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The Effect of Substrate on Quartz Precipitation Rates

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Honors Project

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Introduction

Silica, typically found in the form of quartz, is a pervasive material in the earth's crust.

Formed from the most abundant anion and cation in the earth's crust, quartz's prominence is no

surprise and its importance in geologic systems is great. When considering quartz rich rock, such

as quartzite or sandstone, the mineral very often plays the role of cementing the rock, filling

previously open porosities as are found in fractures and between grains. Cement may form on a

fractured surface, or as overgrowth on existing quartz grains (Fig. 1). Cement can have a

significant effect on the porosity, permeability, and strength of the rock and is often modeled for

systems to assess these properties.
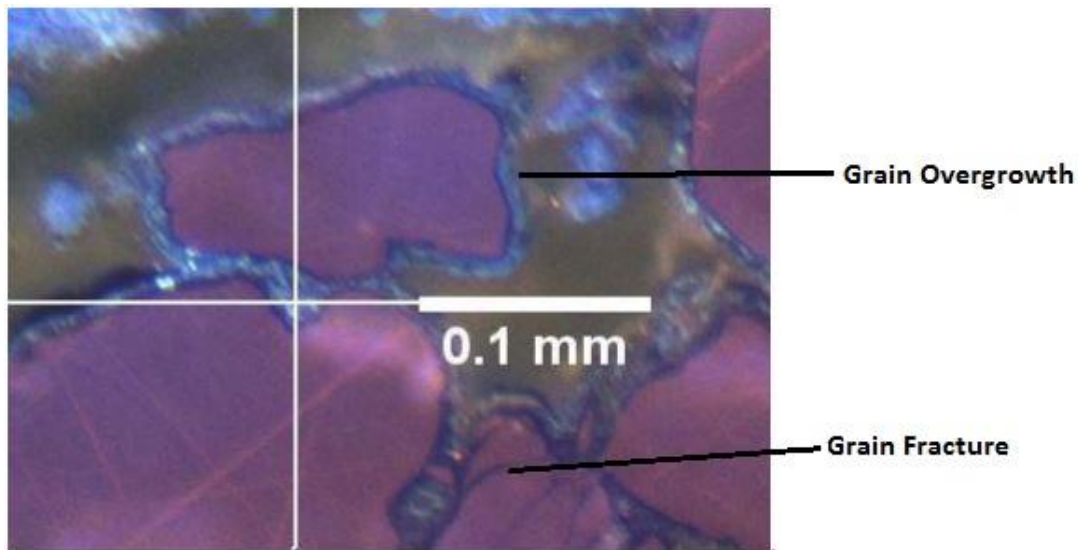
Figure 1: A cathodoluminescence image of quartz grains with overgrowths and fractures. The
overgrowths have a blue luminescence while the grains have a purple luminescence. Adapted from
Williams (2012).

Quartz cementation is accomplished by the precipitation of dissolved silica from an

aqueous solution onto surfaces within a rock unit. Surface types include transgranular fractures

(fractures within individual quartz grains), fractured grain surfaces, and naturally weathered

grain surfaces. Many previous researchers have studied the development of quartz cement, as outlined by Worden and Morad (2000) and references therein. The main questions addressed include: the source of the cement material, what processes are rate limiting for cement formation, how is the silica transportation accomplished, the rate of quartz cementation, and what conditions lead to cementation. Answers to these questions are necessary to understand how quartz cement will develop within a rock unit.

Dissolution and Transport of Silica

Before quartz may precipitate from solution, silica must first enter solution. Many forms of silica (SiO_2) exist and are defined by the arrangement of silica and oxygen atoms forming crystals. The most common form is α-quartz, which has a trigonal crystal type; however other forms exist including β-quartz and cristobalite. In addition, silica may exist in an amorphous form which lacks a regular crystal structure. The crystallinity, or lack of it, changes the solubility of silica in water. The solubility of amorphous silica is much greater (about 10 times greater) than that of quartz and has been studied under a variety of conditions. Fornier and Rowe (1977) examined the solubility of amorphous silica in water at elevated pressures (200-1379 bars) and temperatures (180-382°C) and used experimental data to create a formula modeling the concentration of silica in solution at a fixed pressure and a variable temperature. Later work by Icenhower and Dove (2000) compared the solubility of silica in water to its solubility in NaCl brine and concluded that the NaCl brine greatly increased the solubility of amorphous silica (21 times greater for a 0.05 molal solution when compared to deionized water).

Transport processes are also important for precipitation of quartz cement, moving the dissolved silica from its source to the area where precipitation occurs. This may occur through

advective fluid flow along fracture systems on scales as large as kilometers or a small as micrometers, such as those described in Cook et al. (2006) and Brantley et al. (1990, 1992), respectively. In a more static fluid, diffusion accomplishes a great deal of transport. Watson and Wark (1997) created a model to predict silica diffusivity under varying temperatures at a fixed pressure using experimentally derived data.
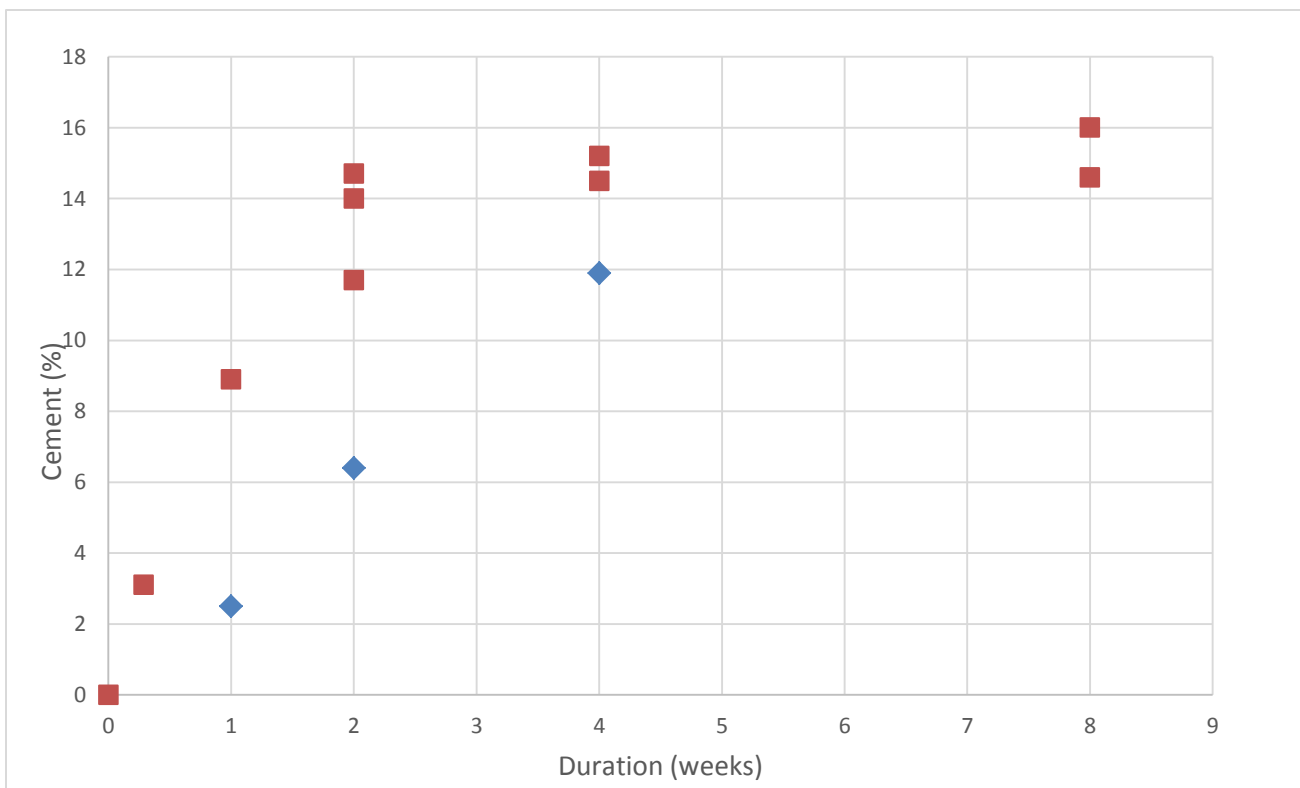
Precipitation of Silica

Precipitation of quartz from an aqueous solution is controlled by the degree of supersaturation of the fluid, the ionic strength of the fluid, time, and the type of substrate precipitation occurs on (Pepple 2007, Winslow 2012, Hilgers and Tenthorey 2004). The effect of temperature, which is typically used to drive quartz precipitation in experiments, was examined by Rimstidt and Barnes (1980) who found that maximum precipitation rates could be achieved by lowering the temperature of a saturated solution 25°C-50°C below the equilibrium solubility temperature. Also, the amount of cement precipitated increased with increases in the degree of supersaturation of the fluid, the ionic strength of the fluid, and the time allowed for the experiment to run.

The role of substrate on quartz cementation is less clearly defined however. As noted in Williams (2012), when comparing precipitation rates on natural quartz grains of two different sizes, smaller grain sizes had slower rates of surface area normalized growth than larger grains. Work by Lander et al. (2008) suggests that growth on smaller grains achieves a slower growing euhedral crystal form much sooner than growth on larger grains. Once growth of the euhedral crystal forms dominate, the overall cement growth rate decreases. They also suggested that a similar effect may be achieved through nucleation discontinuities on the grain surface, formed by weathering damage and/or adhesions of other materials (e.g. clays) to the grain. The findings of

Winslow (2012) and Pepple (2007) do not appear to support the effect of weathering lowering

precipitation rates (Fig. 2). However, the data do support a change in precipitation rate over time.

Whether this is from the development of a euhedral crystal form or a decrease in supersaturation

(due to recrystallization of the amorphous silica source during the experiment) is as of yet

unknown.

Research Importance

Figure 2: Graph showing the amount of quartz overgrowth cement precipitation on a fresh fractured surface (blue diamonds, synthetic quartz of size fraction 125μm-250μm from Pepple 2007) and the quartz cement precipitation on a natural weathered surface (red squares, St. Peters sandstone size fraction 90μm-500μm from Winslow 2012). All run at 450°C and 150 MPa confining pressure.

Permeability and porosity within reservoir rocks are of great concern for hydrocarbon

resources, as they dictate the flow and storage of hydrocarbons within the reservoir. The

permeability of quartz-rich rocks is often controlled by faults and fractures within the unit. As

such, cementation processes have a substantial effect on the permeability and porosity of rock

units, lowering both the permeability and porosity as cement develops within the open spaces of the rock. In quartz-rich reservoir rocks, quartz cement has been found to form preferentially within zones of fracture, dramatically changing the permeability of the reservoir. Work conducted by Williams et al. (2015) showed that precipitation rates within transgranular fractures far exceeded rates on weathered grain surfaces. This may be explained by transgranular fractures healing with locally derived cement. However, the question remains if freshly fractured surfaces and weathered surfaces on quartz grains have different precipitation rates.

The goals of this study are to evaluate: (1) how quartz crystallization on a weathered quartz surface compares to crystallization on a fresh fractured surface, (2) how sealing rates of transgranular fractures produced during pressurization compare with quartz overgrowth rates on a weathered surface, and (3) do cementation rates on a fractured surface and on a weathered surface decrease with time.

Methods

Starting Materials

For each experiment samples of two different surface types were used; naturally weathered surfaces and freshly fractured surfaces. Disaggregated grains of St. Peters sandstone were used for the naturally weathered surfaces. These grains were well-rounded quartz grains, sized 90-125μm. Crushed synthetic quartz grains were used for the freshly fractured surfaces. These grains were angular and were also sized 90-125μm (Fig. 3). By using samples of like grain size any effect of grain size on precipitation rates may be removed.

A.

B.
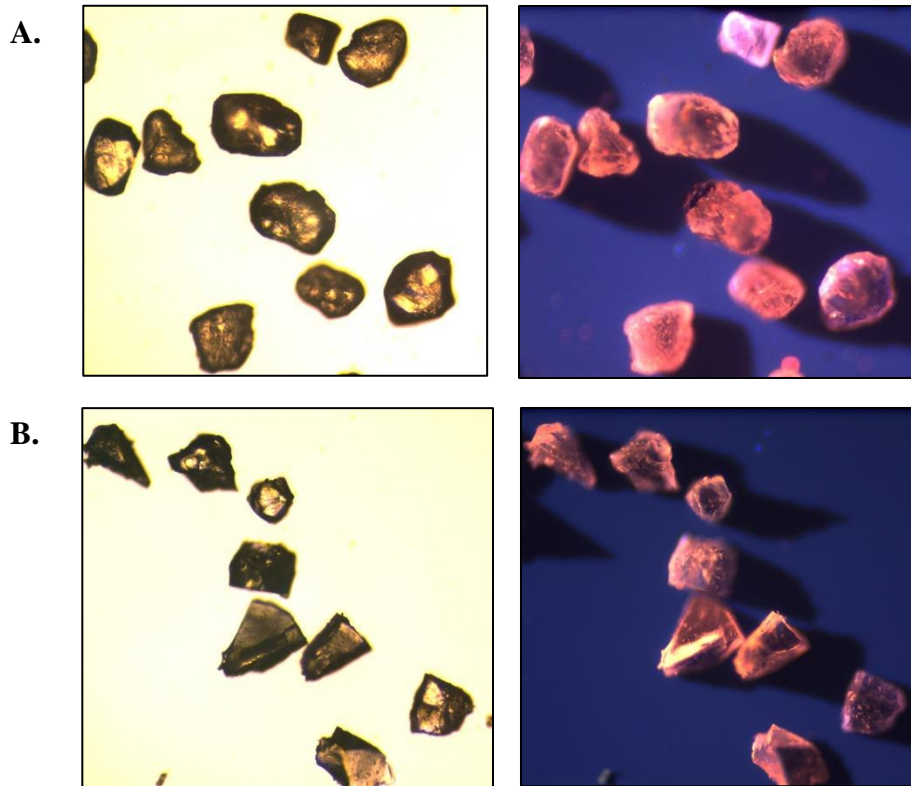
Figure 3: Plane polarized (left) and CL images (right) of disaggregated St. Peters Sandstone grains (A) and crushed synthetic quartz grains (B). Field of view is 1mm.
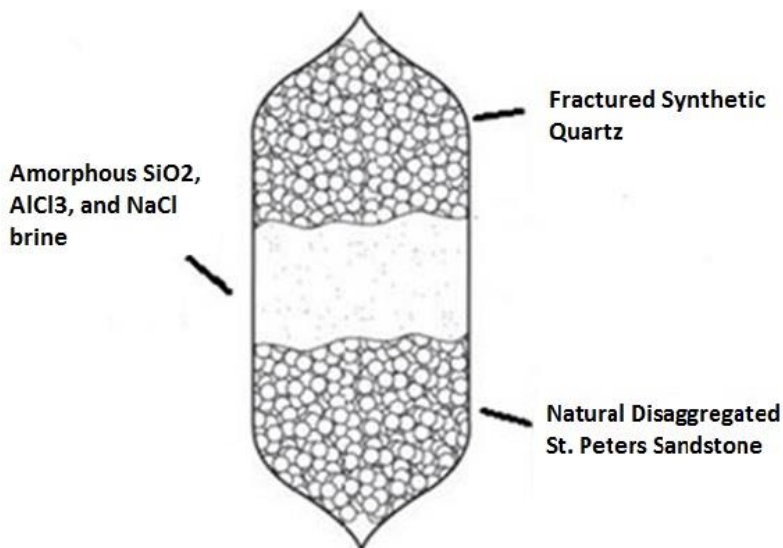
Experimental Design

Much of the experimental design was adopted from Williams et al. (2015) to ensure that the results of the project may be directly compared with previous work. The primary difference is that instead of using a single specific grain size sample of disaggregated St. Peter sandstone, both crushed synthetic quartz and disaggregated St. Peter sandstone of like grain sizes were used.

Experiments were carried out by loading approximately 150 mg of disaggregated St. Peter sandstone, 20 mg of amorphous silica, 10 mg AlCl$_3$, 20 mg amorphous silica, and 150 mg crushed synthetic quartz (composed of entirely fractured surfaces) along with 40 mg of 25 wt% NaCl brine into a gold tube (5mm in diameter and 25mm in length). The disaggregated sandstone and crushed quartz were of like size-fractions (90-125μm). The materials were added in the order

given so that the disaggregated sandstone and the crushed synthetic silica are separated by the

layer of amorphous silica and $AlCl_3$, forming a "sandwich" (Fig. 4). This helped ensure that both

the disaggregated sandstone and the crushed synthetic quartz had equal access to the amorphous silica, which was used as a source for the dissolved silica forming the quartz cement. Amorphous silica was used as it has a higher solubility in water than quartz, causing the solution to be oversaturated in quartz when it is saturated with amorphous silica. The $AlCl_3$ serves as a luminescent tracer which, in cathodoluminescence shows a distinctive blue

Figure 4: The arrangement of the experimental charge, showing the spatial relationship of all materials used. Adapted from Williams (2012).

color. The $AlCl_3$ is incorporated in the new quartz growth, allowing the cement formed during

the experiment to be distinguished from the preexisting quartz (Fig. 5). The addition of NaCl

brine increases the solubility of quartz, aiding growth, and also acts to mimic the brines found in

hydrocarbon reservoir rocks.

The charges were weighed after each addition, then weld sealed and weighed again. The

charges were then placed in a drying oven at 60 °C for one hour then weighed again to check the

integrity of the weld. The charges were loaded vertically into cold-seal vessels, switching the

orientation to ensure that geometry of the vessel does not have an effect on the quartz

cementation. The experiments were then run at 450 °C and 150 MPa confining pressure for 1

week, 2 weeks, and 4 weeks to allow for a measurable amount of quartz growth.
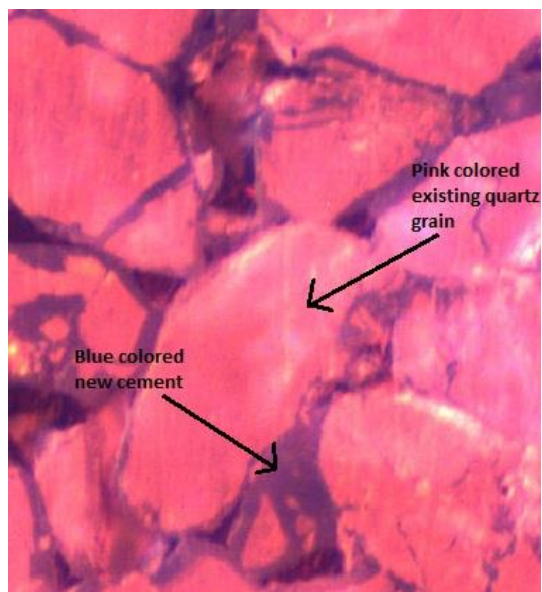
Figure 5: Cathodoluminescence microscope image showing the colors of existing quartz and cement developed during the experiment. Field of view is 1mm.

Analysis Methods

After each run the charges were removed from the cold-seal vessels and placed in a drying over at 60 °C for one hour and weighed to check for any fluid escape during the experiment. The charges were then pierced to allow fluids to evaporate and were dried at 60 °C to a constant weight. The gold tubes were carefully removed and the samples vacuum impregnated with a low viscosity epoxy, dyed blue to more easily show pore spaces within the sample, and allowed to cure for 24 hours. Each sample was sliced in half along the long axis, with one half archived. The remaining half was placed within a brass ring and sealed again in low viscosity epoxy. After curing for 24 hours, the sample was polished with silicon carbide sandpaper to a grit of 3 μm to prepare for analysis.

The samples were analyzed using a Technosyn cold cathodoluminescence system on a Nikon microscope. Images were taken using a cooled chip digital camera and the images mosaiced using Microsoft Image Composite Editor. The new growth, marked by the blue luminescence of the $AlCl_3$, was point counted to determine how much cement had formed in

each sample (Fig. 6). Following William et al. (2015), cement values were normalized to within 2mm of the silica source.
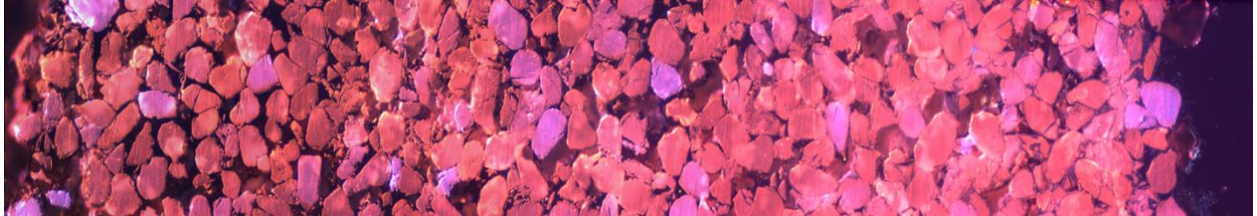
Figure 6: **Figure 4. Photomosaics of CL images of experimental samples showing disaggregated natural St. Peter's sandstone (top) and fresh-fractured synthetic quartz (bottom). These samples were run at 450° C and 150 MPa confining pressure for 2 weeks. In both images the source of silica for cement was to the right. Field of view in the long dimension is 5mm and 8mm respectively.**

Results

Three experiments were run and analyzed for this project. All were run under the same temperature and pressure conditions (450°C and 150MPa) and varying times (1 week, 2 weeks, and 4 weeks). This normally would have given three samples of fractured synthetic quartz and three samples of naturally weathered disaggregated St. Peters sandstone grains; however, the 4 week sample deformed during pressurization in such a way so as to separate the St. Peters side of the sample completely from the amorphous silica cement source. This caused the St. Peters section to remain uncemented. However, the fractured synthetic quartz section of the sample was unaffected and analyzed.

Table 1: A summary of the percentages of overgrowth cement found for each sample. All samples were run at 450°C, 150 MPa confining pressure. Error is estimated to be 1.3% based on Winslow (2012).

Sample Number	Experiment Duration	Sample	Percent Overgrowth Cement
CH-105	1 week	St. Peters	1.96%
CH-105	1 week	Synthetic	4.58 %
CH-107	2 weeks	St. Peters	7.25 %
CH-107	2 weeks	Synthetic	12.43 %
CH-106	4 weeks	Synthetic	23.88 %

After point counting was performed the percentages of overgrowth cement were calculated for the naturally weathered St. Peters sections and the freshly fractured synthetic quartz sections of each sample. As can be seen in Table 1, there is an increase in the percentage of overgrowth cement developed over time. Also, in the 1 week and 2 week samples (the two samples from which both the naturally weathered St. Peters and the freshly fractured synthetic quartz were recovered) the freshly fractured synthetic quartz developed a greater amount of cement than the disaggregated St. Peters sandstone grains. The distribution of overgrowth cement within the sample, observed during analysis, showed greater amounts of cement closer to the amorphous silica cement source, lessening with distance from the source.

When the percentage of overgrowth is plotted against time (Fig. 7) a change in the rate of cementation may be observed between two and four weeks. This change may also be observed in the results of Pepple (2007) and Winslow (2012) for experiments run at the same temperature and pressure, but different size fractions. In the results of this project, however, the freshly fractured synthetic quartz has clearly accumulated more cement than the naturally weathered St. Peters sandstone grains whereas the results of Pepple (2007) and Winslow (2012) show the opposite.
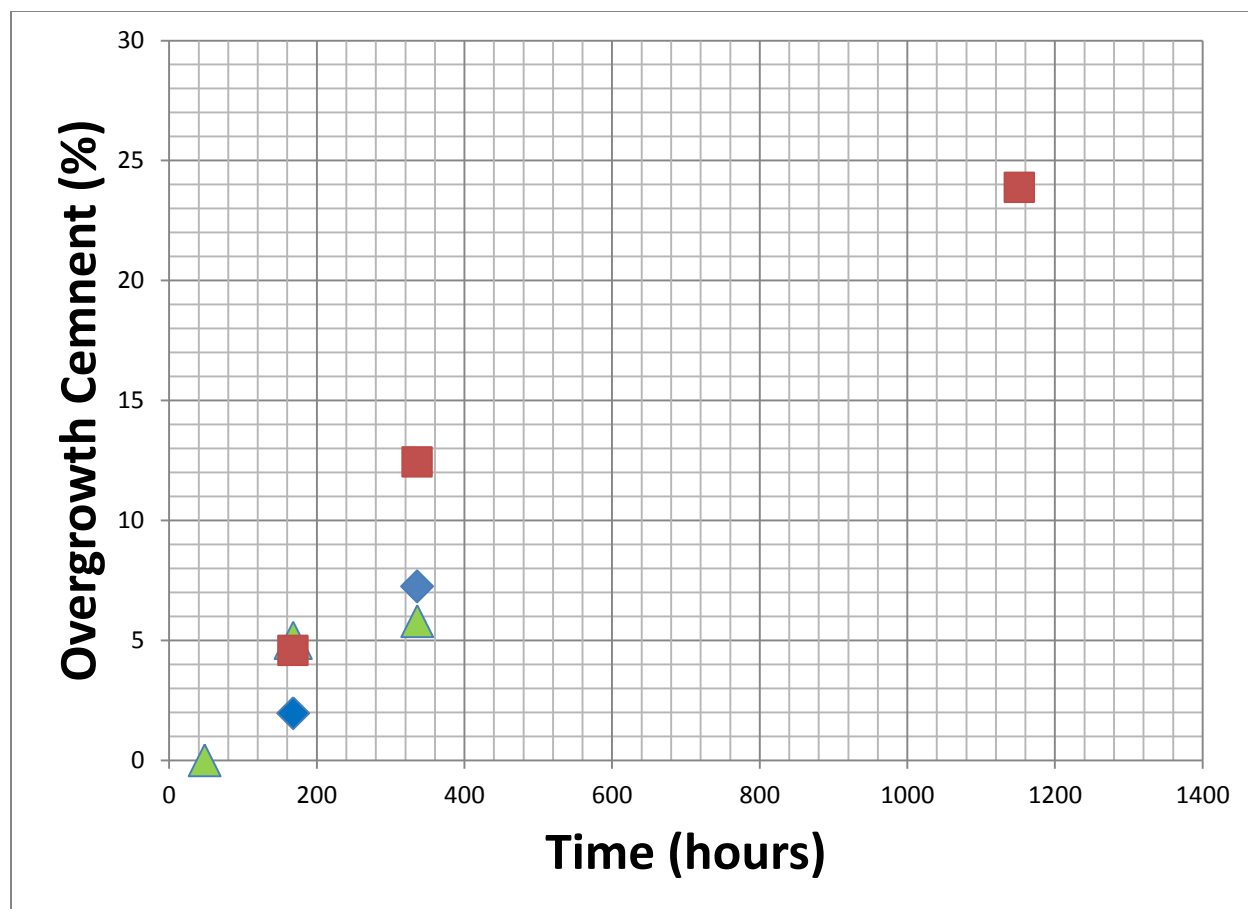
Figure 7: Plot showing the amount of cement formed over time in the naturally weathered disaggregated St. Peters sandstone (blue diamonds) and fresh-fractured synthetic quartz (red squares) of each sample as a function of time. Green triangles are data from Williams et al. (2015) for St Peter samples of the same size fraction run at the same temperature and pressure conditions as in this study. Estimated uncertainty is ±1.3 based on Winslow (2012).

Discussion

The results of this project appear to agree with Lander et al. (2008) who predicted that a freshly fractured surface would develop cement at a faster rate than a weathered surface. Lander et al. (2008) proposed that damage and adhesions to the grain surface would act as nucleation discontinuities for the developing overgrowth cement, causing smaller crystals of quartz cement to form on the weathered grain than the less inhibited fractured grain. These smaller crystals grow into a euhedral crystal form faster than the larger crystals and, as a euhedral grain surface has lower energy than a non euhedral surface, the growth rate on these surfaces slows. This is

illustrated in figure 8, where the grain surfaces with higher surface discontinuities have not only less overgrowth, but a higher percentage of the overgrowth developed is designated as a euhedral surface.
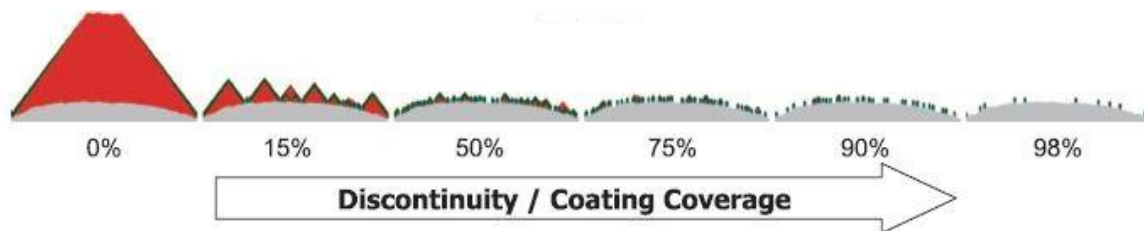
Figure 8: A simulation of quartz grain overgrowth and the effect caused by nucleation discontinuities on the grain surface. In the figure, red color represents a non-euhedral grain surface while the green color represents a euhedral grain surface. Adapted from Lander et al. (2008).

The results of this project do not agree with the findings of Pepple (2007) and Winslow (2012), however. When compared using the same temperature and pressure conditions as this project, the fractured synthetic quartz used by Pepple (2007) shows less growth than the natural disaggregated St. Peters sandstone grains used by Winslow (2015). Several factors may cause this discrepancy, including personal differences in data collection. Also, as found by Williams (2012), the differing grain sizes (125-250μm for the crushed synthetic and 90-500μm for the St. Peters) between the two sample sets may cause an effect similar to the grain surface discontinuities described by Lander et al. (2008). In this case, the smaller grain size cause overgrowths to form euhedral growth forms faster than on larger grains, slowing the rate of overgrowth development. This effect was removed in this project by using samples of like grain size fractions and, with its removal, the data again supports fresh fractured surfaces having a higher rate of precipitation than weathered surfaces.

The consistent decrease in precipitation rate after a two week period at the experimental temperature and pressure, shown both in the results of this project (Fig. 7) and in the results of Pepple (2007) and Winslow (2012) (Fig. 2), remains unexplained. At this time, one or both of

two causes is most probable. As proposed by Lander (2008), this could represent a period when euhedral growth forms dominate the overgrowth crystals, causing a decrease in the precipitation rate. Alternatively, this decrease in precipitation rate could represent a decrease in the degree of supersaturation of the solution as the amorphous silica source recrystallizes to a less soluble form during the experiment. Although an adequate amount of amorphous silica was added to the reaction vessel to fuel crystallization for this amount of time, the temperature and pressure condition of the experiment could cause the amorphous silica to recrystallize into another, less soluble form such as cristobalite. A closer examination of the remaining source material, visible under cathodoluminescence imaging due to the blue color of the $AlCl_3$ tracer, could help to resolve this question.

Conclusion

While preliminary, the results of this project indicate that precipitation rates may indeed be greater for fractured surfaces than weathered surfaces of quartz grains. These data may explain why in quartz-rich hydrocarbon reservoir rocks zones of fracture preferentially develop cement. The effect of cementation on the properties of reservoir rocks is great, controlling the permeability and porosity that dictate transport and storage of hydrocarbons in the rock unit. As understanding of this process progresses, understanding of the properties of hydrocarbon reservoirs may improve.

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