A COMBINED EXPERIMENTAL AND NUMERICAL APPROACH TO UNDERSTANDING QUARTZ CEMENTATION IN SANDSTONES

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ABSTRACT

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Quartz cement formed during diagenesis is the principle cause of porosity and permeability reduction in sandstones and therefore greatly affects reservoir quality. Predictive quartz cement models have provided a basic ability to estimate reservoir quality for quartz-rich rocks under ideal diagenetic conditions. However, examination of more complex, specific diagenetic environments is required to improve the accuracy of predictive models applied to unconventional hydrocarbon reservoirs. Our experimental and numerical approach to this problem has examined quartz cementation processes by: 1) assessing the feasibility of relatively low temperature hydrothermal flow-through experiments for investigating silica dissolution, transport, and precipitation processes during diagenesis in active fluid flow environments, and 2) to assessing the effect of grain size and sorting on the rate of quartz cementation and corresponding pore space evolution in sandstones under static hydrothermal conditions. Hydrothermal flow-through results indicate that small amounts of new quartz cement can be generated in less than 10 days at relatively low temperatures when compared to previous experimental work. Results obtained from static hydrothermal experiments indicate that grain size and sorting effect both the rate of quartz cementation in our experiments and corresponding pore space evolution. The surface area normalized rate is observed to decrease more rapidly in fine grain size experiments when compared to coarse grain size experiments. Additionally, pore space analysis of both experimental and modeled results indicates that while all grain size fractions rapidly converge on similar total porosity values the 2D connectivity of porosity varies markedly as a function of grain size and sorting.
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INTRODUCTION

The relative importance of silica dissolution, transport, and precipitation (DTP) processes in sandstones changes dramatically as a result of differences in temperature, pressure, and fluid chemistry and understanding these effects is of fundamental importance to a wide range of geologic processes ranging from deformation (Cook et al., 2006; O’Kane et al., 2007) to geological CO₂ sequestration (Kaszuba et al., 2003; Xu et al., 2005; Xu et al., 2007) and issues of hydrocarbon migration and reservoir quality (Worden and Morad, 2000; McCullagh and Hart, 2010).

When working with quartz-rich reservoir rocks, reservoir quality is determined principally by porosity and permeability. In these rock units, porosity and permeability are a function of depositional factors such as grain size and sorting, mechanical and chemical compaction processes, and the formation of quartz cement (Worden and Morad, 2000). Quartz cement formed during diagenesis results from the precipitation of syntaxial overgrowths on detrital quartz grains, which provide a surface for nucleation (Worden and Morad, 2000). In lithologies where quartz cementation has reduced porosity and permeability to the point of having little to no connected pore networks, fluid flow is accomplished predominately through fractures and micro-cracks that are unstable and will rapidly seal or heal (Brantley et al., 1990; Worden and Morad, 2000).

Many previous researchers have sought to understand DTP processes through experiments where temperature, pressure, and fluid compositions were held constant (e.g., Lamb, 1996; Teinturier and Pironon, 2004; Pepple, 2007; Winslow, 2012). These studies have provided a basic understanding of how DTP mechanisms proceed in static conditions. However, there is a
clear need for a more detailed understanding of how silica DTP processes evolve with progressive diagenesis.

Predictive models of sandstone diagenesis have been shown to provide accurate estimations of reservoir quality (porosity and permeability) for simplified burial conditions (Walderhaug, 1994; Lander et al., 2008). However, the application of current predictive diagenesis models to sandstone reservoirs experiencing more complex burial conditions has resulted in only limited success (Taylor et al., 2010). Investigation of silica DTP processes under more specific hydrologic (active fluid flow) and sedimentary (differences in grain size and sorting) conditions is necessary to further improve predictive diagenesis models in sandstones.

The objectives of this research are: 1) to assess the feasibility of relatively low temperature hydrothermal flow-through experiments for investigating silica DTP processes during diagenesis in active fluid flow environments, and 2) to assess the effect of grain size and sorting on the rate of quartz cementation and corresponding pore space evolution in sandstones under static hydrothermal conditions.

**Dissolution, Transport, and Precipitation of SiO$_2$**

Many previous research efforts have focused on determining the specifics of mineral kinetics and phase equilibria in pure SiO$_2$-H$_2$O and brine systems (Rimstidt and Barnes, 1980; Watson and Wark, 1997; Farver and Yund, 2000) or SiO$_2$-H$_2$O systems with the addition of volatiles such as CH$_4$ or CO$_2$ (Watson and Brenan, 1987; Frantz et al., 1989; Lamb et al., 1996; Chiquet et al., 2007). In addition, researchers have examined the effects of more complex natural analogues with the addition of phyllosilicates (Anjos, 2003; Worden and Morad, 2003), oxides (Pepple 2007; Winslow 2012), and hydrocarbons (Teinturier and Pironon, 2004). These
previous research efforts have provided basic information concerning the effects temperature, pressure, and fluid chemistry on the rate of silica DTP processes as summarized below.

**Temperature and Pressure**

The solubility of silica in aqueous fluids is greatly enhanced by increasing temperature and pressure (Rimstidt and Barnes, 1980; Dove and Rimstidt, 1994) up to a maximum solubility that occurs near the H₂O critical point (Fornier and Potter, 1982; Okamoto *et al.*, 2010). Increased solubility due to increases in fluid temperature and pressure will result in undersaturation of the fluid with respect to silica leading to dissolution (Dove and Rimstidt, 1994). Conversely, fluids which have become saturated with respect to silica will begin to precipitate when encountering a significant drop in either temperature or pressure due to a decrease in solubility, and hence, saturation of fluid with respect to quartz (Rimstidt and Barnes, 1980; Dove and Rimstidt, 1994).

The transport of silica in solution is also strongly dependent on temperature conditions because the rate of diffusion (the dominate transport mode in the absence of a pressure gradient) increases exponentially with temperature (Rimstidt and Barnes, 1980; Wark and Watson, 1997; Farver and Yund, 2000). This temperature dependency is of particular importance in SiO₂-H₂O systems at temperatures below 300° C. Systems in the 0 to 300° C temperature range experience a maximum precipitation rate at approximately 25 to 50° C below equilibrium temperatures (Rimstidt and Barnes, 1980). Any additional under-cooling of systems in this range will reduce diffusion rates, overriding the effect of increased silica supersaturation and preventing any additional increase in precipitation rate (Rimstidt and Barnes, 1980).
Fluid Chemistry

Aspects of fluid chemistry in hydrothermal systems such as pH, ionic strength, and the presence of dissolved ions are also important to silica DTP processes (Dove and Rimstidt, 1994). The rate of silica dissolution is at a minimum at approximately pH 2 for both low temperature (less than 75° C) systems and those more representative of hydrothermal environments (Dove and Rimstidt, 1994). More basic solutions will result in an increase in silica solubility and therefore an increased rate of dissolution (Rimstidt and Barnes, 1980; Dove and Rimstidt, 1994). The rate of dissolution in these systems is also increased by increased ionic strength in brine solutions (Dove and Crerar, 1990; Dove and Rimstidt, 1994).

Dissolved non-silica constituents also affect dissolution and precipitation processes, as any reaction which forms a complex with the dissolved silica (H₄SiO₄) will drive dissolution of quartz in order to re-establish equilibrium conditions with the surrounding fluid (Dove and Rimstidt, 1994). For example, the presence of dissolved iron was proposed to have increased solubility of silica, driving dissolution of detrital quartz in the Tuscarora sandstone (Morris and Fletcher, 1987). Experimental work conducted by Pepple (2007) using synthetic quartz with and without the addition of iron oxides (goethite) revealed that the amount and rate of quartz cement formation are dependent not only on temperature but the presence of goethite as well. The addition of iron oxides in Pepple’s (2007) experiments was found to increase both the rate of initial grain dissolution and subsequent precipitation in the form of new quartz overgrowths, consistent with the observations of O’Kane et al. (2008) in natural samples. Similar experimental work by Winslow (2012) using natural quartz, however, was unable to confirm this effect.
Okamoto et al. (2010) concluded that the presence of various cation impurities control to some degree which silica polymorphs precipitate in hydrothermal settings. Their experiments were conducted using a hydrothermal flow-through cell and involved examining quartz vein formation on a granite substrate. The fluid input to their flow-through cell consisted either of pure silica solutions (quartz source) or mixed solutions with minor amounts of Al, Na, and K (granite source). In the single component silica experiments, heterogeneous precipitation of metastable silica polymorphs occurred in the reaction vessel whereas only quartz and minor amounts of chalcedony were observed in multi-component solution experiments. These results led Okamoto et al. (2010) to conclude that cation impurities are able to inhibit nucleation of metastable silica polymorphs.

OBJECTIVES

As described in the previous section, large data sets concerning quartz cementation processes in relatively simple scenarios have been generated by previous research efforts. If these data are to be applied to a wider variety of unconventional sandstone hydrocarbon reservoirs additional work is required to constrain how these processes work under variable fluid flow and sedimentary conditions. This research will attempt to provide additional data toward improving predictive diagenesis models in sandstones by examining quartz cementation processes in sandstones in an active fluid flow environment (Chapter One), and assessing the effect of grain size and sorting on the rate of quartz cementation and corresponding pore space evolution in sandstones under static hydrothermal conditions (Chapter Two).
CHAPTER ONE

1.1. INTRODUCTION

Previous research has sought to understand DTP processes under constant temperature, pressure, and fluid compositions (Rimstidt and Barnes, 1980; Frantz et al., 1989; Lamb, 1996; Pepple, 2007; Winslow, 2012). These studies have provided us with a basic understanding of how DTP mechanisms proceed in static hydrothermal experiments. However, these experiments do not provide a direct analog to progressive diagnosis during active fluid flow. Previous experimental work has examined quartz cementation in an active fluid flow apparatus (Okamoto et al., 2010); however, these experiments created a saturation gradient by exceeding the temperature solubility maximum (372 °C; Fornier and Potter, 1982) in downstream portions of the system. The experimental setup of Okamoto et al. (2010) thereby relied on an unrealistic hydrologic scenario where fluid flows from relatively cold to relatively warm regions, greatly decreasing solubility with respect to quartz (supersaturating the solution) while preserving the thermal energy required for nucleation (increased kinetics).

The objective of this research was to design, implement, and test a novel hydrothermal flow-through apparatus based on that described by Okamoto et al. (2010). This experimental apparatus is capable of further constraining factors affecting quartz cementation processes due to the ability to simulate fluid rock interactions in an active fluid flow environment under more geologically reasonable decreasing temperature gradients. The ability to measure and potentially change various experimental parameters such as temperature, pressure, fluid composition, and fluid flow rate during an experiment could allow much more detailed constraints to be placed on the conditions of quartz cementation during diagenesis.
1.2. METHODS

Experimental Design

The hydrothermal flow-through cell is configured as a dual chambered convection system (Fig. 1). Two 15 cm segments of 0.5” OD stainless steel tubing are connected via a tee junction and serve as saturation and precipitation reaction vessels respectively (hereafter referred to as “Rs” and “Rp”). Pressure and flow control are provided by a Jasco pu-2080 High Performance Liquid Chromatography (HPLC) pump connected to the Rs chamber via a check valve assembly to prevent back flow. This pump is designed to provide precise flow-rate control between 0.1 and 10 mL/min at a maximum pressure of 50 MPa and is fed via a 5 gallon reservoir of deionized water. Solution temperature is monitored at the exit of both the Rs and Rp chambers via custom-made K-type stainless steel thermocouples inserted directly into the fluid flow path. Pressure conditions for each experiment are set and maintained via a relief valve and coupled pressure gauge located at the distal end of the fluid flow path.

Heat is provided to the system during run time by two heating tapes (Omega STH101-120LSE) which are capable of a constant heat output of up to 760°C. These heating units were controlled via two temperature controllers (Omega 4001a) which monitored solution temperature using the aforementioned stainless steel thermocouples. Previous cold seal experiments conducted at BGSU have shown the reliability of temperature measurement using similar methods to be < ± 5°C (Pepple 2007; Winslow 2012). Higher temperatures in the Rs chamber than the Rp chamber provide a driving force for both convective fluid flow and solution transport (buoyancy driven convection) and SiO₂ precipitation due to the decrease in equilibrium SiO₂ concentration (hence supersaturation of fluid) upon entering the relatively colder Rp chamber.
In order to test the apparatus prior to conducting advective fluid flow (flow-through) experiments, a simplified convective fluid flow system was used in the experiments described below. Similar to the cold seal vessels (Pepple, 2007; Winslow, 2012) this experimental apparatus is effectively a closed system during experiment runtime; however, the relatively large volumes of convective fluid flow accomplished using this system allows for simulation of fluid flow scenarios encountered in the subsurface.

**Pre-Experiment Setup**

Stainless steel tubing was sized, cut, and deburred prior to assembly. Once attached to the fluid flow path, the assembly is brought to desired temperature and pressure conditions and allowed to equilibrate for a period of approximately 24 hours based on the results of experiment FT-1 (see results). This process results in the formation of a thin iron oxide layer on the inner surface of the stainless steel tubing, thereby reducing iron contamination of the solution during each experiment. Once the reaction vessel assembly was seasoned a pre-measured amount of amorphous SiO$_2$ was placed into the open end of a crimped Au tube and then inserted into the $R_s$ chamber, providing a highly soluble SiO$_2$ source for growth after convective transport of solution to the $R_p$ chamber. NaCl was also added to the $R_s$ chamber in amounts sufficient to create a NaCl brine of approximately 3 to 5 wt % once the system was flooded.

Cataclasite samples (Lower Silurian Tuscarora Sandstone near McCoy’s Ferry, Maryland) were prepared by cutting hand samples into blocks of approximately 2 x 0.5 x 0.5 cm. These blocks were polished to 1µm grit size on one side using silicon carbide sand papers to determine the effect of surface roughness on precipitation during each experiment. Once polished, samples were placed into a 60° C drying oven for 24 hours before weighing.
Approximately 8 to 10 cataclasite blocks were placed sequentially into the \( R_p \) chamber before attachment to the fluid flow path. The system was pressurized to approximately 20 MPa before heating element activation to prevent vaporization of the solution during heating, and continual pressure increases associated with thermal expansion of the solution were manually bled using a shut off valve located at the distal end of the apparatus. Experiments were considered to begin upon reaching a temperature and pressure within 5˚C and 5 MPa of desired conditions, respectively.

Following the completion of an experiment the heat source for the apparatus is disabled and the insulating blocks are removed allowing the system to rapidly cool to room temperature (< 1 h). Reactant remaining in the Au tube was collected from the \( R_s \) chamber and immediately placed into a 60˚C drying oven and allowed to dry for 24 hours before weighing to assess the amount of reactant transported during an experiment. Cataclasite samples were removed from the \( R_p \) chamber and individually rinsed with de-ionized water to remove any particulate matter. Following washing, cataclasite samples were placed into individually labeled weighing pans and allowed to dry for 24 hours at 60˚C before weighing.

Sample Analysis

The absolute amount of precipitation or dissolution was assessed by subtracting the starting weight from the final weight of each sample block. In order to assess the nature of precipitation a scanning electron microscope (SEM, Hitachi S2700, BGSU Biology Department) in secondary electron mode was used to differentiate SiO\(_2\) polymorphs based on observed precipitation textures (quartz versus opaline growth habits). Additionally, energy dispersive x-ray analysis (EDAX) was used to assess elemental composition of new growth observed during
traditional SEM microscopy. Data collected using EDAX were used in conjunction with textural
data collected from SEM to identify any potential iron-sodium silicates which may have
precipitated as a result of iron contamination from the stainless steel reaction chambers.

1.3. RESULTS

Starting conditions for flow-through experiments are summarized in Table 1. Following
testing of the apparatus, these experiments showed a systematic trend in the amount and nature
of new crystal growth as a function of both position in the $R_p$ chamber and surface roughness.
Each of the conducted experiments is addressed individually below.

$FT-1$

$FT-1$ served as a test of the hydrothermal convection cell described above and was
conducted with a $R_s - R_p$ temperature gradient of approximately 315°C to 205°C (230 ppm
equilibrium solubility decrease) at a confining pressure of approximately 40 MPa for a period of
344 hours. Visual inspection of the samples following the experiment revealed significant
amounts of green-black staining on the sample surface with the relative amount of staining
increasing with distance from the silica source.

A clear trend of dissolution of the cataclasite samples is visible as a function of distance
into the $R_p$ chamber with the most substantial dissolution occurring approximately 8 cm into the
$R_p$ chamber (Fig. 2). Beyond 8 cm, the relative amount of dissolution of each sample shows a
systematic decrease before modest weight gains are observed in samples 8 through 11. Samples
12 through 15 were observed to have the largest gains in weight following the experiment;
however these samples also showed the most extensive green-black staining on visual inspection.
Green-black staining of samples 12 through 15 was determined to be goethite based on textural and elemental analysis conducted using SEM and EDAX, respectively.

Analysis of both relative weight change and SEM imagery indicated two primary problems were experienced during the FT-1 experiment. Dissolution trends observed in the upstream portions of the Rp chamber suggested that convective flow was discontinuous between the Rs and Rp vessels. This hypothesized discontinuity in fluid flow would result in samples in the upstream portion of the Rp chamber effectively serving as reactant to the system rather than the amorphous silica in Rs, experiencing dissolution in a solution that was undersaturated with respect to SiO2. Closer inspection of the system following the experiment revealed that the stainless steel mesh separating the two reaction vessels had experienced substantial goethite growth during the experiment, greatly reducing its ability to allow free fluid flow between Rs and Rp. The presence of the iron oxide goethite in such large amounts on downstream samples suggested that corrosion of the stainless steel tubing and fittings contributed greater than anticipated amounts of iron to the solution during the experiment, resulting in the precipitation of goethite in lower temperature regions.

**FT-2**

Analysis of the FT-1 experiment resulted in two modifications to the experimental apparatus: 1) The stainless steel mesh used to confine the amorphous SiO2 to the saturation vessel was removed and amorphous SiO2 was instead placed into a 5 cm length of gold tubing crimped such that the open end was facing the upstream portion of the system, and 2) all stainless steel tubing and connections were first “seasoned” for a period of 24 hours as mentioned in the previous section.
During the startup phase of the FT-2 experiment the Rp chamber temperature rapidly exceeded the desired temperature conditions such that the heating element was disabled and remained so for the duration of the experiment. Temperature conditions in the Rp chamber remained constant at 25°C above the set point for the duration of the experiment despite the lack of a heating element, suggesting that convective flow was now active between Rs and Rp and confirming that it had been restricted in FT-1.

Following completion of the experiment, visual inspection of the cataclasite samples showed no apparent signs of the goethite precipitation observed in the FT-1 experiment, and samples were rinsed with deionized water to remove any particulate matter before insertion into a 60°C drying oven for 24 hours. All samples in the FT-2 experiment experienced at least some degree of new crystal growth (Fig. 3). The trend in weight gain as a function of distance from the silica source suggests that precipitation rates were at a maximum near the central portions of the Rp chamber consistent with that observed by Okamoto et al. (2010). SEM analysis of samples obtained from the FT-2 experiment also exhibit an apparent surface roughness control on the phase being nucleated where opaline textures were observed only on polished surfaces, while rough cut surfaces appear to have been overgrown only by quartz.

**FT-3**

The FT-3 experiment was designed to assess the effect of increased duration (120 h) on the previously describe setup. However, despite the lack of a heating element on the Rp chamber, a smaller thermal gradient of approximately 302°C to 245°C (112 ppm equilibrium solubility decrease) was established within hours of system start and persisted throughout the
duration of the experiment. The exact cause of this increased heat transfer efficiency within the system is unknown.

A trend of new crystal growth similar to that of the FT-2 experiment is apparent in terms of both spatial distribution of growth in the precipitation chamber and absolute growth amount in weight gained (Fig. 4). Again, visual inspection of samples post experiment did not indicate the presence of visible amounts of iron oxide precipitation, and SEM analysis of surface textures again suggests a strong surface roughness control on the SiO₂ nucleation phase. However, despite the increased time in the fluid flow path, the absolute weight gain experienced by the FT-3 samples is comparable to that of the FT-2 experiments (Fig. 4). As a result, it was hypothesized that the weight gains experienced in both the FT-2 and FT-3 experiments may have been largely attributable to a quench effect during the rapid cooling following each experiment.

**FT-4**

To assess the possible amount of new crystal growth attributable to the rapid system cooling, the conditions of the FT-3 experiment were replicated for a period of 4 hours to assure fluid equilibration before the system was quenched. This relatively short duration experiment precluded any significant accumulation of new crystal growth resulting only from the imposed thermal gradient, as such weight gains associated with this experiment would be attributable entirely to quench growth during system cooling. Alternatively, early weight gains may be the result of rapid initial growth and the establishment of slow-growing surfaces that retarded additional growth (Lander et al., 2010).

Samples from the FT-4 experiment gained a maximum of 0.5 mg (Fig. 5), suggesting that only a relatively small amount of the weight gain observed in the previous experiments can be
attributed to quench growth during system cooling. It is therefore concluded that the majority of weight gains experienced in experiments FT-2 and FT-3 are the result of new crystal growth driven by the imposed thermal (i.e., solubility) gradient in the system, and that the magnitude of quench effects in this system is less than 1 mg per sample.

1.4. DISCUSSION

Considerations of Reactant Equilibration

Previous experimental work conducted with a similar apparatus suggests that equilibrium between powdered quartz and water is achieved nearly instantaneously at temperatures above 350°C (Okamoto et al., 2010); however, dissolution experiments conducted using our apparatus failed to reproduce this result. Preliminary experiments conducted with our apparatus using a 3.5 wt % NaCl brine and powdered synthetic quartz on the other hand were in agreement with predicted weight losses based on the equilibrium solubility of quartz. Given the increased solubility and dissolution kinetics of amorphous SiO₂ compared to quartz (Dove and Rimstidt, 1994) it is assumed that experiments conducted using amorphous SiO₂ in conjunction with NaCl brine solutions achieve supersaturation with respect to quartz nearly instantaneously in our experiments.

The potential for crystallization of the amorphous SiO₂ reactant in our experiments has not been fully investigated. Crystallization of the reactant to a more stable (and less soluble) silica polymorph (e.g., opal-C or quartz) will result in the transport of a solution which is less supersaturated with respect to quartz compared to a solution equilibrated with amorphous SiO₂. While the decrease in the equilibrium solubility of quartz resulting from the imposed thermal gradient between the two reaction vessels will still provide a driving force for new crystal growth
following any reactant crystallization, previous experimental work has shown that crystal growth rates are roughly proportional to the degree of supersaturation (Lasaga, 1998; Lander et al., 2008). Data discussed in Chapter 2 indicate that amorphous SiO₂ may crystallize to quartz in 2 weeks or less in NaCl brine solutions at 450° C and 150 MPa confining pressure.

Spatial Trends in the Amount of Crystal Growth

The effect of sample position on growth amount in the R_p chamber can be seen in Figures 3 and 4. Similar to results reported by Okamoto et al. (2010), the amount of new crystal growth experienced by each sample appears to be at least partially dependent on its position in the fluid flow path with samples 3 through 5 (approximately 5 to 15 cm from reactant) experiencing the most substantial crystal growth. However, our results differ from Okamoto et al. (2010) as all samples in the FT-2 and FT-3 experiments experienced at least some crystal growth rather than only dissolution. And while Okamoto et al. (2010) attributed differential growth and dissolution rates in the R_p chamber to changes in SiO₂ supersaturation during reactive transport, it appears as though different processes govern the experimental system, thus producing disparate results.

Previous hydrothermal flow-through experiments have utilized an increase in R_p temperature to provide large equilibrium solubility decreases associated with supercritical fluids (Okamoto et al., 2010). Unlike the experiments conducted by Okamoto et al. (2010), the temperature in our R_p vessel is below the critical point of H₂O and decreases across the chamber resulting in a continual increase in SiO₂ supersaturation during fluid flow. It is possible that the effect of location on new crystal growth in our R_p vessel is the result of the achievement of an optimal balance between supersaturation and temperature where the temperature in the central regions of the vessel is low enough to provide a large degree of supersaturation but high enough
to provide the kinetic energy required for nucleation (Rimstidt and Barnes, 1980). However, the
exact cause of differences in the distribution of precipitation and dissolution regimes between
our experiments and those of Okamoto et al. (2010) remains unknown.

*Surface Roughness Controls on Nucleation and Growth*

Both the FT-2 and FT-3 experiments show apparent surface roughness controls on the
nature of crystal nucleation and growth. The partitioning of apparent quartz growth textures to
rough surfaces and spherical opaline textures to polished surfaces suggests that in supersaturated
hydrothermal experiments the nature and rate of crystal growth is at least partially controlled by
variations in surface roughness. While the exact cause of this result is beyond the scope of this
research it is possible that increased surface energy resulting from polishing and subsequently
increased dislocation density is responsible for the nucleation of these opaline phases, and that
the apparent control of surface roughness is incidental to the buildup of dislocations during
polishing (Blum et al., 1990).

SEM analysis of both polished and rough cut surfaces also illustrates discontinuous
growth zones across the surface of the sample. Generally, this discontinuity in growth across the
sample surfaces is observed as growth on individual grains or grain boundaries while adjacent
grains appear to have experienced little to no growth. Given the relatively short duration of the
experiments, it is possible that differences in maximum growth rate associated with
crystallographic orientation of the quartz lattice may result in the appearance of selective
overgrowth on favorably oriented grains. It is possible that this growth discontinuity is the result
of differences in grain orientation relative to the surface of each sample.
1.5. RECOMMENDATIONS FOR FUTURE WORK

Future work should be directed toward continued diagnostic testing of apparatus functionality. While a tentative hypothesis for the distribution of new crystal growth is given in section 1.4 more data are needed to fully understand this trend which will allow for more efficient experimental design. Data concerning reactant crystallization are also required to assess any changes in boundary conditions following system startup. Future work concerning quartz cement on lithified materials such as cataclasite should discontinue the use of polished surfaces as these may facilitate the nucleation of unwanted meta-stable SiO$_2$ phases.
CHAPTER TWO

2.1. INTRODUCTION

Static Hydrothermal Experiments

While flow-through experiments provide a more direct analog to progressive diagenesis in active fluid flow environments, valuable information can still be obtained from static experiments. Recently, Pepple (2007) reported quartz cementation rates in samples of crushed fragments of synthetic quartz (125 – 250 µm diameter range). The samples were run in weld-sealed Au tubes in cold-seal pressure vessels at constant (static) temperature and pressure conditions. The source of the silica was amorphous silica powder and the cementation was driven by the solubility difference between the amorphous silica powder and the synthetic quartz fragments (Fornier and Rowe, 1977; Rimstidt and Barnes, 1980) rather than a large temperature gradient (Hilgers and Tenthorey, 2004; Okamoto et al., 2010). Using a similar experimental design, Winslow (2012) determined quartz cementation rates in samples of natural disaggregated St. Peter sand grains (180 µm mean diameter).

The results of the static hydrothermal experiments of Pepple (2007) and Winslow (2012) showed measurable quart cementation occurred in experiments run at temperatures as low as 250°C for a few weeks. For experiments run at similar time and temperature, the average amount of cement was found to be similar in the two studies. In both studies, the amount of cement formed increased with increasing temperature and duration of the experiments. However, in long-term (8 weeks) experiments, Winslow (2012) observed a dramatic decrease in the rate of cementation and suggested the apparent change in precipitation rate may reflect a decrease in
available surfaces for nucleation and/or a decrease in growth rate as euhedral faces develop as proposed by Lander et al. (2008).

If the decrease in quartz precipitation rate reported by Winslow (2012) is attributable to the development of euhedral growth surfaces, then this effect should be more pronounced in fine grain size fractions, which require less growth to achieve euhedral terminations (Lander et al., 2010). Alternatively, the apparent decrease in growth rate reported by Winslow (2012) may be the result of crystallization of the amorphous silica reactant during the experiment which would greatly decrease the silica solubility gradient and hence decrease the driving force for cement precipitation.

While similar average amounts of new quartz cement were reported, questions regarding the exact distribution of new cement following the experiments of Pepple (2007) and Winslow (2012) have not been fully explored. In both studies, the amount of quartz cement decreases with increasing distance from the amorphous silica reactant. While it has been qualitatively concluded that this spatial heterogeneity in the amount of new quartz cement is more pronounced in the experiments using crushed synthetic quartz fragments (Winslow, 2012), a quantitative analysis has yet to be conducted.

Mechanical Effects of Quartz Cementation

Quartz cementation during diagenesis also exerts a substantial effect on the evolving hydrological and mechanical properties of sandstones (Cook et al., 2006; O’Kane et al., 2007; Laubach et al., 2010; Cook et al., 2011). The amount of quartz cement in sandstones has been shown to decrease susceptibility to both elastic deformation (Dvorkin and Yin, 1995) and physical and chemical compaction (Hiatt et al., 2007). The preferred deformation mechanism in sandstones has been shown to be in part controlled by the amount of quartz cement (Dunn et al., 2009).
1973) where sandstones with <12% total porosity tend to deform via fracturing while sandstones with >12% total porosity tend to deform via deformation bands. While previous research has provided a general framework for understanding how hydrological and mechanical properties of sandstones change during diagenesis, the specific effects of grain size and sorting on these processes have remained largely unexamined.

Objectives

The objective of this research was to address unresolved issues in the previous research by Pepple (2007) and Winslow (2012) by specifically: 1) quantifying and explaining the apparent changes in precipitation rate through time, 2) quantifying and explaining the spatial distribution and temporal sequence of quartz cementation and, 3) assessing the possibility of amorphous SiO₂ reactant crystallization during hydrothermal experiments. Additionally, new experiments designed to examine the effect of grain size on precipitation rate were conducted and analyzed in conjunction with previous experimental samples (Winslow, 2012) to examine the effect of grain size and sorting on pore space evolution during sandstone cementation.

2.2. METHODS

2.2.1. Experimental Design

Experiments using two different grain size fractions (described below) were conducted in hydrothermal cold seal vessels to examine the effect of grain size on quartz cement growth rate, thereby testing the hypothesis that decreases in growth rate observed in previous experiments (Winslow, 2012) are the result of the development of slow-growing euhedral growth surfaces (Lander et al., 2010; Winslow, 2012). This configuration allows for direct comparison of cementation processes in different grain size fractions by ensuring that chemical and physical
conditions are identical in each. Additionally, these two-grain size fraction experiments also provide an ideal platform for examining the effect of grain size on pore space evolution during quartz cementation.

Charge Assembly

Charges consisted of two different grain size fractions of disaggregated St. Peter sandstone grains separated by a layer of amorphous SiO$_2$ which served as a source for dissolved SiO$_2$. Au tubes were loaded with approximately 150 mg of either coarse (425-500 $\mu$m) or fine grained (90-125 $\mu$m) St. Peter sand, followed by approximately 40 mg NaCl brine (25 wt. % NaCl), 20 mg amorphous SiO$_2$, 10 mg AlCl$_3$ (a luminescent tracer), an additional 20 mg amorphous SiO$_2$, and finally approximately 150 mg of sand of the remaining size fraction (Fig. 6). Charges were weighed following each material addition and following weld-sealing of the Au tube. After welding, charges were placed into a 60˚C oven for 1 h and reweighed to test weld integrity.

Charges were loaded vertically into the cold seal vessel and brought to the pre-selected temperature and pressure conditions for each experiment. The geometry of the charge was reversed (fine or coarse size fraction at the base of the charge) between experiments to demonstrate that there is no effect of loading geometry. Testing by Pepple (2007) indicated that upper and lower portions of the charge receive approximately equal amounts of new quartz cement using this geometry. Experiments were conducted at 300˚ and 450˚C at a confining pressure of 150 MPa (Table 2).

Following removal from the cold seal vessel, charges were placed into a 60˚C drying oven for 1 h and weighed to ensure that no fluid had escaped during the experiment. Charges were then opened and dried in a 60˚C oven to constant weight. Once dry, each sample was
vacuum impregnated with a low viscosity epoxy and allowed to cure for 24 h. Samples were then sliced along the long axis with one half of the sample preserved for archive and the other half mounted into a brass ring for support, and polished using a series of increasingly finer silicon carbide sandpapers down to 1 µm grit size for analysis.

2.2.2. Analysis

Quantification of New Growth

A Technosyn cold cathodoluminescence (CL) system attached to a Nikon microscope was used to quantify the amount of new quartz cement precipitated during each experiment. As quartz cement typically grows in optical continuity with host grains, CL microscopy is necessary to differentiate new from preexisting quartz overgrowths (Millikin, 1994; Laubach et al., 2004). The addition of AlCl₃ to each experiment resulted in blue luminescent overgrowth material, which was easily distinguishable from the red-pink overgrowths found in unaltered St. Peter Sandstone (Winslow, 2012). The CL images were collected at 20x magnification using a cooled chip digital camera (see Appendix).

Using Microsoft Image Composite Editor, multiple images were combined into mosaics representing approximately 5-10 mm². Following the construction of each mosaic, the resulting image was adjusted for brightness and contrast to enhance visibility and subjected to a median filter to reduce unwanted noise.

Point counting was used to quantify the amount of new cement present in these experiments. Because silica supersaturation is assumed to reach a maximum near the reactant substrate interface (RSI; Fig. 6) shortly after the experiment begins, counting of these samples was conducted only within approximately 1 mm of the RSI in order to ensure that comparisons between experiments were made using areas that experienced similar SiO₂ supersaturation (see
below). For each experiment and size fraction, four images were overlain with a 100 point grid and counted for a total of 400 counts per sample and size fraction.

Point counting was also used to quantify the distribution of new quartz cement in previous experiments conducted by Pepple (2007) and Winslow (2012). To quantify changes in new quartz growth with distance from the RSI, mosaics generated by Pepple (2007) and Winslow (2012) were separated into a series of smaller equally-sized images along the long axis of the mosaic. Each image was overlain with a 100-point grid and point counted to quantify the amount of new cement in that segment. Linear regression analysis was used to assess changes in the amount of new cement with distance from the RSI.

Quantification of Porosity

A Hitachi scanning electron microscope (SEM, Hitachi s2700 model) operated at 20 kV and 70x magnification was used in conjunction with a Backscattered Electron detector (BSE) to collect images used to construct mosaics of each experiment. BSE analysis provided a high contrast image where epoxy filled pore space appeared black and quartz grains and overgrowths appeared gray (see Appendix). Similar to the techniques described for the CL images, BSE images were composited using Microsoft Image Composite Editor. Resulting mosaics were converted to binary images using ImageJ. 2D pore space was then quantified using ImageJ’s particle analyzer function. To avoid spurious identifications, a minimum detectable pore area of approximately 100 $\mu$m$^2$ was used. In the interest of minimizing differences in pore space evolution resulting from spatial differences in SiO$_2$ supersaturation (see below), a constant rectangular area of approximately 4 mm$^2$ was placed at the base of each mosaic and used to quantify pores.
Determination of Silica Polymorphs and Crystallization

Micro-Raman analysis is a non-destructive technique for differentiating mineral polymorphs, as it is sensitive to variations in vibrational frequencies associated with differences in crystal lattice structures (Kingma and Hemley, 1994). Micro-Raman spectroscopy was conducted in the BGSU Photochemical Sciences Department to determine which silica polymorphs were present and to assess the possibility of reactant crystallization (see below). A Renishaw inVia Raman microscope equipped with a 785 nm laser (<1 μm lateral resolution) was used at 20x magnification to collect spectra of reactant, grain, and overgrowth material following each experiment. Spectra collected for this research are composite spectra of 16 cumulative acquisitions at 50% beam power. Reference spectra were also collected from amorphous SiO₂ and St. Peter sand starting materials for comparison with spectra collected from experimental samples (Figs. 7, 8).

2.2.3. Modeling

Diffusive Flux and SiO₂ Supersaturation

A diffusive flux model was developed to estimate the degree of SiO₂ super saturation with respect to quartz. Equilibrium dissolved amorphous SiO₂ concentrations of 3000 ppm at 300˚ C and 4500 ppm at 450˚ C were used in this model (Fournier and Rowe, 1977). The bulk diffusivity (Dbulk) of SiO₂ at a given temperature was estimated experimentally by Watson and Wark (1997) and can be approximated via the Arrhenius equation described therein. Using their reported Arrhenius parameters, Dbulk was estimated to be approximately 4.6 x 10⁻¹⁰ m²/s at 300˚ C and 4.5 x 10⁻⁹ m²/s at 450˚ C. However, as diffusion in these experiments occurred in a porous media, an effective diffusivity (Deff) was used. Deff was calculated (Deff = Total Porosity x Dbulk₁³; Boving and Grathwohl, 2001) to be 2.1 x 10⁻¹³ m²/s at 300˚ C and 4.2 x 10⁻¹² m²/s at
450°C for a starting porosity of 30%. It should be noted that this model assumes that the concentration of dissolved SiO2 near the RSI remains constant throughout the duration of the experiments (infinite reservoir) and that the reactant does not experience crystallization thus lowering the SiO2 concentration in the fluid. Issues relating to the crystallization of amorphous SiO2 will be discussed below.

New Cement Growth and Changes in Precipitation Rate

In addition to the SiO2 supersaturation model, a numerical 2D model was generated to calculate the potential amount of new quartz growth for different grain size fractions exposed to equal temperature and pressure conditions. This model was constructed using Microsoft Visual Basic for Applications as an extension of Microsoft Excel. Grains were modeled two dimensionally as circles and growth proceeded concentrically outward from a host grain. The surface area normalized growth rate (SAN rate) was equal between all grain size fractions for each time step. Modeled SAN rates were based on an empirical relationship derived from SAN rate estimation near the RSI in the experiments of Winslow (2012, Fig. 9). Changes in the amount of surface area available for reaction (S) were accounted for during each time step using a relationship based on that described by Lander et al. (2008):

\[ S = Q_s \left( \frac{6}{D} \right)^{2/3} \]  

where \( Q_s \) is the volume of substrate grains, and \( D \) is the mean diameter of substrate grains.

2D Geometric Modeling of Pore Space Evolution

Using Python®, a 2D geometric model was generated to estimate changes in total porosity and pore space connectivity as a function of grain size fraction. This model utilized concentric circles to represent both detrital grain and overgrowth material and generated multiple randomized simulations of pore space evolution using user-defined parameters. These
parameters include the field of view (µm), the grain diameter range (µm), the growth increment (µm / time step), and the number of modeled time steps. The scale of the model output was fixed at 1 µm per pixel.

The initial field of view (1200 x 1200 µm) is generated by randomly placing non-overlapping grains of a predefined diameter into the field until no additional grains can be spatially accommodated. Tests of packing efficiency using this method yielded an average porosity of 17.7% ± 1.5% for coarse grain fractions (420 – 500 µm diameter), 31.9% ± 1.3% for fine grain fractions (90 – 120 µm diameter), and 13.0% ± 1.3% for mixed grain fractions (90 – 500 µm diameter). While these packing efficiencies are consistent with previous experimental determinations of porosity reduction at pressures up to 50 MPa (Chuhan et al., 2002), discrepancies observed between coarse and fine grain size simulations are likely due at least in part to issues of scale associated with the constant field of view dimensions. Following the generation of the initial field of view all grains receive a concentric overgrowth thickness pre-defined by the user at each time step (equal modeled SAN rate). Porosity, volume percent cement, and bond to grain ratio (the number of cemented grain contacts / the number of grains visible in the field of view) are also recorded at each time step. Following the completion of a simulation, resulting images are subjected to pore space analysis using the methods described below.

2.3. RESULTS

2.3.1. Changes in Precipitation Rate

The dual grain size fraction experiments (hereafter CH-100 and CH-101) displayed a difference in precipitation rate as a function of grain size, with the fine grain fraction having a higher volume percent of new cement than the coarse grain fraction (CH-100: FG=12.0%,
Furthermore, close agreement was observed between modeled and observed new quartz cement for the first week of growth (Fig. 10). However, longer duration experiments resulted in an over-prediction of new cement growth in the fine grain fraction by the model, while new cement growth for the coarse grained fraction was under-predicted (Fig. 10). This result is consistent with experiments reported by Lander et al. (2010).

2.3.2. Spatial Controls on Quartz Cement

*Distribution of Quartz Cement in Pepple (2007) and Winslow (2012)*

Volume percent of new quartz cement decreased with increasing distance from the amorphous SiO$_2$ in all experiments reported by Winslow (2012), although this trend was statistically significant in only two of the five 450° C samples (P < 0.05; Table 3). However, this trend was significant in all three samples from the 300° C experiments (P < 0.05; Table 3). Similarly, the two experiments conducted with synthetic quartz (Pepple, 2007) at 450° C (2 weeks and 4 weeks duration) displayed a significant decrease in volume percent of new quartz cement with distance from the amorphous SiO$_2$ reactant (P < 0.05; Table 3). Unlike the experiments of Winslow (2012), however, the experiments of Pepple (2007) displayed a steeper gradient of new cement versus distance from the RSI, with little or no cement observed beyond approximately 2 mm from the amorphous SiO$_2$ reactant (Fig. 11).

*The Effect of Diffusive Flux*

Results of the 300° and 450° C supersaturation numerical models suggested that the distribution of new quartz cement was the result of spatial and temporal variations in dissolved SiO$_2$ concentration (Figs 12, 13). As supersaturated conditions are required to initiate substantial
quartz cementation \( (C_{SiO2} / C_{SiO2eq} > 1) \) these models were used to estimate the time required for new quartz growth to begin at a specified distance from the reactant.

Increased diffusion rates found at 450˚C compared to 300˚C result in more rapid establishment of supersaturated conditions (Figs. 12, 13). Agreement was observed between back-calculated growth rates (based on observed new quartz cement volumes and experiment duration) and modeled SiO\(_2\) supersaturation in the 450˚C experiments. Modest growth rates 1 to 2 mm from the reactant interface at 450˚C were observed at 48 h and correspond temporally with the onset of modest SiO\(_2\) supersaturations (Figs 12, 13). At 1 week, segments 1 to 2 mm from the reactant experienced peak growth rates, which corresponded temporally with the development of a solution which was highly supersaturated with respect to quartz (Figs. 12, 13). Experiments conducted at 300˚C, however, showed only a vague agreement with modeled SiO\(_2\) supersaturation values (see discussion).

**Fracture Sealing**

Microfractures formed during system pressurization were fully healed in cemented regions of all observed experiments. New quartz cement values associated with 48 h experiments CH-97 and CH-102 were predominately attributable to fracture sealing, with little cement observed as grain boundary overgrowths. In longer duration experiments (CH-100, CH-101) new cement growth became increasingly associated with fracture seal cement in distal regions of the sample. The aforementioned distribution of fracture sealing in comparison to grain boundary overgrowths shows that fracture sealing preceded grain boundary overgrowth formation in these experiments. Calculations suggested that the rate of fracture sealing in these experiments may have been faster than the diffusive flux of SiO\(_2\) from the amorphous silica source to the precipitation site (see discussion).
2.3.3. Pore Space Evolution

To assess the effect of average grain size and sorting on changes in porosity and pore space distribution, dual grain size fraction experiments were analyzed in conjunction with the coeval time (1 and 2 week) and temperature (450°C) mixed grain size fraction experiments of Winslow (2012).

Grain Size Effects on Total Porosity

Total porosity decreased with increasing time in all samples and the rate of porosity decrease is a function of average grain size (Fig. 14). Starting porosities estimated for each grain size fraction (total porosity + volume percent new cement) indicate that the efficiency of compaction differed for each grain size fraction during pressurization (Fig. 14). Furthermore, total porosity values for all grain size fractions rapidly converge to approximately 10% porosity after 1 week (Fig. 14).

Theoretical changes in total porosity were calculated using the 2D geometric model described in Section 2.3 and the results show that the rate of porosity decrease differed between grain size fractions (Fig. 15). Despite having the highest average initial porosity of the modeled size fractions, fine grain models quickly reduced total porosity to levels less than both coarse and mixed grain size fractions (Fig. 15). While modeled total porosity reduction proceeded at a similar rate in both coarse and mixed grain size models, total porosity for all grain size fractions converged to approximately 10% after 8 modeled time steps (Fig. 15).

Grain Size Effects on Pore Space Connectivity

The number of pores per unit area was used to estimate pore space connectivity which varied markedly between grain size fractions at all time intervals (Fig. 16), even though the total
porosity was similar. Despite the small number of samples, these data suggest that pore space evolution was a function of grain size.

Theoretical results obtained from the 2D geometric model also showed that pore space connectivity differed greatly between size fractions for a similar total porosity (Figs. 17, 18, 19). Decreases in the number of pores at approximately 10% total porosity in the fine grain experiments were confirmed in modeled results; however, similar decreases observed in coarse grain experiments were not observed in 2D models (Figs. 17, 18, 19). Comparison of pore space connectivity between coarse and fine grain size fractions showed that for similar total porosity values, the pore space was 8 to 10 times more disconnected in fine grain fractions (Figs. 17, 18).

### 2.3.4. Determination of Silica Polymorphs and Crystallization

#### Factors Controlling Crystallization

The micro-Raman analysis of experiments conducted at 450°C and containing AlCl₃ indicate that amorphous SiO₂ crystallization to quartz does not occur for at least 4 weeks. Spectra collected from amorphous SiO₂ in experiments during this time period exhibit broad, poorly defined peaks similar to those observed in amorphous SiO₂ starting material (Fig. 7). At 4 weeks, however, two well-defined peaks are observed at approximately 227 and 415 cm⁻¹ (Fig. 20). It appears as though the AlCl₃ is preventing crystallization, as experiments conducted at 450°C without AlCl₃ appear to have experienced amorphous SiO₂ crystallization in as little as 2 weeks (Fig. 21).

#### Occurrence and Distribution of Cryptocrystalline Quartz

Previous analysis of the 4 week, 450°C experiment (CH-71) revealed the presence of anomalous overgrowth textures on grains near the base of the charge in contact with the amorphous silica layer (Fig. 22). While these textures are observed in other experiments, they
are only present in sufficient quantities for micro-Raman analysis in sample CH-71. Anomalous overgrowth textures observed in CH-71 were found to have Raman spectra similar to moganite or chalcedony and were interpreted as cryptocrystalline quartz overgrowths (Figs. 23). These overgrowths were located predominately near the base of the charge. Additionally, in all experiments sand grains within approximately 200 μm of the RSI consistently displayed no grain boundary overgrowths.

2.4. DISCUSSION

2.4.1. Grain Size Effects on Precipitation Rate

*Differences in Cementation Rate between Fine and Coarse Grain Sizes*

It is concluded that the change in apparent growth rate through time reported by Pepple (2007) and Winslow (2012) was the result of a differential decay in growth rate between coarse and fine grain fractions where fine grain fractions experience a more rapid decrease in rate (Lander et al., 2008). The observed differences in the SAN rate decrease in different size fractions are consistent with previous work conducted by Lander et al. (2010) who concluded that this decrease results from the progressive development of euhedral overgrowths, which develop more rapidly on fine grains when compared to coarse grains under equal growth conditions. Comparison of modeled results to the 1 week 450 °C experiment CH-100 indicate that the initial or maximum SAN rate experienced by both grain size fractions is equal, and that apparent differences in growth rate are attributable to a more rapid decrease in this rate in fine grain experiments. Individual fine grains are able to achieve euhedral faces more quickly than coarse grains, and as such fine grain size fractions experience a decrease in SAN rate in a shorter time period under equal growth conditions (Lander et al., 2010).
Effect of Precipitation Rate Change on the Distribution of Cement

It is possible that non-significant trends observed in the 450°C experiments of Winslow (2012) are the result of both temporal requirements for SiO$_2$ supersaturation establishment and decreases in SAN rate following the onset of growth. While regions near the RSI experience new crystal growth relatively early in an experiment, back-calculated growth rates for the Winslow (2012) experiments show that growth rate decreases rapidly within several days of the onset of growth. If SiO$_2$ supersaturation is considered as a wave front which travels away from the RSI with time then it follows that distal regions of the charge can experience peak SAN rates at the same time that regions near the RSI experience a SAN rate minimum. This contrast in SAN rate between proximal and distal regions would result in the partial homogenization of total crystal growth for each growth region. While a similar mechanism would also operate in 300°C experiments, it appears that the greatly reduced diffusive flux operating in these experiments results in a statistically significant decrease in new quartz cement with distance from the RSI.

2.4.2. Diffusive Flux

Effect on Temporal Sequence of Cementation

Differences in the rate of diffusive flux between 300° and 450° C experiments result in markedly different distributions of new quartz cement in these experiments. It is hypothesized that fracture sealing is the precursor step to grain boundary overgrowth formation at each discrete section of the charge as SiO$_2$ supersaturation is achieved. In longer duration experiments a brief zone of fracture sealing is observed immediately next to grain boundary overgrowth cemented regions, indicating that this zone was experiencing the onset of peak SiO$_2$ supersaturation near the end of the experiment. While not fully explored, it is hypothesized that
300°C experiments will follow a similar trend in temporal sequence, albeit at a reduced rate consistent with decreased diffusive flux.

It is possible that highly supersaturated conditions near the RSI resulted in the precipitation of cryptocrystalline quartz observed in CH-71. While textural evidence of cryptocrystalline quartz varieties is rarely observed in other experiments, grain boundary overgrowths are generally absent in regions immediately adjacent to the RSI. These observations are consistent with previous research, which showed that the deposition of a nanolayer of cryptocrystalline quartz can inhibit the formation of syntaxial grain boundary overgrowths during cementation (Worden et al., 2012).

**Comparison of Fracture Sealing Rate to Diffusive Flux**

While it was empirically confirmed that fracture sealing precedes grain boundary overgrowths in these experiments, it is hypothesized that the process of fracture sealing may actually retard the onset of grain boundary overgrowth formation in areas of sufficient fracture density. Calculations of the SAN rate required to seal 10 µm wide fractures within 48 h at 450°C reveal these rates approximate the rate of diffusive flux to the precipitation site. If the rate of fracture sealing is able to match or exceed the rate of diffusive flux to the precipitation site, then both slow growing grain boundary surfaces and distal portions of the charge would effectively be starved of dissolved SiO₂ until the fractures are sealed. Previous research has shown that fractures equal to the maximum width observed in these experiments of 10 µm may heal in as little as 10 h at 450°C (Brantley et al., 1990).

Similar effects are observed in the 450°C crushed synthetic quartz experiments of Peppe (2007), where new cement growth is observed to be heavily concentrated near the RSI. As the
synthetic quartz used in those experiments was obtained via crushing of a single synthetic quartz crystal, all available growth surfaces can effectively be considered fracture surfaces. It is possible that the greater free energy on these surfaces in comparison to the 450°C experiments of Winslow (2012) resulted in rapid growth similar to that experienced by fractures in St. Peter sandstone experiments, thereby reducing SiO₂ transport to distal regions of the charge and slow growing (transport rate limited) grain boundary surfaces.

The observations presented above indicate that the rate-limiting factor to crystal growth in these experiments may alternate between transport and precipitation at different regions of the charge through time. Further research is required to empirically constrain both the rate of fracture sealing and the rate of diffusive flux to the fracture site. Should the rate of fracture sealing be confirmed to be equal to or faster than the rate of diffusive flux, then transport of dissolved SiO₂ can be said to be the rate-limiting factor in the early stages of crystal growth following the establishment of supersaturation. This situation would persist until a sufficient number of fractures had been sealed, and growth on relatively slow growing grain boundaries becomes the dominant mode of crystal growth. Following the re-establishment of grain boundary overgrowth formation, transportation may resume unimpeded and precipitation will once again become the rate-limiting reaction.

Discrepancies in SiO₂ Supersaturation Model

The SiO₂ supersaturation model described in section 3.3 appears to effectively predict peak growth rates in the 450°C experiments; however, it is less effective at predicting growth in the 300°C experiments. As the onset of crystal growth depends not only on supersaturation but on temperature as well, it is likely that differences in growth kinetics between the 300°C and 450°C
C experiments result in differences in the timing of nucleation between these temperatures. Errors in the estimation of the amount of new cement in these charges will also inevitably effect the estimation of SAN rate. While a variety of possibilities exist as to why this discrepancy occurs it should be noted that these models were generated to illustrate the theoretical differences in diffusive flux for identical conditions between the 300˚C and 450˚C experiments.

2.4.3. Pore Space Analysis

Discrepancies between Experimental and Modeled Results

Several discrepancies exist between the experimental and modeled pore space results which arise primarily from limited sample size and non-ideal shapes in the experimental data. The starting porosity estimated for the fine grain fraction experimental samples is approximately 10% less than that of the modeled starting porosity for an equal grain size distribution. Starting porosities observed for coarse and mixed grain size fractions are comparable between experimental and modeled results. While modeled starting porosities are consistent with previous experimental work on quartz sand packing efficiencies up to 50 MPa (Chuhan et al., 2001), it is possible that the increased confining pressure in these experiments (150 MPa) resulted in more efficient packing in fine grain size fractions during pressurization (Houseknecht, 1987).

A decrease in the number of pores at approximately 10% porosity in coarse and fine grain size fraction experimental samples is confirmed in modeled results for fine grain size fractions but not for coarse grains. Examination of BSE mosaics for coarse grain size experiments reveals that grain crushing occurred during pressurization. Fragments of crushed grains are found to be infilling pore space around larger grains in some areas, resulting in the generation of numerous,
small pores which are rapidly destroyed during new cement growth. It is hypothesized that the presence of these small grain fragments results in an erroneous calculation of a decrease in the number of pores where a plateau is observed in modeled results.

Observations of the number of pores in fine grain size experiments are consistently 2 to 3 times lower than that reported by modeled results for a similar porosity. The number of pores observed in coarse and mixed grain size experiments is consistent with that reported by modeled results. As BSE mosaics were first subjected to a median filter in ImageJ, it is possible that this discrepancy results from incidents of boundary blurring between grains in fine grain BSE images. As modeled results used in pore space analysis are simple tri-color images, the accuracy of pore space detection is 100% whereas images obtained through BSE analysis and image processing are prone to some degree of error. Additionally, the aforementioned differences in starting porosity between experimental and modeled fine grain results may result in the more rapid destruction of small pores in the experiments.

*The Effect of Pore Space Connectivity on Effective Diffusive Flux*

In the absence of effective porosity (the amount of interconnected pore space), total porosity can be used to estimate the effective diffusivity ($D_{\text{eff}}$) of a species through a saturated porous media (Boving and Grathwohl 2001). However, as the total porosity does not account for the amount of pore space unavailable for diffusive transport, calculations utilizing the effective porosity of a sample will likely provide the most accurate estimation of $D_{\text{eff}}$ (Boving and Grathwohl 2001). This is particularly true in the case of the experiments reported herein. Experimental and modeled results show that for the same total porosity, pore space is much more disconnected in fine grain size fractions. It can be concluded that $D_{\text{eff}}$ will decrease much more
rapidly in fine grain size fractions than coarse or mixed grain size fractions under equal time and temperature conditions.

2.4.4. Amorphous SiO$_2$ Crystallization

*Timing in AlCl$_3$ Experiments*

Raman spectra collected from the remaining reactant in the 4 week experiment at 450˚C (CH-71) shows that crystallization of the amorphous SiO$_2$ reactant may have begun during the experiment. While these spectra are not consistent with alpha quartz the development of well defined peaks is indicative of crystallization to an unknown phase other than amorphous SiO$_2$. It is therefore concluded that experimental boundary conditions (i.e., SiO$_2$ supersaturation near the RSI) breakdown after 4 weeks experimental duration at 450˚C in the presence of AlCl$_3$. Unfortunately no data points are available for experimental durations between 2 and 4 weeks to further constrain exactly when this transition occurs.

*The Effect of Al on Amorphous SiO$_2$ Crystallization*

Micro-Raman analysis reveals the amorphous SiO$_2$ reactant used in a 2 week AlCl$_3$ free experiment at 450˚C (CH-42) has undergone complete crystallization to quartz during the experiment. The fact that crystallization of the amorphous SiO$_2$ reactant appears to be complete in sample CH-42 when sample CH-71 appears to have only begun crystallizing suggests that the presence of aluminum in solution is slowing the rate of amorphous SiO$_2$ crystallization. This result is counter to previous research suggesting that trivalent cations such as aluminum may facilitate the transition from opaline phases to alpha quartz (Hinman, 1999). The mechanism for this effect remains unknown, but future research efforts should focus on determining the nature of this mechanism and assess if other trivalent cations such as Fe have a similar effect.
2.5. CONCLUSIONS

The results of this research show that the amount and distribution of new quartz cement in hydrothermal cold seal experiments is a function of systematic variations in SAN rate, diffusion controlled SiO₂ supersaturation, grain size, and fracture density. Measured SAN rates are shown to decrease in a manner consistent with that proposed by Lander et al. (2008), wherein decreases in rate are more pronounced in relatively fine grain size fractions. Back-calculations of apparent SAN rate for discrete sections of each experiment show that peak rates are experienced following the modeled onset of SiO₂ supersaturation.

The observed temporal sequence of cementation in conjunction with modeling efforts of SiO₂ supersaturation shows that the rate limiting factor in quartz cementation may vary between transport and precipitation in areas of sufficient fracture density. However, the relatively high temperature nature of our experiments in comparison to typical diagenetic conditions precludes the possibility of making a direct comparison to diagenesis in highly fractured sandstones. Despite the discrepancy in temperature, our results suggest that it is possible the rate limiting factor in quartz cementation following brittle deformation (shear zone diagenesis) may be variable when transport is diffusion dominated. As open fractures have long been considered to be effective conduits for subsurface fluid flow it is critical that this possibility be explored in greater detail at temperatures more reflective of diagenesis.

Pore space analysis conducted during this research shows that for an equal amount of total sample porosity the connectivity of the pore space varies greatly as a function of grain size and sorting. This effect is most clearly illustrated in modeled results, where a total sample porosity of approximately 10% in both coarse and fine grain size fractions is segmented into 8 to
10 times as many pores in the fine grain size fraction. This result shows that previous efforts to tie specific hydrological or mechanical effects to total porosity in sandstones may provide limited predictive capability by not considering the effect of grain size and sorting during progressive diagenesis. While empirical results are currently limited, this research has provided an initial framework for understanding these effects.

Our results indicate that future efforts to predict sandstone diagenesis would benefit greatly from considering the complexities of diagenesis under a wider variety of hydrologic and sedimentary conditions. While previous efforts have been successful in accurately modeling sandstone diagenesis under idealized burial conditions, increased demand for unconventional sandstone reservoirs necessitates the examination of a wider variety of more specific diagenetic environments. This research has provided a basic foundation for understanding the effects of fracture density as well as grain size and sorting on silica DTP processes and how these processes combine to determine pore space morphology in sandstones. Future efforts should focus on further constraining these effects under more realistic experimental conditions.
REFERENCES


FIGURES AND TABLES

Table 1. Experimental run conditions for convection cell cataclasite experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (hours)</th>
<th>Thermal Gradient (R₀ – R₁ °C)</th>
<th>Number of Samples</th>
<th>Reactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT-1</td>
<td>344</td>
<td>315 - 205</td>
<td>15</td>
<td>5.5189 g Pwd Qtz</td>
</tr>
<tr>
<td>FT-2</td>
<td>50</td>
<td>305 - 225</td>
<td>9</td>
<td>1.1844 g AmSil</td>
</tr>
<tr>
<td>FT-3</td>
<td>122</td>
<td>302 – 245</td>
<td>7</td>
<td>1.1500 g AmSil</td>
</tr>
<tr>
<td>FT-4</td>
<td>4</td>
<td>301 - 253</td>
<td>7</td>
<td>1.1060 g AmSil</td>
</tr>
</tbody>
</table>

* All experiments run with NaCl addition equivalent to between 3 and 5 wt % of solution. AmSil – amorphous silica.
Table 2. Dual grain size fraction experiments conducted to assess changes in precipitation rate and pore space geometry as a function of grain size.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH-100</td>
<td>168</td>
<td>450</td>
<td>150</td>
</tr>
<tr>
<td>CH-101</td>
<td>336</td>
<td>450</td>
<td>150</td>
</tr>
<tr>
<td>CH-102</td>
<td>48</td>
<td>450</td>
<td>150</td>
</tr>
<tr>
<td>CH-99</td>
<td>168</td>
<td>300</td>
<td>150</td>
</tr>
<tr>
<td>CH-103</td>
<td>336</td>
<td>300</td>
<td>150</td>
</tr>
</tbody>
</table>
Table 3. Experiments of Pepple (2007) and Winslow (2012) used in linear regression analysis of new quartz cement distribution with distance from the reactant interface. All samples showed a decrease in the amount of cement with distance from the RSI.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
<th>Substrate</th>
<th>P-value &lt; .05</th>
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</thead>
<tbody>
<tr>
<td>CH-88</td>
<td>1344</td>
<td>450</td>
<td>150</td>
<td>St Peter</td>
<td>No</td>
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<tr>
<td>CH-74</td>
<td>336</td>
<td>450</td>
<td>150</td>
<td>St Peter</td>
<td>No</td>
</tr>
<tr>
<td>CH-83</td>
<td>336</td>
<td>450</td>
<td>150</td>
<td>St Peter</td>
<td>No</td>
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<tr>
<td>CH-73</td>
<td>672</td>
<td>450</td>
<td>150</td>
<td>St Peter</td>
<td>Yes</td>
</tr>
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<td>450</td>
<td>150</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>672</td>
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<td>150</td>
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<tr>
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<td>150</td>
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</tr>
<tr>
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<td>150</td>
<td>Syn Qtz</td>
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<td>150</td>
<td>Syn Qtz</td>
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</tr>
</tbody>
</table>
Figure 1. Diagram of hydrothermal flow-through apparatus showing reaction chambers $R_s$ and $R_p$ as well as corresponding thermocouple locations $T_s$ and $T_p$. 
Figure 2. The change in weight (g) for each cataclasite sample in the Rp chamber following the completion of the 344 hour FT-1 experiment. Substantial dissolution is observed in more upstream samples, while equilibrium conditions occur near the center of the chamber. Weight gains observed in regions 24 through 30 cm from the silica source are attributed to the precipitation of the iron oxide goethite.
Figure 3. The change in weight (g) for each cataclasite sample in the Rp chamber following the completion of the 50 hour FT-2 experiment. In contrast to the FT-1 experiment (Fig. 2) all samples in the Rp chamber experienced positive weight change indicating new crystal growth. Maximum growth is observed near the center of the reaction chamber.
Figure 4. The change in weight (g) for each cataclasite sample in the R_p chamber following the completion of the 122 hour FT-3 experiment. All samples in the R_p chamber experienced positive weight change indicating new crystal growth, however the amount of total growth experienced was similar to that observed in the 50 hour FT-2 experiment (Fig. 3).
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Figure 8. Raman spectrum collected from disaggregated St. Peter Sandstone starting material using a 785 nm laser at 50% power. Spectrum is the result of 16 acquisitions collected at 20x magnification.
Figure 9. Back calculated surface area normalized growth rates for regions within 1 mm of the reactant substrate interface at 450°C for use in new quartz cement models. Apparent rates are observed to decrease logarithmically throughout each experiment.

\[ y = -9E-12 \ln(x) + 7E-11 \]

\[ R^2 = 0.9454 \]
Figure 10. Output of new quartz growth model implementing rate decay back calculated from the experiments of Winslow (2012, Fig. 4). Good agreement is observed between experiments of Winslow (2012) and predicted new quartz cement values. While 1 week dual grain size fractions show good agreement with modeled results, two-week experiments are over and under predicted for fine and coarse grain size fractions, respectively.
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Figure 13. Theoretical SiO$_2$ supersaturation as a function of distance from the reactant interface and time in the experimental reactor at 450˚ C. Regions experiencing SiO$_2$ supersaturation < 1 are considered undersaturated and no growth can occur until SiO$_2$ supersaturation > 1 is achieved.
Figure 14. Total porosity decrease in coarse, fine, and mixed grain size fraction experiments as a function of time in the reactor at 450˚ C. Starting porosities were estimated by the sum of new quartz cement and remaining porosity in two-week experiments. Total porosity values quickly converge after only one week in the reactor.
Figure 15. Modeled total porosity for coarse, fine, and mixed grain size fractions. While the modeled starting porosity of fine grain size fractions is approximately 10% higher than that of experimental estimates, total porosity for all grain size fractions is observed to quickly converge to similar values following eight modeled time steps.
Figure 16. The number of pores per unit area in coarse, fine, and mixed grain size fractions as a function of time in the reactor as determined by pore space analysis. While all grain size fractions share a similar total porosity following one week in the reactor, the connectivity of that porosity varies markedly between grain size fractions as is shown above.
Figure 17. Modeled results of pores per unit area in coarse (425 – 500 µm) grain size fractions. Decreases in the total number of pores observed in experimental results are not confirmed in this model for similar total porosity values or total volume new quartz cement. Despite sharing a similar porosity, the number of pores in coarse grain size models is 8 to 10 times less numerous than those observed in fine grain size fraction models. Error bars represent the standard error of pores-/mm² following five simulations.
Decreases in the number of pores per unit area observed in experimental results are confirmed in this model as small pores are increasingly destroyed with progressive additions of new cement. Despite sharing a similar total porosity, the number of pores observed in fine grain size fraction models is approximately 8 to 10 times more numerous than those in coarse grain size fractions. Error bars represent the standard error of pores/mm$^2$ following five simulations.
Figure 19. Modeled results pores per unit area for mixed grain size fractions. Mixed grain size fraction models generally show good agreement with experimental results. Error bars represent the standard error of pores/mm$^2$ following five simulations.
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Figure 21. Raman spectrum collected from amorphous SiO$_2$ source layer in the 2 week, 450° C AlCl$_3$ free CH-42 experiment (Pepple, 2007). The collected spectra are consistent with alpha quartz (Fig. 8), indicating that amorphous SiO$_2$ in this experiment has been fully crystallized to the stable quartz phase within two weeks of experiment start.
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Appendix A (1) Cathodoluminescence (CL) mosaic of the coarse-grain section (425 – 500 µm) of the 48 hour at 450 °C experiment CH-102.
Appendix A (2) Cathodoluminescence (CL) mosaic of the fine-grain section (90 – 120 µm) of the 48 hour at 450 °C experiment CH-102.
Appendix A (3) Cathodoluminescence (CL) mosaic of the coarse-grain section (425 – 500 µm) of the 1 week at 450 °C experiment CH-100.
Appendix A (4) Cathodoluminescence (CL) mosaic of the fine-grain section (90 – 120 µm) of the 1 week at 450 °C experiment CH-100.
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Appendix B (2) Back-scattered electron (BSE) mosaic of the fine-grain section (90 – 120 µm) of the 48 hour at 450 °C experiment CH-102.
Appendix B (3) Back-scattered electron (BSE) mosaic of the coarse-grain section (425 – 500 µm) of the 1 week at 450 °C experiment CH-100.
Appendix B (4) Back-scattered electron (BSE) mosaic of the fine-grain section (90 – 120 µm) of the 1 week at 450 °C experiment CH-100.
Appendix B (5) Back-scattered electron (BSE) mosaic of the coarse-grain section (425 – 500 μm) of the 2 week at 450 °C experiment CH-101.
Appendix B (6) Back-scattered electron (BSE) mosaic of the fine-grain section (90 – 120 μm) of the 2 week at 450 C experiment CH-101.