approaches are essentially those we have reported elsewhere (Anovitz et al., 2009, 2011, 2013a,b, Wang et al., 2013) and will, therefore, only be briefly summarized. Small and ultrasmall angle neutron scattering were used to probe porosity over length scales from approximately 10 nm to 30 μm . This was expanded to scales up to approximately 1 cm using autocorrelation functions calculated from backscattered electron (BSE) images taken on a scanning electron microscope (SEM) at 10 and 20x of the samples. Transmission electron microscopy (TEM), electron diffraction (ED), and cathodoluminescence (CL) imaging were also used to examine porosity and the structure of new as well as diagenetic overgrowths.

Small angle neutron scattering (SANS) measurements were conducted on the NG7 instrument at the Center for Neutron Research at the National Institute of Standards and Technology (NIST/NCNR; Glinka et al., 1998), and the General Purpose SANS Instrument at the High Flux Isotope Reactor at the Oak Ridge National Laboratory (HFIR; Littrell et. al., 2008). SANS measurements were performed on polished thin sections (0.15 mm thick) of each sample with the beam incident along the surface normal. Because of the experimental limitations somewhat smaller samples were used than those previously reported (Anovitz et al., 2009, 2013a). For variable sample sizes we used cadmium masks with different size openings that allowed neutrons

to access the sample: 1/8" and 1/4" round, and 0.3" x 0.2" and 0.5" x 0.2" rectangular dimensions. At NIST, the wavelength (λ) was 8.09 Å with a wavelength spread ($\Delta\lambda/\lambda$) of 0.11. Three sample-to-detector distances (1.0, 4.0 and 15.3 m) were used to increase the observed angular range and, therefore, the Q-range. Typical Q-resolution was between 5 and 10 percent depending on Q and the sample-to-detector distance. At the 15.3 m distance we used a set of biconcave MgF₂ lenses to further increase the Q range and provide better overlap with the USANS data at lower Q (Choi et al., 2000). The resultant scattering vector ranged from 0.0009 to 0.43 Å⁻¹, which corresponds to sizes from approximately 15 to 7000 Å. At HFIR, three sample-to-detector distances (1.1, 4.7 and 19.3 m) were used with the wavelength $\lambda = 4.75$ Å at 1.1 and 4.7m, and $\lambda = 19$ Å at 19.3m with a wavelength spread $\Delta\lambda/\lambda = 0.14$. The measurements were performed with the detector offset to extend the Q range measured at each setting and provide better overlap between settings. The resultant scattering vector ranged from 0.0009 to 0.9 Å⁻¹, which corresponds to sizes from approximately 7 to 7000 Å. Data were corrected for empty-beam scattering, background counts and detector uniformity, sample transmission and scattering volume, and reduced to an absolute scale (differential scattering cross-section per unit volume) by normalization to the intensity of the direct beam. The two-dimensional data were always isotropic, and thus were circularly averaged to produce one-dimensional intensity profiles (Kline, 2006).

Ultra-small angle neutron scattering (USANS) measurements were performed on the BT5 instrument at the Center for Neutron Research at the National Institute of Standards and Technology (Barker et al., 2005). A pair of triple-bounce channel-cut perfect silicon (220) crystals was used in this instrument for the monochromator and analyzer. The wavelength was 2.38 Å with a wavelength spread $\Delta\lambda/\lambda = 0.059$. Data were collected over a Q range from 4.19 x 10⁻⁵ to 2.66 x 10⁻³ Å⁻¹, which corresponds to length scales from 0.24 μm (2400 Å) to 15 μm. The

horizontal Q resolution (full width at half maximum) is $2.5 \times 10^{-5} \text{ \AA}^{-1}$. The same cadmium sample apertures used for the SANS measurements were used for the USANS measurements which, therefore, probed the identical volume. Scattering intensity data were corrected for empty beam and constant background levels. The corrected data were converted to an absolute scale by measuring the attenuation of the direct beam through the sample. Further data reduction and de-smearing were accomplished through the USANS data reduction software provided by NIST/NCNR (Kline, 2006). The combination of USANS and SANS allows us, in principle, to probe length scales over four orders of magnitude from 7 Å to 15 µm.

Specimens for examination in the TEM were prepared by first impregnating samples of the sandstones with epoxy. Samples were then extracted using a Hitachi NB-5000 FIB-SEM focused-ion-beam instrument and imaged using a Hitachi HF-3300 cold-field-emission TEM, operated at 300 kV accelerating voltage at the High Temperature Materials Laboratory at ORNL. Bright-field images were recorded on a Gatan 2K Ultrascan CCD camera.

Backscattered electron images of the pore space were used to extend the scattering curve to larger scales and to provide two-dimensional information on the lacunarity and multifractal spectrum of the pore system (Debye et al., 1957, Anovitz et al., 2013, Wang et al., 2013). Images were obtained using a Hitachi S3400 environmental SEM. The samples were not coated, and a pressure of 50 Pa was used to eliminate charging. Images were obtained at 10, 20 and in some cases 40x, the first yielding an image size of 12.7 mm x 9.5 mm. The images consisted of 5120 x 3840 pixels, yielding a pixel edge length of 2.480 microns. Thus the maximum pixel size overlapped the maximum spacing observable by USANS by approximately one order of magnitude. Cathodoluminescence images were obtained on a similar Hitachi S3400 SEM also

running at a pressure of 50 Pa on uncoated samples, using a Gatan PanaCL system with a parabolic mirror in the Department of Geoscience at the University of Wisconsin-Madison.

Fluid chemistries were analyzed using a Varian model GTA120/AA240Z graphite-furnace atomic absorption spectrometer (GFAA). Standards were made by diluting 1000 ppm Si and Fe standards (Fisher lot 102251 and 102053 respectively) with DI water for Si, and 0.2 wt% HNO₃ for Fe. Si was diluted to a range from ~27 to 134 ppb, and Fe from ~3 to 15 ppb. Samples were diluted twice for Si and once for Fe with DI water as necessary to reach the linear range in the GFAA.

3.0 Experimental Results and Discussion

3.1 Scanning and Transmission Electron Microscope Imaging and X-ray diffraction

Figures 1-4 show selected SEM/BSE images of different samples from the four experimental conditions run for varying lengths of time. There are several trends observable in these images. From three days and onward newly-formed overgrowths begin to be visible along grain edges and, especially in the 100°C experiments, finer material begins to fill the pores, a result which is likely to increase the number of small pores detected in the scattering. The formation of this finer material is less evident, however, in the 05Wi30 (25.8 % initial porosity) experiments than in those using the 04Wi17b (4.8% initial porosity) starting material.

Most surprisingly, however, in sample 04Wi17 there is a distinct increase in the porosity between the starting material and the sample after three days at both 100°C and 200°C. Therefore these experiments did not exhibit the simple decrease expected in pore volume with time in the early stages of reaction. Careful examination of Figure 1a shows that pre-existing overgrowths are visible in BSE mode around many of the grains, and many of these have

disappeared after 3 days (Figure 1b). This would suggest these are a different material from the core (i.e. original detrital) quartz grains. However, Kelly et al. (2007) noted that the diagenetic overgrowths in these samples are optically continuous with the quartz cores. Their identification as quartz would also seem to be supported by the crystal faces observable on fractured surfaces on overgrowth surfaces in pores (Figure 5), and when seen in cross section (Figure 5b) the overgrowths are smoother and show less visible porosity at this scale than that observable in the core grains.

There are, however, several reasons besides the dissolution behavior to argue that these pre-existing overgrowths are not identical to the cores of the quartz grains. Figure 6 shows a cathodoluminescent (CL) image of the sample. There are clearly multiple layers of overgrowths present, some of which appear to be fibrous, whereas others do not. The latter appear to be largely at the exterior surface of each grain, which may explain the features observed in the SEM images (Figure 5). Griffin (2000) has noted that charge contrast imaging (CCI) in the SEM under environmental conditions may yield images identical to those obtained by CL, and that “high sensitivity, low kV BSE detectors are also light sensitive and consequently also will respond to this phenomenon in varying degrees”. This may explain the contrast observed in the BSE images. Thus both the SEM and CL images are consistent in identifying the pre-existing overgrowths as differing from the core quartz grains. We tested this hypothesis by conducting selected area diffraction on both the core and pre-existing overgrowth materials using the TEM, but beam focusing appeared to amorphize the sample, although this effect was much more severe in the overgrowths than in the grain cores. This was not observed for samples of Brazilian quartz analyzed on the same instrument under the same conditions. Similar results have been previously reported by McLaren and Phakey (1965a,b), van Aken et al. (1998), Stenina (2004) and Page et

al. (2004) who suggested this phenomenon could be due to water and/or trace elements dissolved in the quartz, or the presence of a truly amorphous phase, either of which could explain the observed dissolution during the experiment.

TEM imaging was also used to examine the structure of the precipitation products at finer scales. Figure 7 shows TEM images and TEM/energy dispersive analysis (EDA) X-ray maps of the precipitate in sample 04Wi17B run at 100°C for 7.5 months. Most of the precipitate is platy, and primarily consists of silicon and oxygen, as would be expected. This habit is common in opal-CT (Graetsch, 1994, Keene, 2006, Gaillou et al., 2008), as well as at coarser scales in epithermal gold deposits where it is thought to be a pseudomorph after calcite (Lindgren, 1933; Urashima, 1956; Simmons and Browne, 1990, Simeone and Simmons, 1999; Simon et al., 1999, Etoh et al., 2002), which is not a likely origin here. It has also been observed in phytoliths in fossil forests (Kodama et al., 1992). As shown by electron diffraction (Figure 7G), however, the plates are crystalline, and thus not opal, and analysis of the pattern shows that they are composed of alpha-quartz. However, some opal spheres (Figure 7H) are present, and electron diffraction shows that these are, indeed amorphous (Figure 7I). These data suggest that the experimental silica may have originally precipitated as opal, then recrystallized to quartz. A small Na-bearing layer on the plate surface suggests that some sodium hydroxide or silicate may have precipitated during the quench.

At 200°C (Figure 8) at least two phases appear to be present: silica, and a Na-Fe-silicate. XRD analysis of the sample as a whole shows no evidence of the presence of either aegerine, an amphibole, or any other phase, although one could be present in percentages too small to be observed, or the material may be amorphous. This phase undoubtedly formed by incorporating small amounts of iron during dissolution and reprecipitation, but as this was quite small and

some remained in solution (Table 2) the total abundance of this material in the pores is, therefore, quite small as well and unlikely to affect the scattering results.

3.2 Fluid Chemistry

Figure 9 and Table 2 show the silica composition of the fluid (post quench) in each experiment as a function of time. At 200°C the solution begins at or near equilibrium with amorphous silica and, over time, approaches equilibrium with quartz. Although amorphous silica was still present in each experiment, the fluid seems to have equilibrated more easily with the quartz, perhaps due to consolidation or crystallization of the Cab-o-Sil. The results of the 100°C experiments are, however, significantly different. Although the silica concentrations in some samples rise to the level expected for quartz solubility, most have concentrations that are significantly below that expected for equilibrium with either quartz, amorphous silica, or some mixture thereof. The most likely explanation is that this is a quench phenomenon caused by the fact that the 100°C experiments were run in quartz glass tubes, whereas the 200°C experiments were performed in Teflon-lined steel vessels. At 100°C silica may have metastably adsorbed on the quartz glass, silica wool, or amorphous silica surface. In this case, it would be the higher concentration samples that more closely reflect conditions during the experiment.

3.3 Scattering Curves

Figure 10 shows Porod-transformed, background-subtracted scattering data (including the results from the image processing at larger scales) for selected times for each experimental condition and material. Several features of the scattering curves are clear from these diagrams. As we have shown previously (Anovitz et al., 2009, 2013) scattering data provide a

quantification of the surface and mass fractal dimensions, and thus the surface roughness and size dependent number density of potential nucleation sites, and interpore distribution of pore structures. In a Porod plot smooth surfaces should yield a zero slope, surface fractals slopes fall between 0 and 1, mass fractals exhibit slopes between 1 and 2, and slopes greater than 2 are indicative of fuzzy interfaces. It is clear that none of these data sets can be simply described by only one of these models. Instead, each appears to be composed of several steps and changes in slope at different Q ranges, and both the position and intensity of these steps varies with time. This is similar to the results we reported for samples of the St. Peter sandstone from SW Wisconsin which contain varying levels of porosity due to overgrowth formation (Anovitz et al., 2013a). Thus, at least to a first approximation, the results of the experimental quartz precipitation experiments are consistent with those for the natural samples.

Both the SEM/BSE imagery and the (U)SANS scattering data can be used to obtain the porosity of the samples. For the SEM imagery this is, of course, obtained directly from the pore fraction in the binary images. For the scattering curves porosity is obtained from the invariant (Y) as:

$$Y \equiv \int_0^{\infty} Q^2 I(Q) dQ = 2\pi^2 (\Delta\rho)^2 \phi(1 - \phi) \quad (1)$$

assuming a two-phase (rock, pore) approximation (Radlinski, 2006), where $\Delta\rho$ is the difference in scattering length density between the quartz ($4.18 \times 10^{-6} \text{ \AA}^{-2}$) and the empty pores (assumed to be zero), and ϕ is the porosity. Figure 11 and Table 1 show the changes in the (U)SANS scale, image-scale, and total porosity as a function of time, although it is important to point out that there is significant overlap between the image and (U)SANS scales. We observe that porosity initially increases in the two 04Wi17b samples due to the dissolution mentioned above, and then decreases in all four cases as precipitation occurs at larger scales with little absolute change in

small-scale porosity. Fitted curves are shown for the USANS and total pore fractions to better show the trends. Although at small scales there is significant scatter attributable to the small absolute values, it is apparent that, with the exception of 04Wi17b at 200°C there has been a significant decrease in both the larger and smaller-scale porosity in all four experiments. In fact, the percentage change at this scale is as large or larger than that at bigger scales. This suggests that, on a percentage basis, the smaller pores are filling more rapidly than larger ones, although the mass of precipitated material is likely larger at larger scales.

In order to examine this effect in more detail we need to quantify porosity as a function of pore size. As we have previously shown (Anovitz et al. 2013a,b, Wang et al., 2013) the scattering curves shown in Figure 10 can be modified to extract cumulative porosity as a function of pore diameter. However, we can take this one step further by taking the derivative of the cumulative porosity as a function of r (normalized to account for variations in step size so that the integral is equal to the cumulative porosity). This yields the pore volume distribution as a function of pore diameter. These results are summarized for selected reaction times for each set of experiments in Figures 12-15.

To quantify these changes the data must be fitted as the sum of several pore distributions. The choice of distributions is, however, somewhat arbitrary. Although the data could be fitted assuming either a suite of log-normal distributions or a combination of fractal distributions modified slightly by small log-normal sets, following our previous work (Anovitz et al., 2013a) we have selected the second approach. The log-normal probability distribution functions are given as:

$$V(r)_{LN} = \frac{I}{r\sigma\sqrt{2\pi}} e^{-\frac{(\ln r - \mu)^2}{2\sigma^2}} \quad (2)$$

where I is the overall intensity of the distribution, r is the pore radius, e^{μ} is the median of the distribution, and σ defines the width of the distribution. The fractal distributions are given as:

$$V(r)_F = IQ^3 \left(1 + \frac{\sqrt{2}}{3} Q^2 r_0^2 \right)^{\frac{D_s-6}{2}} \quad (3)$$

where I is again the intensity of the distribution and r the pore radius, Q is the scattering vector ($= 2\pi/r$), r_0 is a position variable for the distribution (but not the peak of the distribution), and D_s is a surface fractal dimension that defines the low- r slope of the curve. This has the advantage of describing both the nature of the pore clusters and the individual pores making up those clusters. All data were, therefore, fitted as the sum of three fractal distributions. These were modified at the largest and smallest scales by log-normally distributed pore sets. This approach was adopted for data at either end of the size range as there was insufficient data to constrain additional fractal distributions, but is consistent with the unified approach adopted by Beaucage and co-workers (Beaucage et al., 1995; 2004; Beaucage, 1995, 1996) to account for samples with scatterers at multiple structural levels. Figures 12-15 show fits to the pore volume distributions for each run. Fitting coefficients for all of the samples, along with R^2 values for the fits are given in Table 3.

Examination of Figures 12-15 shows that there are clearly at least two pore-size distributions for the 100°C and 200°C experiments on both sample types: one with a peak around 200 microns, the other with a peak near 0.5 microns. As noted above, and as shown by the dashed lines in these figures, fitting shows that the larger length-scale features must be modified from a strictly fractal distribution by the addition of a second, log-normal set. The fact that these largest pores cannot be fitted as a strictly fractal distribution is apparent in several other datasets as well (Radlinski et al., 2002, 2004; Anovitz et al., 2013a). A third fractal distribution is also apparent

in most samples near 0.1 microns. Figure 16 shows the volumes of each of the fitted pore distributions as a function of time for each experiment.

The relative volumes of each of these distributions change with time, as is evident both qualitatively in the plots (Figures 12-15) and in the fitted results (Figure 16, Table 3). In sample 04Wi17b the volumes of all distributions increase during initial dissolution at both temperatures. At 100°C the total volume of the both the larger-scale fractal and log-normal distributions then slowly decrease. There is little apparent overall change at this scale for the 200°C experiments after the initial dissolution out to 6.5 months, although the fitted results do show a decrease in the log-normal modification. At 100°C the volume of the mesoscale distribution increases slowly. The nanoscale distribution increases initially with overgrowth dissolution, followed by a significant decrease for the first two weeks and then a slow continuous increase to values near those of the starting and 3 day (after dissolution) samples. At 200°C the mesoscale porosity increases for the first two to three weeks, followed by a decline to final values less than half those observed at 100°C. The nanoscale porosity also increases for approximately three weeks and then decreases sharply, although the 6-week experiment is an exception to this rule.

The primary difference between the 04Wi17b and 05Wi30 samples is that the latter initially had a smaller percentage of overgrowth on the core quartz grains, and thus little or no dissolution and increase in porosity at short times. In fact, as shown in Figure 16, the overall patterns of change in the various distributions are very similar between the two samples at each temperature. At 100°C there is relatively little change with time at larger scales although, again, the log-normal modification decreases with time and the whole decreases slightly, indicating large-scale pore filling. There is a slight increase in the mesoscale and nanoscale distributions although the final values are not quite as large as those in 04Wi17b, possibly a result of an increase in the

silica concentration in the pores of the latter caused by the initial dissolution. At 200°C some dissolution clearly occurred in sample 05Wi30, as porosity increased at all scales for approximately 1 week (longer at the nanoscale). Porosity in the large log-normal modification and the mesoscale and nanoscale distributions then decrease proportionately until the pore volume distribution at 6.5 months looks very similar to that of the original sample, although there may still be slightly greater porosity at the smaller scales. This is supported by the fitted results, which show initial increases, followed by decreasing porosity at all three scales.

Most of the fractal dimensions fitted for the mesoscale distribution are extremely uncertain, as the small- r end of this distribution is typically limited by the smaller-scale structures, the fractal dimensions of which are similarly rendered uncertain by background effects and even smaller structures. However, the largest-scale pore structures typically cover a larger range of scales than the other two, and thus their fractal dimensions are better constrained. Although the upper end of this distribution is largely defined by the imaging data, the fractal slope is largely controlled by the USANS data set and is thus at a smaller scale than the multifractal results based on the imaging data. For the 04Wi17b experiments the primary change is an initial decrease in the fractal dimension from an initial value of 2.43 to a final value near 2.25 correlated with the increase in porosity due to the initial dissolution. There is little change at longer times. For sample 05Wi30, however, the decrease in porosity with time correlates with an increase in the fractal dimension from a starting value of 2.17 to values near 2.3.

3.4 Multifractal Analysis

As we have shown in previous work (Anovitz et al., 2013a), in addition to calculating the low- Q range of the scattering curve, SEM/BSE images of the pore structure in a sample can also

be used to calculate the multifractal dimensions and lacunarity of that sample. These provide information about the distributions of pixels, and therefore pores, within an image, and significant quantification of the pore structure at this scale. They are, therefore, quantifiable measures of the relation between porosity and permeability, as well as reactive surface area within the sample. Multifractal values provide a quantification of how the image behaves if magnified, and whether multiple scaling rules are present. Mandelbrot (1989), in an extension of his original description of multifractal systems (Mandelbrot, 1974) notes that:

“The generalization of fractal sets to multifractal measures involves the passage from geometric objects that are characterized primarily by one number, namely a fractal dimension, to geometric objects that are characterized primarily by a function”

Typically, then, multifractals describe distributions that are not just present or absent, but have varying fractal dimensions depending on their concentration – such as the distribution of copper within an orebody (Mandelbrot, 1989), or porosity in space. There are several ways to quantify this. One is the Rényi spectrum in which the distribution of the measure (porosity in our case) is distorted by raising it to some arbitrary power, q , calculating the resultant fractal dimensions $D(q)$ and plotting $D(q)$ as a function of q . $D(0)$ in this case is equivalent to the box-counting or capacity dimension, for which there is no weighting relative to the distribution of porosity. Larger values of q weight the calculation in favor of more porous areas (denser distribution of the measure), and values of q less than zero place greater emphasis on less porous areas (rarified regions). $D(q)$ typically either decreases with increasing values of q or, in the case of a simple monofractal where there is no dependence of the fractal dimension on concentration, there will be no change in $D(q)$ with q . A simple method of quantifying the extent of multifractal behavior is, therefore, to calculate the difference between $D(0)$ and $D(q)$ at some higher value of q , such as

between $D(0)$ and $D(2)$. $(D(0) - D(q))$ then provides a measure of the multifractality of the image. For a monofractal $D(0) - D(2)$ will be equal to zero, and the larger this value is the more the fractal behavior is scale-dependent.

The lacunarity, Λ , provides a measure of the inhomogeneity or “gappiness” (from the latin word lacuna, meaning a gap or a lake, which is commonly used in stratigraphic analysis for a gap in the stratigraphic record at some location) of the pore structure. Lacunarity is, therefore, a quantitative measure of how clustered the pore structure is, and serves as an addition to the concept of fractal analysis (cf. Mandelbrot, 1983, 1994, 1995). It can also be viewed as a measure of the translational homogeneity of an image. From the point of view of understanding the relationship between porosity and permeability, therefore, this provides a quantification of how isolated each pore, or group of pores is from others.

For a binary image divided into a given number of boxes of a given box size, ϵ , and grid orientation, g , the box-size specific lacunarity (λ) is calculated from the mean, σ , and standard deviation, μ , of the number of pixels “turned on” in each box as:

$$\lambda_{\epsilon,g} = (\sigma_{\epsilon,g}/\mu_{\epsilon,g})^2 \quad (4)$$

The overall lacunarity of the image, Λ , is then the average of the single box size lacunarities (λ) over all box sizes and grid positions. Analysis of these values is, of course, limited by the resolution of the images in question.

In this paper multifractal calculations were performed using the Fractalac plugin version 2.5 for ImageJ (Karperien, 1999-2012). Figure 17 and Table 4 show the multifractal and lacunarity results for samples from the four experimental conditions. For experiments on sample 04Wi17b (Figure 17a,b) which began with significant dissolution there is an initial increase in the fractal dimensions at all q (roughening, $D(0)$ and $D(2)$ shown), but a decrease in the multifractality

($D(0)$ - $D(2)$) and lacunarity of the samples. At the longest times, however, as the pores begin to refill this pattern is reversed, with the pore network getting smoother and lacunarity and multifractality increasing, an effect that is especially clearly demonstrated in the 100°C experiments. This latter pattern is also generally consistent with results from sample 05Wi30 in which little or no initial dissolution occurred. In most of these samples the overall fractal dimensions decrease with time, and both the multifractal and lacunarity behavior increase, although there does not appear to be a significant increase in multifractality for the 200°C experiment on 05Wi30.

4.0 Conclusions

The data discussed above yield a number of multiscale observations of the process of quartz precipitation in sandstone pores during these experiments. SEM and TEM imagery shows that, in addition to the initial dissolution of original overgrowths in 04Wi17b, with time quartz not only precipitated on the grain edges, but as plates extending into the larger pores as well. The presence of larger-pore filling precipitates likely increased the concentrations of smaller pores due to the spaces between precipitate grains, explaining the increase in the nano-scale porosity at the longest times.

Multifractal and lacunarity analysis of the SEM images showed that, as porosity decreases, the overall fractal dimension $D(0)$ also decreases. That is, the image-scale pores get smoother. However, the multifractality (shown here as $D(0) - D(2)$) and the lacunarity increase. Thus, the roughness of the pore structure becomes more scale dependent, and the pores become more isolated. This is completely consistent with the observation by Anovitz et al. (2013a) that

changes in image-scale fractal dimension and multifractality (given there as $D(0) - D(q_{\max})$) correlate with changes in porosity due to natural overgrowth formation (silcrete formation) in the St. Peter Sandstone from SW Wisconsin, and thus shows a generalized relationship between changes in pore structure due to overgrowth formation.

Interestingly, the decrease in $D(0)$ with decreasing porosity observed at the image scale is opposite to that observed in the larger fractal pore distributions in the scattering data. This is also consistent with the results of Anovitz et al. (2013a), who found that, with increasing overgrowth abundance (decreasing porosity) $D(0)$ tended to decrease, and the fractal dimension obtained from the scattering data increased. Thus, as overgrowths form (as porosity decreases) the pore structure at the micron to centimeter scale becomes smoother and more clustered, whereas at finer scales the surfaces become rougher.

As noted above, Wong et al. (1986) suggested that, although fractal scattering from sandstones is often dominated by interstitial clay particles, for materials that precipitate from solution (carbonates in their study) surface roughness is determined by the relative magnitudes of surface tension and thermal fluctuations. In this case, by analogy to the pure Ising model, there should be a transition temperature above which surfaces roughen with time. As the surface tension is lowered by the presence of impurities in the solution, this tends to lower this transition temperature (cf. Huse and Henley, 1985; Grinstein and Ma, 1983; Wong et al., 1984; Cohen and Anderson, 1985, Cohen, 1987). Thus, at the smaller scales, an increase in roughness occurs during quartz overgrowth formation such as that investigated here and by Anovitz et al. (2013a).

To the extent that the fractal dimension, or surface roughness can be viewed as a configurational entropy (Nosonovsky, 2010), the differences between the behavior at larger and smaller scales may be explained by a scale-dependent entropy transfer, even in an otherwise

closed system. Nosonovsky and Esche (2008) note that thermal fluctuations at the nanoscale require energy, which must be dissipated to maintain a constant temperature. The result is that entropy is transferred from larger scales, where grains tend to grow or smooth and entropy decreases, to smaller scales, where entropy increases and the surface becomes rougher.

The details of the pore structure at the sub-10 micron scale obtained from the scattering data are also qualitatively similar to those observed in other natural sandstones. The pore structure is not composed of a single, polydisperse distribution, but of several pore-size distributions with maxima at different scales. Anovitz et al. (2013a) suggested that this may be the effect of smaller grains filling spaces between larger ones, much in the manner of an Apollonian Gasket. While sand grains are not spheres, although in a mature arkose like the St. Peter they are well rounded, in a well-sorted sandstone the particles are of similar sizes, and thus leave between them pore spaces that tend to fall into a defined size range. If some of these are filled by smaller-sized grains a second pore distribution will be formed with a size distribution smaller than, and distinct from, the first. The observed correlations between the precipitate infilling and the development of new or increase in the overall volume of preexisting smaller pore distributions tends to support this suggestion. However, these distributions may also represent pores of different types (cf. Swift et al., 2014), the prevalence of which is enhanced or diminished during precipitation/dissolution processes.

Nelson (2009) summarized the prevailing ideas about the distribution of pore and pore-throat sizes in sandstones. Summarizing data from Wardlow and Cassan (1979) he noted that pore sizes, fitted as the largest inscribed circles in pores in resin casts, were typically about $\frac{1}{2}$ to one order of magnitude smaller than the grain sizes of the rocks, and the pore throats an order of magnitude smaller yet. The ratio observed by Wardlow and Cassan (1979) between grain sizes

and pores is very consistent with that observed in tetrahedral or octahedral coordination between identical spheres, where the radius ratio of the pore should be about 0.225 and 0.414 that of the grains, respectively. Later work described by Nelson (2009), based largely on mercury porosimetry, suggests pore throat sizes that are somewhat smaller than those suggested by Wardlaw and Cassan (1979), ranging from approximately 0.01 to 10 microns, which agrees very well with the r -values for the mesoscale and nanoscale fractal distributions in our data (~ 1 micron and ~ 0.1 micron).

There were significant differences in the temporal evolution of the various pore size distributions for the four experiments, as well as in comparisons of the image-scale and (U)SANS-scale overall porosity, beyond that due simply to the initial dissolution of overgrowths. At the (U)SANS scale, it was clear that, whereas the bulk of the precipitation by mass was in the larger pores, on a percentage basis, precipitation at the smaller scales was dominant. In all cases the log-normal “modification” to the largest pore distribution decreases with time. It disappears completely in both 100°C experiments by 7.5 months but is still present in both 200°C experiments at 6.5 months. There is much less relative decrease in the volume of the largest fractal distribution itself, although the absolute decrease at this scale is much larger, and dominates changes in the overall porosity. This is consistent with the suggestion by Stack et al. (2014) that small pore filling is dominant during homogeneous precipitation. Differences in reaction behavior between the 04Wi17b and 05Wi30 samples appear to be related primarily to the initial dissolution of some of the overgrowths in 04Wi17b, and to in-pore concentration changes caused by the initial dissolution of overgrowths in 04Wi17b, which led to larger porosity changes at longer times.

Differences between the 100°C and 200°C results appear to be due to the nature of the precipitation process itself. As shown in the SEM and TEM images (Figures 1-8) at the longest times at 100°C much of the precipitate is present as platy material partially filling the larger pores, but clearly creating significant meso- and nanoscale porosity between the grains. At 200°C, however, the new material has clearly formed as overgrowths on the initial grains with some, but limited, porosity within these newly formed parts of the sample. The cores of the larger pores, however, remain largely empty. Thus, at 200°C, much less new, fine-scale porosity is formed.

The origins of the rest of the pore distributions can also be determined by examination of the SEM and TEM images. As is evident from the SEM images from which these data were derived, the largest pore distribution clearly involves two pore types: large open pores, and variable-length scale grain-grain boundary porosity. This may explain why the volume distribution for pores in this size range cannot be described simply as either a fractal, or a log-normal distribution, but can be reasonably fitted as a combination of the two. The reduction of the log-normal part of this pair with time may also, then, be related to the decrease in multifractal behavior and lacunarity with precipitation. Furthermore, this can be expected to affect the relationship between pore bodies and pore throats, and thus the overall permeability of the sample.

The separation between the mesoscale and nanoscale pore distributions is very clearly delineated in the data for 05Wi30, but less so in that for 04Wi17b (Figures 12-15). This suggests that the finer-scale distribution is partially obliterated by overgrowth formation. This is supported by the results of the 200°C experiments in which overgrowth formation was the primary deposition mechanism and, in both cases, the volume of the nanoscale fractal

distribution decreased dramatically at longer times. As there is little clay in this material these pores must be due to contacts between the quartz grains themselves. As they change with precipitation they cannot be isolated pores, but must be connected to the pore network.

The form of the precipitate also provides interesting potential insights into quartz precipitation in sedimentary basins. As noted above, the platy texture observed is commonly associated with opal-CT, although the material tested in our experiments was alpha quartz. This suggests that the silica may originally have precipitated as opal and converted during the experiment. Although the experimental temperatures are higher than would be expected for silcretes (For example, Kelley et al., 2007 suggested that quartz cementation in the samples of the St. Peter sandstone from southwestern Wisconsin later examined by Anovitz et al., 2013 occurred at 10 – 30°C.), these temperatures are within the range observed in deep sedimentary basins (e.g. North Sea, ~ 170°C, Bjørlykke and Egeberg, 1993; Illinois Basin, ~ 200°C, Proffitt et al., 2013), geothermal systems and elsewhere. Although opal-CT is commonly observed at temperatures up to about 70 to 90°C (Bjørlykke and Egeberg, 1993; Kameda et al., 2012) at higher temperatures it is replaced by quartz, a conversion whose rate has been studied by several investigators (Ernst and Calvert, 1969; Stein and Kirkpatrick, 1976; Mizutani, 1977; Williams et al., 1985; Williams and Crerar, 1985). It has been suggested that formation of quartz from opal-CT involves dissolution/reprecipitation. If, however, the crystal form in our experiments does imply that the precipitate was originally opal-CT, it appears that it converted first to quartz. At sufficiently long times this could be followed by dissolution/reprecipitation reducing the large surface area of the platy precipitate.

In summary, then, the experiments described here have shown that, even for a relatively simple, nearly monomineralic, static system, the multiscale evolution of the pore structure

during burial diagenesis can be quite complex. Pore structures in sandstones are composed of several pore-size distributions, changes in each of which can affect others, possibly leading to feedback mechanisms transferring entropy between scales. In addition, it is clear that both absolute and relative pore filling rates have to be considered. The effects of additional factors such as fluid composition and flow, heterogeneous precipitation stress/strain etc. remain to be addressed, but will surely further complicate this picture.

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7.0 Figure Captions

Figure 1: SEM/BSE images of selected samples of sample 04Wi17b run for a) 0 days, b) 3 days, c) 8 weeks and d) 7.5 months at 100°C. Arrows show several areas of precipitate. Individual image width = 3.175 mm. Width of insert images in (c) and (d) = 0.793 mm.

Figure 2: SEM/BSE images of selected samples of sample 04Wi17b run for a) 0 days, b) 3 days, c) 6 weeks, 2 days and d) 6.5 months at 200°C. Arrows show several areas of precipitate. Image width = 3.175 mm.

Figure 3: SEM/BSE images of selected samples of sample 05Wi30 run for a) 0 days, b) 3 days, c) 8 weeks and d) 7.5 months at 100°C. Arrows show several areas of precipitate. Image width = 3.175 mm.

Figure 4: SEM/BSE images of selected samples of sample 05Wi30 run for a) 0 days, b) 3 days, c) 6 weeks, 2 days and d) 6.5 months at 200°C. Arrows show several areas of precipitate. Image width = 3.175 mm.

Figure 5: Secondary electron images of overgrown quartz grains in the starting 04Wi17b material showing well-formed crystal faces. Note the apparent porosity differences between the overgrowths and the core detrital quartz grains at this scale.

Figure 6: Cathodoluminescent (CL) image of sample 04Wi17b. There are clearly multiple layers of overgrowths present, some of which appear to be fibrous, whereas others do not. Image obtained on a Hitachi S-3400 scanning electron microscope at 20 kV and an air pressure of 50 Pa equipped with a Gatan PanaCL system with a parabolic mirror. The image is approximately 1.27 mm across, and pixel size is 0.496 microns.

Figure 7: TEM images and TEM/EDA X-ray maps of the precipitate in sample 04Wi17B run at 100°C for 7.5 months. A) image of initial FIB sample take across one of the partially filled

large pores. B, C) TEM images of SiO_2 plates deposited in the pore, D) Si map, E), O map, F) Na map, G) electron diffraction image of silica plates showing indexing as alpha quartz, H) opal sphere, I) electron diffraction image of opal sphere shown in (H).

Figure 8: TEM images and TEM/EDS X-ray maps of the precipitate in sample 04Wi17B run at 200°C for 6.5 months. A, B) Images showing the presence of a second (brighter, rice-shaped) material. C, D, E, F) Si, O, Na, Fe maps showing that this second phase appears to be a sodium iron silicate.

Figure 9: Silica composition of the fluid (post quench) in each experiment as a function of time. As samples of 04Wi17b and 05Wi30 were run together in each reaction vessel to assure that each saw the same fluid composition, temperature, and time, there are only two sets of analyses, one for each temperature. Solid circles (100°C), open circles (200°C), solid lines equilibrium solubility of amorphous SiO_2 at the experimental pH, dashed lines, equilibrium solubility of quartz at the experimental pH.

Figure 10: Selected, Porod-transformed, background-subtracted scattering data (including the results from the image processing at larger scales) for selected times for each experimental condition and material. Data are offset for clarity. Note the changes in step size and position and the slope of the background curve. A) 04Wi17b, 100°C , solid squares (starting material), open squares (3 day), solid circles (8 weeks), open circles (7.5 months); B) 04Wi17b, 200°C , solid squares (starting material), open squares (3 day), solid circles (6 weeks, 2 days), open circles (6.5 months); C) 05Wi30, 100°C , solid squares (starting material), open squares (3 day), solid circles (8 weeks), open circles (6.5 months); D) 05Wi30, 200°C , solid squares (starting material), open squares (3 day), solid circles (6 weeks, 2 days), open circles (6.5 months);.

Figure 11: Changes in porosity at the (U)SANS scale (triangles), image-scale (open circles), and total porosity (squares) as a function of time. The (U)SANS porosity is calculated from the invariant of the scattering data without addition of data points from the imaging calculations. The image-scale data is obtained from the binary transformation of the image used to define the pore structure. A) 04Wi17b, 100°C, B) 04Wi17b, 200°C, C) 05Wi30, 100°C, D) 05Wi30, 200°C. As zero time cannot be represented on a log time scale the starting values are shown as grey symbols at 1 day.

Figure 12: Pore volume distributions for samples of 04Wi17b run at 100°C. A) starting material, B) 3 days, C) 8 weeks, D) 7.5 months. The solid line is the total fit, the dashed lines show the individual fitted distributions. The asymmetrical dashed lines are the fractal distributions, the symmetrical dashed lines are the log-normal distributions.

Figure 13: Pore volume distributions for samples of 04Wi17b run at 200°C. A) starting material, B) 3 days, C) 6 weeks, 2 days, D) 6.5 months. The solid line is the total fit, the dashed lines show the individual fitted distributions. The asymmetrical dashed lines are the fractal distributions, the symmetrical dashed lines are the log-normal distributions.

Figure 14: Pore volume distributions for samples of 05Wi30 run at 100°C. A) starting material, B) 3 days, C) 7 weeks, D) 7.5 months. (note that because the 8 week sample was small the data were more scattered and were not fitted). The solid line is the total fit, the dashed lines show the individual fitted distributions. The asymmetrical dashed lines are the fractal distributions, the symmetrical dashed lines are the log-normal distributions.

Figure 15: Pore volume distributions for samples of 05Wi30 run at 200°C. A) starting material, B) 3 days, C) 6 weeks, 2 days D) 6.5 months. The solid line is the total fit, the dashed lines

show the individual fitted distributions. The asymmetrical dashed lines are the fractal distributions, the symmetrical dashed lines are the log-normal distributions.

Figure 16: Volumes of each of the fitted pore volume distributions as a function of time. A) 04Wi17b, 100°C, B) 04Wi17b, 200°C, C) 05Wi30, 100°C, D) 05Wi30, 200°C. Solid squares (largest fractal distribution), open circles, (large log-normal distribution), open squares (mesoscale fractal distribution), solid circles (nanoscale fractal distribution). As zero time cannot be represented on a log time scale the starting values are shown as grey symbols at 1 day.

Figure 17: Multifractal and lacunarity results for samples from the four experimental conditions. A) 04Wi17b, 100°C, B) 04Wi17b, 200°C, C) 05Wi30, 100°C, D) 05Wi30, 200°C. Solid squares ($D(0)$), open circles, ($D(2)$), open squares (lacunarity), solid circles ($D(0) - D(2)$). As zero time cannot be represented on a log time scale the starting values are shown as grey symbols at 1 day.

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Table 1: Experimental Conditions and Pore Volumes

Sample	T (°C)	Time (days)	sample wt (gms)	fluid wt (gms) *	Image Magnif	Image pore fraction	Invariant Volume Total	Invariant Volume (U)SANS	% Change total	% Change (U)SANS	% Change image
04Wi17b	0	0			10	0.0500	0.0551	0.0149	-70.25	-56.06	-71.66
04Wi17b	100	3	0.578	1.266	10	0.1764	0.1854	0.0352	0.00	0.00	0.00
04Wi17b	100	3			20	0.1652					-6.37
04Wi17b	100	7	1.015	1.892	10	0.1643	0.1667	0.0266	-10.06	-42.23	-6.88
04Wi17b	100	7			20	0.1571					-10.97
04Wi17b	100	14	0.724	1.875	10	0.1544	0.1561	0.0233	-15.78	-41.49	-12.45
04Wi17b	100	14			20	0.1550					-12.13
04Wi17b	100	21	0.929	1.726	10	0.1286	0.1383	0.0261	-25.41	-46.80	-27.07
04Wi17b	100	21			20	0.1385					-21.49
04Wi17b	100	28	0.961	1.884	10	0.1366	0.1383	0.0244	-25.42	-45.82	-22.57
04Wi17b	100	28			20	0.1333					-24.46
04Wi17b	100	35	1.130	1.845	10	0.1362	0.1425	0.0262	-23.12	-34.88	-22.78
04Wi17b	100	35			20	0.1349					-23.54
04Wi17b	100	42	1.050	2.012	10	0.1238	0.1276	0.0214	-31.15	-55.42	-29.81
04Wi17b	100	42			20	0.1264					-28.34
04Wi17b	100	42			40	0.1352					-23.37
04Wi17b	100	49	1.030	1.782	10	0.1360	0.1424	0.0266	-23.18	-29.44	-22.89
04Wi17b	100	56	1.000	1.418	10	0.1340	0.1573	0.0260	-15.13	-35.71	-24.06
04Wi17b	100	56			20	0.1297					-26.49
04Wi17b	100	228	0.940	1.654	10	0.0633	0.0738	0.0238	-60.20	-33.56	-64.10
04Wi17b	100	228			20	0.0537					
04Wi17b	0	0			10	0.0500	0.0551	0.0149	-63.37	-57.47	-63.73
04Wi17b	200	3	1.092	6.409	10	0.1378	0.1340	0.0268	-10.98	-32.14	0.00
04Wi17b	200	3			20	0.1330					-3.53
04Wi17b	200	7	0.898	4.388	10	0.1295	0.1506	0.0311	0.00	-13.78	-6.07
04Wi17b	200	7			20	0.1238					-10.20
04Wi17b	200	15	1.135	3.845	10	0.1217	0.1334	0.0256	-11.42	-32.20	-11.69
04Wi17b	200	15			20	0.1177					-14.63
04Wi17b	200	21	0.905	5.024	10	0.1134	0.1322	0.0359	-12.17	0.00	-17.77
04Wi17b	200	21			20	0.1103					-19.97
04Wi17b	200	29	1.879	5.406	10	0.1171	0.1317	0.0272	-12.55	-21.62	-15.02
04Wi17b	200	29			20	0.1080					-21.66
04Wi17b	200	35	1.995	5.301	10	0.1120	0.1268	0.0284	-15.80	-35.89	-18.74
04Wi17b	200	35			20	0.1202					-12.79
04Wi17b	200	44	1.543	4.938	10	0.1112	0.1280	0.0309	-15.00	-24.45	-19.33
04Wi17b	200	44			20	0.1095					-20.56
04Wi17b	200	198	1.578	4.545	10	0.1154	0.1246	0.0252	-17.25	-44.20	-16.28
04Wi17b	200	198			20	0.1127					-18.21
05Wi30	0	0			10	0.1600	0.1467	0.0310	-5.97	-11.62	0.00
05Wi30	100	3	0.565	1.266	10	0.1469	0.1561	0.0267	0.00	-23.08	-8.19
05Wi30	100	3			20	0.1482					-7.39
05Wi30	100	7	0.738	1.892	10	0.1495					-6.58
05Wi30	100	7			20	0.1372					-14.24
05Wi30	100	14	1.043	1.875	10	0.1406	0.1444	0.0228	-7.46	-30.65	-12.13

05Wi30	100	21	0.692	1.726	10	0.1409						-11.93
05Wi30	100	28	0.804	1.884	10	0.1288	0.1307	0.0238	-16.25	-31.60		-19.52
05Wi30	100	35	0.562	1.845	10	0.1190	0.1259	0.0242	-19.31	-29.84		-25.63
05Wi30	100	35			20	0.1141						-28.69
05Wi30	100	42	0.831	2.012	10	0.1254	0.1434	0.0361	-8.15	0.00		-21.61
05Wi30	100	42			20	0.1318						-17.61
05Wi30	100	49	0.608	1.782	10	0.1267	0.1353	0.0261	-13.29	-30.21		-20.84
05Wi30	100	49			20	0.1186						-25.89
05Wi30	100	56	0.279	1.418	10	0.0833	0.0987	0.0248	-36.74	-97.55		-47.94
05Wi30	100	56			20	0.1033						-35.42
05Wi30	100	228	0.569	1.654	10	0.1154	0.1310	0.0393	-16.09	-61.64		-27.86
05Wi30	100	228			20	0.1288						-19.48
05Wi30	0	0			10	0.1600	0.1467	0.0310	-11.62	-41.61		0.00
05Wi30	200	3	1.098	6.409	10	0.1418	0.1522	0.0319	-8.31	-28.16		-11.36
05Wi30	200	7	0.349	4.388	10	0.1389	0.1660	0.0465	0.00	0.00		-13.16
05Wi30	200	7			20	0.1314						-17.90
05Wi30	200	15	1.057	3.845	10	0.1346	0.1494	0.0341	-10.04	-27.47		-15.90
05Wi30	200	15			20	0.1328						-17.02
05Wi30	200	21	1.505	5.024	10	0.1317	0.1577	0.0452	-5.00	-21.78		-17.71
05Wi30	200	21			20	0.1344						-15.98
05Wi30	200	29	1.767	5.406	10	0.1378	0.1514	0.0343	-8.82	-41.22		-13.86
05Wi30	200	29			20	0.1251						-21.83
05Wi30	200	35	0.717	5.301	10	0.1336	0.1364	0.0271	-17.83	-98.54		-16.48
05Wi30	200	35			20	0.1318						-17.61
05Wi30	200	44	0.789	4.938	10	0.1357	0.1505	0.0345	-9.33	-27.94		-15.21
05Wi30	200	44			20	0.1289						-19.44
05Wi30	200	198	0.776	4.545	10	0.1222	0.1300	0.0250	-21.68	-59.27		-23.60
05Wi30	200	198			20	0.1207						-24.58

* one reaction vessel contained both the 04Wi17b and 05Wi30 samples for each temperature and time

Table 2: Post experiment fluid chemistry

Sample	molality SiO ₂	molality Fe
tube 1 - 100°C	1.731E-01	
tube 2 - 100°C	1.259E-01	3.957E-04
tube 3 - 100°C	2.463E-01	7.764E-04
tube 4 - 100°C	1.521E-01	1.183E-03
tube 6 - 100°C	1.409E-01	4.632E-04
tube 7 - 100°C	1.522E-01	4.628E-04
tube 8 - 100°C	6.552E-01	3.013E-03
tube 9 - 100°C	2.864E-01	7.071E-04
tube 10 - 100°C	1.500E-01	5.026E-04
vessel 1 - 200°C	3.585E-01	1.774E-03
vessel 2 - 200°C	3.911E-01	8.368E-04
vessel 3 - 200°C	3.278E-01	0.000E+00
vessel 4 - 200°C	3.558E-01	6.387E-04
vessel 5 - 200°C	3.510E-01	8.115E-04
vessel 6 - 200°C	3.184E-01	
vessel 7 - 200°C	3.003E-01	9.313E-04
vessel 8 - 200°C	3.124E-01	1.723E-03

Table 3: Fitting Coefficients for individual pore distributions

Sample	T (°C)	Time (days)	log normal Intensity 1	sigma	R(med)	log normal Intensity 2	sigma	R(med)	Fractal 1 Intensity	r	Ds	volume	Fractal 2 Intensity	r	Ds	volume	Fractal 3 Intensity	r	Ds	volume	R ²
04Wi17b	0	0				1.85E-02	8.47E-01	1.24E+07	1.70E-01	1.00E+03	2.10	1.20E-06	1.70E+02	7.00E+03	2.00	2.31E-05	3.50E+09	9.00E+05	2.43	3.66E-02	1.76E-02
04Wi17b	100	3	2.00E-08	1.00E+00	2.00E+02	2.69E-02	5.53E-01	1.81E+06	1.10E+00	1.10E+03	2.10	6.27E-06	1.70E+02	7.00E+03	2.00	2.32E-05	2.26E+10	1.01E+06	2.23	1.66E-01	3.90E-02
04Wi17b	100	7	1.50E-08	1.00E+00	2.00E+02	5.00E-02	5.53E-01	2.50E+06	7.00E-04	2.50E+02	2.00	7.47E-08	1.00E+02	7.00E+03	2.30	1.60E-05	1.21E+10	8.96E+05	2.32	1.19E-01	8.94E-03
04Wi17b	100	14	1.00E-09	1.00E+00	2.00E+02	3.93E-02	4.51E-01	2.09E+06	4.00E-05	1.00E+02	2.00	2.85E-08	8.50E+01	5.00E+03	2.00	2.25E-05	1.00E+10	8.00E+05	2.20	1.15E-01	1.17E-02
04Wi17b	100	21	3.00E-08	1.00E+00	2.00E+02	4.45E-02	4.48E-01	2.80E+06	1.00E-03	2.50E+02	2.00	1.07E-07	2.75E+02	7.00E+03	2.10	3.94E-05	6.00E+09	7.00E+05	2.25	9.31E-02	1.26E-02
04Wi17b	100	28	5.00E-08	1.00E+00	2.00E+02	3.50E-02	4.38E-01	2.65E+06	1.00E-03	2.50E+02	2.00	1.07E-07	3.50E+02	7.00E+03	2.10	5.02E-05	7.70E+09	7.50E+05	2.22	1.02E-01	1.62E-02
04Wi17b	100	35	2.00E-08	1.00E+00	2.00E+02	1.50E-02	5.44E-01	2.42E+06	1.00E-03	2.00E+02	2.00	1.68E-07	3.00E+01	3.00E+03	2.00	2.23E-05	1.20E+10	8.50E+05	2.20	1.23E-01	4.48E-03
04Wi17b	100	42				2.64E-02	4.64E-01	2.10E+06	1.70E-03	2.50E+02	2.00	1.81E-07	1.50E+01	3.00E+03	2.00	1.11E-05	6.89E+09	6.92E+05	2.20	1.06E-01	2.24E-02
04Wi17b	100	49	9.00E-09	7.27E-01	2.05E+02	1.45E-02	3.38E-01	2.65E+06	2.00E-03	2.50E+02	2.10	2.24E-07	4.00E+02	9.00E+03	2.20	3.66E-05	1.30E+10	9.30E+05	2.30	1.17E-01	9.11E-02
04Wi17b	100	56	2.00E-08	1.00E+00	1.00E+02	1.10E-02	6.00E-01	1.50E+06	1.80E-03	2.50E+02	2.10	2.02E-07	5.00E+01	4.00E+03	2.20	2.32E-05	1.40E+10	9.00E+05	2.20	1.28E-01	3.55E-02
04Wi17b	100	228							8.00E-02	5.00E+02	2.40	2.67E-06	2.50E+03	1.50E+04	2.50	9.89E-05	6.50E+09	8.25E+05	2.20	7.07E-02	9.49E-03
04Wi17b	0	0				1.85E-02	8.47E-01	1.24E+07	1.70E-01	1.00E+03	2.10	1.20E-06	1.70E+02	7.00E+03	2.00	2.31E-05	3.50E+09	9.00E+05	2.43	3.66E-02	1.76E-02
04Wi17b	200	3				3.00E-02	5.50E-01	2.70E+06	2.80E-01	7.00E+02	2.35	4.64E-06	1.00E+04	2.00E+04	2.00	1.67E-04	7.50E+09	7.50E+05	2.23	9.99E-02	1.97E-02
04Wi17b	200	7	7.80E-08	1.20E+00	2.00E+02	2.00E-02	5.53E-01	2.50E+06	8.50E-01	9.00E+02	2.05	7.20E-06	2.20E+03	1.10E+04	2.00	1.21E-04	9.50E+09	7.50E+05	2.23	1.27E-01	2.84E-02
04Wi17b	200	15	7.00E-08	1.20E+00	2.00E+02	3.00E-02	5.53E-01	2.00E+06	3.00E+00	1.40E+03	2.10	1.07E-05	8.00E+02	9.00E+03	2.00	6.59E-05	1.00E+10	8.50E+05	2.23	1.04E-01	3.17E-02
04Wi17b	200	21	5.00E-08	1.20E+00	3.20E+02	1.50E-02	5.53E-01	2.50E+06	4.00E+00	1.20E+03	2.00	1.85E-05	5.50E+03	1.50E+04	2.00	1.63E-04	7.50E+09	7.00E+05	2.23	1.15E-01	5.01E-03
04Wi17b	200	29	6.00E-08	1.05E+00	3.16E+02	1.00E-02	5.53E-01	3.00E+06	3.81E+00	1.49E+03	2.12	1.22E-05	1.50E+03	1.02E+04	2.00	9.66E-05	9.50E+09	7.50E+05	2.13	1.20E-01	7.61E-03
04Wi17b	200	35	4.50E-08	1.05E+00	3.16E+02	1.50E-02	5.53E-01	3.00E+06	2.50E-01	1.00E+03	2.35	2.02E-06	2.75E+02	6.00E+03	2.00	5.10E-05	7.50E+09	7.00E+05	2.24	1.16E-01	1.32E-02
04Wi17b	200	44	5.50E-08	1.05E+00	3.16E+02	1.00E-02	4.64E-01	2.50E+06	4.50E+00	1.50E+03	2.10	1.40E-05	5.00E+02	9.00E+03	2.00	4.12E-05	9.50E+09	7.70E+05	2.23	1.20E-01	3.31E-02
04Wi17b	200	198	1.00E-08	1.00E+00	1.00E+02	2.00E-02	5.53E-01	2.50E+06	2.30E-03	2.50E+02	2.30	2.87E-07	1.15E+02	4.50E+03	2.10	3.99E-05	7.70E+09	7.50E+05	2.23	1.03E-01	6.91E-03
05Wi30	0	0				4.29E-02	9.36E-01	1.05E+07	7.00E-03	3.50E+02	2.10	4.03E-07	4.00E+01	4.00E+03	2.00	1.67E-05	8.00E+09	7.50E+05	2.17	1.03E-01	1.78E-01
05Wi30	100	3	3.00E-08	1.20E+00	1.88E+02				3.20E-03	3.00E+02	2.10	2.49E-07	5.90E+01	4.00E+03	2.00	2.46E-05	1.50E+10	8.50E+05	2.20	1.53E-01	2.24E-02
05Wi30	100	7*																			
05Wi30	100	14	2.50E-08	1.20E+00	1.88E+02	2.00E-02	4.64E-01	2.10E+06	6.00E-03	4.00E+02	2.10	2.63E-07	7.00E+02	9.00E+03	2.10	6.07E-05	1.35E+10	8.90E+05	2.20	1.26E-01	1.95E-02
05Wi30	100	28	3.50E-08	1.20E+00	1.88E+02	2.30E-02	4.77E-01	1.82E+06	3.00E-03	4.00E+02	2.10	1.32E-07	6.25E+02	8.00E+03	2.10	6.86E-05	7.50E+09	7.20E+05	2.20	1.07E-01	1.20E-02
05Wi30	100	35	3.00E-08	1.20E+00	1.88E+02	2.00E-02	4.64E-01	2.50E+06	2.00E-04	1.50E+02	2.10	6.82E-08	8.00E+01	5.00E+03	2.40	2.66E-05	7.50E+09	7.20E+05	2.20	1.07E-01	1.71E-02
05Wi30	100	42	6.00E-08	1.20E+00	1.88E+02	1.07E-02	2.99E-01	2.82E+06	1.20E-03	2.00E+02	2.10	2.10E-07	1.20E+03	1.00E+04	2.20	8.90E-05	1.20E+10	8.70E+05	2.35	1.28E-01	9.69E-03
05Wi30	100	49	9.00E-09	7.27E-01	2.05E+02	1.45E-02	3.38E-01	2.65E+06	2.00E-03	2.50E+02	2.10	2.24E-07	4.00E+02	9.00E+03	2.20	3.66E-05	1.30E+10	9.30E+05	2.30	1.17E-01	3.43E-03
05Wi30	100	56*																			
05Wi30	100	228							6.97E-03	2.58E+02	2.35	8.38E-07	1.05E+02	5.00E+03	2.40	3.50E-05	1.35E+10	9.00E+05	2.30	1.31E-01	3.16E-01
05Wi30	0	0				4.29E-02	9.36E-01	1.05E+07	7.00E-03	3.50E+02	2.10	4.03E-07	4.00E+01	4.00E+03	2.00	1.67E-05	8.00E+09	7.50E+05	2.17	1.03E-01	1.78E-01
05Wi30	200	3				2.67E-02	3.75E-01	2.08E+06	2.52E-01	7.84E+02	2.41	3.44E-06	1.14E+04	2.06E+04	2.38	2.21E-04	1.52E+10	9.39E+05	2.23	1.29E-01	1.28E-02
05Wi30	200	7	8.00E-08	7.48E-01	1.57E+02	1.50E-02	3.75E-01	3.00E+06	7.00E-01	8.00E+02	2.06	7.53E-06	1.30E+03	8.00E+03	2.06	1.40E-04	7.40E+09	6.00E+05	2.23	1.55E-01	1.96E-02
05Wi30	200	15	3.50E-08	9.36E-01	1.14E+02	3.20E-02	3.95E-01	2.58E+06	6.50E-01	9.50E+02	2.00	4.84E-06	5.00E+02	8.00E+03	2.00	5.21E-05	1.03E+10	8.40E+05	2.35	1.18E-01	2.53E-02
05Wi30	200	21	5.00E-08	8.15E-01	1.58E+02	1.56E-02	3.65E-01	2.78E+06	3.20E+00	1.20E+03	2.05	1.52E-05	5.00E+02	8.00E+03	2.00	5.22E-05	1.10E+10	8.00E+05	2.35	1.39E-01	9.10E-03
05Wi30	200	29	4.00E-08	9.07E-01	2.05E+02	2.00E-02	4.64E-01	2.50E+06	5.99E-01	1.06E+03	2.19	3.91E-06	7.00E+02	8.50E+03	2.18	7.10E-05	1.30E+10	8.50E+05	2.20	1.33E-01	5.54E-02
05Wi30	200	35	4.00E-08	9.07E-01	2.05E+02	9.43E-03	5.94E-01	1.37E+06	5.00E-01	1.06E+03	2.19	3.28E-06	7.00E+02	8.50E+03	2.18	7.10E-05	1.30E+10	8.50E+05	2.20	1.25E-01	5.72E-02
05Wi30	200	44				1.00E-02	4.64E-01	2.50E+06	5.00E-03	3.00E+02	2.25	1.18E-07	2.00E+02	6.00E+03	2.25	4.19E-05	1.30E+10	8.50E+05	2.30	1.41E-01	2.82E-02
05Wi30	200	198				6.66E-03	5.23E-01	1.57E+06	3.00E-03	2.70E+02	2.25	1.01E-07	1.50E+02	6.00E+03	2.25	3.16E-05	2.00E+10	1.10E+06	2.30	1.29E-01	3.21E-02

* not fitted because data too scattered

Table 4: Lacunarity and Multifractal Dimensions for the images

Sample	T (°C)	Time days	Lacunarity	D(0)	D(1)	D(2)
04Wi17b	0	0	0.6615	1.5911	1.4657	1.4266
04Wi17b	100	3	0.3605	1.7719	1.7124	1.6839
04Wi17b	100	7	0.3178	1.7713	1.741	1.7144
04Wi17b	100	14	0.3248	1.7341	1.7266	1.7185
04Wi17b	100	21	0.2716	1.7972	1.7735	1.7502
04Wi17b	100	28	0.3226	1.8172	1.7832	1.757
04Wi17b	100	35	0.3817	1.7661	1.7406	1.7209
04Wi17b	100	42	0.3714	1.815	1.8032	1.7864
04Wi17b	100	49	0.2852	1.8164	1.7926	1.7764
04Wi17b	100	56	0.3462	1.7999	1.7875	1.775
04Wi17b	100	228	0.6801	1.7298	1.6329	1.5719
04Wi17b	0	0	0.6615	1.5911	1.4657	1.4266
04Wi17b	200	3	0.4797	1.7413	1.6861	1.6575
04Wi17b	200	7	0.392	1.7263	1.723	1.711
04Wi17b	200	15	0.3992	1.7462	1.708	1.6736
04Wi17b	200	21	0.3257	1.7834	1.7592	1.7431
04Wi17b	200	29	0.4052	1.7512	1.7261	1.7064
04Wi17b	200	35	0.3783	1.7345	1.6941	1.6638
04Wi17b	200	44	0.5107	1.7732	1.7477	1.7179
04Wi17b	200	198	0.3367	1.7328	1.6892	1.6628
05Wi30	0	0	0.2773	1.7331	1.6785	1.6609
05Wi30	100	3	0.3181	1.7972	1.7589	1.7291
05Wi30	100	7	0.3639	1.7349	1.7159	1.7019
05Wi30	100	14	0.3448	1.6822	1.6119	1.5914
05Wi30	100	21	0.4044	1.7234	1.6757	1.638
05Wi30	100	28	0.4615	1.7291	1.68	1.6529
05Wi30	100	35	0.3827	1.7654	1.7103	1.6692
05Wi30	100	42	0.3661	1.7835	1.7393	1.7028
05Wi30	100	49	0.387	1.7476	1.6876	1.6524
05Wi30	100	56	0.7741	1.625	1.4779	1.4065
05Wi30	100	228	0.6614	1.7335	1.623	1.5555
05Wi30	0	0	0.2773	1.7331	1.6785	1.6609
05Wi30	200	3	0.3628	1.7709	1.705	1.6688
05Wi30	200	7	0.3885	1.7237	1.7333	1.7237
05Wi30	200	15	0.4631	1.7642	1.7328	1.7051
05Wi30	200	21	0.373	1.7546	1.7116	1.6766
05Wi30	200	29	0.3589	1.752	1.7083	1.6784
05Wi30	200	35	0.4744	1.7217	1.6215	1.5713
05Wi30	200	44	0.4654	1.7474	1.6785	1.6479
05Wi30	200	198	0.5366	1.6806	1.6802	1.6538

Figure

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 11

Figure 9

Figure 10

Pore Fraction (Image and Total)

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

Figure 17