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Analysis of Quartz Dissolution Rims

by

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INTRODUCTION

The ancient Chinese invented porcelains thousands of years ago. With much different technology, they were able to create many unique bodies and glazes. One of the mysteries of ceramic engineering is how they were able to make such ceramics and what parameters did they use. Specifically, the firing parameters they used to create their ceramics.

The properties of porcelain make it very appealing to artists and engineers alike. It is hard, smooth, chemically inert, resistant to sharp changes in temperature, and translucent. Porcelain is created from raw materials mined from the earth. Clay, quartz, and feldspar are the primary materials, though this can vary. These raw materials are mixed together to create clay, and water is added to change the formability of the clay, otherwise known as plasticity. Clay provides plasticity that allows to be formed into shapes. It is this property that allows clay to be manipulated into objects like cups, bowls, and plates. These objects are made by throwing clay on a pottery wheel. A potter takes a ball of clay and throws it on a rotating wheel, where it is centered and manipulated by the potter's hands and tools. More complex objects, such as toilet bowls, toilet tanks, and sinks can also be created out of clay using a process known as slip casting. Ceramic slip is created by adding clay and other materials to water and mixing. The ceramic slip is then poured into a gypsum mold, which is in the shape of a desired product. The gypsum will absorb the water from the slip and leave a hollow clay body, which is in the shape of the mold.

Once a body is made, it must be dried to eliminate moisture before firing in a kiln. Firing is the most important step in the ceramic process. It transitions the body from clay

into porcelain. Chemical reactions occur within the clay that changes the composition of the body, thus changing the properties. Porcelain is much harder and tougher than clay.

One proposed model involves using the microstructure of the ancient porcelain samples to determine the firing parameters, specifically dwell (firing) time and temperature. When the porcelains reach a dwell temperature of approximately 1200° C, a chemical reaction occurs where quartz is aggressively dissolved into the glass phase. During this reaction, a rim can be seen around the border of quartz particles. It is proposed that measuring these quartz dissolution rims will indicate what temperature they were fired at and for how long. This information could potentially be of great use to archaeologists in analyzing the history of ancient ceramics. It was proposed that the onset of quartz dissolution rims depends on firing temperature and dwell time and that it is constant at those conditions.

Samples created by a previous student (Jindaporn Juthapakdeeprasert) were included because the firing conditions could potentially lead to results proposed in this problem. Nine samples were obtained. Three samples were fired at 1200° C, 1250° C, and 1300° for dwell times of 1 hour, 10 hours, and 100 hours.

Samples were also fired using a gradient furnace. They were placed in a tube so that each sample would have a slightly different firing temperature (a gradient). This will show the gradual change in microstructure and rim size as temperature changes. Ten samples were fired for 10 hours, and ten samples were fired for 32 hours in the gradient. It is proposed that both firing temperature and dwell time play a role in the firing process, and specifically in the development of quartz dissolution rims in porcelain.

All samples were prepared for viewing under the scanning electron microscope (SEM). This is a tool that is used to view the microstructure of materials, and in this case, to view the microstructure of porcelain. The microstructure can be viewed at very high magnifications. This project used magnifications of 1000x and 5000x. *Analyzing Digital Images*, an image analysis software package, was used to measure the quartz dissolution rim images.

Juthapakdeeprasert's porcelain samples showed some trends in terms of quartz dissolution rim thickness. Thickness increases with dwell time. If dwell time is kept constant, change in rim thickness is not present at 1200° C as much as it is at 1250° C and 1300° C. From 1250° C to 1300° C, the rim thickness increased the most. The difference between rim size at 1200° C at 1 hour and 1300° C at 100 hours is large.

SEM work shows that samples less than 1100° C will show dissolution rims. The 10-hour samples show dissolution between 1082°-1149° C. The micrographs show the transition to dissolution between these temperatures. For the 32-hour samples, the second lowest sample up peaked at 1119° C and shows dissolution rims.

A problem encountered in this experiment was that the dissolution rim measurements collected from the gradient furnace was scattered and did not show much trend. This made it difficult to evaluate the original hypothesis. The data collected did, however, provide an opportunity to solve a different problem. The temperature at which dissolution rims formed could be determined for each set of data based on the use of linear regression analysis with several sets of samples and data.

To determine the onset of quartz dissolution rims in these samples, a linear equation was created for each set of samples. The temperature at which the rim thickness

would be 0.1 μm, which can be easily seen in the SEM, was calculated. With the exception of one set of samples, these temperatures formed a linear relationship between firing temperature and dwell time. As dwell time increased, the onset temperature decreased. This is because the samples underwent more heat work, allowing the microstructure to develop to the point where dissolution rims would form.

Error analysis provided reasons why the data might be scattered. Assuming that the quartz particles are spherical, if the spheres are sliced at any location other than the center, then the quartz dissolution rim thickness will be altered. It is also unclear if the rim is uniform around the quartz particle. This may be why some rims are larger or smaller than others. It would be beneficial to measure more quartz particles per sample to get a better average of the rim thickness for each sample.

Quartz dissolution rims were analyzed to determine if the thickness could be linked to firing temperature and dwell time. Analysis of gradient runs shows that dissolution rims depend on both temperature and dwell time. Quartz dissolution was found to begin before 1200° C, thus disproving the original hypothesis of this work. A different problem arose that was more solvable with the data collected. The onset of quartz dissolution rim formation was calculated using linear regression analysis. This can be seen when comparing samples at the same temperature, but with significantly different dwells. Future work could help narrow down the effects of dwell time on quartz dissolution rims. Performing a 100-hour gradient could provide a broader range of dissolution rims at various temperatures. More rim measurements per sample will provide a better idea of average rim size per sample. This would be able to further study the effect of dwell time on the onset temperature of quartz dissolution rims.

The results of this study have shown that the formation of quartz dissolution rims is a function of both firing temperature and dwell time. In general, as firing temperature and dwell time both increase, the quartz dissolution rim thickness increases. Similarly, the onset temperature of dissolution rims decreases as dwell time increases. This result is a large step towards helping to identify firing conditions of ancient Chinese pottery.

ANALYSIS OF QUARTZ DISSOLUTION RIMS

BY

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ABSTRACT

Previous thesis work has recently built on the fact that quartz dissolution rims are dependent on dwell temperature. It was sought after to determine if the dissolution rims were also dependent on the temperature at which dwells were held. With results from gradient runs not yielding reliable data, the scope of the thesis was changed. It was thought that analyzing both dwell temperature and time would help determine the onset temperature of quartz dissolution. With analysis of existing samples, which were fired at fixed temperatures and times, the onset temperature of quartz dissolution could be calculated using linear regression analysis. A linear regression analysis was used on each set of samples to obtain the onset temperature. This yielded a linear relationship between dwell time and onset temperature. Error analysis determined that the some differences in rim thicknesses could be attributed to where the quartz particles were sectioned. Future work to further observe this relationship could include a 100-hour run to help further determine the data. Analyzing more rims per sample will result in a more accurate average rim thickness.

I: INTRODUCTION

Porcelains have been used to make objects for a long time. They are one of the most widely used and complex ceramic systems known. Of particular interest is the microstructural evolution of porcelain during the firing stage. Above 1200° C quartz begins to dissolve into the glass phase leaving behind a dissolution rim around the quartz particles. [1-3] The thickness of this rim can be measured and used to determine the firing conditions (time and temperature) of porcelain.

The objective of this experiment is to discover an algorithm that can relate dissolution rim thickness to firing temperature and to determine the minimum temperature that quartz dissolution rims begin to appear in the microstructure. With future work this information may potentially applied to ancient pottery to help determine the historical firing conditions of pottery.

II: LITERATURE REVIEW

Lundin, Iqbal, and Lee have studied the microstructural evolution of porcelain. They all found that above 1200° C quartz begins to dissolve into the glass phase, leaving behind a dissolution rim around the quartz grains.[1-3] Experiments by Lerdprom[4] and Ouyang[5] provided possible methods for analyzing firing behavior of porcelains. In particular, Lerdprom and Ouyang determined that measuring the quartz dissolution rims would be crucial for analyzing firing temperatures and times. Lerdprom previously had developed a method for accurately measuring the quartz dissolution rim around a particle. Measurements were taken perpendicularly to the particle edge to accurately measure the thickness, as show in Figure 1.[4] The figure also shows that eight measurements were taken on each particle. All particles within a field of view were measured, which increases the ability of obtaining an accurate dissolution rim average.

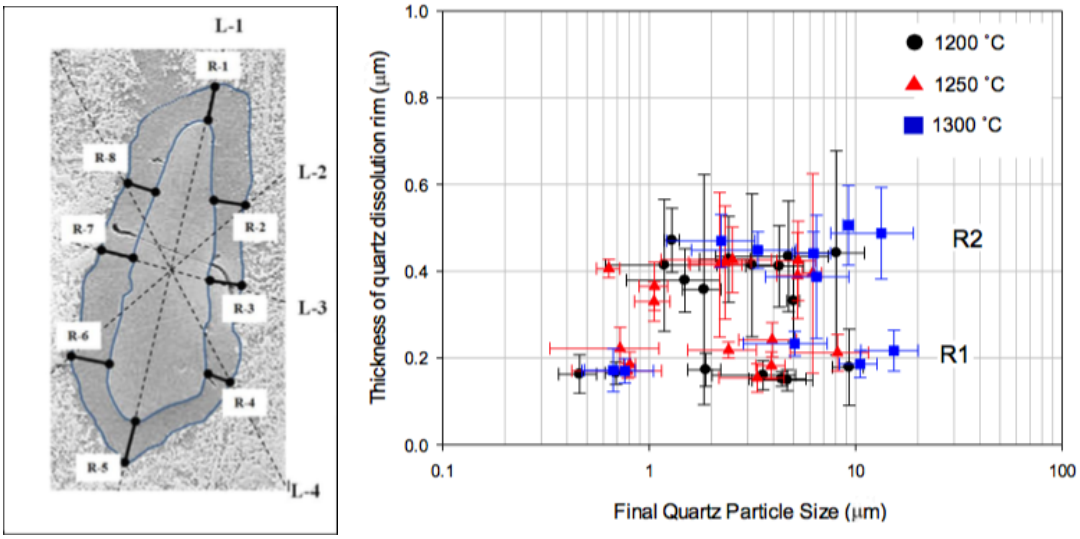

Figure 1. Sample quartz particle with measurement lines, along with dissolution rim thickness as a function of final quartz particle size.

III: EXPERIMENTAL PROCEDURE

Two sets of samples were used to analyze and measure quartz dissolution rims. Previous porcelain bodies fired by Jindaporn Juthapakdeeprasert[6] were used to analyze the microstructure. Green body rods prepared by an undergraduate lab (ENGR 112, Spring 2015) were also used, with a different set of firing conditions. Both sets of fired and analyzed samples were then compared against work completed by Wirat Lerdprom.[4]

Heat Treatment

Samples by Juthapakdeeprasert were fired at temperatures of 1200°C, 1250°C and 1300°C for 1, 10 and 100 hours each.[6] For the green body rods, 20 samples were cut down to 2.54cm pieces. Using a "D" tube as the holder, samples were spaced evenly along the tube. Starting at the peak hot zone, eight samples where spaced 2.54cm apart towards the front of the tube, and one sample was spaced 2.54cm away, towards the back of the tube. Two runs were completed, each with ten samples set up identically, with the first gradient run going for 10 hours and the second run going for 32 hours. Periodically throughout the run, samples were individually checked for temperature, below in Table I the measurements can be seen, along with the plot of temperatures in Figure 2.

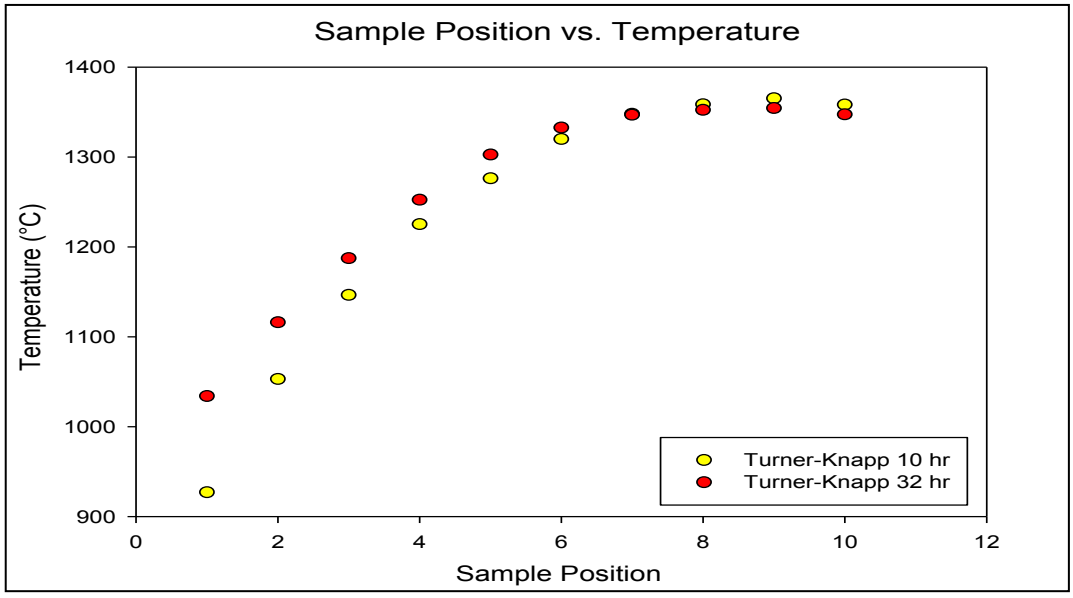

Figure 2: Temperature as a function of sample position.

Table I. Gradient run temperatures.

Position	10-Hour	32-Hour
1	927 ± 16	1040 ± 8
2	1053 ± 29	1118 ± 3
3	1146 ± 2	1190 ± 5
4	1225 ± 2	1254 ± 3
5	1276 ± 4	1305 ± 5
6	1320 ± 3	1334 ± 2
7	1348 ± 2	1347 ± 1
8	1359 ± 1	1353 ± 1
9 (Peak)	1365 ± 1	1355 ± 1
10	1358 ± 1	1348 ± 2

Sample Preparation

Each of the samples were cut and then mounted. From here samples were grinded and polished, with each sample run on four different grits (60, 180, 320, 600) and two diamond slurries (1μm, 6μm). At each step the sample was run for five minutes, with five pounds of force. With each sample polished to a satisfactory level, they were then HF etched using 20% HF for 10

seconds each at 0°C, to remove the glass phase on the surface. After grinding and polishing were complete, all samples (except 10-hour, sample 1) were imaged using the SEM. Each sample was imaged with the intent of producing a section of the sample most populated with quartz particles.

Rim Analysis

All quartz particles were analyzed and measured by the method developed by Lerdprom, which was outlined previously.[4]

Error Analysis Associated With Curvature

During the grinding and polishing step, particles are being cut into at angles, which are indeterminable. Figure 2 below shows how a random slice through a plane of spherical particles may lead to various different cross-sectional cuts.

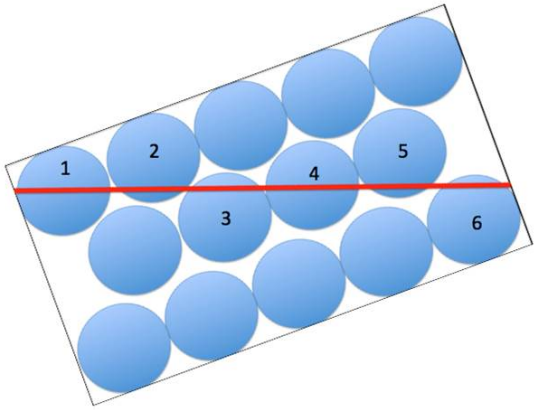

Figure 3. Hypothetical sample plane with particles being cut.

As seen in the figure, each particle is not cut evenly, with some being cut directly through the middle and others more towards the top or bottom of the particle. Due to this issue, a quartz particle in the sample may give a misleading rim size during measurement. During measurement, a particle may give a dissolution rim measurement larger than the temperature may allow. The

more off-center the particle measurement is, the larger the dissolution rim will appear to be. Figure 3 shows how position within the particle will change dissolution rim, along with Figure 4, which shows a plot of how rim size increases.

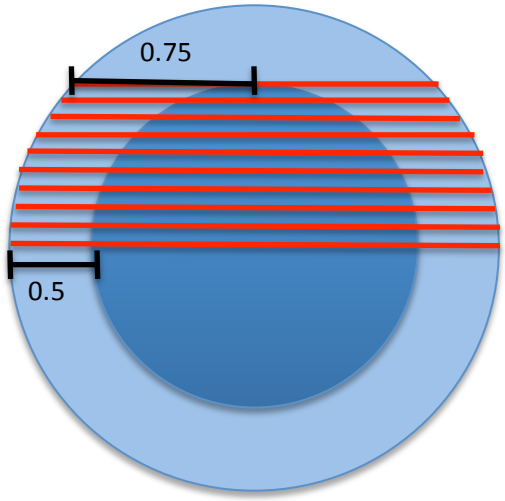

Figure 4. Hypothetical particle and dissolution rim with different cross-sectional cuts.

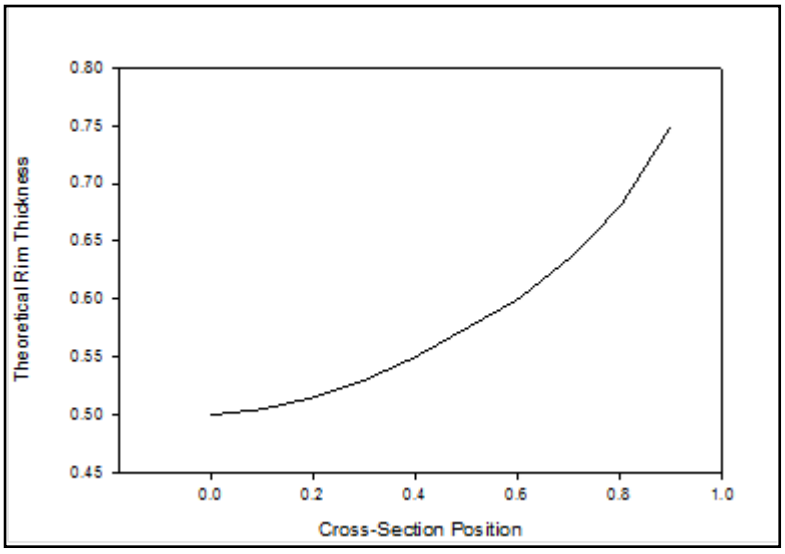

Figure 5. Rim Thickness as function cross-section position

As illustrated, the dissolution rim thickness increases as the cross-sectional cut moves further from the center-point of the particle. With this being shown, it can be estimated that the quartz dissolution rim may be up to 50% greater when the particle is not cut through its center-line

IV: RESULTS AND DISCUSSION

In Juthapakdeeprasert's porcelain samples, thickness increased with temperature and dwell time. With dwell time kept constant, the dissolution rims are smaller because the dissolution was less aggressive in samples fired for shorter times at lower temperatures. Rim thickness increased as temperature and time increased. From 1200° C to 1300° C, for all three dwell times examined, a significant change in rim thickness was observed. The smallest rim was observed at 1200° C for 1 hour and the largest rim was observed at 1300° C for 100 hours.

In the gradient furnace, two batches of porcelain were fired at 10 and 32 hours to determine the lowest temperature that quartz dissolution rims begin to form. The data was plotted to compare temperature and rim thickness. Linear regression was used to determine the temperature at the onset of quartz dissolution rims, with the condition that rims would be first visible at 0.1 μm in the SEM. The 10-hour batch began showing rims at 941° C, which according to the phase diagram, is impossible since there is a eutectic at 990° C. As seen by error analysis, up to a 50% increase in quartz dissolution rims can be seen. For the 10-hour gradient run, some samples produced dissolution rims that were deemed to be larger than possible. Table II shows the average dissolution rim thickness for the 10 samples in the run. Samples 9 and 10 both exhibited dissolution rims larger than expected. Due to the larger rims, data was shown that onset dissolution had to begin around 941°C. With knowing that this is not possible due to the eutectic point, the particles analyzed were determined to have cross sections further away from their

midpoint. If the samples experience a 50% increase in rim size, samples 8 and 10 would expect to have a 3.51μm and 2.85μm dissolution rims, respectively.

Table II. Average rim size (μm) and temperature (°C) for each sample for both the 10 and 32-hour run, respectively.

Position	Temperature (10 hour)	Average Rim Size	Temperature (32 hour)	Average Rim Size
1	927 ± 16	-	1040 ± 8	-
2	1053 ± 29	1.53 ± 0.51	1118 ± 3	0.58 ± 0.1
3	1146 ± 2	1.12 ± 0.15	1190 ± 5	1.59 ± 0.2
4	1225 ± 2	2.24 ± 0.34	1254 ± 3	2.71 ± 1.04
5	1276 ± 4	3.67 ± 1.02	1305 ± 5	4.15 ± 0.65
6	1320 ± 3	-	1334 ± 2	10.71 ± 3.88
7	1348 ± 2	1.38 ± 0.35	1347 ± 1	13.46 ± 4.83
8	1359 ± 1	5.26 ± 0.41	1353 ± 1	-
9 (Peak)	1365 ± 1	-	1355 ± 1	-
10	1358 ± 1	4.28 ± 1.31	1348 ± 2	7.66 ± 6.14

In both runs, some samples produced no particles with a measureable quartz dissolution rim. The 32-hour samples had a more realistic onset temperature of 1142° C. The onset of quartz dissolution rims started at higher temperatures as firing time increases. The gradient furnace data has a different slope than the data collected by Lerdprom and the samples fired by Juthapakdeeprasert. The data is still trending in the same direction, however. Figure 6 shows the trend lines of each set of data. Figure 7 shows the onset temperature of quartz dissolution rim formation.

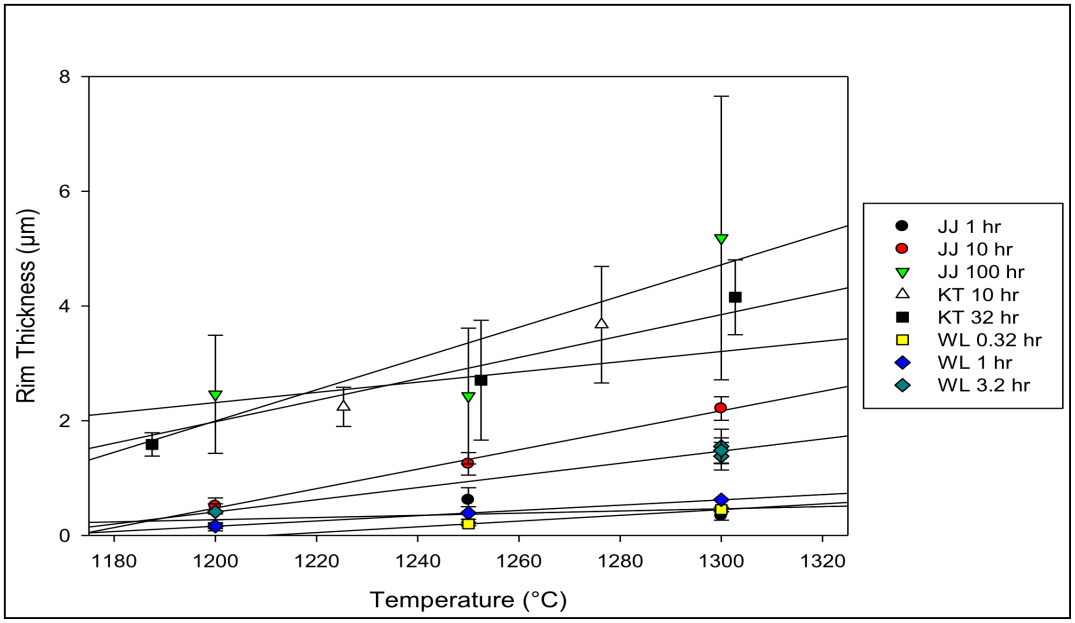

Figure 6. Change in rim thickness as temperature changes for data from gradient furnace samples, Juthapakdeeprasert's samples, and Lerdprom's samples.

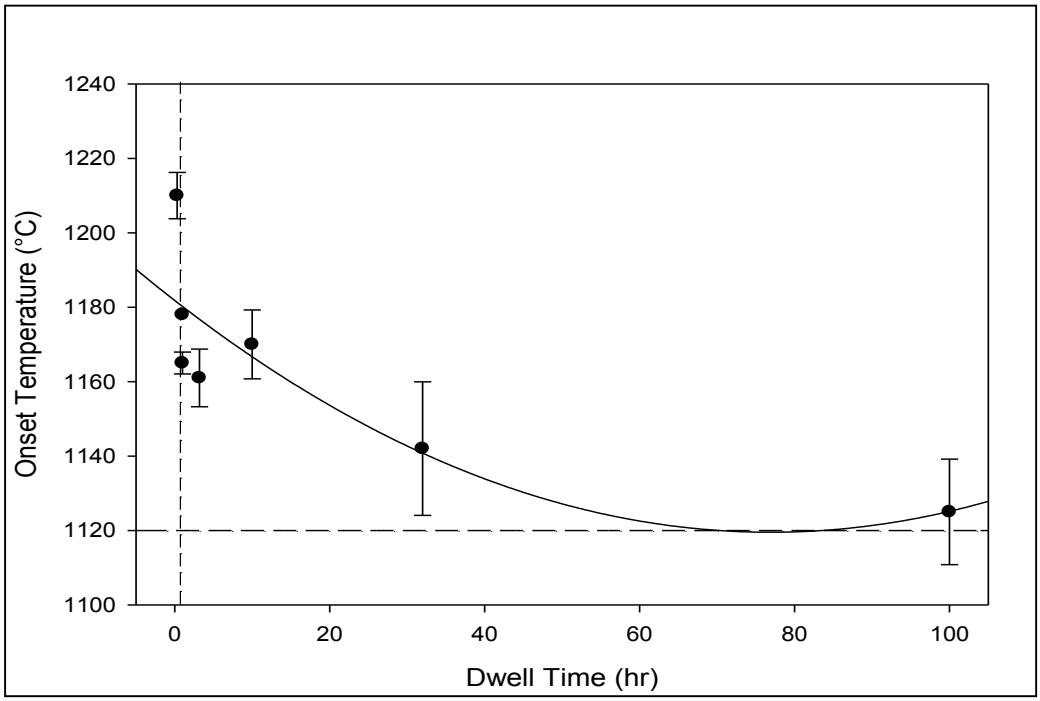

Figure 7. Onset temperature of quartz dissolution rims.

The data collected from the 10 and 32-hour gradient furnace runs was compared to data taken from Lerdprom's thesis and Juthapakdeeprasert's samples. The gradient furnace samples did not correlate as well as Juthapakdeeprasert and Lerdprom's samples did. A possible reason for this apparent poor correlation could be that the specimens were not sectioned around the centerline. Limited sample size also may play a role in obtaining data. With a specimen only containing a few quartz particles, a greater chance for a particle to skew data is possible. A solution to this problem would be to obtain measurements from enough quartz dissolution rims to negate a large standard deviation and yield a better dissolution rim average. Lastly, the chemistry of all three data sets was different. This may lead to a difference in the ability of the quartz particle to begin dissolving.

V: CONCLUSION

In this experiment, 10 and 32-hour gradient runs were carried out to compare to samples fired from different experiments. The quartz dissolution rims were analyzed on each set of sample to see if any trends could be seen. While the data did not line up perfectly between each sample, it was observed that quartz dissolution rim thickness correlates with temperature and dwell time.

For each set of samples, linear regression was used to determine the onset of quartz dissolution rims (when the rim thickness was 0.1 μm). With one exception, this trend was linear. This also suggests that quartz dissolution rim thickness depends on temperature and dwell time. As seen, the onset of quartz dissolution rims can start at 1120° C, with a longer dwell time. This data shows that quartz dissolution will not begin any lower, no matter the length of the dwell time.

Future work to further understand this project would involve performing a 100-run in the gradient furnace. Measuring several different quartz dissolution rims per sample would yield more reliable rim thicknesses. With this work, a maximum of two dissolution rims were measured per sample, which led to a bit of misleading data. More images per sample would prove itself to be helpful, by allowing enough dissolution rims per sample to be measured. With a large set up samples, the rim size average would be more refined and allow for less scatter in the data.

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VII: APPENDIX

Table III. Raw data of 10-hour gradient furnace run.

10-Hour					
Sample	**1**	**4**	**9**	**AVERAGE**	**STDEV**
1	913	924	944	927	16
2	1024	1053	1082	1053	29
3	1145	1146	1149	1147	2
4	1224	1225	1227	1225	2
5	1273	1275	1281	1276	4
6	1318	1319	1323	1320	3
7	1347	1347	1350	1348	2
8	1358	1358	1360	1359	1
9	1365	1365	1366	1365	1
10	1359	1359	1357	1358	1

Table IV. Raw data of 32-hour gradient furnace run.

32-Hour						
Sample	**1**	**12**	**24**	**29**	**AVERAGE**	**STDEV**
1	1022	1035	1039	1040	1034	8.29
2	1112	1116	1118	1119	1116	3.10
3	1180	1188	1191	1191	1188	5.20
4	1248	1253	1254	1255	1253	3.11
5	1296	1301	1306	1308	1303	5.38
6	1330	1332	1334	1335	1333	2.22
7	1346	1347	1347	1348	1347	0.82
8	1352	1352	1353	1353	1353	0.58
9	1354	1354	1355	1355	1355	0.58
10	1345	1349	1348	1348	1348	1.73