

Augustana College Augustana Digital Commons

Celebration of Learning

Effects of Heat Treatment of Spinel as Determined by VIS/NIR and Raman Spectroscopy and XRD

Jill Reale

Augustana College, Rock Island Illinois

Dr. Michael B. Wolf

Augustana College

Follow this and additional works at: <https://digitalcommons.augustana.edu/celebrationoflearning>



Part of the [Geology Commons](#)

Augustana Digital Commons Citation

Reale, Jill and Wolf, Dr. Michael B.. "Effects of Heat Treatment of Spinel as Determined by VIS/NIR and Raman Spectroscopy and XRD" (2019). *Celebration of Learning*.

<https://digitalcommons.augustana.edu/celebrationoflearning/2019/posters/11>

This Poster Presentation is brought to you for free and open access by Augustana Digital Commons. It has been accepted for inclusion in Celebration of Learning by an authorized administrator of Augustana Digital Commons. For more information, please contact digitalcommons@augustana.edu.

Effects of Heat Treatment on Spinel Determined by VIS/NIR and
Raman Spectroscopy

A senior thesis written by

By Jill Reale

5/3/19

Augustana College
Rock Island, Illinois

Abstract:

Heat treatment is done to improve the color and clarity and, therefore, the value of gemstones. The objectives of this study include observing color and inclusion changes in pink spinels after heat treatment and analyzing structural changes within differently colored spinels using Raman Spectroscopy. We expected the heat treatment to yield color changes and fading of small inclusions. To determine changes, Vis/NIR spectroscopy data were taken before and after heating. Raman spectroscopy was used in this study to observe structural changes in spinels that were exposed to heat. Five experiments involved cutting and polishing spinel samples and tracking their color and inclusion changes after heat treatments. Three other experiments contain differently colored spinel samples that have been halved, heated, and compared spectroscopically. This study contains 73 spinel samples that have been heated and analyzed.

Introduction:

Spinel is a gem-quality mineral that is rising in popularity within the gem industry. According to the Gemological Institute of America (GIA), spinel has desirable attributes as a gemstone, such as its variety in color, abundance, hardness, and lower prices. Because of spinel's formula, $(\text{Mg}, \text{Mn}, \text{Zn}, \text{Fe}^{2+})(\text{Al}, \text{Fe}^{3+})_2\text{O}_4$, trace elements are often present and can produce a wide variety of colors. The most popular colors in the gem industry for spinel are red and pink (Rosett, 2018). Currently, blue and purple gemstones are also in high demand for jewelry (GIA). In the article, *Spinel History and Lore*, GIA mentions that spinel crystals are abundant and often mined in South-Eastern Asian countries like Thailand and Myanmar. Spinel do not only make good jewelry for their vivid colors, but also their hardness. The hardness of spinel gems falls between 7.5-8 on the Mohs Hardness Scale which protects its surfaces from everyday scratches (Perkins, 1998).

With all these great characteristics, one may ask, “Why is spinel cheaper than other valuable gemstones?” In its history, spinel has often been mistaken for corundum (sapphire and ruby) because of its wide range in colors and beauty. Because of this confusion, spinel is often sold as a less expensive alternative (Rosett, 2018). Yet, spinel has many redeeming qualities for the gem industry and its customers. This research project is working towards improving the color and clarity of spinel samples and increasing their value in the market. The objectives here are to use heat treatment to change the spinel samples’ colors in a desirable way. This research project is also determining if heat treatment can diminish inclusions, or impurities, that may decrease the gem values. With desirable colors and clarities, the demand for this mineral may increase in the gem industry.

Inclusions are impurities that grow or appear within a mineral as it forms. GIA prices gemstones by using the set guidelines of the “4Cs of Gem Quality”. The 4Cs are cut, color, clarity grade, and carat weight. If a gemstone has few to no inclusions, it has high clarity which may increase a gem’s price. This study works towards improving two of out of the 4Cs, color and clarity.

This research project includes two types of data collection to understand the causes of color change with heat treatment. VIS/NIR (Visible Light and Near Infrared) spectra has been taken before and after heating to see if the treatments change any of the samples’ spectra. Raman Spectroscopy, a digitized way to read a mineral’s crystalline structure, data was also collected in an effort to determine if the gems’ crystalline structures changed during heat treatment. Performing these data collections may provide an answer as to why spinels change as they do. A heating pattern that could predict similar color change results could also be discovered.

Discovering a heating pattern would be valuable to the gem industry so results could be predicted, and heat treaters would not need to deal with trial and error.

Background:

The formula for spinel is $(\text{Mg,Mn,Zn,Fe}^{2+})(\text{Al,Fe}^{3+})_2\text{O}_4$, however, the more general way to write its formula is, AB_2O_4 . The formula is written this way because the cations of the A-sites and B-sites can vary. The A-site is often Mg, Mn, Zn, or Fe^{2+} , but can sometimes be Co, V, Cr, Ti, and Ni. The B-site is often Al but can be Fe^{3+} as well. These cations are always bonded to O_4 (Rosett, 2018).

The National Programme on Technology Enhanced Learning (NPTEL) discusses spinel's crystal structure and how its elements bond. Spinel is part of the cubic crystal class and grows octahedral crystals. Figure 1 comes from a course taught by NPTEL and shows the atoms bonded within the crystal system. The octahedral and tetrahedral sites bond with the oxygen atoms to form spinel crystals.

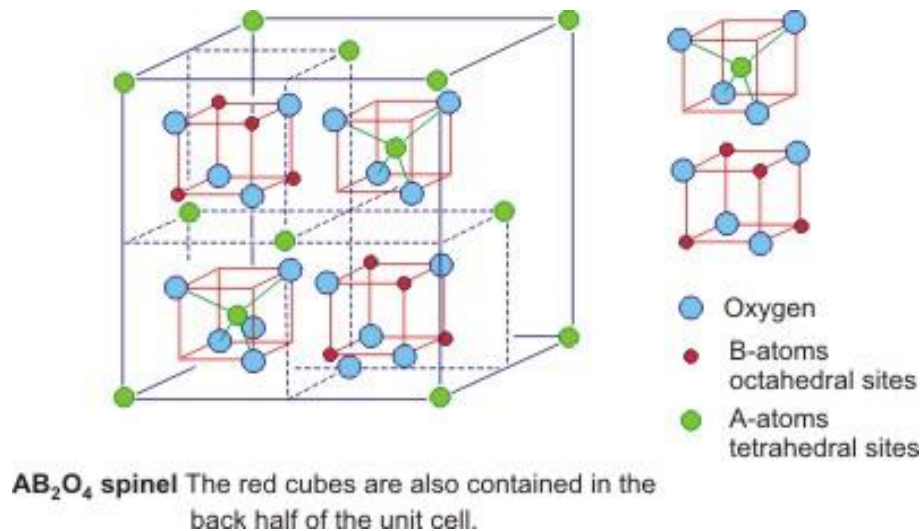


Figure 1: Shown are the bonds with spinel's crystal structure. A-site and b-site atoms pattern can range between certain elements. Spinel is part of the cubic crystal class and maintains octahedral and tetrahedral sites bonded together (NPTEL).

In an experiment studying bonds between certain alloy materials, Lee *et al.* discuss how their results of their samples reacting to heat. The alloys being studied consist of gold, platinum, and indium. The study found that if the alloy is heated at a lower temperature, its bonds will remain stronger than if they were exposed to higher temperatures. Lee's results show that certain heats change their bonding strengths at a molecular level (Lee *et al.*, 2009). Though heat by itself will not change the spinel samples compositionally, the tetrahedral sites, octahedral sites, and their bond strengths can change (Widmer *et al.*, 2014). This research on spinels includes gathering Raman Spectroscopy before and after heat treatment to determine whether heat can change the bonds of samples. Gemstones get their hues from their composition, or the elements that make them up. How an element is bonded within the crystal lattice can also affect the gem's physical appearance. An example is provided in a previous study: if cobalt is bonded in the a-site, or tetrahedral site, the spinel could maintain a dark blue hue. If cobalt is bonded in the b-site, or octahedral site, the spinel may be pink (D'Ippolito, 2018).

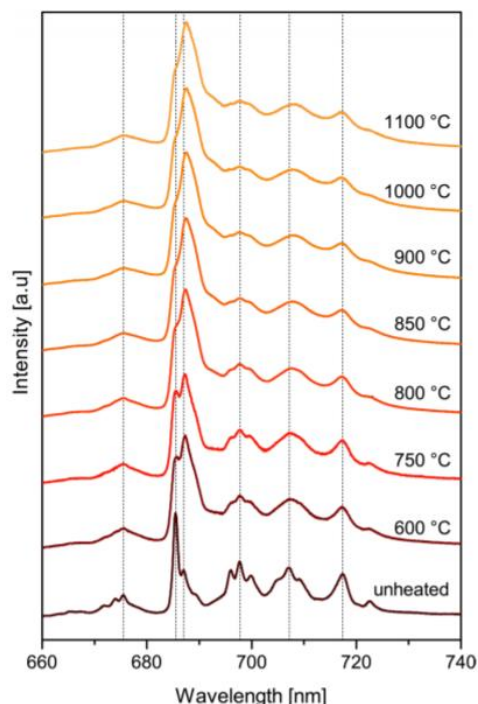


Figure 2: Example of Raman Spectra from Widmer *et al.*, 2014 research on spinel bonding after heat treatment. The peaks widen along the x-axis which shows that the bond strength has changed in some way (Widmer *et al.*, 2014).

Raman Spectroscopy has been used by previous heat-treating experiments to understand a mineral's crystal structure and bonds. Samples are typically analyzed before and after heating, so the results can be compared. Widmer *et al.* (2014) share their experimental results in their research on spinel spectra. Their spinels were exposed to 600, 700, 800, 850, 1000, and 1100°C. The spectra show a normal spinel signature for the non-heated sample, but with each increase in temperature, the peaks in the spectra widen. The peaks widths are measured and show that the bond strengths have changed in these samples after being exposed to temperatures starting at 600°C (Widmer et al., 2014). These spectra examples are shown in Figure 2.

This research project does not have chemical or bond strength data, so another analysis must be taken. A Principal Component Analysis (PCA) is a function of *R*, a data software that can perform a multiple variable analysis which compares a dataset's variance (Varmuza and Filzmoser, 2009). This function shows variance in samples but does not tell what the variance entails.

Visible/Near Infrared (VIS/NIR) data were collected using a spectrometer with an UV laser. Spectroscopy is the measurement of intensity of light interacting with absorbency of an object, like spinel. A light or laser applies its wavelength to the sample and an absorbance pattern, or spectra, is produced (Martin and Pretzel, 1991).

Methods and Materials:

Methods for experiments analyzing color and inclusion changes:

Over 100 pink spinel samples were donated to Augustana College's Geology Department by Michael Couch and Associates, a gemstone trading company in Iowa. Fifty-four of these pink spinel samples were prepared for color and inclusion analyses. From these set of experiments,

Experiments 4, 5, 6, 12, and 13, our goals included capturing pictures of colors, inclusions, and spectrum before and after heating experiments and further comparing the results.

Before heating, each gem was cut flat and polished smoothly, so that the inclusions could be viewed and analyzed with a microscope. An ISOMET Diamond Blade Saw was used to cut each sample. After the first cut was made, the sample was moved about 3 millimeters closer to the diamond saw and a parallel cut was made. This created 36 flat slices that were ready to be polished. The diamond saw used is shown in Figure 3. Polishing was done on an automatic polishing disc that is pictured in Figure 3. The discs were covered in grit-varying diamond paste that range from 45 μ m to 3 μ m. The 45 μ m grit is coarse and grinds away any large scratches that are left behind from the saw. After this grit, 30 μ m diamond paste is used to grind away the smaller scratches left behind by the 45 μ m grit. Following 30 μ m grit, comes 15 μ m, then 6 μ m, and 3 μ m. By 3 μ m, the spinel surfaces are so clear that the inclusions can be viewed with a microscope and captured by a camera. To get a clear polish, it took about 30 minutes per spinel.



Figure 3: On the left shows the saw that was used to cut the spinel samples. On the right shows the polishing wheel. This machinery was used at Augustana College in Rock Island, Illinois.

The coarser grits (45 and 30 micrometers) polished the samples for about 1-2 minutes. The finer gritted diamond pastes took around 5 minutes to make a difference.

To capture the color of each sample, a digital camera, DinoCapture 2.0, was inserted into a microscope and pictures were taken. After completing Experiments 4 and 5, it became clear that before and after pictures are not the best way to compare colors. The camera used is not good enough quality to capture to exact color of the sample. For Experiments 6, 12, 13, samples were cut in half after they were polished. Now, heated samples can be compared to their original color because every sample has been cut into a non-heated half and a heated half.

Before samples are heated, however, their spectra are taken with a GL Gem Spectrometer and a laser with a wavelength of 850 nm. The Visible/Near Infrared (VIS/NIR) data are captured with the spectrometer that is attached to a computer and is processed using a spectroscopy software called Spectragryph. Spectragryph lays spectra on top of each other and compares their differences. This research project is taking VIS/NIR data to answer if samples have the same spectra before and after heating and if change depends on temperature.

Heating was done in either of two furnaces at Augustana College. The hottest temperature achievable by the Sentro Tech Corp furnace is 1600°C. Experiments 4, 5, 6, 12, and 13 are listed in Table 1 along with their results. These experiments were done in the programmable furnace which was programmed to heat and cool down the samples slowly to avoid breaking. The temperatures shown in Table 1 were chosen with trial and error and research from other projects that involve heating spinels.

Samples from Experiments 1, 2, 3, 6, 12, and 13 all have a non-heated half and a heated half. These can be compared and analyzed separately, now. Samples from Experiments 4 and 5 are not cut into halves so their color change data are less noticeable and trustworthy.

Experiments analyzing color and inclusion changes:

-Table 1:

Experiment	Samples	Temperature	Time Interval	Average Results
Exp. 4	S_21, 18, 20, 15, 33, 23, 29a, 29b, 28, 32	1400°C	50 hours	Dulling of hue
Exp. 5	s_23, 33, 28, 32, 29a, 29b, 20, 15, 21, 18, 49, 53, 47, 14, 12, 52, 54, 16, 50, 68	850°C	72 hours	Dulling of hue
Exp. 6	s_58, 61, 63, 65, 59, 62, 64, 66	1500°C	167 hours	Dark pink to dark purple
Exp. 12	s_19, 22, 35, 37, 38, 79, 80, 81	1300°C	100 hours	Pink to peachy pink
Exp. 13	s_25, 60, 67, 69, 70, 71, 78, 72	1350°C	125 hours	Dark pink to dark purple

Experiments 1, 2, and 3 were not cut and polished as these samples are only being analyzed for color changes and their spectra. Three pink, three blue, three purple, three lavender, three green, and three black spinels were chosen and split between three experiments. Each of these experiments has one of each color. These samples have also been halved so the heated and non-heated halves can be compared. Each sample is labeled with its color and experiment (s1_B = “the blue spinel from experiment 1). The samples from Experiments 1, 2, and 3 are laid out in Table 2.

Experiments 1, 2, and 3 to be analyzed with VIS/NIR and Raman Spectroscopy:

-Table 2:

Experiment	Samples (all 6 colors)	Temperature	Time Interval
Exp. 1	s1_PP, s1_Pk, s1_B, s1_Bk, s1_G, s1_L	850°C	24 hours
Exp. 2	s2_PP, s2_Pk, s2_B, s2_Bk, s2_G, s2_L	1600°C	6 hours
Exp. 3	s3_PP, s3_Pk, s3_B, s3_Bk, s3_G, s3_L	1200°C	6 hours

Results:

Color Change Results:

The color change and inclusions results vary from experiment to experiment. The samples in Experiments 4 and 5 do not have accurate before and after pictures because of when and how their pictures were taken. The eight spinels in Experiment 6 underwent 1500°C for 167 hours. Six of these samples were originally dark pink while the other two samples were originally a light pink. As shown in Figure 4, all pink hues turned to purple hues after being exposed to the heat treatment. Samples 59 and 64 did not turn a deep purple as the others, but the dull purple hue is present.

The eight spinels in Experiment 12 underwent 1300°C for 100 hours. These samples yielded a less significant color change than in Experiments 6 and 13. Samples 19, 22, 37, and 79 yielded a peachy pink hue apart from their original pink hues. Samples 35, 38, 80, and 81 dulled into a lighter pink. The results can be viewed visually in Figure 5.

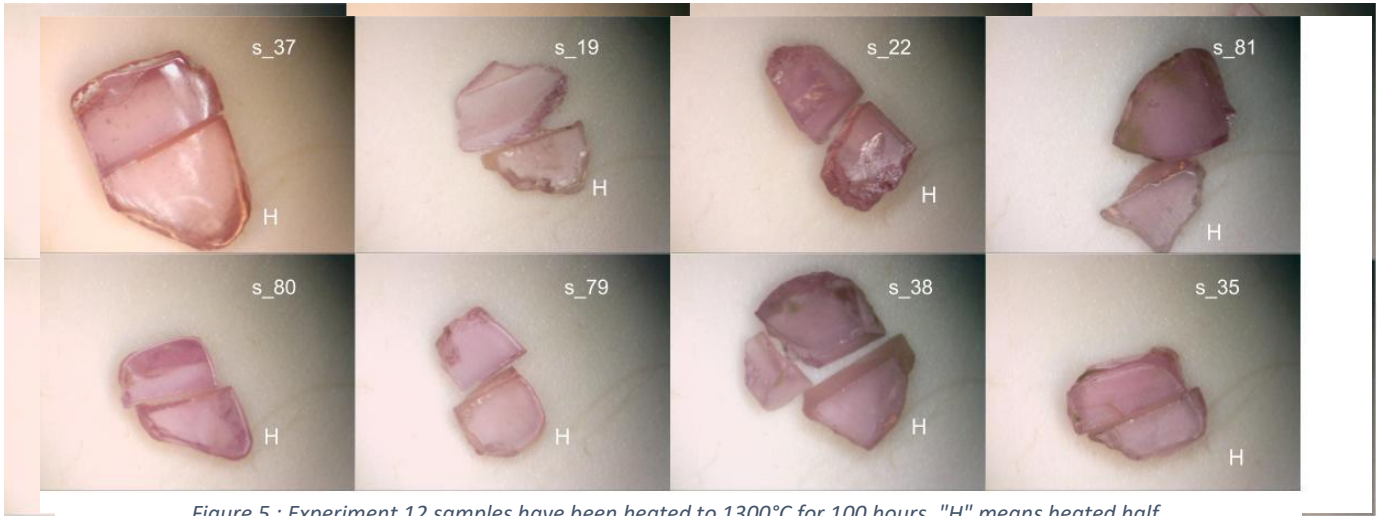


Figure 5 : Experiment 12 samples have been heated to 1300°C for 100 hours. "H" means heated half.
 Figure 4. Experiment 6 samples have been heated to 1300 °C for 107 hours. "H" means heated half.

The eight samples in Experiment 13 underwent 1350°C for 125 hours. These samples yielded purple hues after heat treatment. Samples 60 and 25 were originally lighter pink but also turned darker purple. The color changes of Experiment 13 can be seen in Figure 6.

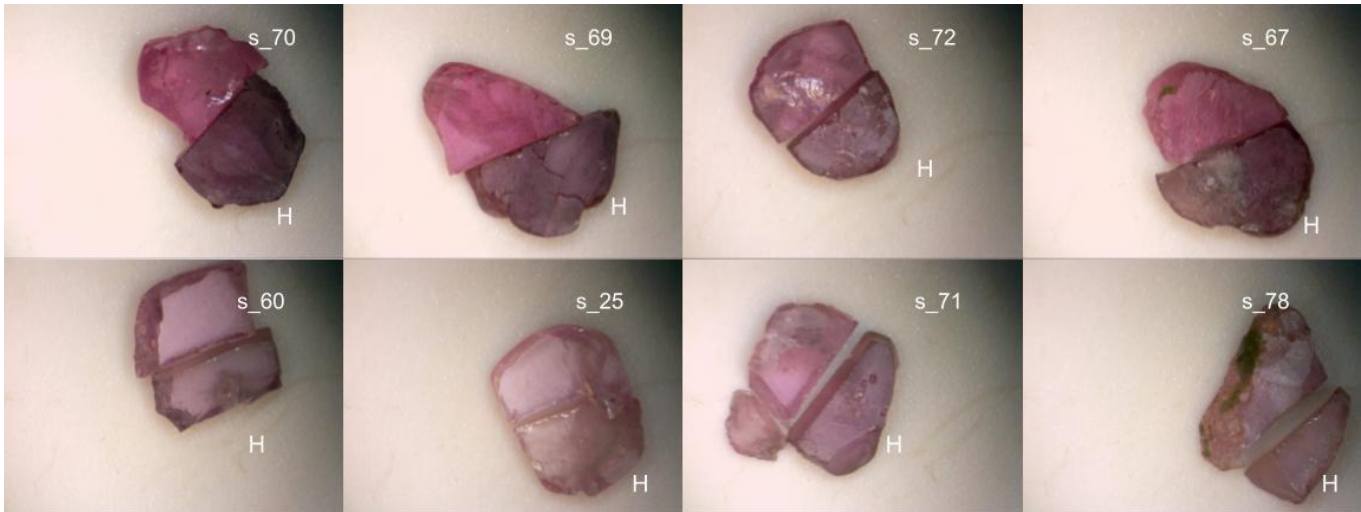


Figure 6: Experiment 13 samples have been heated to 1350°C for 125 hours. "H" means heated half.

Inclusion Results:

Only a handful of inclusions changed in some way after heating. Some inclusions diminished in size or faded, others spread or got worse, but most inclusions did not change

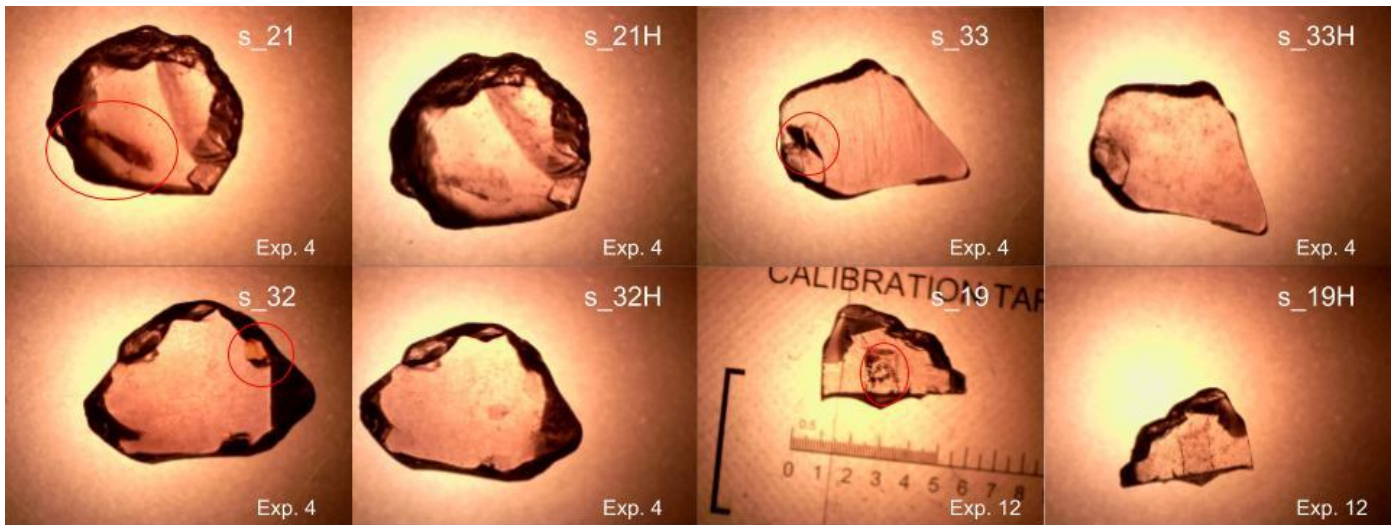


Figure 7: Some dark inclusions faded after heat treatments. These samples are from Experiments 4 and 12. The original inclusions are circled in red.

noticeably. Samples s_33, s_32, and s_21 of Experiment 4 saw a diminishing in some of their inclusions. Samples s_52 and s_49 of Experiment 5, s_19 of Experiment 12, and s_60 of Experiment 13 also contain diminishing inclusions. Experiment 6 samples did not have any increase in clarity.

Sample s_21 had a larger tubular inclusion that seemed filled or stained with a dark brown color. After heat treatment, this stain has left the tubular structure. Similar black stains disappeared from s_33, s_19, and s_49 after heating. Before heating, s_32 had an orange impurity that diminished. Samples s_52 and s_60 had more solid inclusions that faded after heating. In Figures 7 and 8, clarity changes can be viewed.

After heating, some inclusions became worse by either darkening or spreading throughout the crystal. Only samples from Experiment 5, which were exposed to 850°C for 72 hours, had inclusions to worsen. S_16 contained a crystal inclusion that evaporated into a white powder which has left a white, opaque hole. S_14's inclusions spread darker and longer. These inclusion changes can be viewed in Figure 9. Experiments 4, 6, 12, and 13 do not contain any

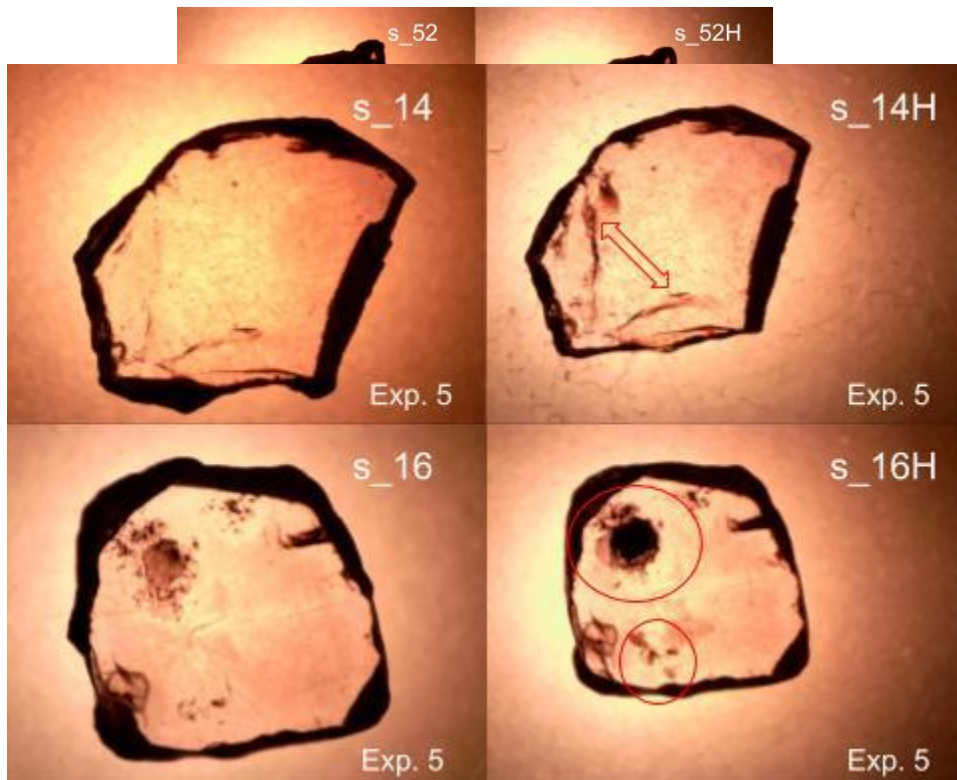


Figure 9: Two samples from Experiment 5 had inclusions spread or become more noticeable. The changed inclusions are circled or arrowed to in red.

samples with worsening inclusions.

Spectra Results:

VIS/NIR results show that each sample has its own spectra. Although each plot is similar, their peaks' structures show the same changes. An example of this study's spectra is shown in

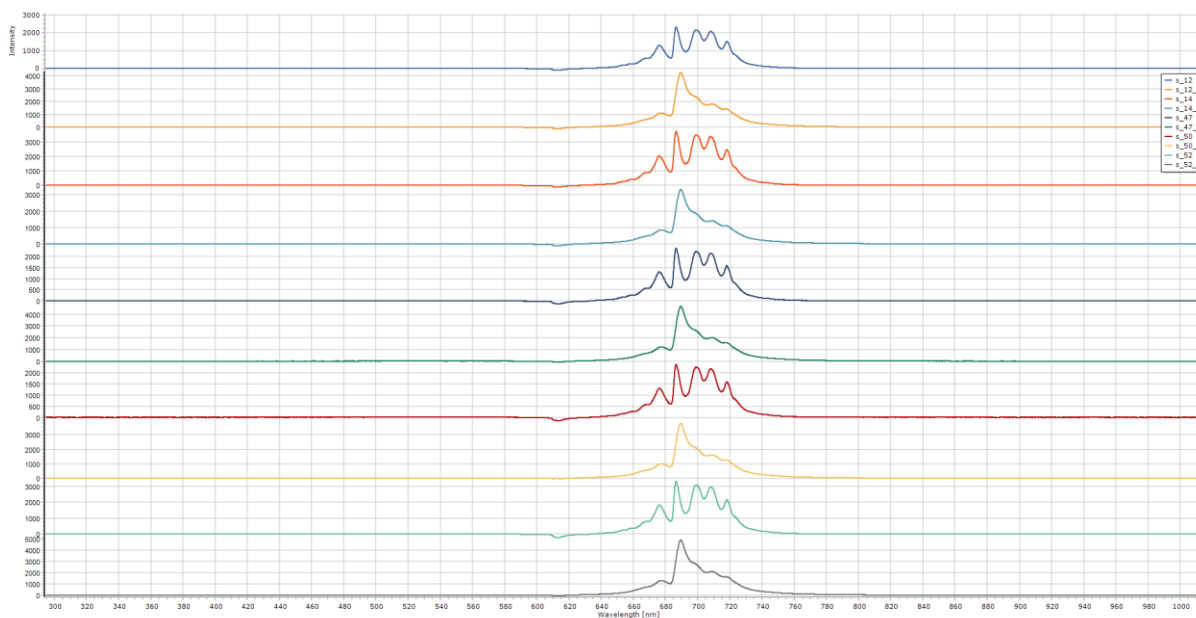


Figure 10: This spectra data comes from Experiment 5 for an example of how all samples' spectra are changing when exposed to heat.

Figure 10. All non-heated samples of spinel show signature 5 peaks. After every heat treatment of this research project, all peaks change similarly. The four outside peaks maintain the same wavelength (x-axis) but shrink along the y-axis which shows intensity. These peaks may be shrinking after heating because the samples have a different intensity when in contact with the spectrometer's laser.

Raman data was collected at the University of Michigan, Ann Arbor with the use of their Raman Spectrometer. Before the Raman spectra was collected, it was hypothesized that all eighteen non-heated spinel samples would produce the same spectra. It was also hypothesized that heat treatments would change the spectra. Experiments 2 and 3 were expected to produce the most change as they contain high temperatures and heating times. Experiment 1 was not

expected to produce as much change. As Figure 11 shows, non-heated spectra have the same peaks and heated spectra peaks show significant change. However, Experiments 1, 2, and 3 heated samples seem to also have changed in the same way. Their peaks have stretched or increased along the x-axis. The widening of the peaks points to evidence of the bond strengths within the crystal structure mentioned in research by Widmer *et al.*, 2014.

The spectra changes are noticeable in Figure 11 but it should be confirmed in another way. To prove that the spectra are different, a PCA analysis was made to compare the same colored spinels from each experiment. The PCA analyses are shown in Figures 12 -17. The axes are PC1 and PC2 which are unknown variables that are used to measure variance between a

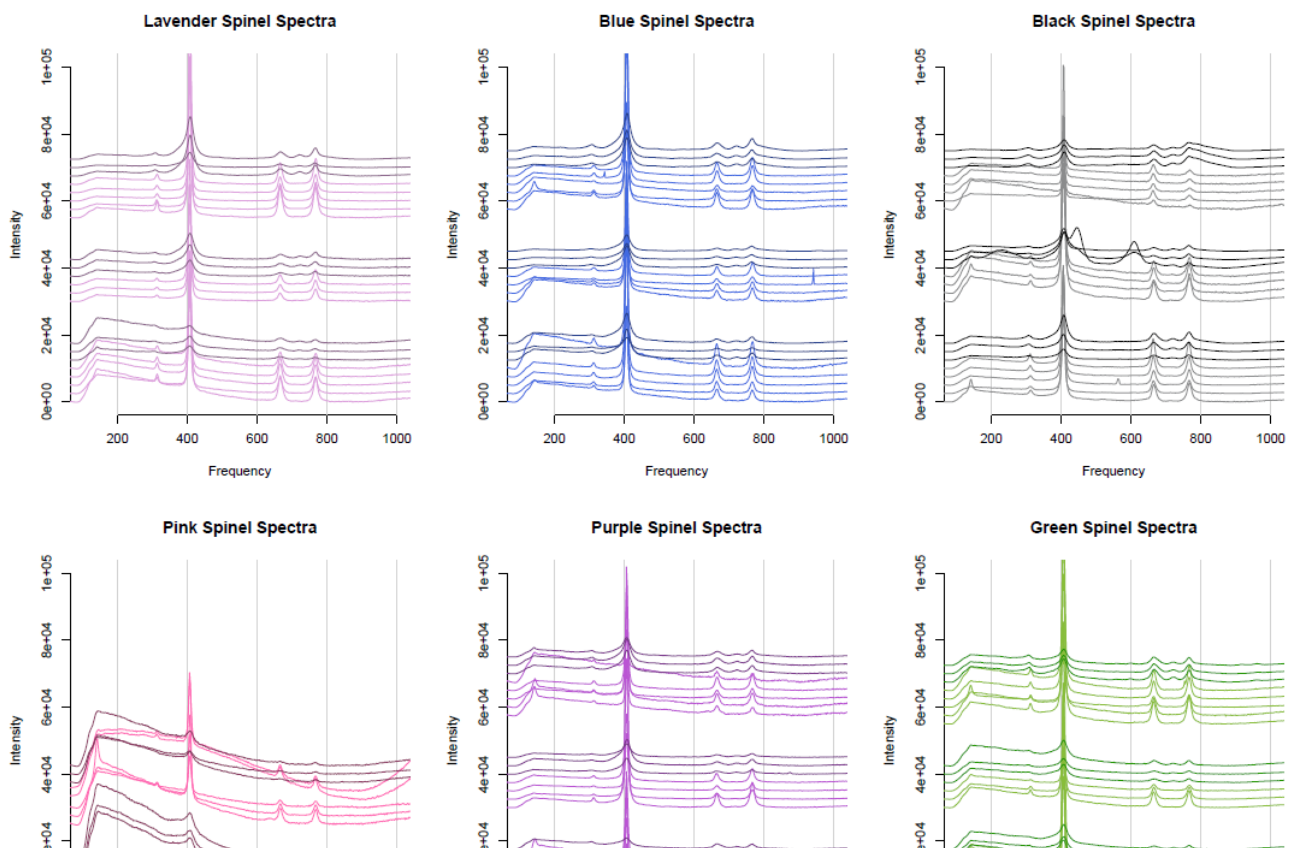


Figure 11: The Raman Spectra from this study is pictured here. The first set of Raman spectra lines on each graph show data collection from Experiment 1, the middle set of lines show Experiment 3, and the top set of lines show Experiment 2. The dark lines represent heated samples and the light lines represent non-heated samples. The pink spinel spectra were not read or collected properly. Therefore, the pink spectra are not uniform with the other colored spinels.

dataset (Varmuza, 2009). The percentages next to PC1 and PC2 show what percentage this variable accounts for variance in the dataset.

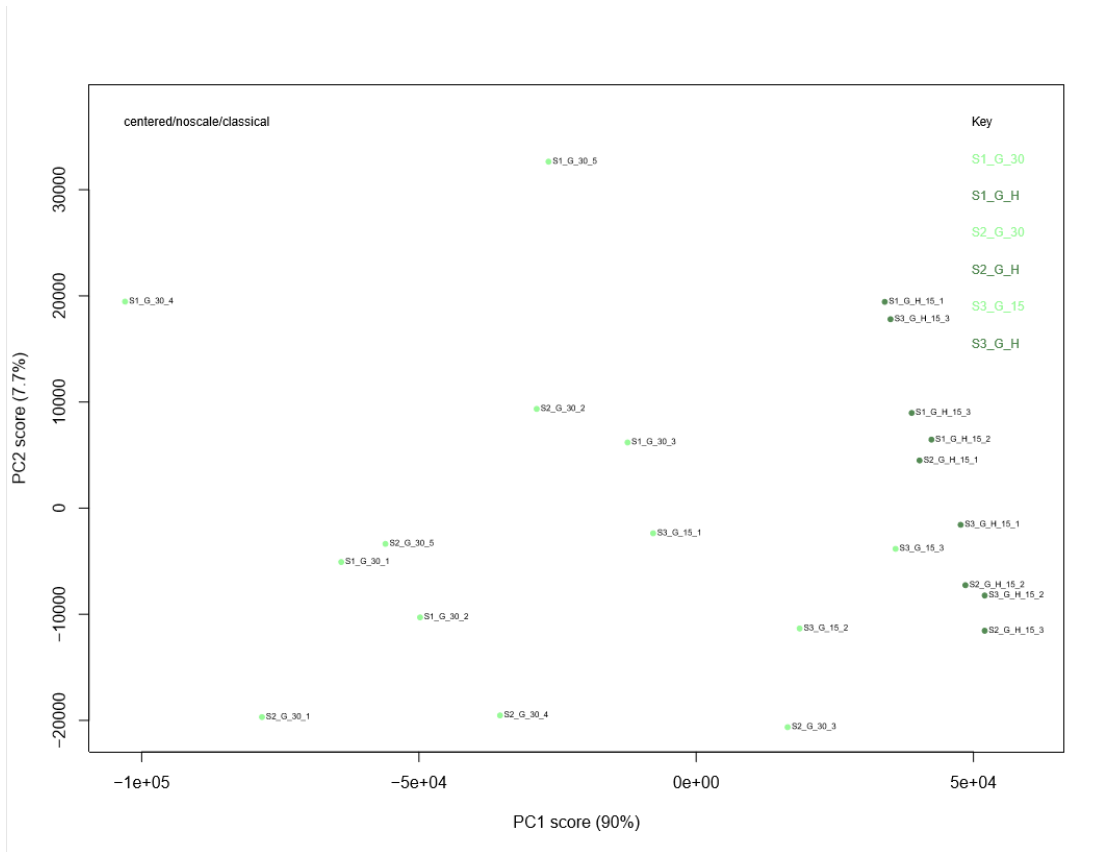


Figure 12: This is the PCA for the green dataset.

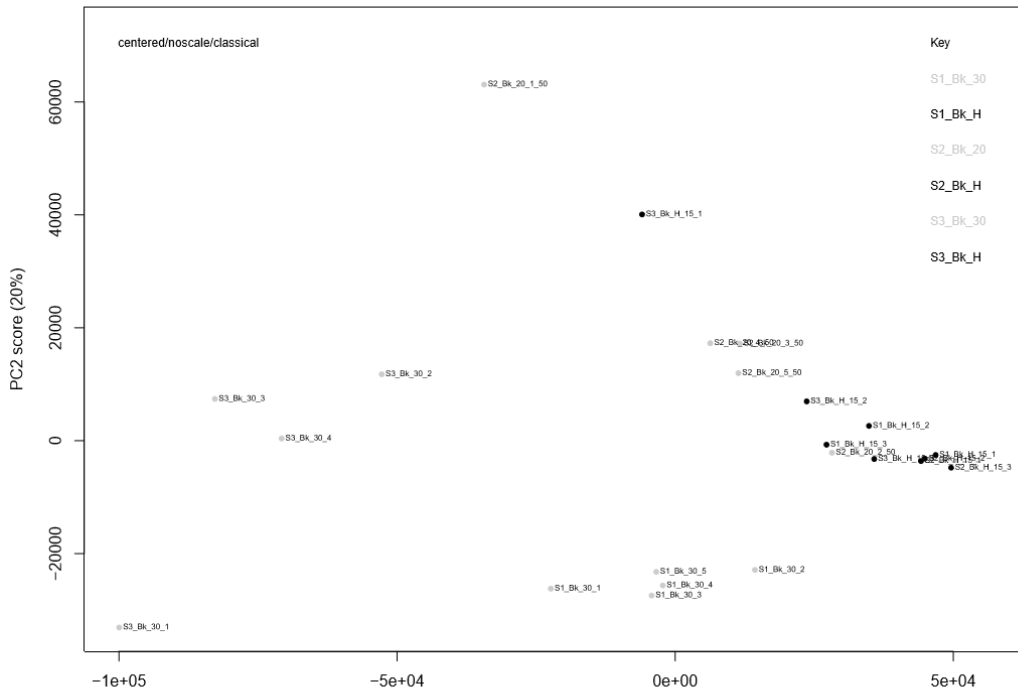


Figure 13: This is the PCA for the black dataset.

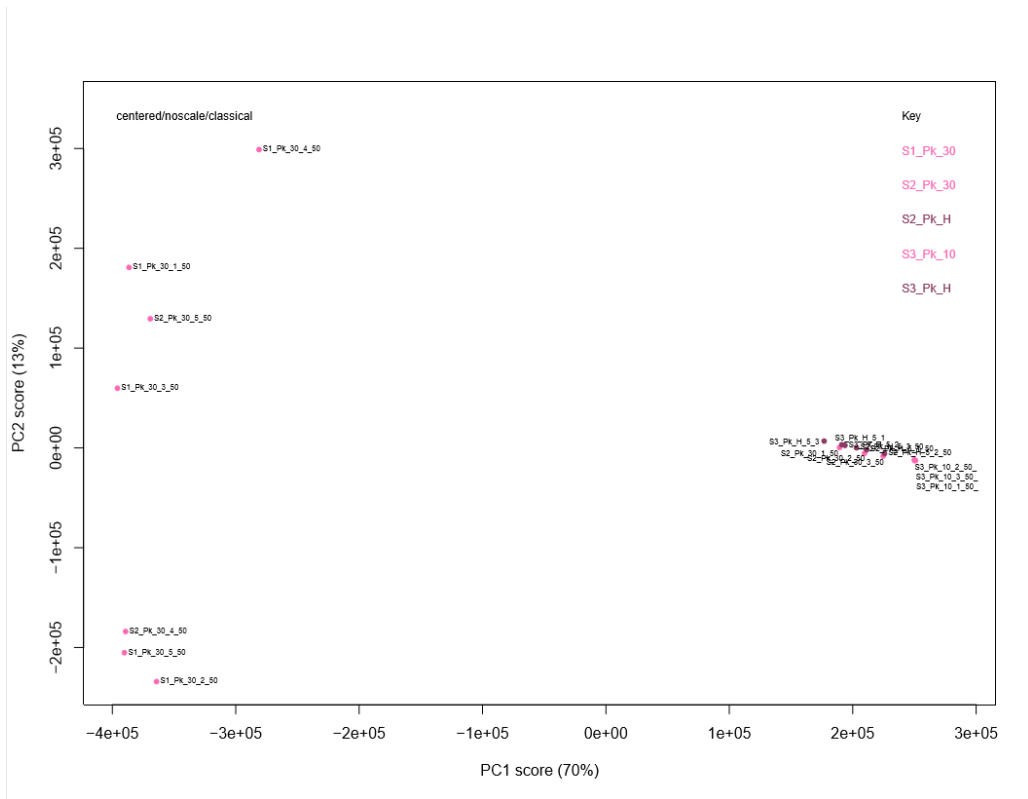


Figure 14: This is the PCA for the pink dataset.

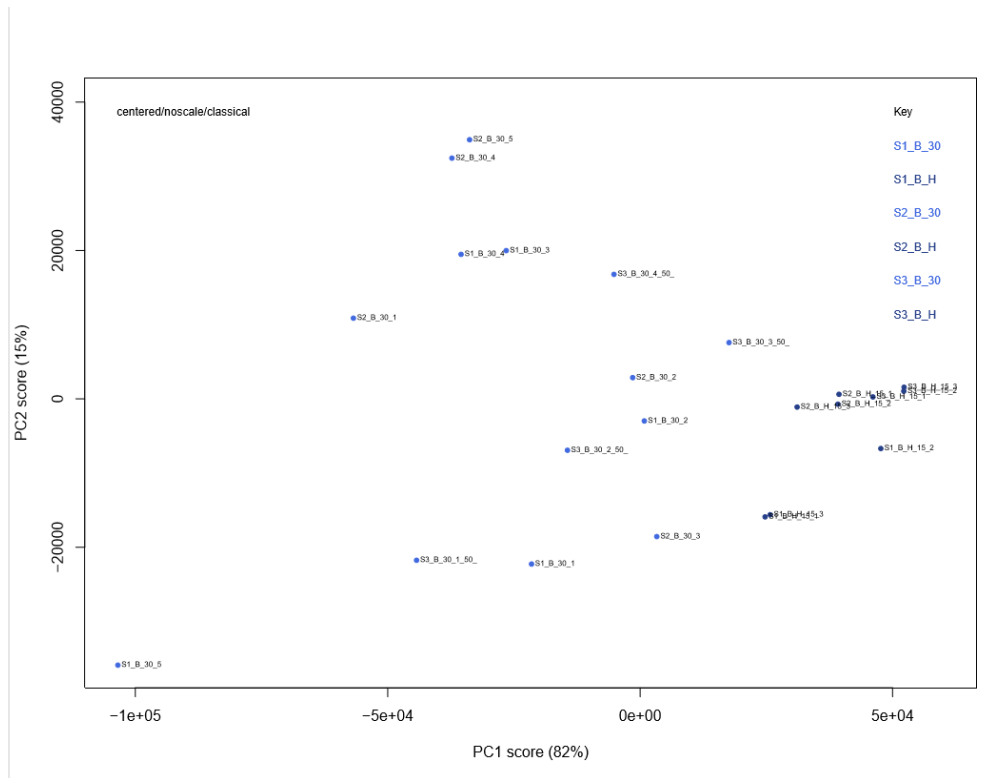


Figure 15: This is the PCA for the blue dataset.

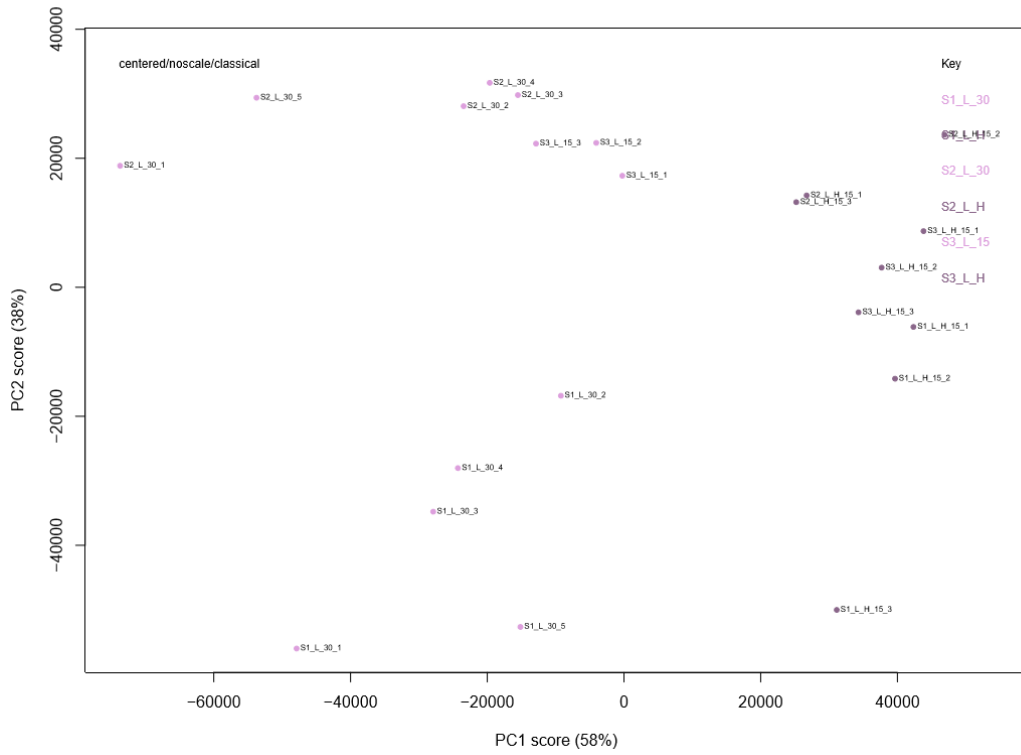


Figure 16: This is the PCA for the lavender dataset.

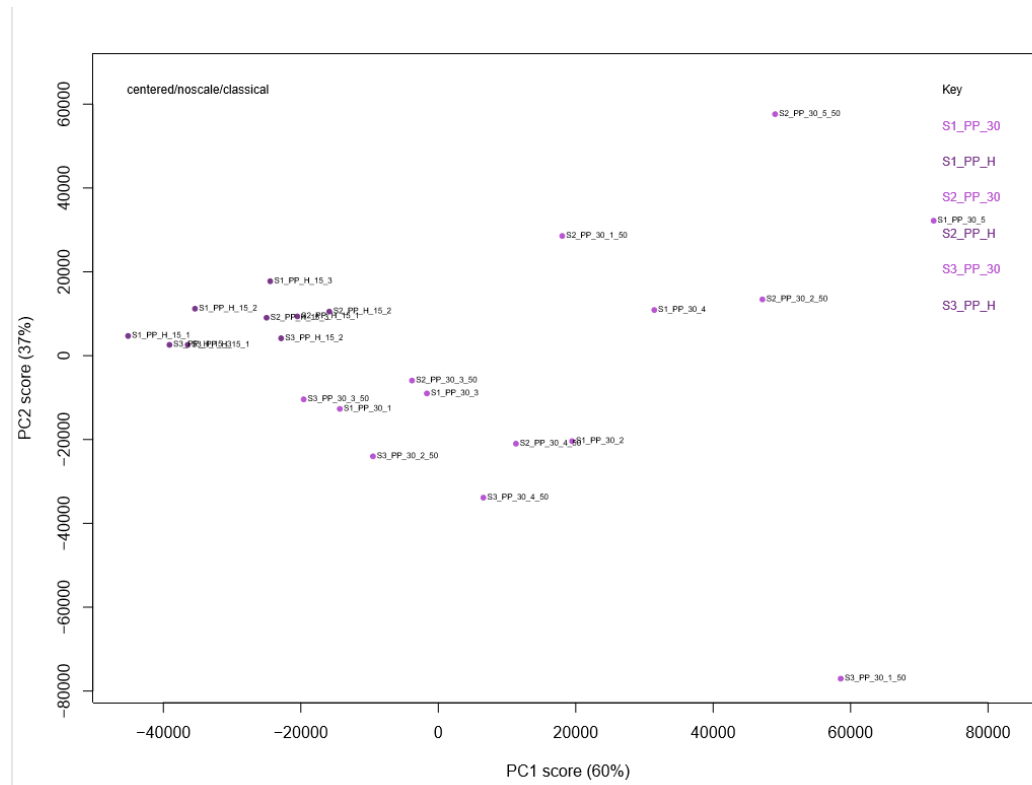


Figure 17: This is the PCA for the purple dataset.

Discussion and Conclusions:

These research experiments show that spinel undergoes color change starting around 850°C. However, the samples exposed to 850°C gain a more dull, purple hue which may be less desirable than their original pink hue. Color darkens to a dark purple beginning at 1350°C. This darker purple is desirable in the gem industry. This portion of the study partially supports the hypothesis that spinel's color can be changed in a desirable way with heat-treating.

The changes in inclusions observed within this study do not show a pattern. Experiment 6 saw no changes in inclusions, Experiment 5 saw worsening and diminishing of inclusions, and Experiments 4, 12, and 13 experienced diminishing inclusions. Since not all inclusions act the same, it is difficult to predict inclusion change results for future experiments. This portion of the study supports the hypothesis of heat changing impurities within spinel, although results are not predictable.

The spectral data collection of the study supports the hypotheses that VIS/NIR and Raman Spectra change with heat treatments. After completing a PCA analysis, it has been noticed that spinel samples have wider variance when they are not heated. When spinel samples are heated, their variance decreases as they become more similar. It is important to remember that PC1 and PC2, the axes, are not known in a PCA analysis but R has calculated all variables that can make samples different from the others. A general observation made is that most of the heated samples from Experiments 1, 2, and 3 group together and have little variance on the x-axis and y-axis.

This research has explored the possibilities of improving clarity and color of gemstones and understanding how heat and time can change samples. Exciting results in the spinel samples have been discovered with research of multiple studies and lab work. Color and inclusions

changes have occurred in the lab and further research is being done on the changing spectra of spinels.

Suggestions for Future Work:

With spinels showing signs of rising in the gem industry, it could be proactive for more research on their heat treatment to be done. This research maintained a heavy methods and background research load. For heat treatment of spinels or any gemstone, it is suggested that the crystalline structure, composition, and gem spectra is understood by the researcher through extensive background research. Within the methods section, we realized that samples should be halved so heated and non-heated samples can be properly compared. While planning your heat treatments, results from other research projects should be compared to each other to find which temperatures and time interval yield desirable color change.

Acknowledgements:

Augustana College funded and provided equipment for this research project. University of Michigan and PhD student, Allison Pease, facilitated the use of the Raman Spectrometer. Each sample of spinel was gifted to this project by Michael Couch & Associates. This research would not be possible without the funding and support of Augustana College's Dr. Michael Wolf, Dr. Jeffrey Strasser, Dr. Kelsey Arkle, Professor Jenny Arkle, Susan Wolf, and Todd Kull.

References:

Minerals.net, 1997, The Spinel Mineral

Series: <https://www.minerals.net/mineral/spinel.aspx> (accessed 4 May, 2019).

GIA, 2019a, 4Cs of Diamond Quality: <https://4cs.gia.edu/en-us/4cs-diamond-quality/> (accessed 5 May, 2019).

GIA, 2019b, Spinel Description: <https://www.gia.edu/spinel-description> (accessed 6 May, 2019).

GIA, 2019c, Spinel History and Lore: .

Martin, G., and Pretzel, B., 1991, UV-VIS-NIR spectroscopy: What is it & what does it do? v. 01, .

NPTEL, Structure of Ceramics: https://nptel.ac.in/courses/113104005/lecture3/3_9.htm (accessed 5 May, 2019).

Perkins, D., 1998, Mineralogy: Upper Saddle River, New Jersey, Prentice-Hall, Inc., p. 7-26.

Rosett, A., 2018, Geochemical Fingerprinting and Heat Treating of Spinel from Tanzania and Mozambique to Address Supply Challenges in the Colored Gemstone Market: p. 1-42.

Varmuza, K., and Filzmoser, P., 2009, Introduction to Multivariate Statistical Analysis in Chemometrics: Boca Raton, eBook, p. 58-102.

Widmer, R., and et al., 2014, Effects of heat treatment on red gemstone spinel: single crystal X-ray, Raman, photoluminescence study: Physics and Chemistry of Minerals: Geology, v. 42, p. 251-260.