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Geochemical Analysis and Heat-Treatment of Natural Sapphires from Madagascar and Tanzania in Oxidizing and Reducing Conditions

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Abstract

Natural or synthetic sapphires can be heat-treated to improve the clarity by removing "silk" (inclusions) and to change color by introducing color-inducing elements (i.e., chromophores) into the lattice structure or changing their valency. Due to these reasons, sapphires can be heat-treated to increase their monetary value. Twenty natural blue (C1), 20 green (C2), and 20 clear (C3) sapphires from Madagascar and Tanzania were heat-treated in a muffle furnace in oxidizing and reducing conditions, from 1200 to 1600°C, for 10-hour soak time. In total, 5 experiments were conducted in which soak time remained constant: experiment 1 was performed at 1200°C, exp. 2 at 1300°C, exp. 3 at 1400°C, exp. 4 at 1500°C, and exp. 5 at 1600°C. Each experiment contained 4 sapphires from C1, C2, and C3 respectively, and half of the sapphires were exposed to oxidizing conditions, while the other half to reducing conditions. To achieve reducing conditions, graphite slabs were used to create the CCO buffer; the oxidizing conditions were achieved simply with air. The clear (C3) sapphires remained clear under both conditions from 1200 to 1500°C exclusively and up to 1600°C in oxidizing conditions. The blue (C1) sapphires either underwent no change of color or became lighter with increasing temperature and some received a yellowing effect resulting in green in oxidizing conditions. In reducing conditions, the blue (C1) sapphires became darker in color, especially from 1400°C and up. Green/blue (C2) sapphires became lighter and increased the green intensity from 1200 to 1400°C exclusively and up to 1600°C in oxidizing conditions. Starting at 1400°C heat-treatment of the stones in reducing conditions turned almost all of the samples grey/black. Electron microprobe analyses were used to determine concentrations of chromophores at minor and trace element concentrations, including: Ca, Ti, Zn, Mg, Si, Ga, Fe, Mn, and Cr to evaluate the geochemical effects of heat-treating sapphires. C1 sapphires contained the highest amount of Ti

and Fe (Ti > 100ppm, Fe 8000-10000 ppm), C2 sapphires contained much less Ti but the same amount of Fe (Ti 40-50ppm) and C3 samples contained the same amount of Ti as C2 but the least amount of Fe (Fe 400-700 ppm).

Introduction

A gemstone is a mineral with appealing visual attributes and is used to produce jewelry or other embellishments. Recently, the price of gemstones such as sapphires (gem corundum) has been increasing (Hugi and Krzemnicki, 2015). In 2007, the price per carat of gem-quality blue sapphire was $700-1375 depending on the color, clarity, cut, and provenance (van der Wal and Hann, 2010; Collet et al., 2013). A carat is a unit of measurement used to measure the mass of gemstones. One carat is equal to 200 mg or 0.00705 oz. Today, fine sapphire samples are almost never found for under $1000 USD independent of size (Gemselect, 2018). This trend of increasing natural sapphire prices is negatively impacting many people's acquisition of sapphire jewelry.

Heat treatment of gems is a process in which a mineral of non-gem grade quality such as sapphire, ruby, spinel, etc. is subjected to a high temperature in a furnace or high-temperature microwave oven to improve the clarity and enhance the color. This, in turn, changes the sample from a non-gem grade to gem-grade and increases the value as jewelry many times over. Heat treating non-gem grade sapphires, however, supplies the gem market with heat-treated sapphires that are much more affordable. Figure 1. shows sapphire prices of non-origin specific, heat-treated sapphires, Burma sapphires, Ceylon sapphires, and fancy green heat-treated sapphires over a four-month period (November 2019 to March 2020). The natural Burma and Ceylon
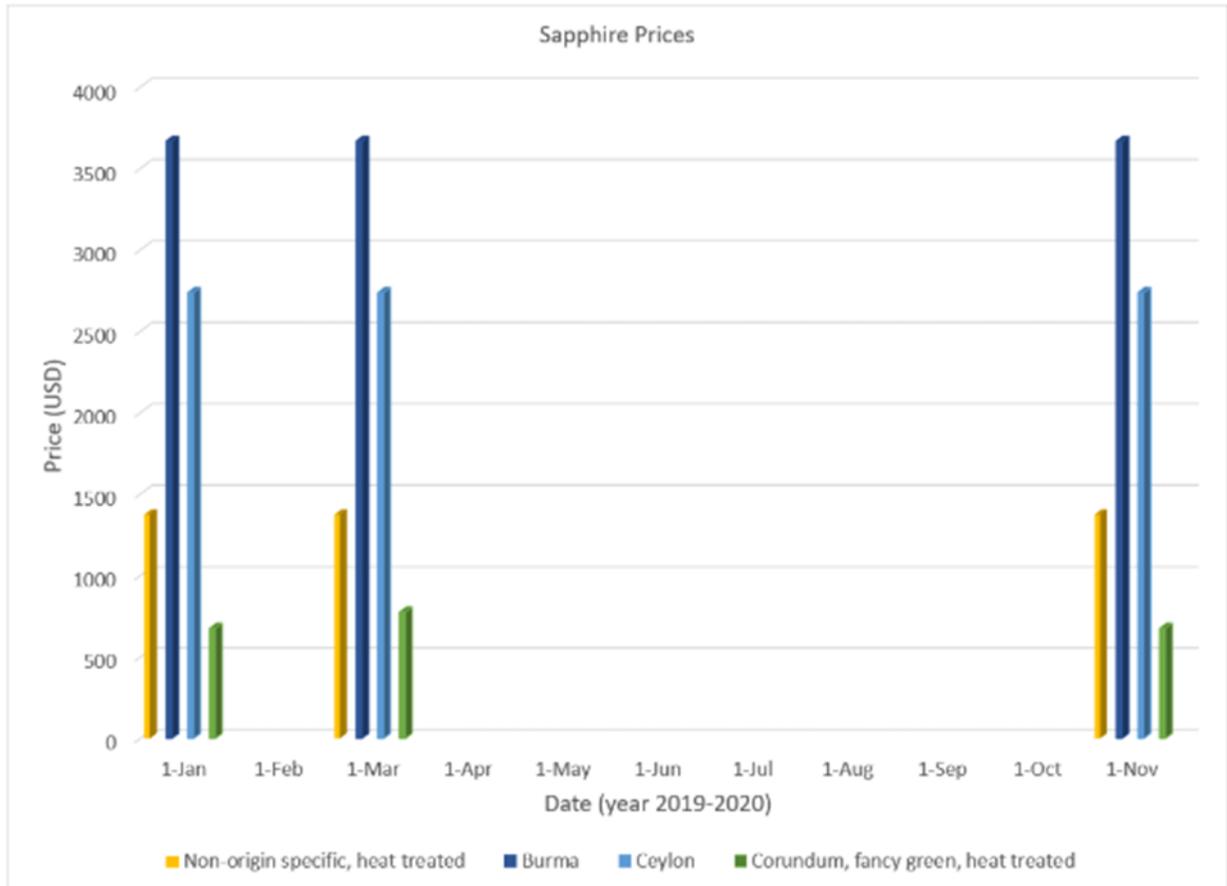
Figure 1. A bar graph showing several natural and heat-treated sapphire prices over a four-month period. From (Gemguide, 2020).

sapphires are selling for more than double than non-origin specific heat-treated sapphires and more than triple than fancy green, heat-treated sapphires. Burma sapphires are mined in a country formerly named Burma which is now called Myanmar. Ceylon sapphires are from a country formerly called Ceylon, which is now Sri Lanka (Figure 2.).

Modern heat treatment techniques are mostly performed by the use of high-temperature furnaces that can achieve 2000°C. The heat treatment of corundum (Al_2O_3) to improve clarity and enhance the color has been heavily researched and there are many different hypotheses on what causes the color in corundum. The science behind colors in gemstones is very complex and

Figure 2. Blue sapphires from Myanmar (Burmese), Sri Lanka (Ceylon) and Thailand. From (Navneetgems 2020).

always improving due to the betterment of technology available. Also, no specific instructions are provided in the scientific literature due to their economic impact and proprietary value. The goals of this research were to experimentally determine the optimal temperature of corundum heat treatment in both oxidizing and reducing conditions of sapphires from Tanzania and Madagascar by using a high-temperature furnace and to geochemically analyze the natural and heat-treated sapphires.

Background

To understand how heat treatment affects gems such as sapphires, one must first understand the science behind color in minerals. Sapphire is a variation of corundum, Al_2O_3, which also has industrial uses such as being used as an abrasive because of its hardness of 9 in Mohs hardness scale. Pure corundum is an allochromatic gem, meaning that it receives its color

from impurities and is colorless by itself (Emmett et al., 1993). For corundum to be considered a sapphire, the gemstone can have every color except red. If the gemstone is red, then it is considered a ruby.
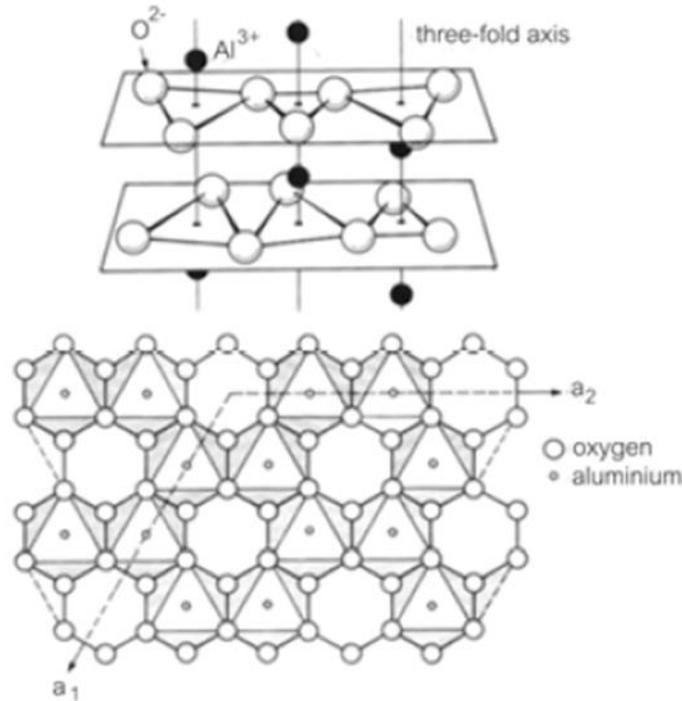
Figure 3. The polyhedral model of the structure of corundum (Mungchamnankit, A. et al, 2012).

One hypothesis for the blue color comes from metal-metal charge transfer which is governed by the molecular orbital theory. Molecular orbital theory can be considered as the best explanation of the cause of color in minerals where the involved electrons are present in multi-centered orbits (Nassau, 1978). The results of charge transfer explained by molecular orbital theory vary depending on if the centers involved are metal-metal, metal-nonmetal, nonmetal-nonmetal bonding environments. Metal ions that color gem corundum are 3d transition ions, such as Cr3+, Ni3+, Fe3+, Ti4+, and so on. Metal ions themselves do not color gemstones, it is the transition of the electron structure that corresponds to changes in visible light emitted from

the corundum. The metal ions substitute for Al3+ ions in the vacancies present in the Al layer.

For every 3 Al ions in the Al layer, there is one Al ion missing, creating a vacancy, as seen in

Figure 3 and Figure 3a. Blue sapphires very often contain Fe and Ti impurities which can exist in

two valence states (Fe2+ and Fe3+; Ti4+ and Ti3+) and create two scenarios of mixed oxidation

states (1) Fe2+ and Ti4+ and (2) Fe3+ and Ti3+. One electron can be caused to transfer from Fe

Here's the trioctahedral O-layer, with all octahedral spaces totally filled (with +2 cations, like Mg or Fe^{+2}):

Mark every 3rd octahedron for removal...

... and you get the dioctahedral O-layer:

VACANCIES: a place where a cation could be but isn't

Even with cations missing, the whole O-layer can charge-balance the corresponding T-layer because the cations are now Al^{+3}
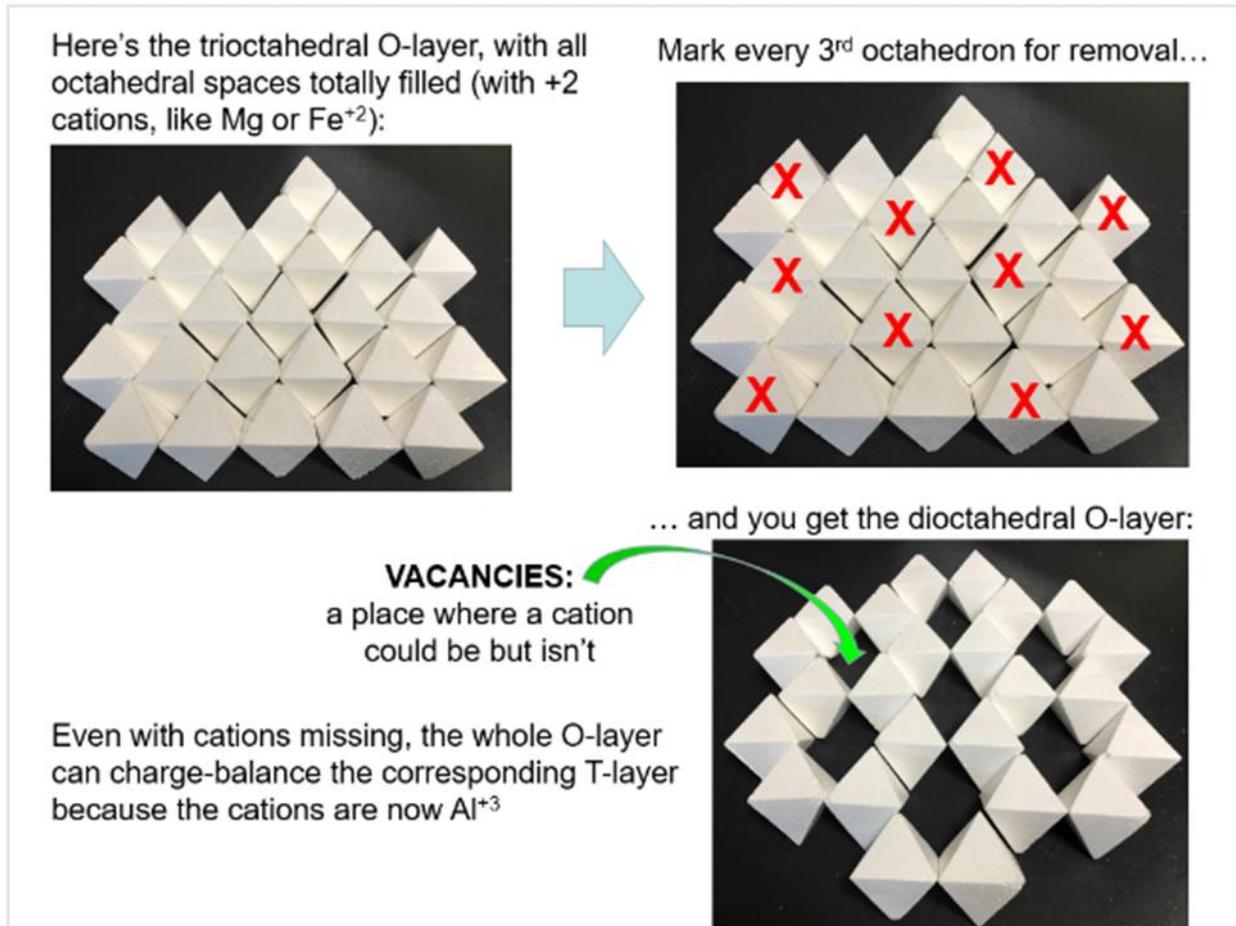
Figure 3a. An explanation of why there is one Al ion missing for every 3 Al ions. This also explains the vacancies that are caused by the missing Al ions and that the vacancies can be filled with other ions such as Fe^{2+} or other (M. Wolf, personal communication).

to the Ti by light absorption and back again. This electron transfer from (1) to (2) involves the

absorption of energy and produces sapphire's trademark: the deep blue color (Nassau, 1978).

This means that the Fe and Ti ions are substituted into the Al layer and transfer electrons

between each other and produce the blue color. Fe^{3+}-Fe^{3+} and Fe^{3+} cause a yellow color in corundum in a process called electronic transitions (Mungchamnankit et al, 2012).

The inclusions in sapphires are mainly composed of rutile, TiO_2 which is commonly referred to as silk in sapphire, since the human eye perceives rutile needles as "spots of grey" in corundum. In most cases, rutile crystals are referred to as an unwanted constituent of a gem-grade sapphire, however, sometimes those crystals can produce a desirable asterism effect where the crystals align in a shape of a star just like in Figure 4.

Figure 4. Asterism effect caused by rutile crystals (Kwansirikul et al 2016).

Historically, it has been hypothesized that rutile inclusions in sapphires are a result of secondary exsolution upon cooling, and this has significant implications on how sapphire is heat treated. However, a recent study by Palke et al., (2017) performed analytical tests on rutile inclusions in gem corundum and have hypothesized that rutile inclusions are a result of syngenetic growth due to several reasons: (1) The presence of glassy melt inclusions with

oriented rutile inclusions in sapphires from Anakie gem fields of Queensland, Australia are a result of rapid cooling of the corundum which contains the melt inclusions because of the lack of nucleation and crystal growth from the melt. Exsolution of rutile inclusions only occurs when corundum is held at a temperature lower than that of the initial formation for a lengthy period of time to enable the oriented rutile inclusions to nucleate and grow. (2) laser ablation inductively coupled mass spectrometry (LA-ICP-MS) and nano-resolution secondary ionization mass spectrometry (SIMS) detected "unusual" trace elements which have ionic radii and/or cation charges significantly different from Al3+ such as Zr, Nb, Ta, W in rutile inclusions and not the corundum lattice. These elements are also known to be highly compatible in rutile. This means that the presence of these unusual trace elements suggests that they were originally incorporated into the rutile inclusions which coprecipitated with the corundum (Palke et al., 2017). Therefore, if the rutile inclusions in sapphire are from syngenetic growth instead of secondary exsolution processes, heat alone will not dissolve the rutile inclusions into the surrounding corundum structure and thus not improve the gemstone clarity.

Oxygen fugacity (fO2) is a master variable in magmatic and magmatic-hydrothermal systems and it plays a fundamental control on the behavior of redox-sensitive elements such as Fe, V, Cr, and Ti (Simon and Ripley, 2011). Oxygen fugacity is the partial pressure of oxygen in a geologic system and is constrained by the reaction of redox-sensitive mineral phase assemblages (i.e., solid buffers). A fO2 vs T graph showing the different buffers can be seen in Figure 5. If those minerals are exposed to a different buffer than their own, then they become unstable and change their chemical characteristics. This buffering technique can be applied to many different types of minerals such as rutile (Zhao et al., 1999). Rutile is stable above and at the RI (rutile-ilmenite) buffer, and is defined by the reaction:

$$2Fe_2O_3 \text{ (in ilmenite)} + 4TiO_2 \Leftrightarrow 4FeTiO_3 \text{ (ilmenite)}$$

but if exposed to reducing conditions such as the NNO (Ni-NiO) buffer or CCO (CO-CO2) the

rutile inclusions will plausibly dissolve into the corundum lattice. This is the reason why heat

treatment of sapphires is conducted under oxidizing or reducing conditions, since simply heating

it would make no difference to the rutile inclusions.
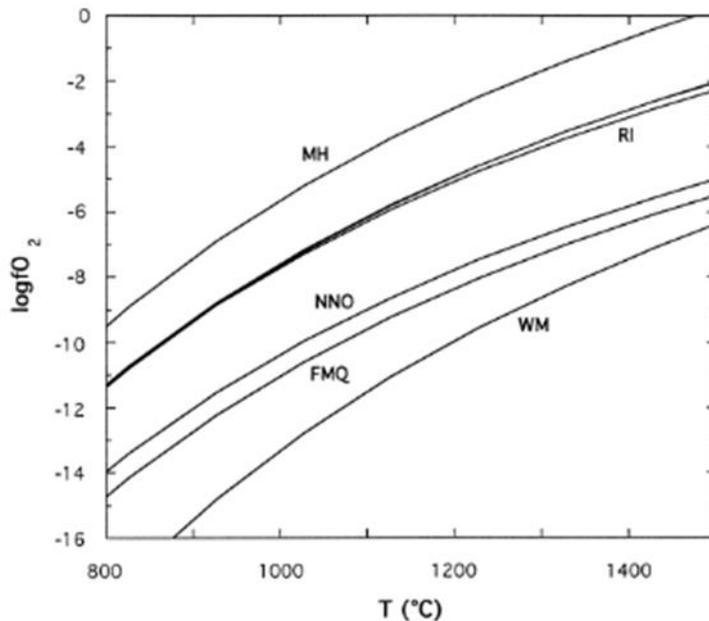
Figure 5. A fO_2 vs T graph showing the different buffer curves.
MH= magnetite-hematite; RI= Rutile-ilmenite; NNO= Ni-NiO;
FMQ= Quartz-fayalite-magnetite and WM= Wüstite($Fe_{0.947}O$)-magnetite
(Zhao et al., 1999).

      Heat treatment has several important considerations: (1) the temperature-time

relationship, (2) the oxidation-reduction conditions, and (3) the presence of chemical substances

that can interact with the gemstone (Nassau, 1981). Once rutile is heat-treated under reducing

conditions, it becomes destabilized and dissolves into the surrounding corundum lattice. The

increase in Ti ions in the structure allows for more Fe-Ti charge transfer to occur. This, in turn,

improves the clarity of the gem and deepens the blue color, which can be seen in Figure 6.

Figure 6. Left, milky white (geuda) corundum from Sri Lanka heat-treated under reducing conditions to deepen the blue color and improve clarity. Right, is the result of heat treatment under reducing conditions. From (Nassau, 1981).

Clarity is defined as impurities in the gem such as a fracture or inclusion with an index of refraction (RI) different from the native material that will scatter light by reflecting it off its surfaces, resulting in the reduction of clarity of the host (Emmett et al., 1993). If a dark blue sapphire sample is present, then oxidizing conditions can be applied to lighten the color. This process is the reverse of reduction and its results can be seen in Figure 7. One more thing to note


Before heating   1200°C
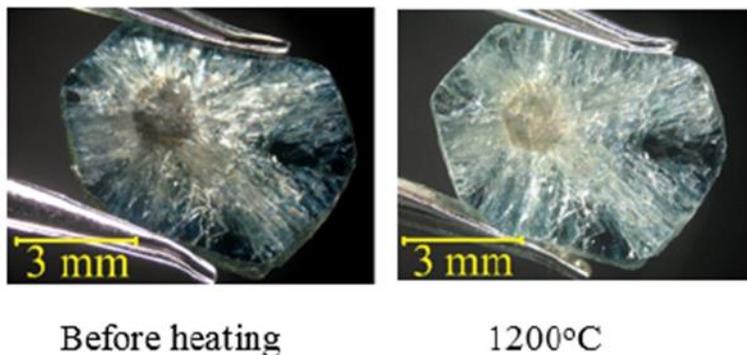
Figure 7. Heat treatment of Trapiche-like sapphires under oxidizing conditions (Kwansirikul et al., 2016).

is that once all the silk has disappeared due to heat treatment, the samples are cooled rapidly, about 30°C/min. This is so that the rutile needles do not re-form (Nassau, 1981).

If a sapphire lacks iron and titanium then no amount of heating will improve the color (Kwansirikul et al., 2016). This, however, can be potentially fixed by the process of diffusion heat treatment. By painting the gem with aluminum titanate (Al2TiO5) in water and then heat treating it for several days under reducing conditions a thin layer of "color" just below the surface can form (Nassau, 1981). This process is extremely slow, meaning that it will take days to complete and the depth of the layer penetration is small, only about one-tenth of one millimeter. However, this is one way to heat treat already faceted sapphires that do not contain enough Fe or Ti. The diffusion heat-treated sapphires must already be faceted prior to heat treatment since any polishing or grinding would destroy the thin color layer.

Equally as important to the process of heat treatment is the compositionally controlled provenance of the corundum samples. The sapphires mined in Montana, United States, are extremely high in iron. The concentration of Fe in Rock Creek sapphires is usually 100 times more than any other impurity (Emmett et al., 1993). This has some implications on heat treatment, such as the degree of reducing conditions. If the sapphires containing large amounts of iron are heat-treated in very highly reducing conditions, then hercynite, an iron spinel (FeAl2O4) will precipitate. Hercynite precipitation can be seen in Figure 8. If further reduction takes place, then the hercynite precipitation and metallic iron will continue until the exterior is opaque. Sapphires from Sri Lanka on the other hand, have much less iron and as a result, do not have hercynite precipitation issues during heat treatment.

Goethite is another mineral that can affect the heat treatment of sapphires. Some sapphire stones may contain brown to yellow hydrous ferric oxide such as goethite. Goethite is one of the

Figure 8. Hercynite precipitation in Fe-rich sapphires from Rock Creek, Montana due to heat treatment in over reducing conditions. Prior heat treatment, the wafer was colorless and transparent and after heat treatment, it turned translucent gray (Emmett et al., 1993).

primary constituents of limonite with the chemical formula of α-FeO(OH) and is deposited in the inclusions found in corundum epigenetically. If goethite is subjected to just 350°C, it is converted into rusty red hematite by following this chemical reaction 2α-FeO(OH) $\rightarrow$ heat 350°C $\rightarrow$ α-Fe2O3 +H2O. This effect can be seen on heat treated sapphires from Sri Lanka in Figure 9.

A study by Emmett et al., (1993) heat-treated more than 75,000 sapphires from Rock Creek, Montana, USA, and found that 65-70% of pale blue, pale green and near-colorless sapphires could be transformed to saturated blue and yellow colors. The sapphires from Rock Creek varied in color: colorless, pale blue, pale green, pink, and pale yellow. However, only 5-10% of the sapphires contained enough silk to substantially reduce visual quality. The heat treatment in this study was performed with a Thermal Technology Group 1000A graphite hot
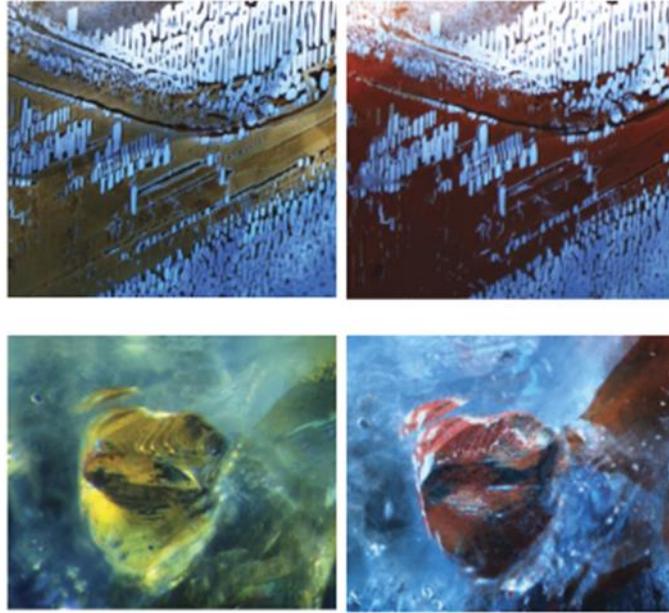
Figure 9. Sri Lankan sapphires untreated (left) and heat-treated (right). The dark yellow goethite undergoes dehydration and turns into the rusty red hematite (Koivula, J.I., 2013).
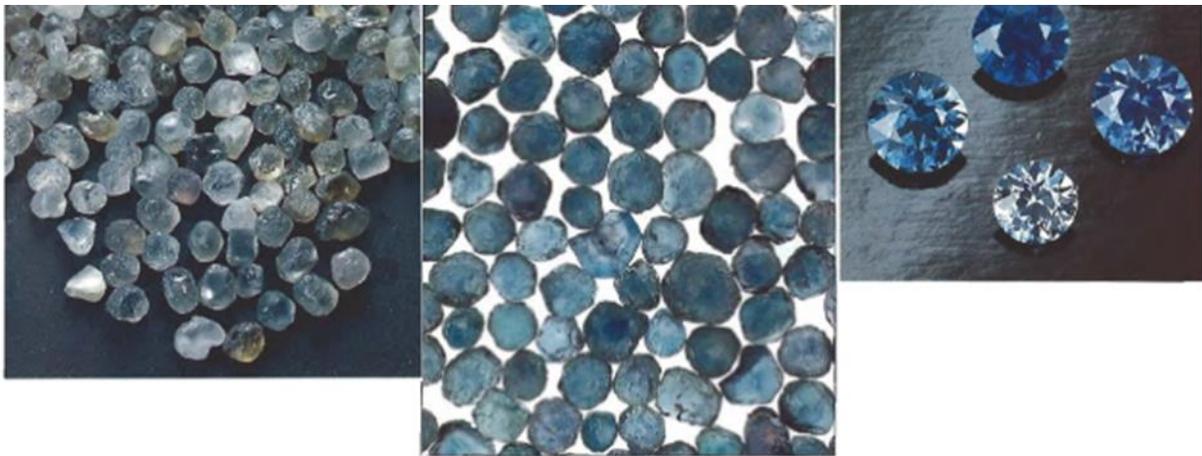
Figure 10. Left, rough Rock Creek sapphires. The pale blue, pale green and near-colorless colors represent the majority of Rock Creek Sapphires. Middle, the previous samples heat-treated under reducing conditions. The different saturations of blue are due to different amounts of rutile concentration. Right, the heat-treated Rock Creek sapphires that are now cut and faceted. This represents the expected color range of heat treating the pale green, pale blue, and near-colorless Rock Creek sapphires (Emmett et al., 1993).

zone furnace which has the capacity of heating to 2200°C. The non-gem grade quality blue sapphires were heat-treated at 1650°C in reducing conditions and the progress can be seen in Figure 10. These stones were then faceted into gem-grade sapphires that cost much less than natural sapphires of the same clarity and color.

Methods

Non-heat-treated corundum samples from Madagascar and Tanzania were obtained from Rosett (2018). This set contained 60 samples divided into 20 sample groups, C1, C2, and C3. Generally, all C1 stones were dark blue, C2 stones were light blue with some stones containing green, and C3 were all colorless or cloudy. All samples were graciously supplied by Michael Couch, of Michael Couch and Associates, a wholesaler, supplier and distributer of colored gemstones, who has invested in numerous Augustana College geology undergraduate students who are interested in doing gemological research.

The preparation for the heat treatment process to determine optimal temperature under oxidizing and reducing conditions started with capturing photos of the sapphire samples. Then, the samples were analyzed with a gem spectrometer (Figure 11) to obtain UV-vis spectra data. The UV-vis spectroscopy data provides us with the absorbance data of ions present in the sample. Higher absorbance means that more of the light is absorbed by the sample. Introducing reducing conditions during heat treatment of corundum has been shown to improve color and clarity (Nassau, 1981), (Emmet et al, 1993). The standard method of creating reduced conditions during heat treatment is to use a CO2 gas-mixing furnace; since Augustana does not own a gas-mixing furnace, a novel, economical experimental design was conceived to achieve these
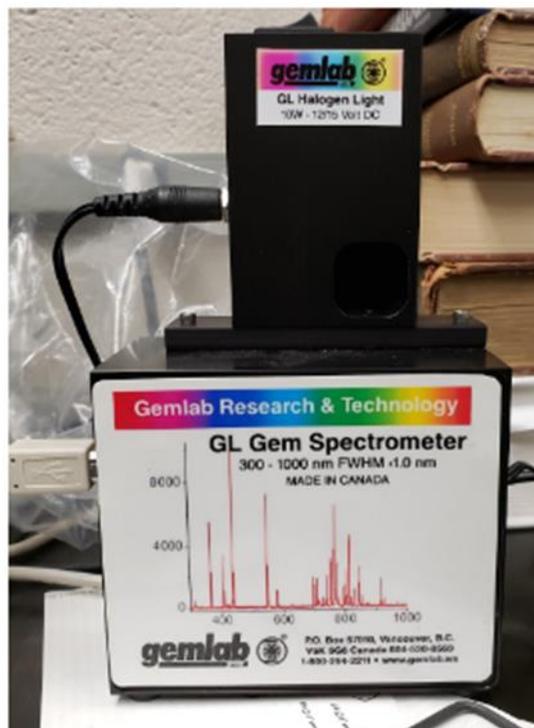
Figure 11. GL Gem Spectrometer that was used to obtain UV-vis spectra data

conditions (M. Wolf, personal communication); boat-shaped grooves were carved out in

graphite slabs and used to create reducing conditions in an alumina chamber. The reducing

conditions are created when the carbon atoms which are present in the graphite interact with the

oxygen in the surrounding atmosphere. This creates CO and CO_2 which comprise the CCO

buffer which destabilizes the rutile present in the corundum samples. The higher the temperature

and the larger the amount of oxygen exposed to the graphite causes the graphite to be consumed

quicker. The graphite slabs were cut so that they fit into a chamber consisting of two opposing

alumina crucibles. The grooves were used to house the sapphire stones. Two alumina crucibles

with graphite slabs in each were then pressed against each other and the gaps filled with alumina

fiber and cemented with Si rigidizer liquid to create a seal and minimize oxygen exposure to the

graphite. This was done to achieve a closed system so that CO and CO_2 did not leak out outside

the reduced crucible and to prolong the time interval that the graphite slabs were present and able to create the CCO buffer. The CCO buffer was proved to be a novel, cost-effective alternative to using a gas-mixing furnace. The graphite slabs and sealed crucible can be seen in Figure 12 below.

Figure 12. Graphite slabs with boat-shaped grooves and alumina crucible on top (left). Two alumina crucibles with two graphite slabs facing each other while housing corundum stones. Sealed off with alumina fiber. Also the inside of the furnace (right).

The heat-treatment experiments contained two crucibles at once, one with an open-top so that the sapphires were exposed to air for oxidizing conditions and one crucible which was sealed for reducing conditions. Each crucible contained six stones, two from C1, C2, and C3 respectively. To confirm if the reducing conditions were achieved by using the (magnetite-hematite) MH oxygen fugacity buffer, the first experiment also contained hematite powder in both sealed and open crucibles. If the hematite powder becomes magnetic, then the conditions are reduced, but if the powder remains non-magnetic, then the conditions are oxidizing. This can be seen in Figure 13.
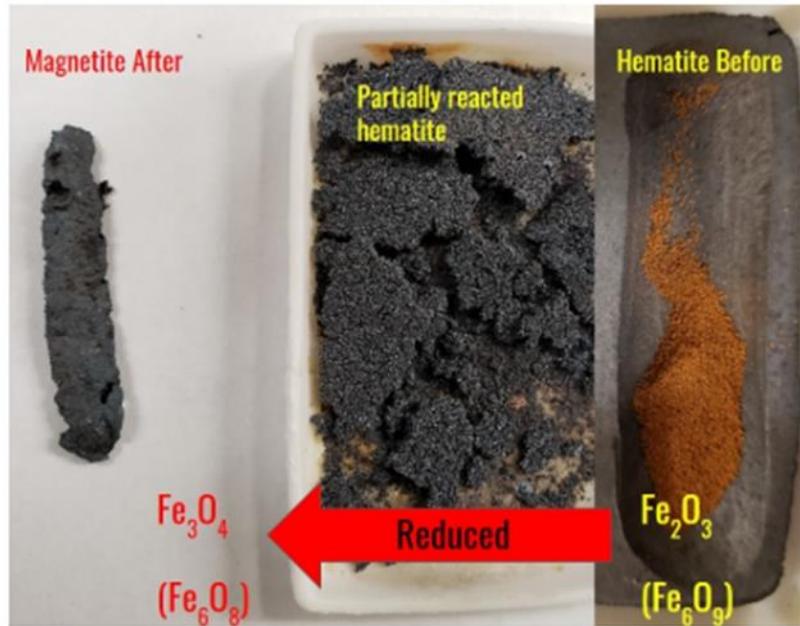
Figure 13. (Right) Hematite before heat-treatment. (Middle) partially reacted hematite which was exposed to oxidizing conditions. (Left) magnetite which was formed by exposing hematite in reducing conditions.

Heat treatment conditions for each experiment can be seen in Table 1. Soak time is the duration of time that the sapphires are exposed to the maximum temperature. So, for experiment 1, sapphires were exposed to 1200°C for 10 hours. The stones were then cooled by letting the furnace cool off to ambient temperature. There were 14 previous heat-treatment experiments that were conducted to get acclimated to the process of heat-treatment.

Run Conditions			
	Temperature(°C)	Soak Time(h)	Heating rate(°C/min)
Exp. 1	1200	10	5
Exp. 2	1300	10	5
Exp. 3	1400	10	5
Exp. 4	1500	10	5
Exp. 5	1600	10	5

Table 1. Heat treatment conditions for each experiment.

After the heat treatment, the UV-vis spectra data and pictures of the stones were retaken and the samples were sent for electron probe microanalysis (EPMA) to Augustana geology alumnus Dr. Brian Konecke '14 at Astromaterials Research and Exploration Science (ARES) lab, NASA Johnson Space Center, Houston, Texas. EPMA was used to determine concentrations of chromophores at minor and trace element concentrations, including: Ca, Ti, Zn, Mg, Si, Ga, Fe, Mn, and Cr to evaluate the geochemical effects of heat-treating sapphires. This compositional and trace element data were also used to create a Fe vs Ga/Mg chart which then can be used to determine the sapphires' geological environment of formation, whether the sapphires are magmatic or metamorphic (Peucat et. al 2007). If the Ga/Mg ratio is > 10, then the corundum stones are magmatic. On the other hand, if the Ga/Mg ratio is < 10, then the samples are metamorphic. The C2 and C3 sapphire stones were mounted in 2.54 cm epoxy-resin rounds as polished to a 1-micron surface roughness by using polycrystalline diamond suspension. C1 samples followed the same preparation routine except that instead of polycrystalline diamond suspension, a 1-micron alumina oxide powder was used for polishing. This resulted in less reliable results because the surfaces were not as smooth, hence using polycrystalline diamond suspension is superior for polishing corundum stones.

Results

Color changes due to heat treatment varied from almost no change to drastic changes. Common color change trends across the experiments can be seen in Figures 14 and 15. In experiment 1, oxidized C1 samples became slightly lighter and reduced C1 samples underwent almost no visual changes. C2 oxidized and reduced samples became lighter and received a yellowing effect changing the color from dark blue to green. The C3 samples underwent no
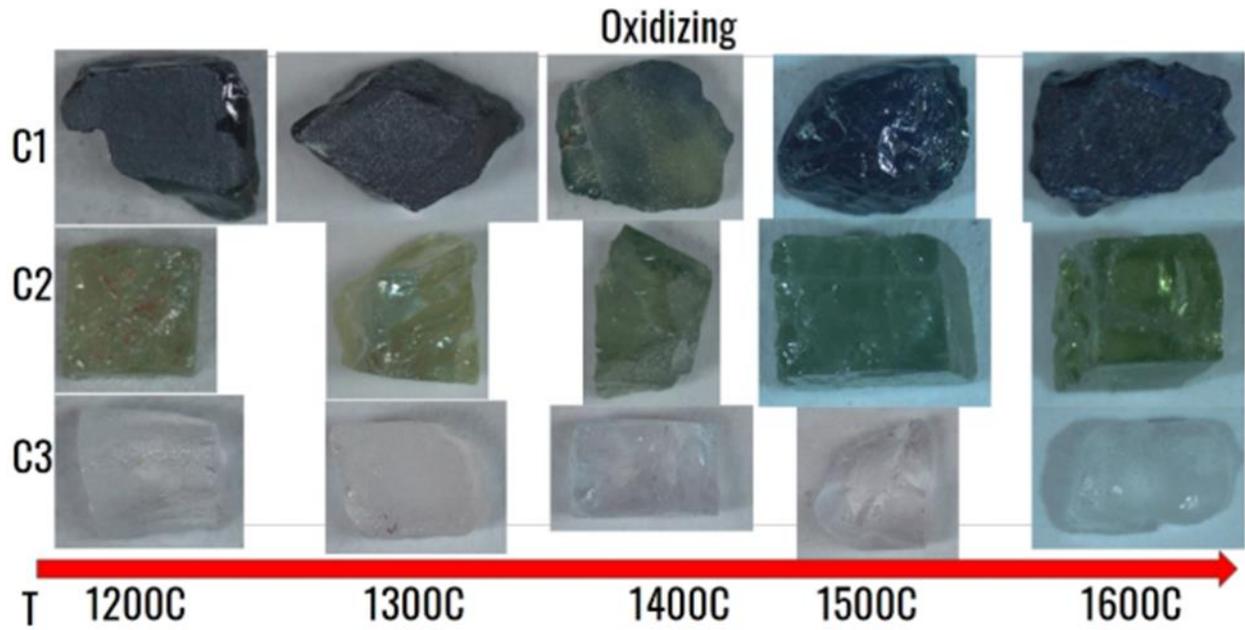
Figure 14. C1, C2, and, C3 sapphire samples after being heat-treated under oxidizing conditions.
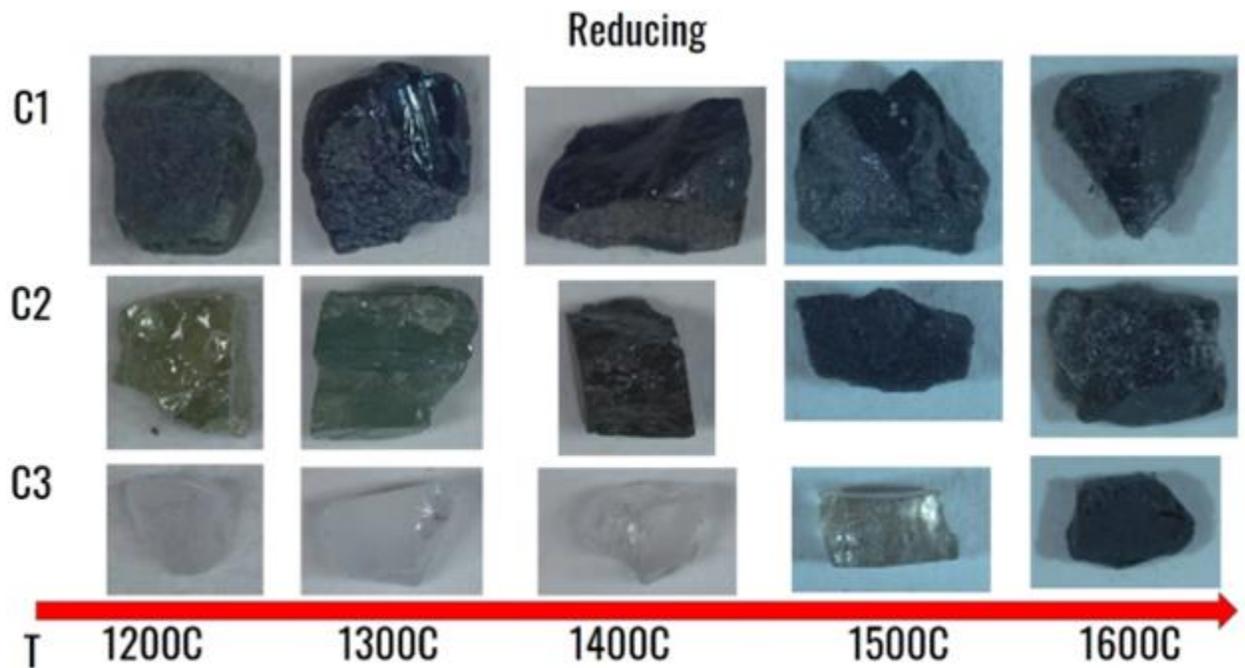
Figure 15. C1, C2, and, C3 sapphire samples after being heat-treated under reducing conditions.

obvious color changes. In experiment 2, oxidized C1 samples underwent no obvious color change while reduced C1 samples became slightly darker. Oxidized and reduced C2 samples underwent the same transition as experiment 1, and C2 oxidized and reduced samples, became lighter and gained a yellowing effect. The oxidized C3 samples underwent no visual change while C3-8 sample expanded the area of dark blue and the brown inclusions disappeared. In experiment 3 oxidized C1 samples had the same effect as experiments 1 and 2- some received a yellowing effect but all became lighter in color. Reduced C1 samples, on the other hand, changed from dark blue to even darker blue. Oxidized C2 stones followed the trend of experiment 1 and 2- became lighter and received a yellowing effect. Reduced C2 samples became much darker blue. Oxidized C3 samples had no visible color change but C3-11 from the reduced group received a blackening effect, changing the color from colorless/slightly yellow to grey/black. In experiment 4, oxidized C1 samples underwent almost no visible change in color, but the reduced C1 samples became black, and obtained a "charcoal" like outer pattern. Experiment 4 C2 oxidized samples followed the same trend as the previous 3 experiments- became lighter and received a yellowing effect while the reduced C2 samples became much darker, almost black with the same charcoal-like outer pattern as reduced C1 samples. C3 oxidized samples remained the same visually but the reduced C3 samples gained a dark grey color. In experiment 5, C1 oxidized samples became slightly lighter and exhibited a gorgeous sapphire blue color. C1 reduced and C2 and C3 samples all followed the same trend as in experiment 4.

Experiment 2 EPMA data in Table 2 is subdivided into three regions: not heat-treated, oxidized, and reduced. The table includes n- the number of data points, Ca, Ti, Zn, Mg, Si, Ga, Fe, Mn, and Cr concentrations in ppm along with their standard deviation for each stone that was used in the experiment. Raw EPMA data for Experiment 1, 2, 3, 4, and 5 can be seen in the

Exp2 Not heat treated	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-5	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-6	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-7	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-8	18	202.889	110.398	432.529	73.6661	166.9	59.7419	111.778	42.8097	389.667	110.513	205	125.252	9480.5	514.489	79	4.5	83.3333	6.94422
C2-5	15	36	18.0957	27.8	18.7232	100.167	78.4887	24.9	12.6842	38.75	24.1113	207.083	98.2043	9400.67	194.683	37.4444	18.3006	51	27.6647
C2-6	15	37.6364	19.662	52.9231	30.1036	120.8	68.1569	19.8571	14.0756	59.8	29.878	135.167	95.3177	9892.33	167.06	60.2	27.2646	39.4	30.5064
C2-7	15	39.25	20.909	33.2	23.2886	121.778	77.1417	29.7143	16.1043	49.6923	24.0397	192	132.057	8981.93	167.997	47	26.1151	43.9	27.9587
C2-8	15	24.0714	15.2852	47.5455	23.4496	78.8889	65.6039	28.8571	7.75387	54.2143	19.9756	234.571	111.265	8215.27	94.1449	41.75	29.265	40.7778	53.9522
C3-5	15	23.5714	15.1644	30.8	18.5462	99.875	88.8685	18	16.9652	69.9333	36.917	197.125	97.1499	1168.67	95.1845	36.8333	19.3427	52.8333	31.4506
C3-6	15	37.2727	23.0418	37.3333	27.5025	101.111	45.3932	31.2857	15.984	44.8	27.2817	118.875	95.7411	1814.6	98.8607	33.5714	42.0879	60.75	22.4095
C3-7	15	41.2	32.3475	70.8667	35.5225	106.333	69.8395	50.3571	18.9835	114.2	25.5948	158	85.3147	311.8	62.5824	46.6	46.8085	56.6	33.9211
C3-8	15	39	31.4219	52.0667	29.8897	125.333	88.2585	22.4	13.6763	62.9231	22.0923	170.091	108.446	638.533	86.5809	68.2	36.0744	45.875	31.2547
oxidized	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-5#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-6#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C2-5#	15	38.1667	22.9123	47.4286	31.8651	98.1429	72.7921	19.1818	10.8696	50.6429	29.7984	191.786	127.292	9488.33	171.487	29.125	18.4894	37.1667	22.5493
C2-6#	15	38.1429	53.6228	46.6429	33.1395	74.625	58.4849	27.4444	14.2057	68.6	40.0197	182.2	127.859	9283.33	406.797	41.8333	37.8876	63.7778	50.4992
C3-5#	15	35.8571	24.692	57.1429	20.7428	64	36.6918	33.1429	27.6608	51.9286	37.0607	134.25	106.327	1209.87	98.2981	38.7143	12.3255	59.125	39.1613
C3-6#	15	97.7143	60.2441	46.7143	17.6935	223.333	61.8457	41.6667	24.3698	48.9333	22.4335	207.769	122.125	2141.8	65.4739	34.5714	31.5769	50.5	27.3176
reduced	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-7#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-8#	12	92.2	13.644	341.5	74.3511	161.75	88.8492	85.25	24.6361	257.417	179.469	201.286	115.791	11538.1	1255.21	103.667	18.5712	82.6667	6.84755
C2-7#	15	46.3846	21.8052	38.5	23.81	97	84.6389	21.1667	15.4857	34.0714	20.7828	264.4	120.729	8976.73	108.64	72.3333	19.7034	67.2	52.0976
C2-8#	15	37	23.1912	44.9286	29.6611	94.6154	96.3923	12.6667	3.39935	75.7857	78.7212	199.667	86.4864	8259.67	178.765	59.3333	29.2271	43.25	29.857
C3-7#	15	45.5	30.7015	74.0667	36.5595	152.167	56.7521	62.9333	32.8339	65.0714	19.3334	206	116.489	323.4	56.507	37.9091	21.1164	52.8333	36.5487
C3-8#	15	29.7143	18.8355	67.9231	27.7252	59.1429	45.4452	30.4545	12.361	36.2143	18.5749	179.1	132.059	721.6	78.0784	56	20.8746	51.2857	32.7751

Table 2. EPMA data for Exp 2 in ppm. Ti and Fe outlined in red.

appendix. Generally, C1 stones contained the highest amount of Ti, while C2 and C3 have close to an equal amount. C1 and C2 also contained a considerably higher amount of Fe than C3. In Exp 2, the C2 oxidized stones decreased in Ti slightly but increased in Fe while the reduced stones decreased slightly in Fe and Ti. In C3 stones, Fe and Ti increased both in reducing and oxidizing conditions. C1 reduced stones decreased in Ti and increased in Fe. The degree of change in minor and trace element concentrations varies highly in each experiment. In experiment 1 C2 stones decreased in Fe and Ti in oxidizing conditions and increased in both concentrations in reducing conditions. C3 stones in oxidizing conditions gained Fe and Ti remained the same, but in reducing conditions, Ti increased and Fe decreased. In experiment 5. C1 samples increased in Fe and Ti under oxidizing conditions and reducing conditions. C2 samples decreased slightly in Fe and Ti under oxidizing conditions and remained almost equal in reducing conditions. C3 samples experienced almost no change under both conditions.

The Ga/Mg ratio for the majority of C3 and C2 samples and all of the C1 samples is below 10 (Figure 16). A few C2 and C3 samples do possess a Ga/Mg ratio higher than 10. C1, C2, and C3 are all in specific regions of the graph and never intersect. C3 has an overall low Fe concentration while C2 and C1 both contain high concentrations of Fe. Ga concentration is very similar across C1, C2, and C3 stones.

UV-vis spectra data for experiment 2 (Figures 17, 18, and, 19) shows that all sapphires contained a peak at 450 nm which is known to be a pair of Fe^{3+}-Fe^{3+} ions (Pardieu, V., 2017). C1 sapphires have a broad band of lower absorbance from 520 nm to 600 nm and some of C2 and C3 stones have an even larger band of lower absorbance. C1 sapphires have almost identical absorption spectra between pre and post-heat-treatment for both reducing and oxidizing conditions. Oxidized C2 sapphires exhibited higher absorbance after heat-treatment while

reduced C2 samples exhibited an interesting transition of absorbance. The pre-heat-treatment stone indicates higher absorbance than the post-heat-treatment except from 500 nm to 710 nm in which the post-heat-treatment sapphire has higher absorbance. C3 samples indicate higher absorbance in post-heat-treatment samples. The C3 oxidized sample also contained a peak at 690 nm. The absorbance is lowest in C1, C2 is higher and C3 has the highest absorbance. These trends are consistent throughout each experiment except Experiment 4 and Experiment 5 reduced stones always resulted in lower absorbance than the untreated stones. All UV-vis spectrums for Experiments 1, 2, 3, 4, and 5 can be seen in the appendix.
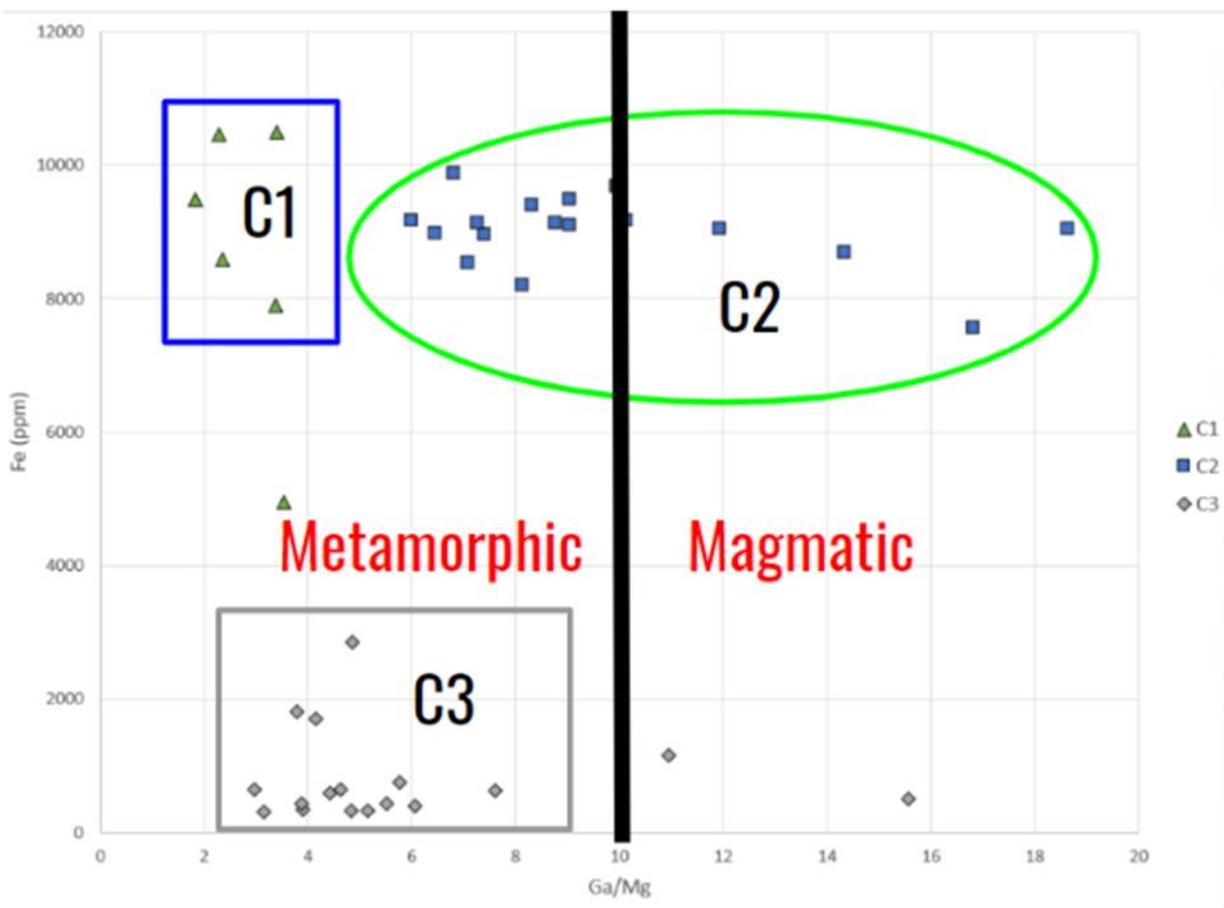
Figure 16. A Fe vs Ga/Mg graph. If the stone contains Ga/Mg ratio < 10, it is considered metamorphic. If Ga/Mg ratio > 10 then it is considered magmatic.
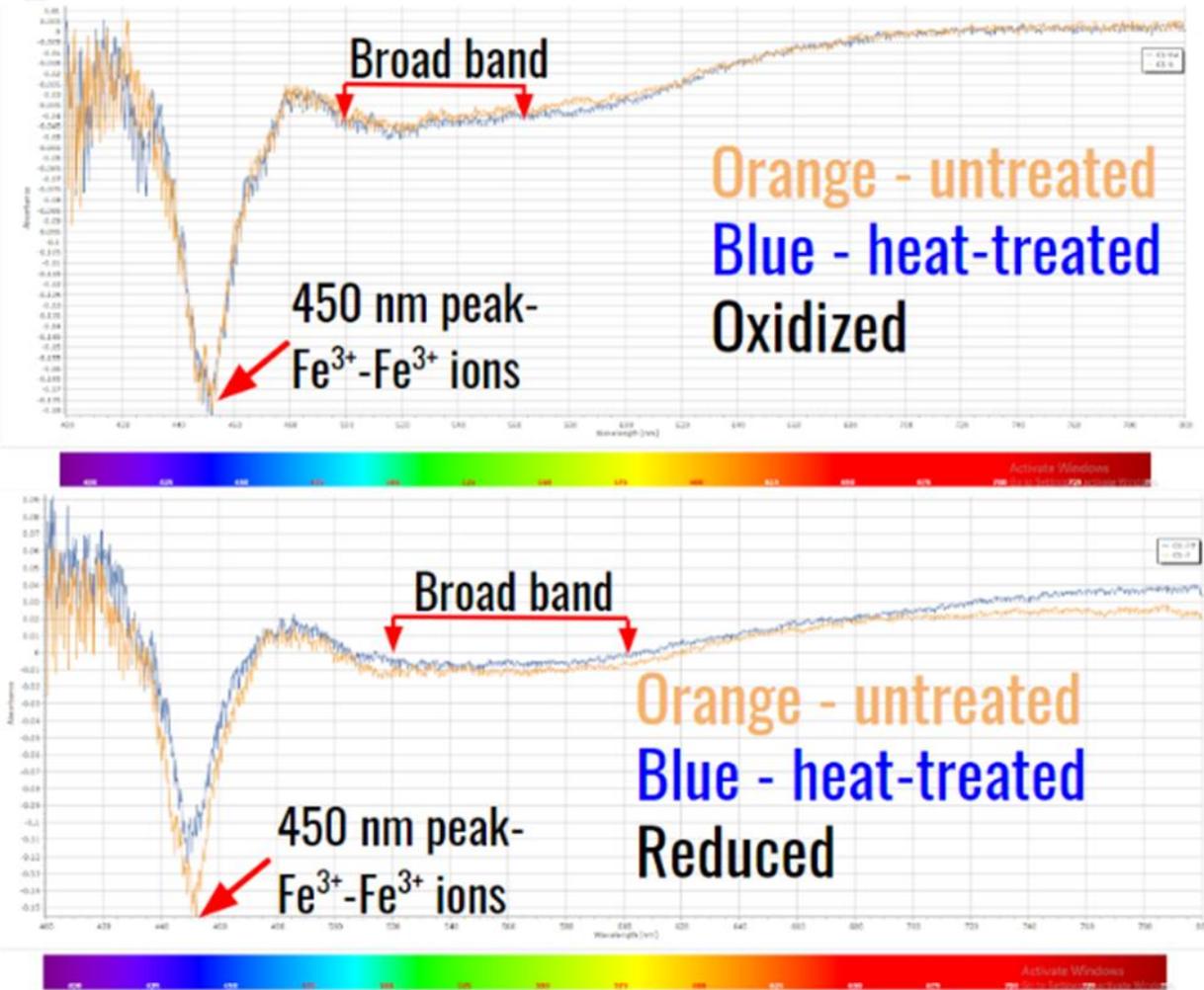
Figure 17. UV-vis spectra data for Exp 2 C1 sapphires. (Top) oxidized, (bottom) reduced. The orange line shows untreated and blue shows heat-treated data.
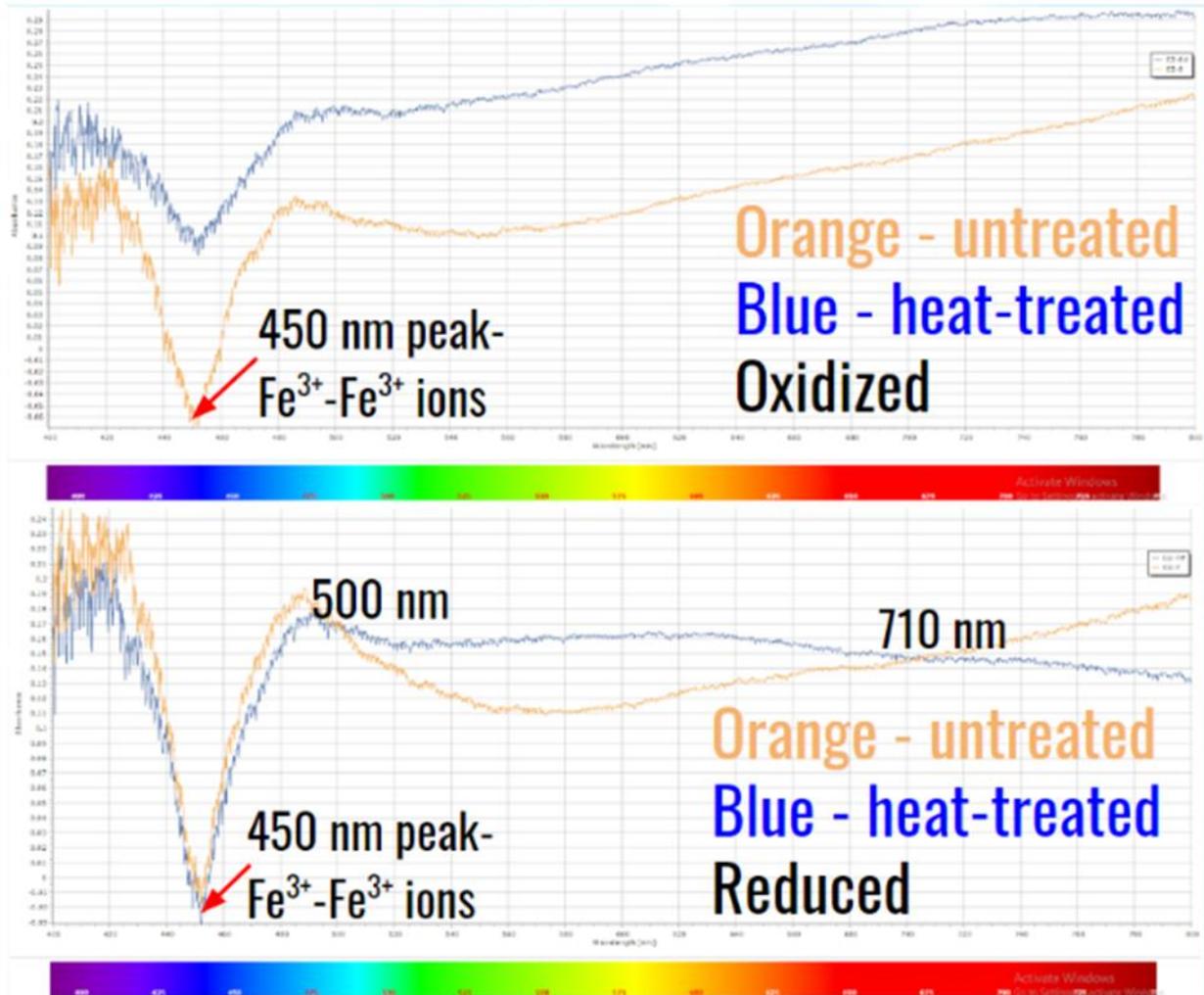
Figure 18. UV-vis spectra data for Exp 2 C2 sapphires. (Top) oxidized, (bottom) reduced. The orange line shows untreated and blue shows heat-treated data.
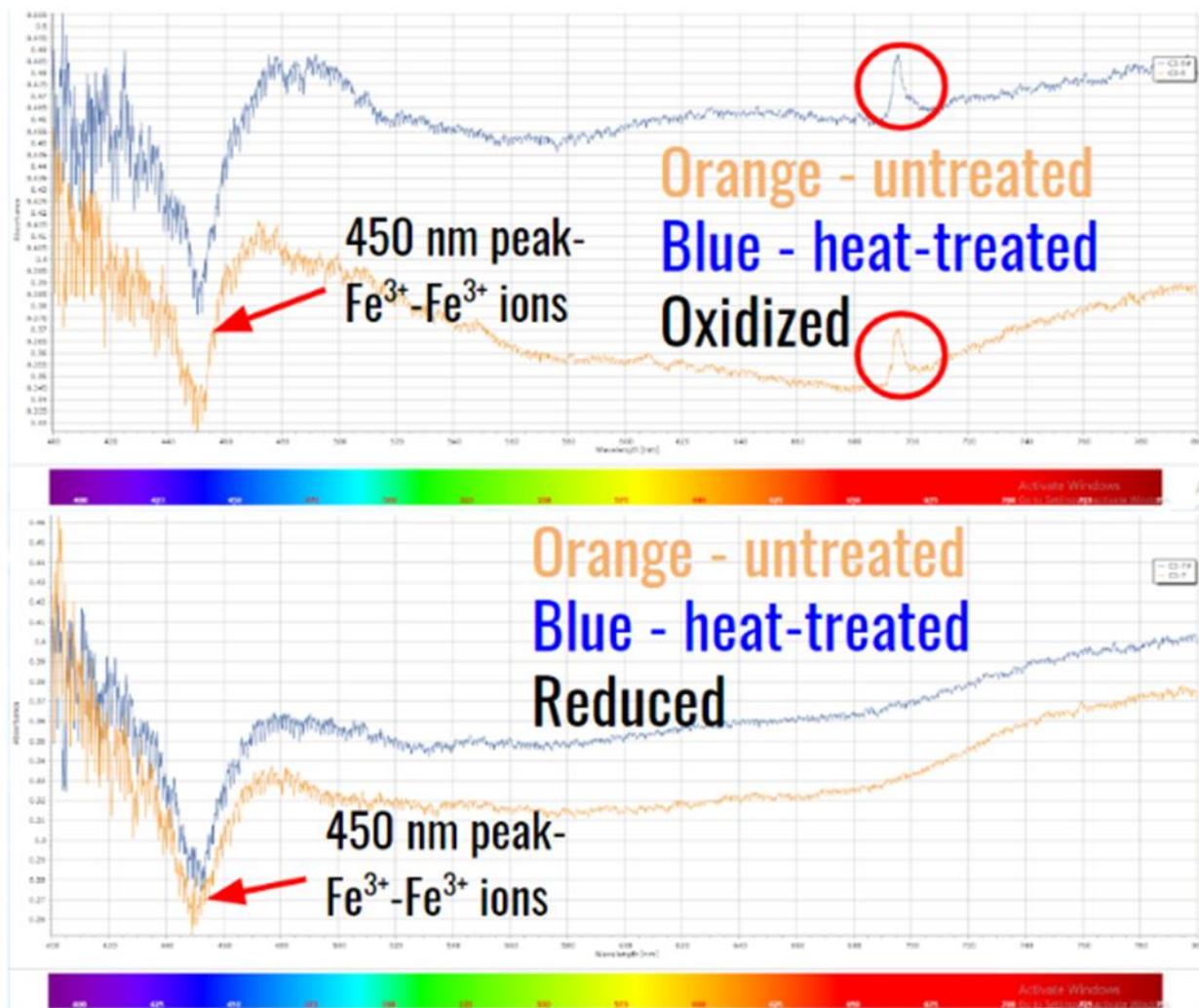
Figure 19. UV-vis spectra data for Exp 2 C3 sapphires. (Top) oxidized, (bottom) reduced. The orange line shows untreated and blue shows heat-treated data.

Discussion

In most of the cases, C1 samples contained the highest amount of Ti, resulting in more Ti and Fe chemical interactions and producing dark blue color in the stones. C2 samples contained a substantially decreased amount of Ti but an equal amount of Fe as C1. Since there is less Ti to interact with the still high amount of Fe, more of the Fe ions form the Fe^{3+}-Fe^{3+} ion pairs. The Fe^{3+}-Fe^{3+} ion pair results in the yellowing color, hence why most C2 samples are lighter blue

and some contain areas of green coloration. C3 samples contained an almost identical amount of Ti as C2 samples but, had substantially less Fe than C1 and C2. This possibly means that there simply is not enough Fe and Ti in the stone to produce the deep blue or any other color. To add color to C3, diffusion heat treatment is most likely necessary.

For the best heat-treatment results, 1200°C for 10 hours soak time should be avoided due to goethite forming rusty red hematite. As described in the background section, goethite is one of the main constituents of limonite and is deposited in the corundum inclusions epigenetically. Figure 20 shows this effect. The dark brown goethite changes to rusty red hematite. The red inclusions are not ideal for sapphires that are meant to be used for jewelry. Figure 21 shows the pre (left) and post-heat treatment (right) pictures of the experiment 2 stones. C1-6 on top, C2-6 middle, and C3-5 bottom. Visually, C1-6 undergoes minimal to no visible color changes and as seen in Figure 17 the spectra data are almost identical for pre and post-heat-treatment. C2-6 becomes lighter and receives a yellowing effect resulting in an overall change from blue/green to light green stone and C3-5 also has no visible color changes.

Figure 20. C2-1 sapphire pre-heat-treatment (left) and post-heat-treatment (right). The dark brown filled inclusions changed to dark red (transition from goethite to hematite)
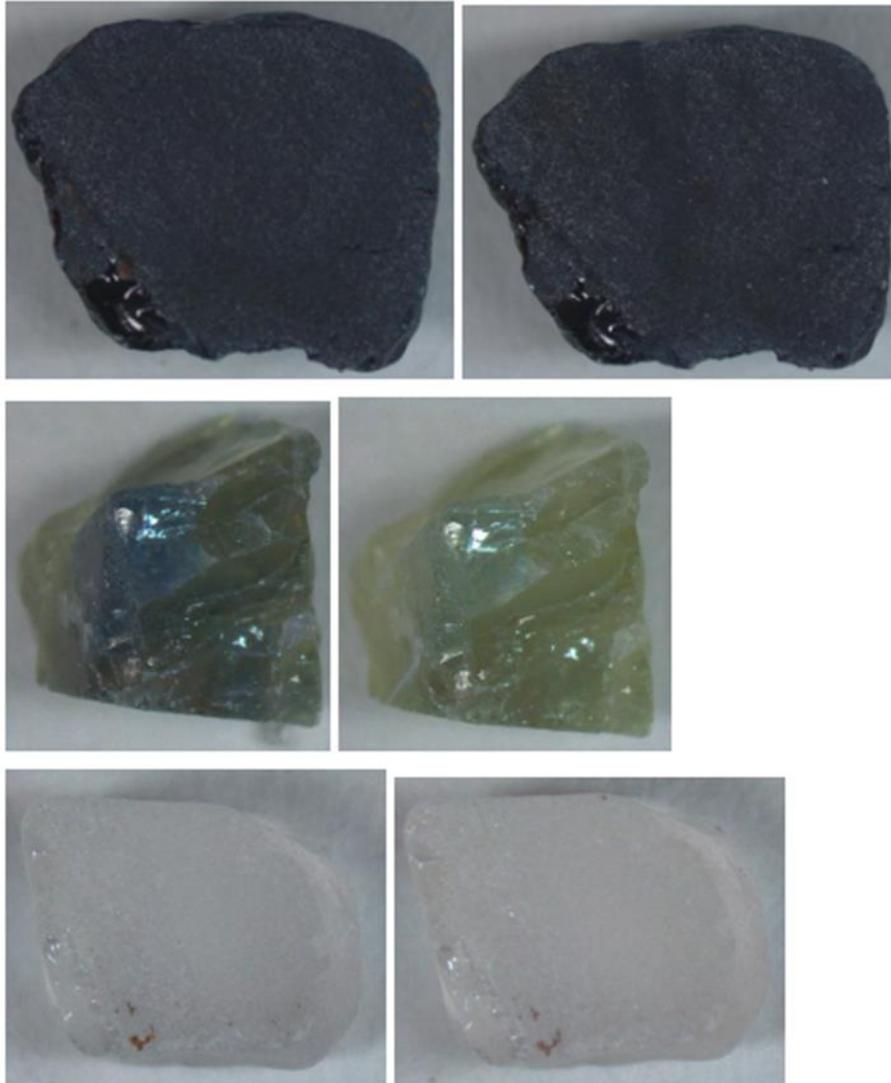
Figure 21. Experiment 2 oxidized stones. C1-6 (top), C2-6 (middle), and C3-5 (bottom). Pre- heat-treatment (left), post-heat-treatment (right)

One issue with the data provided by EPMA for this project is that the standard deviation is quite high. This means that the samples are quite heterogeneous. In sample C1-14# which was exposed to oxidizing conditions, the amount of Ti measured was 39561.8 ppm which is more than 20 times the C1-13# value which was also exposed to oxidizing conditions. The standard deviation for C1-14# is also incredibly high at 67666. This most likely means that one or more of

the analyzation spots for this sample encountered a rutile inclusion which resulted in much higher than average values.

The EPMA data for C2-6 indicates that Ti concentration has marginally decreased and Fe concentration has also decreased. This is difficult to tell if it is a result of the sample heterogeneity or if some chemical changes occurred in the lattice structure. The yellowing effect which lightens the stone can be explained by an increase in Fe^{3+} due to the oxidation of Fe^{2+} ions in the structure. The Fe^{3+} ions form the $Fe^{3+}-Fe^{3+}$ ion pair which results in a yellow color and the 450nm peak in UV-vis spectra which is consistent across all UV-vis spectroscopy data. The UV-vis spectra data also indicates an increase in absorption after heat-treatment which means that more of the light is absorbed and less is detected by the spectrometer. Sapphire C3-5 EPMA data shows an increase in Ti however Fe remained almost the same after heat-treatment. This could be due to the increase in Ti^{4+} ions which do not partake in the corundum's lattice structure. Just like for C2-6, the C3-5 UV-vis data indicates an increase in absorption after heat-treatment. The C3-5 UV-vis data also demonstrates a peak at 690 nm which corresponds to a fine-grained, titanium-containing, calcium aluminum oxide mineral - hibonite which is black to brownish black in color (Colors in minerals, 2009). Hibonite can be commonly found in Madagascar, one of the countries of origin for the sapphire stones (Hibonite Mindat). Hibonite that is present in C3-5 can be seen in Figure 21.

Experiment 2 reduced stones before and after can be seen in Figure 22. C1-7 follows the same trend as the oxidized C1-6, meaning almost no visual changes and almost exact UV-vis spectra for pre and post-heat-treatment. C2-7 is the same as the oxidized C2-6 except with even fewer changes to the concentrations of Fe and Ti. However, the UV-vis data differs in that C2-7 pre-heat treatment absorption is higher until 500 nm and then after 710 nm. Sapphire C3-7 has

almost no visual changes as well as no changes to Fe and Ti concentration. The UV-vis data follows C3-5 in that the post-heat treatment produced higher absorption than the pre-heat treatment.
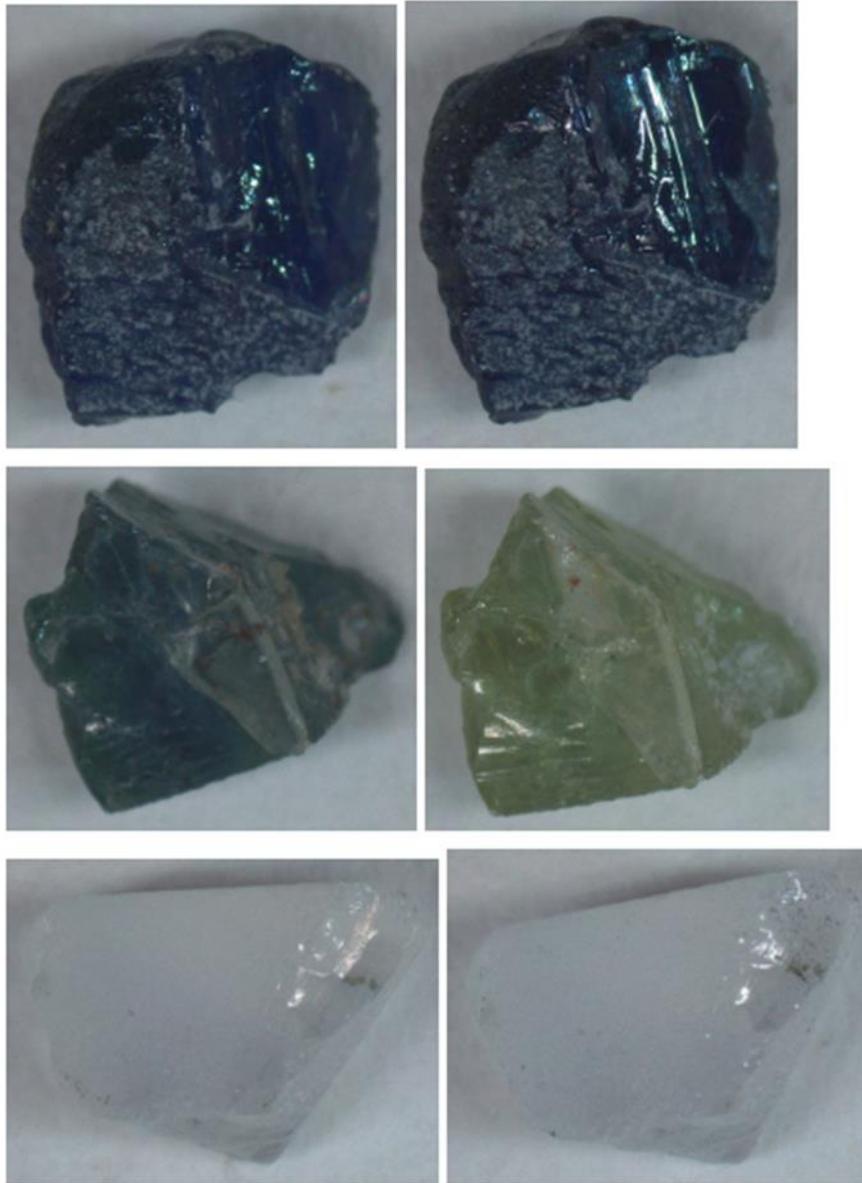

Figure 22. Experiment 2 reduced stones. C1-7 (top), C2-7 (middle), and C3-7 (bottom). Pre-heat-treatment (left) and post-heat-treatment (right)

Experiment 3 sapphires behaved slightly differently in reducing conditions than

Experiment 1 or 2. The reduced C1-11 and C2-12 both got darker after heat treatment (Figure

23). According to EPMA data, C1-11 decreased in Ti and Fe while C2-12 had less change but
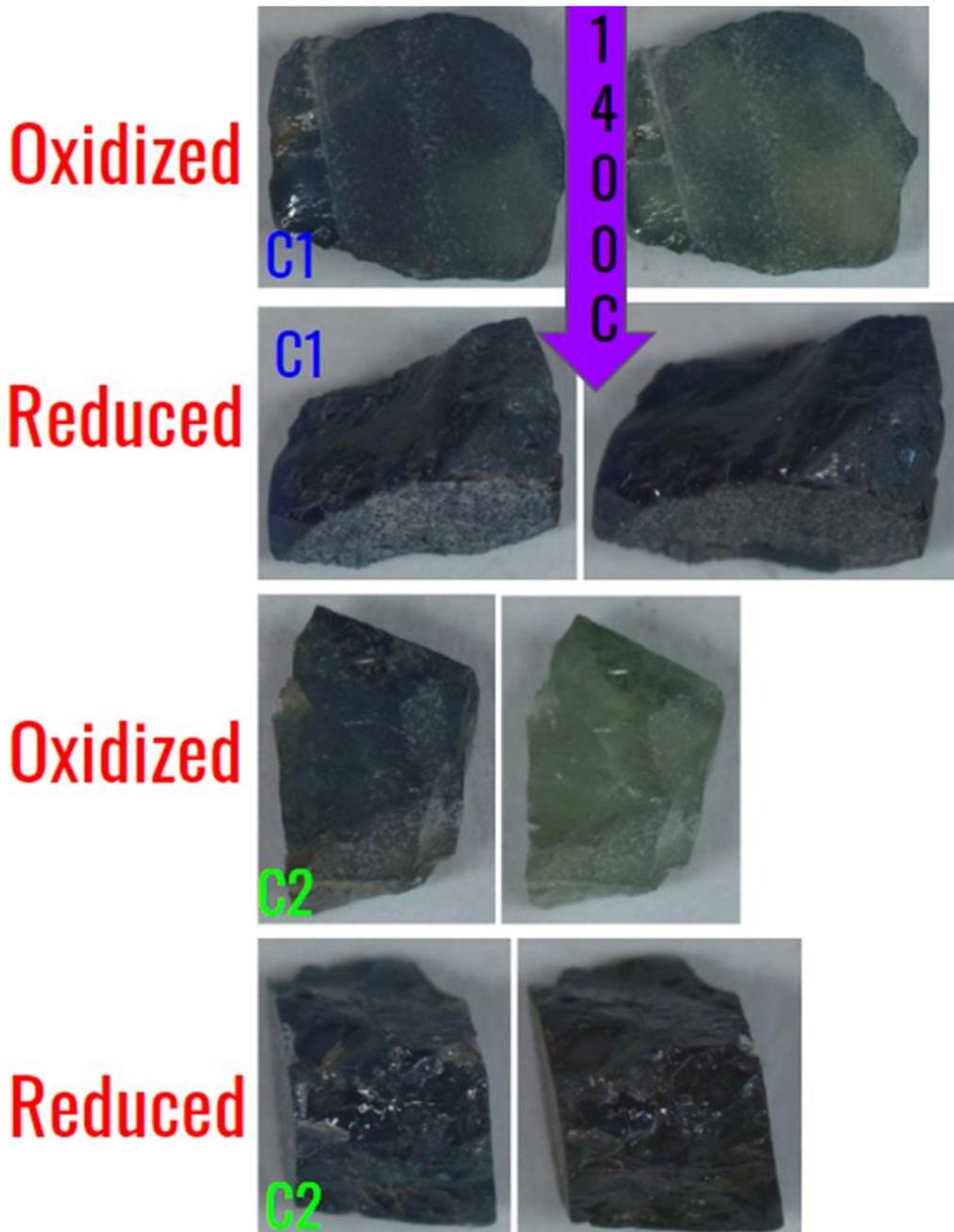
Figure 23. Experiment 3 C1 and C2 oxidized and reduced sapphires. Oxidized C1-10 (top), reduced C1-11 (top middle), oxidized C2-10 (bottom middle), and reduced C2-12 (bottom). Pre-heat treatment (left) and post-heat treatment (right)

decreased in Ti and increased in Fe slightly. For C1-11 this could be interpreted that more of the Ti and Fe are forming ion pairs and are incorporated into the structure and less are stuck in inclusions. C2-12 changes to chromophore concentrations are very minor so it is difficult to tell what causes the darkening of the stone. UV-vis data indicate that both samples, before and after heat-treatment contain the 450 nm Fe^{3+}-Fe^{3+} pair. C1-11 has almost identical before heat-treatment and after heat-treatment spectra, while C2-12 decreases in absorbance substantially post-heat treatment.

Experiments 4 and 5 both have very similar outcomes. Exp 5 oxidized samples can be seen in Figure 24. C1 and C2 samples became lighter while C3 remained the same.
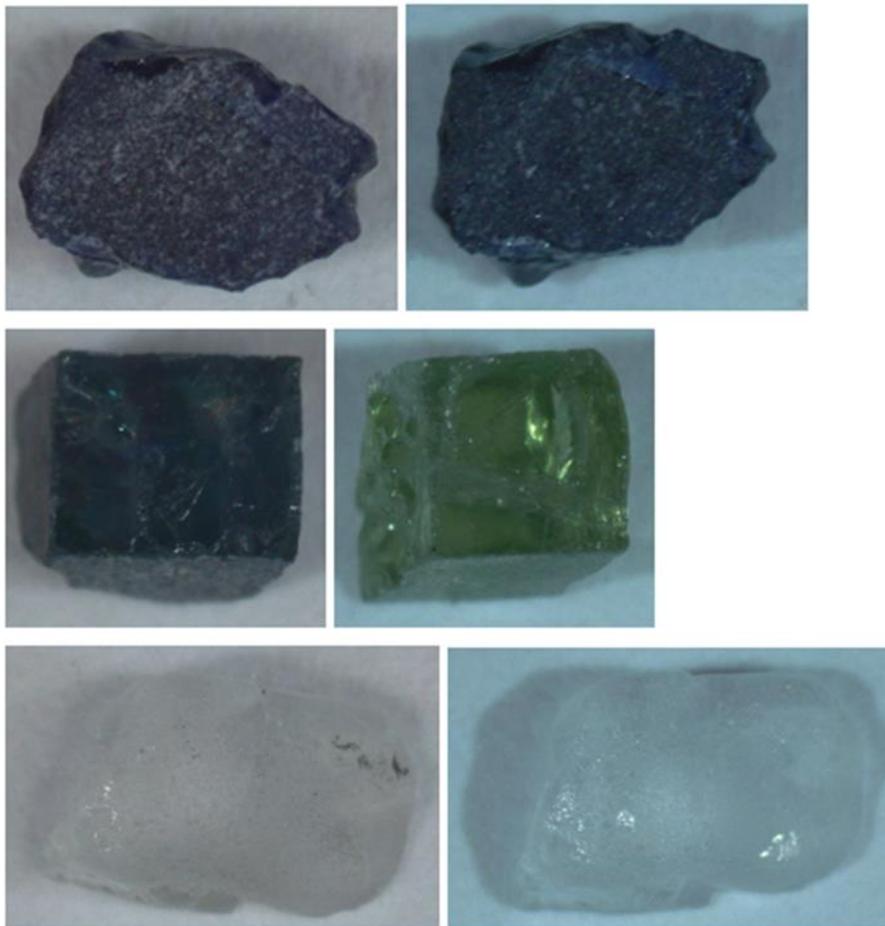

Figure 24. Experiment 5 oxidized samples. C1-18 (top), C2-17 (middle), and C3-18 (bottom). Pre-heat treatment (left), post-heat treatment (right)

C2 stones were also exposed to the yellowing effect causing a change of color from dark blue to green. EPMA data shows that C2-17 and C3-18 both had insignificant Fe concentration changes but C2-17 had a slight increase in Ti after heat-treatment. A possible cause for the increase in Ti is that the increased amount of Ti^{4+} ions results in less Ti partaking in the corundum's lattice structure. The UV-vis data shows that the absorption increased for all stones after heat-treatment. The 450nm peak was present in each stone as well. Interestingly, the absorption difference between un-heat treated and heat-treated varied from sample to sample. C1 had the lowest absorbance difference, C2 slightly higher and C3 even higher. Exp 4 and 5 reduced samples behaved differently from previous experiments. The samples became much darker/black and obtained an external layer with a charcoal-like look (Figure 25). This is most
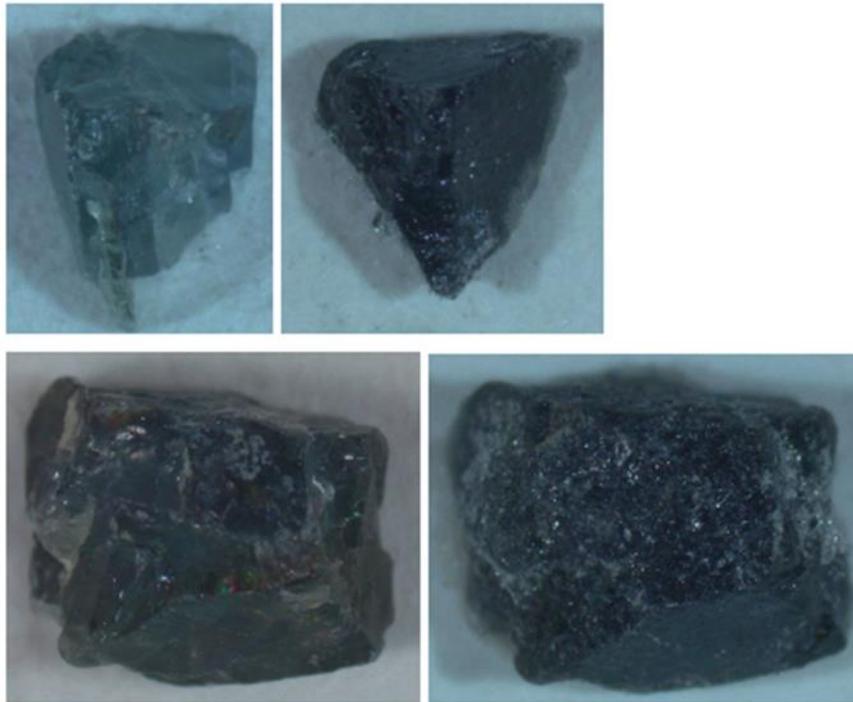
Figure 25. Experiment 5 reduced samples. C1-19 (top) and C2-20 (bottom). Pre-heat treatment (left), post-heat treatment (right)

likely due to a surficial carbon deposition from the graphite slabs that were used to achieve reducing conditions by using the CCO oxygen fugacity buffer. The UV-vis spectra data was also different from other experiments. Generally, untreated had higher absorbance than heat-treated in this case. C1-19 sapphires had a larger than previous C1 stones absorption difference between untreated and heat-treated. C2-20 sapphire consisted of the untreated sapphire having a higher absorbance everywhere except at 450nm peak where it was the same as the heat-treated.

Peucat et. al (2007) demonstrated that the Ga/Mg ratio versus the Fe concentration discriminates between "metamorphic" and "magmatic" sapphire-forming environments. Figure 16 plots the Fe and Ga/Mg data obtained from the EPMA and shows that C1, C2, and C3 each cluster separately which may indicate formation environments. One interpretation of this is that, even though specific mine data were not provided for the raw sapphire samples, clues to the original geologic source for the samples may be deduced from the geochemical compositional data;   each of these C1, C2, C3 groups of samples perhaps comes from different mines located in Tanzania and Madagascar, since the compositional concentrations are all different. All three groups consist of samples that contain Ga/Mg ratio < 10, meaning that the sapphires are of metamorphic origin. C2 and C3 contain a few stones that possess a Ga/Mg ratio > 10, however, this could be due to Ga, Mg or Fe inclusions that spike up the average value of those concentrations in the stone. However, the larger spread of data for C2 sapphires could also indicate an open system behavior, meaning that the sapphires may have formed in areas subjected to contact metamorphism or in other open system environments. This data can be matched with the bedrock geology of the countries of origin. The bedrock geology of Tanzania (Figure 26) indicates a mostly metamorphic geology which agrees with the findings of the Fe and Ga/Mg graph.
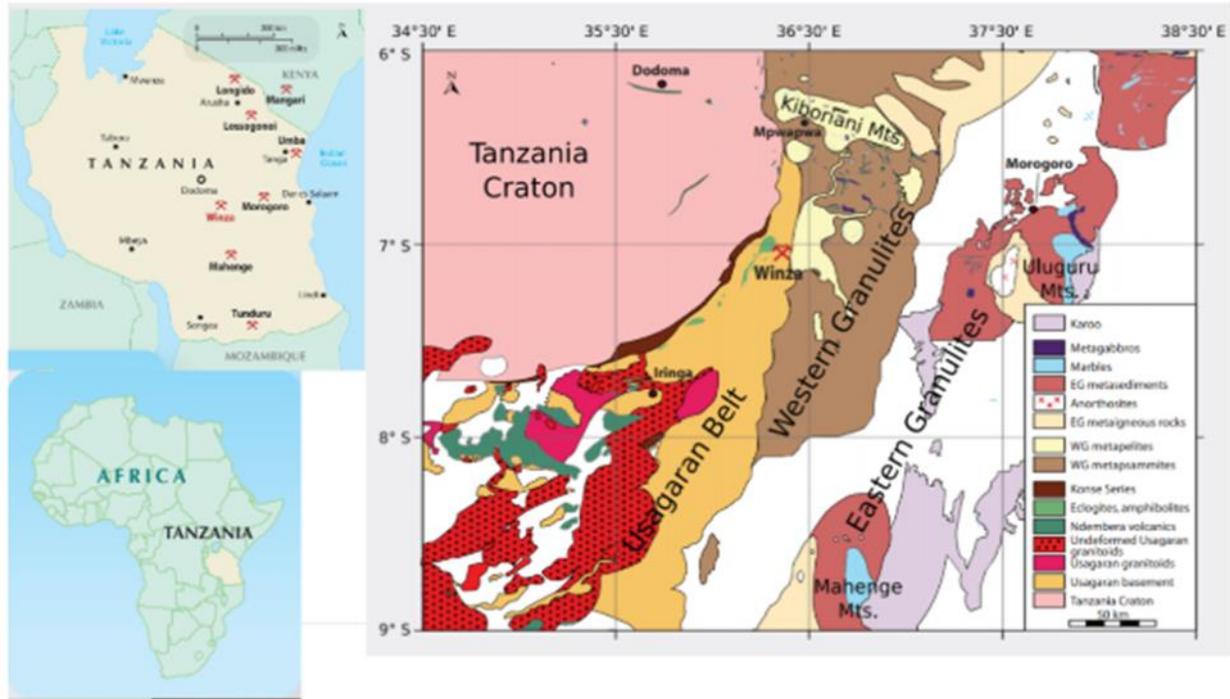
Figure 26. Bedrock geology map of Tanzania. It is mostly composed of metamorphic rocks (Schwarz, D. et al, 2008)

Conclusions

The sapphires from Madagascar and Tanzania can be used for heat-treatment purposes to increase their monetary value. The three different groups of sapphires (C1, C2, and C3) all seem to have different mine locations based on the Fe vs Ga/Mg ratio plot. C1 sapphires were mostly dark blue, C2 sapphires were lighter blue with some containing green and C3 sapphires were mostly colorless. When using graphite slabs to induce the CCO buffer for reducing conditions several experimental provisions must be taken into account: the graphite slabs must be sealed off from as much oxygen as possible and the graphite slabs should only be used for reducing heat treatment experiments of less than 1500°C, due to the carbon depositional coating with temperatures at or higher than 1500°C. Heat treatment in oxidizing conditions had no effect on color for C1 stones until 1400°C with most notable differences in 1600°C where the color

became lighter. C2 samples always had a yellowing effect and became lighter independent of temperature. C3 samples had almost no effect on color independent of conditions and temperature with the sole exception that the stones became black if used for reducing conditions in higher or at 1500°C. Goethite formed hematite at 1200°C but was minimized to zero at 1300°C. Knowing this, it is most likely best to heat treat sapphires under oxidizing conditions: C1 at 1600°C, C2 at 1300°C and C3 with diffusion heat treatment.

UV-vis data proved useful in that the 450 nm peak for $Fe^{3+}-Fe^{3+}$ ion pairs was always present and can be used to identify if the stone is corundum or not. The heat-treated spectra usually showed an increase in absorption with a few exceptions such as when the samples were coated with the black layer.

EPMA data were useful for determining the sample chromophore trace and minor element concentrations especially Fe and Ti which are the main elements that cause the blue color in sapphires. C1 sapphires contained the highest amount of Ti and Fe (Ti > 100ppm, Fe 8000-10000 ppm), C2 sapphires contained much less Ti but the same amount of Fe (Ti 40-50ppm) and C3 samples contained the same amount of Ti as C2 and the least amount of Fe (Fe 400-700 ppm). The heterogeneity of the samples made it difficult to draw confident conclusions from the differences between pre- and post-heat-treatment since sometimes the values were increasing and decreasing between two samples that were used in the same temperature and conditions. However, high standard deviation values of some of these analyses could indicate that inclusions rather than the matrix were sampled and probably should not be included in the average composition. Also, many of the concentrations were below the detection limit, meaning that LA-ICP-MS analyses might have been better for this project.

The sapphires from Tanzania and Madagascar are worthy of being heat-treated for business. The dark blue sapphires are better heat-treated separately from the lighter sapphires that may contain some green. The colorless sapphires require more than just heat-treatment, possibly diffusion heat-treatment. If an EPMA instrument is readily available and inexpensive to use, then samples with high Ti and Fe must be heat-treated differently (as described before) from samples with low Ti and high Fe and vice versa. If heat-treatment proves successful, the sapphire prices would be less than half of the natural sapphires and would be therefore more readily accessible to the general public.

Acknowledgements

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Appendix
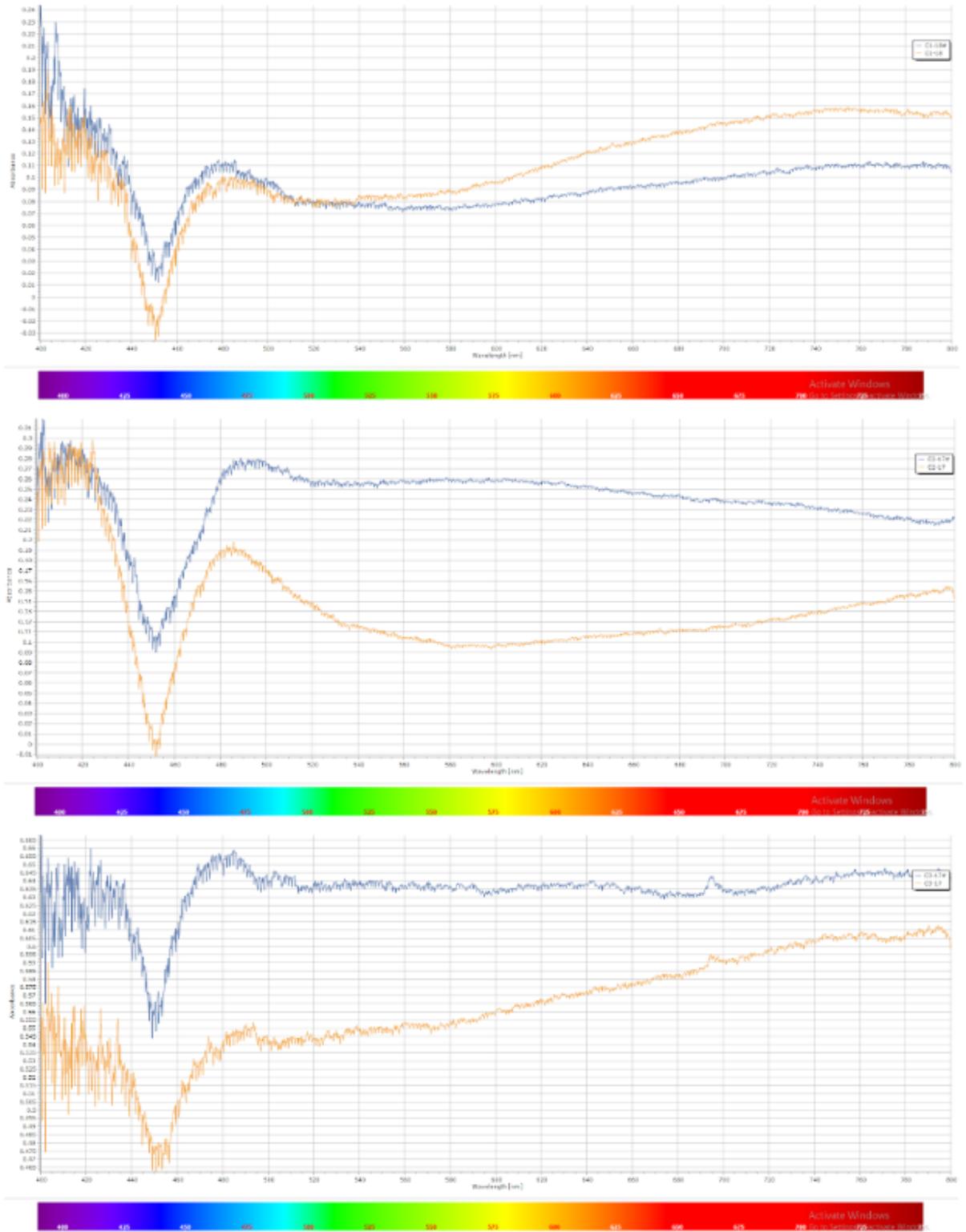
UV-vis spectra data for oxidized sapphires in experiment 5. C1-18 (top), C2-17 (middle), C3-18 (bottom)
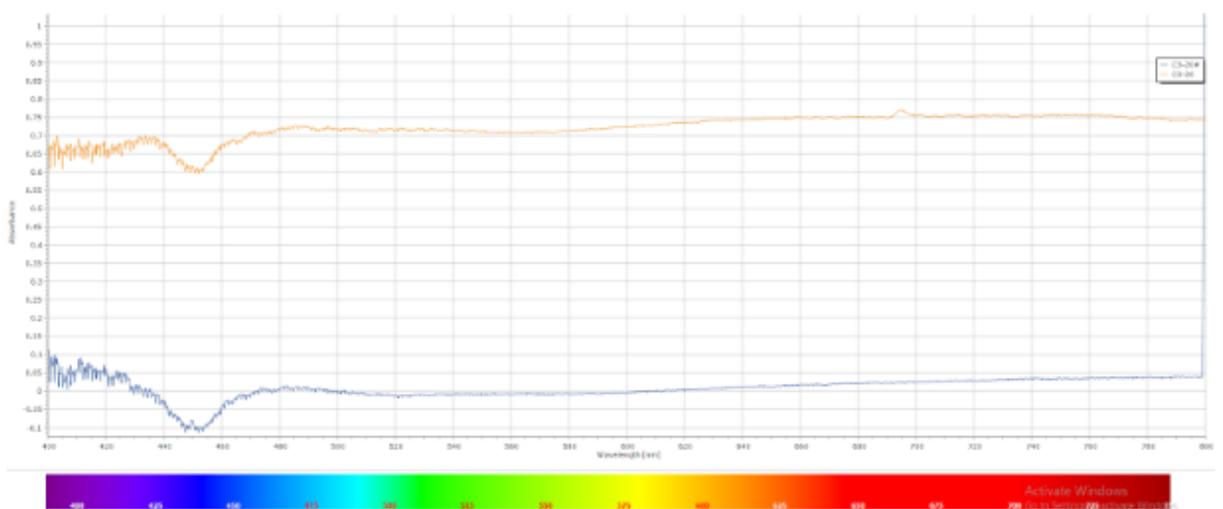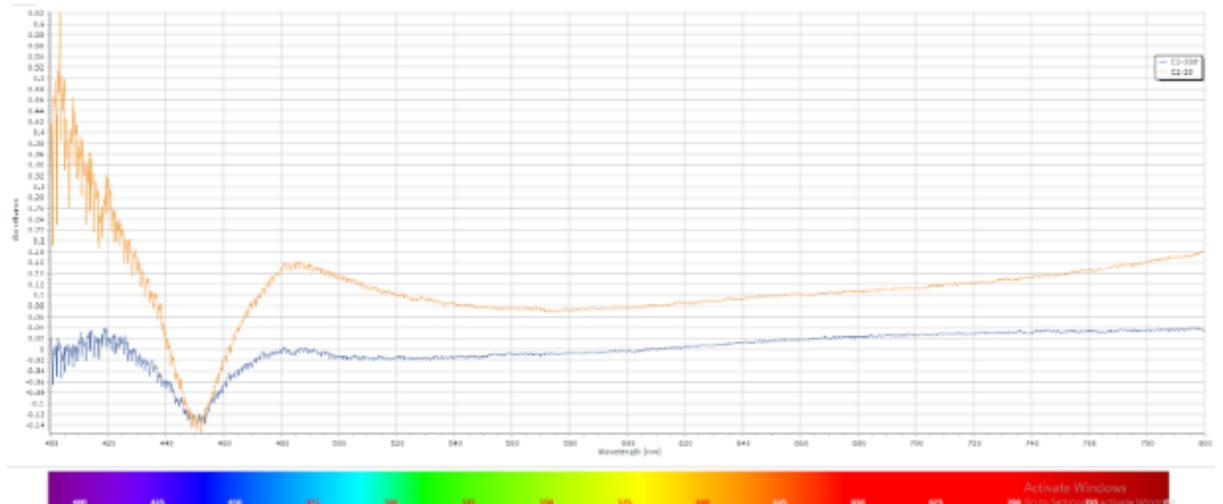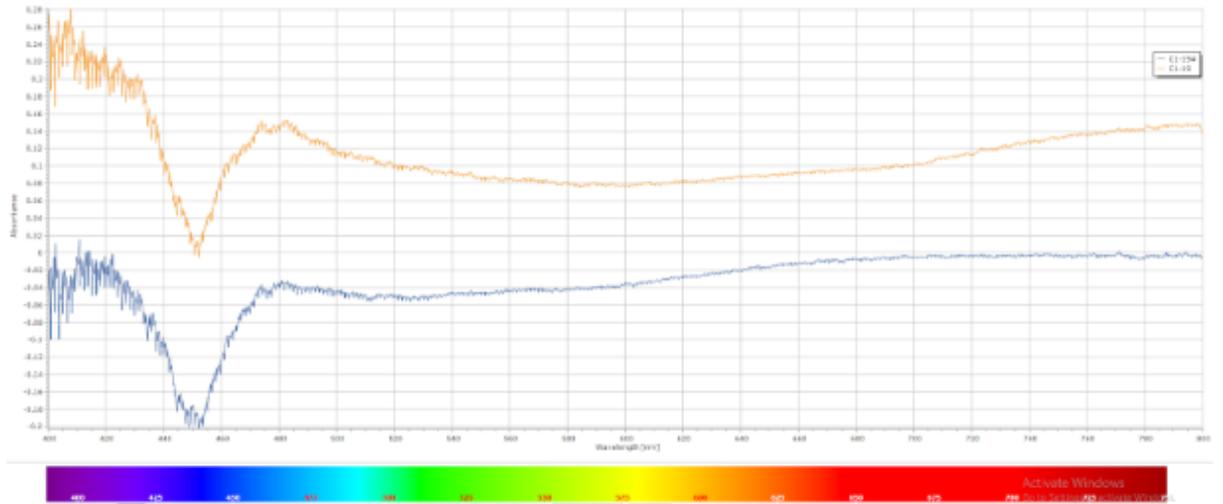
UV-vis spectra data for the reduced sapphires in experiment 5. C1-19 (top), C2-20 (middle), and C3-20 (bottom)
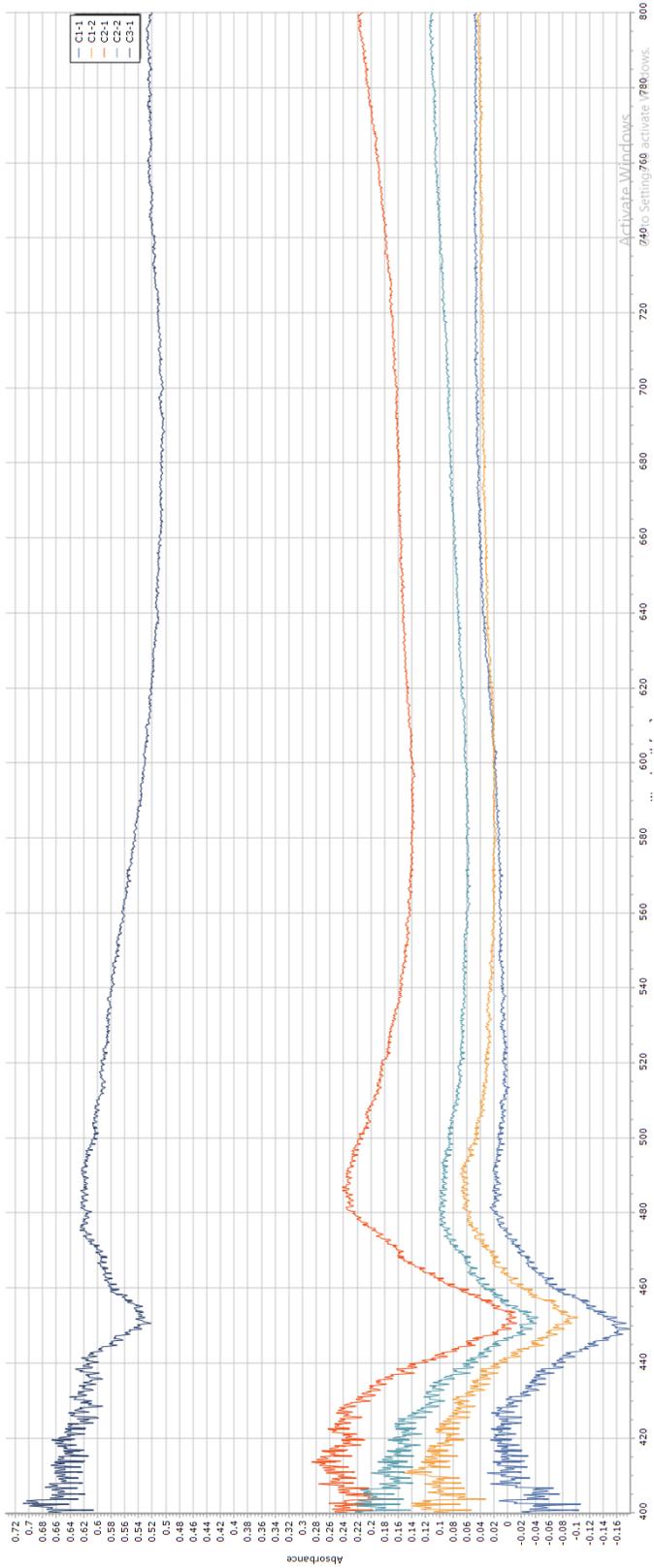
UV-vis spectra of Exp 1 oxidized C1, C2, and C3 stones. Pre and post heat-treatment (labeled with #)
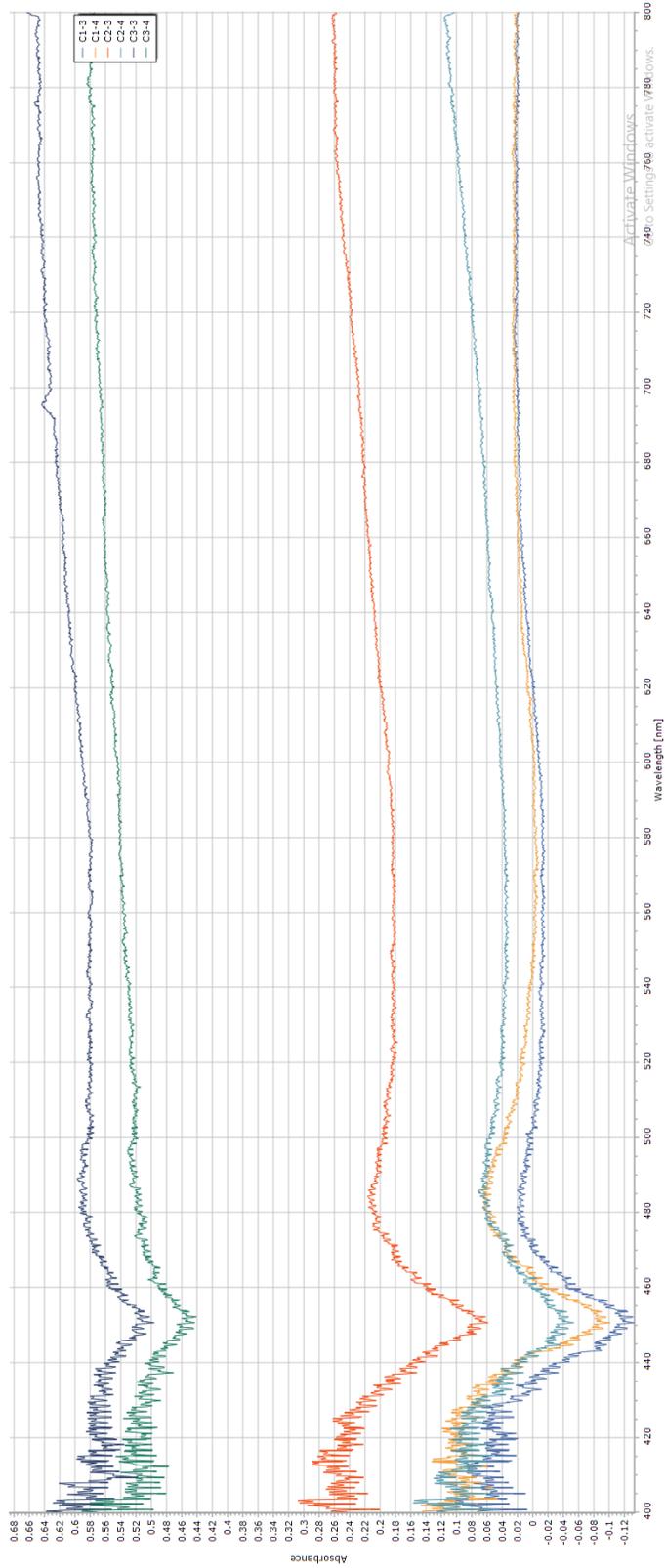
UV-vis spectra of Exp 1 reduced C1, C2, and C3 stones. Pre and post heat-treatment (labeled with #)
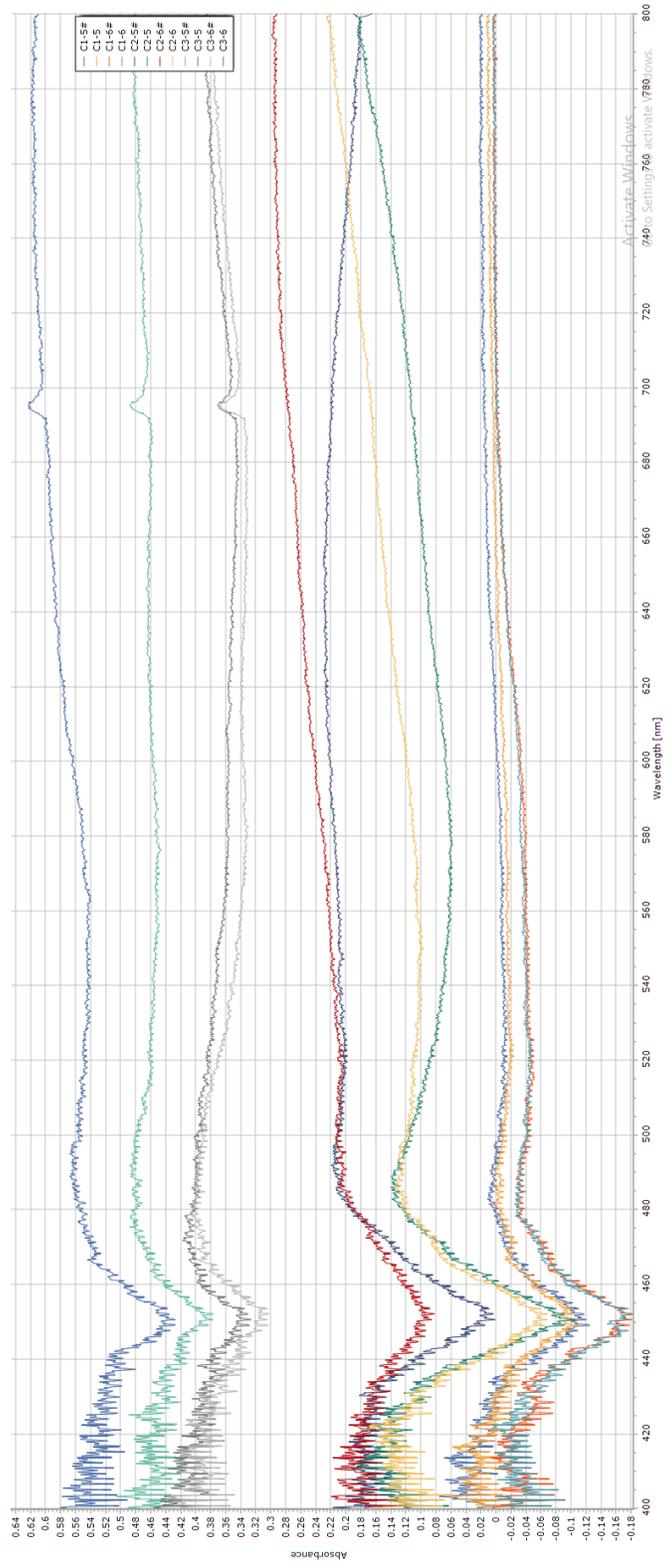
UV-vis spectra of Exp 2 oxidized C1, C2, and C3 stones. Pre and post heat-treatment (labeled with #)
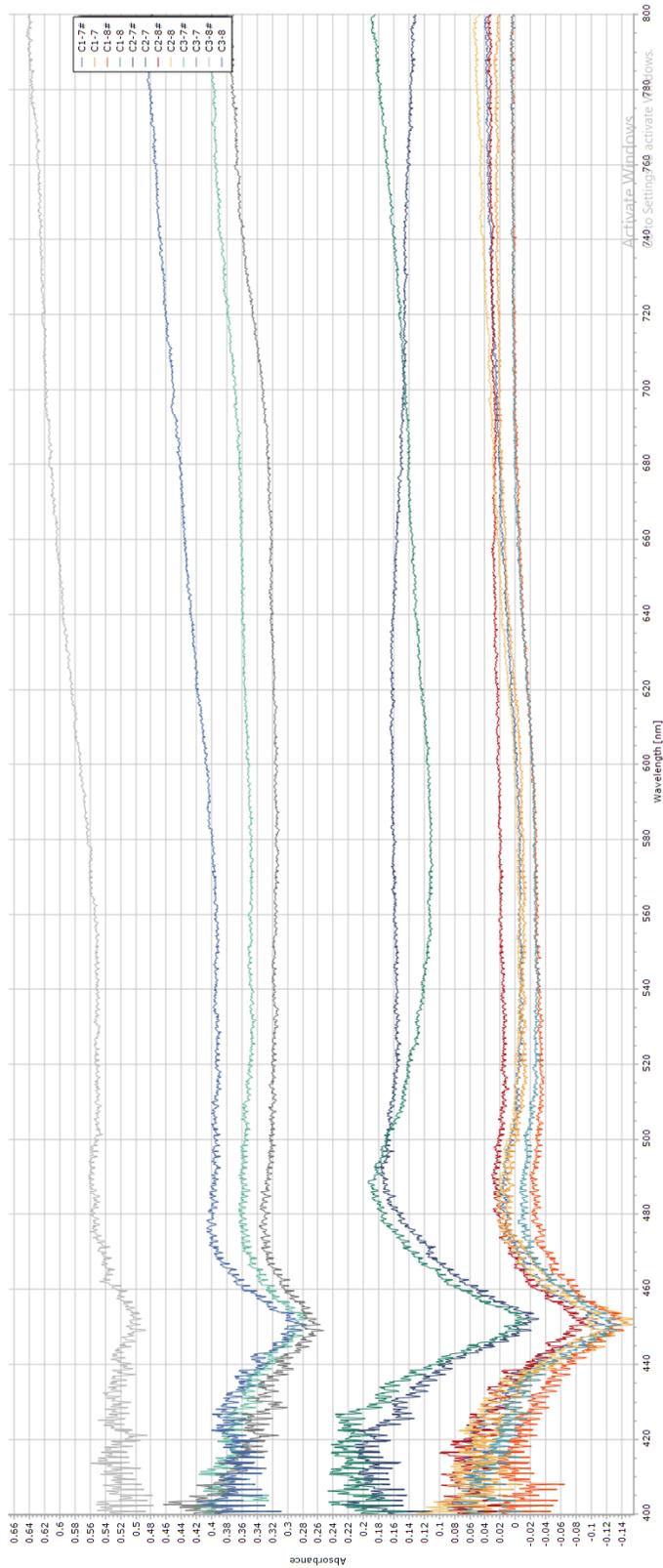
UV-vis spectra of Exp 2 reduced C1, C2, and C3 stones. Pre and post heat-treatment (labeled with #)
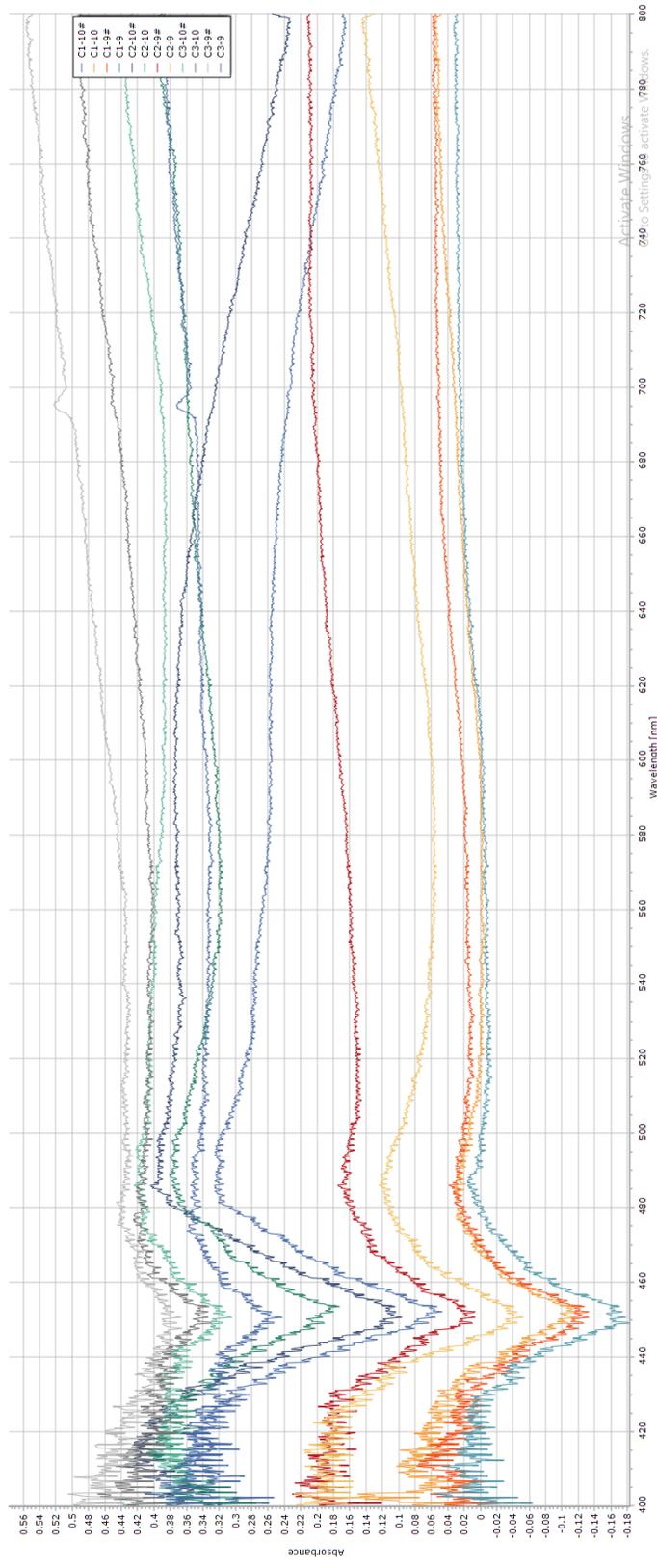
UV-vis spectra of Exp 3 oxidized C1, C2, and C3 stones. Pre and post heat-treatment (labeled with #)
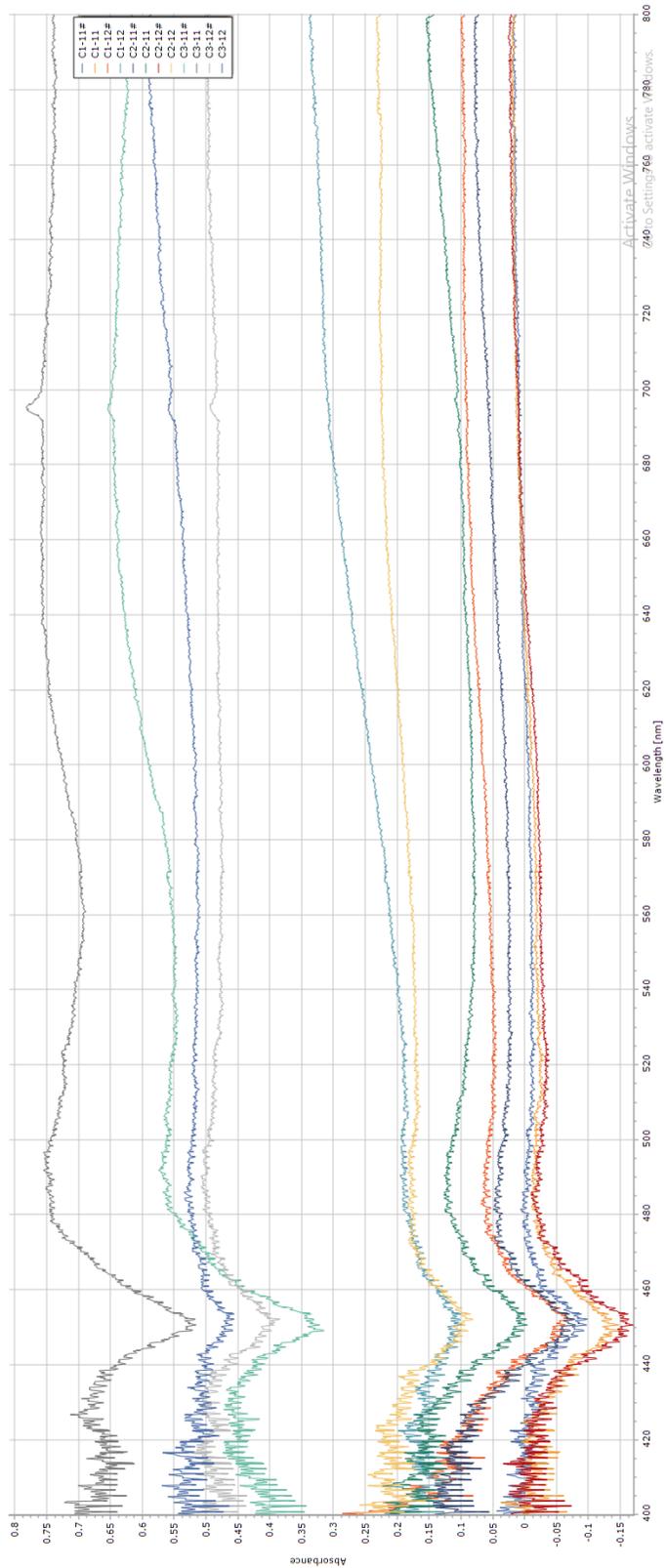
UV-vis spectra of Exp 3 reduced C1, C2, and C3 stones. Pre and post heat-treatment (labeled with #)
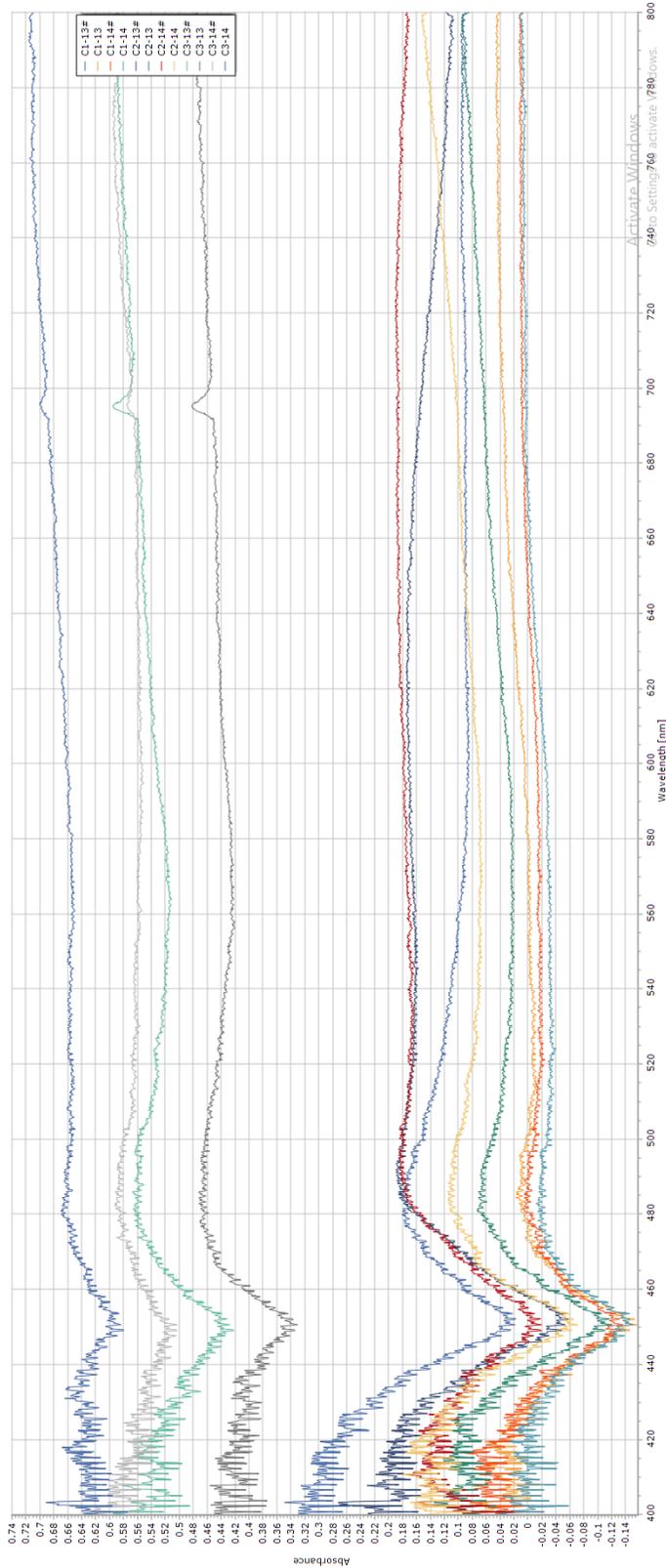
UV-vis spectra of Exp 4 oxidized C1, C2, and C3 stones. Pre and post heat-treatment (labeled with #)
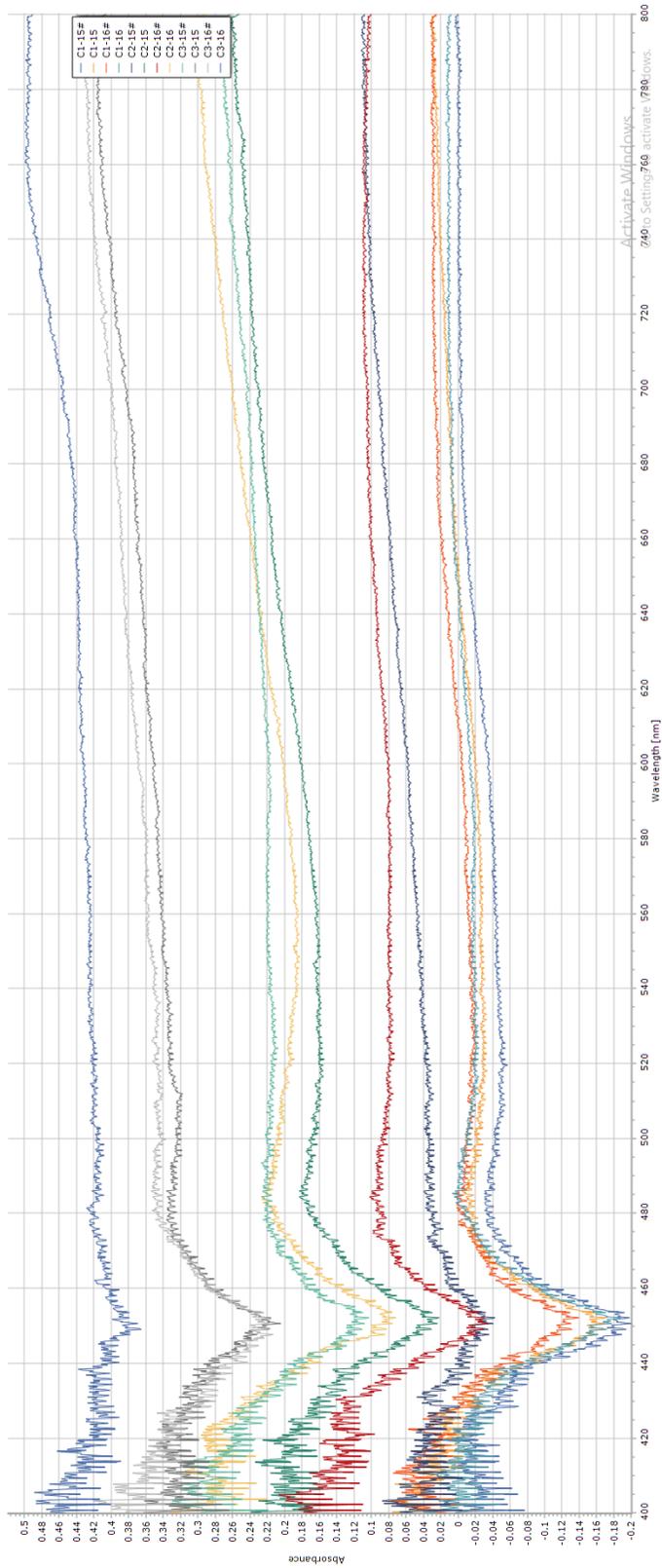
UV-vis spectra of Exp 4 reduced C1, C2, and C3 stones. Pre and post heat-treatment (labeled with #)
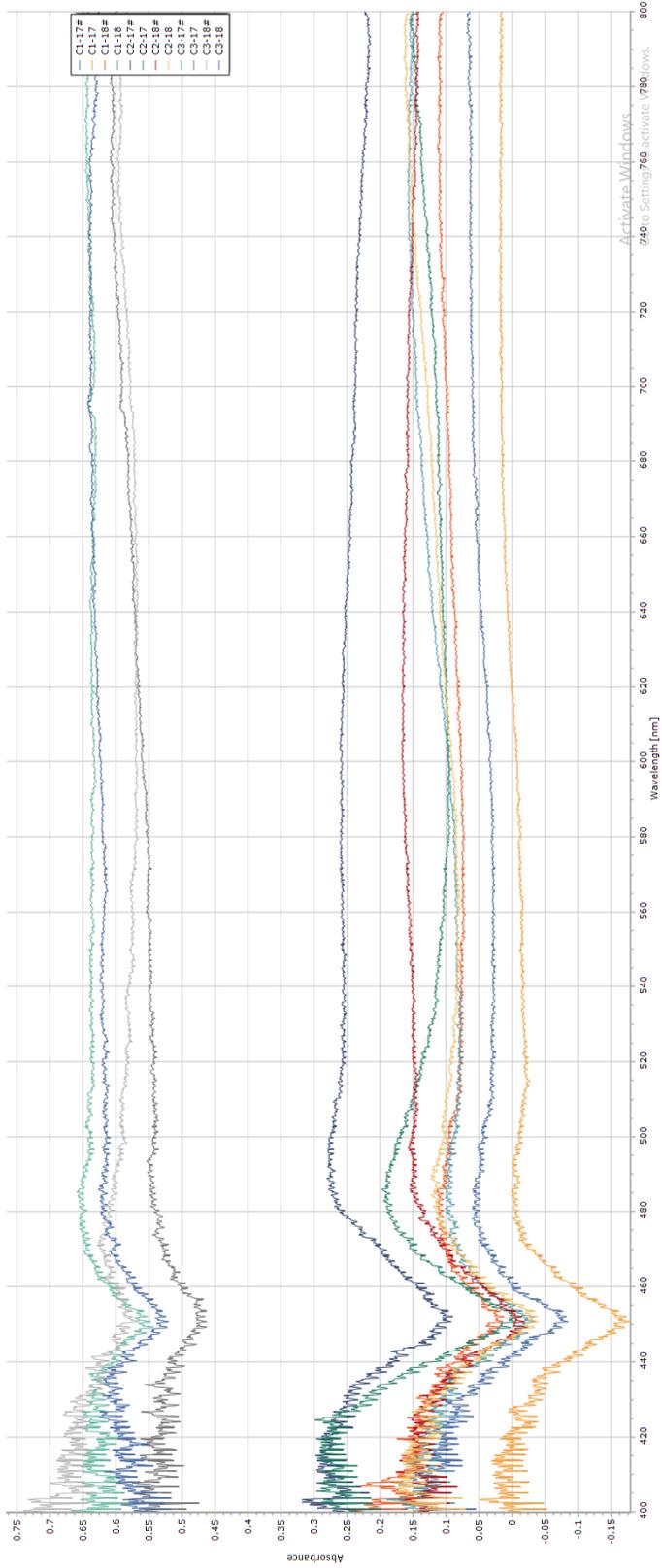
UV-vis spectra of Exp 5 oxidized C1, C2, and C3 stones. Pre and post heat-treatment (labeled with #)
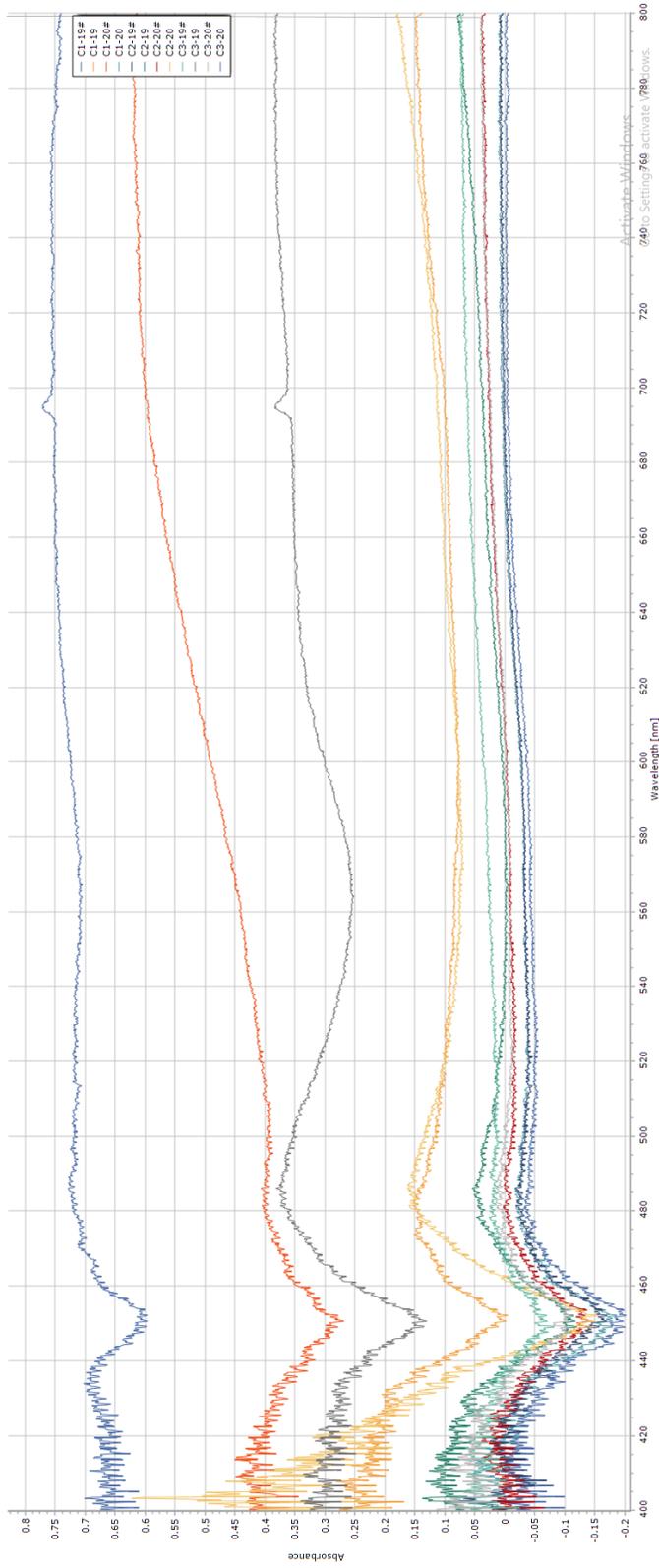
UV-vis spectra of Exp 5 reduced C1, C2, and C3 stones. Pre and post heat-treatment (labeled with #)

| Exp1																			
Not heat treated	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-3	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C2-1	15	37.75	22.2921	39.9091	23.7159	144.333	49.0057	13.7778	10.0529	101.2	35.1723	256.818	104.191	9049.27	204.581	46.3333	15.2388	51.8889	54.694
C2-2	15	26.9167	24.4726	47.8889	28.6994	107.556	55.1001	12.6667	11.1006	243.533	43.6087	181.455	102.477	8682.67	151.171	14.25	13.6816	41.25	23.896
C2-3	15	44.5556	28.841	49.9167	26.7191	151.333	110.121	14.8889	12.7754	47.9231	23.5616	134.667	86.5971	9473.07	265.449	39.8	22.1441	39.625	42.1187
C2-4	15	37.9091	18.5249	40.5	24.3156	136	101.617	16.125	9.62338	43.7143	24.1082	114.286	92.0104	8521.8	175.377	35	16.8819	53.9091	40.7686
C3-1	15	46.9333	43.3704	40.4167	22.3475	68.1429	61.4525	21.2727	12.8636	78.7143	35.724	109.286	68.7245	328.933	71.6077	63.5	23.1463	53.7778	38.2848
C3-2	15	34.0833	25.2701	73.3333	50.5129	118.8	90.7918	32	20.3848	226.667	87.5577	185	28.2489	762.4	54.7623	49.2	29.0751	34.4286	36.6562
C3-3	15	33.4167	23.4466	51.25	15.3413	82	73.6672	14.6667	11.1255	94.6	40.6314	228.214	97.3955	503.067	51.064	46.2222	41.0062	65.4444	48.4862
C3-4	15	44.0909	15.6812	23.5	21.7428	82	62.4927	50.1429	16.3919	126	31.1341	231.571	106.23	650.4	91.7604	45.1111	23.6617	28.375	15.8346
oxidized	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-1#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-2#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C2-1#	15	29.3333	20.4179	29	26.007	70.6667	75.4954	16.4286	8.56667	50.8333	17.363	164.231	106.598	9104.87	133.792	47.7778	21.9078	51	33.6987
C2-2#	15	33.8	21.6555	40.4545	26.8544	142.556	108.658	24.5	10.9506	50.1429	26.4382	298.462	95.279	8567.2	167.893	48.5556	31.0917	52.5455	40.9042
C3-1#	15	43.8182	22.6829	40.8333	30.9727	145.167	89.3055	28	9.90959	135.4	35.4021	113.5	85.2912	330.8	54.9002	37	40.3691	29.25	18.7133
C3-2#	15	31.2727	23.6685	71.0667	27.1624	102.25	68.0418	29.6364	11.4992	34.8571	17.6629	126.077	81.7787	2168.33	137.458	51.6	43.8023	55.1111	49.6777
reduced	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-3#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-4#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C2-3#	15	41.75	15.0948	44.4667	29.3754	149.333	100.457	30	13.68	41	23.3752	214.667	141.568	9876.67	142.475	51.4286	24.7609	83	60.6333
C2-4#	15	28.4	13.3955	48.1667	27.9816	88	50.9967	17.1111	8.71071	47.7692	20.7778	179.462	99.4103	8729.53	169.378	65.2857	35.74	35.25	34.0725
C3-3#	15	54.5455	56.5	39.5	20.6631	147.286	116.664	17.3077	18.1209	53.5	21.0433	188.083	122.095	526.533	59.9498	37.2857	18.2734	41.1111	27.8306
C3-4#	15	41.0714	22.8956	248.067	36.3563	113.083	102.266	75.4	21.8778	87.6	25.8658	191.636	71.0535	495.267	67.8316	66.6667	73.8076	47.2222	23.8317

EPMA data for Exp 1

Exp2																			
Not heat treated	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-5	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-6	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-7	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-8	18	202.89	110.4	432.53	73.666	166.9	59.742	111.78	42.81	389.67	110.51	205	125.25	9480.5	514.49	79	4.5	83.333	6.9442
C2-5	15	36	18.096	27.8	18.723	100.17	78.489	24.9	12.684	38.75	24.111	207.08	98.204	9400.7	194.68	37.444	18.301	51	27.665
C2-6	15	37.636	19.662	52.923	30.104	120.8	68.157	19.857	14.076	59.8	29.878	135.17	95.318	9892.3	167.06	60.2	27.265	39.4	30.506
C2-7	15	39.25	20.909	33.2	23.289	121.78	77.142	29.714	16.104	49.692	24.04	192	132.06	8981.9	168	47	26.115	43.9	27.959
C2-8	15	24.071	15.285	47.545	23.45	78.889	65.604	28.857	7.7539	54.214	19.976	234.57	111.26	8215.3	94.145	41.75	29.265	40.778	53.952
C3-5	15	23.571	15.164	30.8	18.546	99.875	88.868	18	16.965	69.933	36.917	197.13	97.15	1168.7	95.184	36.833	19.343	52.833	31.451
C3-6	15	37.273	23.042	37.333	27.503	101.11	45.393	31.286	15.984	44.8	27.282	118.88	95.741	1814.6	98.861	33.571	42.088	60.75	22.41
C3-7	15	41.2	32.347	70.867	35.523	106.33	69.839	50.357	18.983	114.2	25.595	158	85.315	311.8	62.582	46.6	46.809	56.6	33.921
C3-8	15	39	31.422	52.067	29.89	125.33	88.258	22.4	13.676	62.923	22.092	170.09	108.45	638.53	86.581	68.2	36.074	45.875	31.255
oxidized	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-5#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-6#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C2-5#	15	38.167	22.912	47.429	31.865	98.143	72.792	19.182	10.87	50.643	29.798	191.79	127.29	9488.3	171.49	29.125	18.489	37.167	22.549
C2-6#	15	38.143	53.623	46.643	33.14	74.625	58.485	27.444	14.206	68.6	40.02	182.2	127.86	9283.3	406.8	41.833	37.888	63.778	50.499
C3-5#	15	35.857	24.692	57.143	20.743	64	36.692	33.143	27.661	51.929	37.061	134.25	106.33	1209.9	98.298	38.714	12.326	59.125	39.161
C3-6#	15	97.714	60.244	46.714	17.694	223.33	61.846	41.667	24.37	48.933	22.434	207.77	122.12	2141.8	65.474	34.571	31.577	50.5	27.318
reduced	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-7#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-8#	12	92.2	13.644	341.5	74.351	161.75	88.849	85.25	24.636	257.42	179.47	201.29	115.79	11538	1255.2	103.67	18.571	82.667	6.8475
C2-7#	15	46.385	21.805	38.5	23.81	97	84.639	21.167	15.486	34.071	20.783	264.4	120.73	8976.7	108.64	72.333	19.703	67.2	52.098
C2-8#	15	37	23.191	44.929	29.661	94.615	96.392	12.667	3.3993	75.786	78.721	199.67	86.486	8259.7	178.77	59.333	29.227	43.25	29.857
C3-7#	15	45.5	30.702	74.067	36.559	152.17	56.752	62.933	32.834	65.071	19.333	206	116.49	323.4	56.507	37.909	21.116	52.833	36.549
C3-8#	15	29.714	18.835	67.923	27.725	59.143	45.445	30.455	12.361	36.214	18.575	179.1	132.06	721.6	78.078	56	20.875	51.286	32.775

EPMA data for Exp 2

Exp3	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
Not heat treated	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-9	16	178.333	106.364	460.4	529.911	179.5	92.3837	60.5	13.0671	945.733	914.402	203.455	93.1737	7901.38	237.097	154	34.0294	70	11
C1-10	15	87.6667	30.8941	94.9333	25.9036	112.143	55.6531	N/A	N/A	100.385	39.3672	232.25	131.364	7814.73	145.786	106	48	89.8333	23.3053
C1-11	15	138.444	93.0151	620.667	273.749	139.857	52.428	101.667	32.7041	431	339.628	357.733	145.112	4936.47	1039.14	72.25	13.3487	78	2
C1-12	15	189.917	107.007	305.6	86.0928	145.25	53.8116	65.5556	11.7295	141.533	77.0765	149.556	105.345	10444.9	1361.33	65	4	N/A	N/A
C2-9	15	188.385	499.05	48	21.3842	84	53.5062	24.875	20.2326	174.8	193.125	247.643	117.343	9693.4	112.862	46.4444	23.3243	24	17.855
C2-10	15	34.4545	18.7634	41.2727	29.1769	103.167	85.0322	20.3333	5.4365	38.5455	24.1411	242.583	122.156	9057.87	152.067	45.1429	43.8811	50.4	34.8804
C2-11	15	35.3846	29.6817	34.7273	28.8415	90.8	54.3375	23.4	15.7048	56.5	21.3667	233.091	102.531	9691.13	114.737	46.8571	40.0479	66.25	38.7193
C2-12	15	33.3	28.7891	58.7143	35.1841	90.4286	92.234	24.2222	13.9106	59.7857	24.4224	178.778	110.462	8958.67	198.721	41.4	24.5406	22.6	11.1642
C3-9	15	35.6154	24.3833	80.6	34.0779	157.375	30.1949	45.8462	19.9802	138.667	26.7224	179	104.127	357.667	63.0319	69.1667	54.1461	71	48.3368
C3-10	15	59.6923	29.5749	132.8	31.7998	90.8571	35.8785	72.7333	26.9158	56.6667	24.4231	214.429	91.2921	648.333	73.9474	76.7143	22.3908	45	41.0853
C3-11	15	35.1667	17.9482	53.8	33.9081	98.4286	60.377	36.7	25.9039	76.8	22.0641	178.333	107.128	2863.13	113.371	42.625	35.5033	53.75	34.5063
C3-12	15	45.8462	31.4957	46.5	19.7505	123.667	57.0429	29.2727	13.7978	49.1429	33.0883	129.182	94.872	585.067	51.03	35.5714	41.928	50.6	36.1807
oxidized	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-9#	17	2580	7992.22	549.882	789.415	139.167	90.9348	138	78.1281	930.412	1384.62	254.714	83.2273	8373.06	391.443	84	5	70.2	25.4039
C1-10#	15	190.417	142.702	74.5	22.3439	174	66.6453	56.5	2.5	396.667	341.016	198.364	117.476	7249.73	218.92	106	0	95	0
C2-9#	15	34.9	30.2207	33.3333	15.6436	82.4	55.2941	18.1111	13.4779	67.4286	18.2276	204.5	89.4697	9428.07	122.339	48.1818	36.1105	33	22.6421
C2-10#	15	17.9286	9.17656	44.5	24.5571	112.125	99.0195	26.9091	12.236	67.2857	32.3627	193	128.824	9146.8	221.159	49.1111	29.5576	39.625	20.4935
C3-9#	15	40.3846	24.0529	61.8462	31.6516	85	46.7394	51.6	14.6187	71.4667	24.9209	73.8	49.5112	303.067	57.7921	44	37.2424	28.875	23.0892
C3-10#	15	45.25	22.0232	120.2	29.6765	105.778	76.0201	69.1333	28.8649	65.0667	26.2436	142.5	95.9753	503.467	72.7478	49.7143	33.8219	34	31.6825
reduced	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-11#	15	154.091	84.6076	545.533	179.004	142.5	41.6323	77.3333	17.6131	550.6	321.234	445.4	166.002	4332.07	280.03	69.6667	12.8149	112	53.1852
C1-12#	15	152.636	124.683	314.867	171.082	72.75	32.5682	75.2	27.5783	172.538	126.407	196.125	81.3579	10410.7	1384.16	53.5	3.5	74	12.2474
C2-11#	15	29	18.2866	52.3333	30.2967	75.25	37.7947	24.8889	17.1234	52.2	24.8843	148	80.3039	10010.2	160.398	30.625	28.4383	37.5	28.5132
C2-12#	15	31.2727	21.3503	50.8667	21.7895	108.091	66.8859	14.6667	10.9798	74.7143	22.5339	201	85.8971	9002	115.226	60.5	21.2955	21.1667	22.2442
C3-11#	15	38.6154	22.5134	38.0769	21.6029	89.2	66.4542	23.9167	17.4091	34.75	21.2255	162.308	110.903	2876.93	111.486	29.5	21.1187	63.9091	51.089
C3-12#	15	38.4286	23.3994	51.0714	20.7174	82	53.3667	38.6154	13.0593	69.0714	30.1175	123.091	82.5199	615	92.2504	55.2	48.5197	57	41.5788

EPMA data for Exp 3

Exp4	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
Not heat treated	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-13	11	131.889	91.2499	180	170.881	109.222	51.1507	N/A	N/A	210.364	128.618	194.875	100.416	9127.91	480.994	64.5	9.5	64	0
C1-14	16	176.75	124.434	561.813	187.579	112.667	38.3956	66.25	6.79614	479.375	242.266	226.167	111.202	10503	567.86	90.3333	3.77124	72.4	24.1214
C1-15	11	322.727	352.408	411.455	202.715	170.429	56.3734	91.8	53.5552	206.3	227.459	217.1	69.2408	8585.36	269.423	76.3333	17.932	67	0
C1-16	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C2-13	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C2-14	15	42	23.3381	48.2	32.6603	105.545	80.2874	19.4286	14.3513	68.6667	20.8412	197	111.565	9172.93	149.076	32.1429	24.5265	19.5556	10.7921
C2-15	15	34	19.1398	50.8462	22.776	99	58.5358	28.6667	15.9861	80.8	25.4275	171.214	121.96	9181.6	113.702	48.2	25.9338	52.4	53.3089
C2-16	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C3-13	15	35.5455	13.9959	99.2667	25.6527	54.7778	32.5057	46.4286	31.7236	121.467	27.5097	193.5	135.972	1698.6	84.5157	25.8889	20.344	93.4	55.9199
C3-14	15	49.4286	30.9371	31.75	22.7527	91.4	73.2109	34.1429	19.2311	93.3333	38.1185	188.1	113.967	430.533	101.893	45.125	28.0599	50.625	40.1744
C3-15	15	36.9231	28.4239	36	21.6009	102.167	57.889	30.1818	16.4969	72.6	19.8286	183.143	109.458	382.733	63.2323	37.2	22.6663	31.8571	19.8453
C3-16	15	53.3333	42.2183	50.8	30.1622	124.667	38.3956	39.0833	21.1796	195.8	50.3166	151.769	93.9944	427.733	39.8187	25.2	19.0882	44.3333	23.7253
oxidized	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-13#	15	155.364	55.802	185.667	36.7036	195.667	29.1014	N/A	N/A	962.933	652.417	304.429	104.026	9115.33	259.349	89.6667	13.5974	83.25	12.617
C1-14#	20	158.056	109.374	39561.8	67666	131.6	52.131	677.143	401.819	165.867	123.711	164.889	67.7863	36082.8	44262	2509.18	3810.09	73.8	19.3018
C2-13#	30	22.3889	18.7473	38.625	22.431	110.75	82.6465	16.4706	13.1064	83.2857	41.9641	215.731	116.284	9232.93	176.245	34.6111	23.9841	50.5294	29.7284
C2-14#	15	34.3	23.6983	39.2857	26.8473	72.75	31.5387	17.5	7.95299	94.6667	55.1394	190.25	106.833	8781.53	134.849	57.375	35.2631	81.125	39.7977
C3-13#	15	34.1538	24.1465	106.467	38.9459	83.9	50.2821	47.8667	20.6523	63.7692	20.6403	147.6	88.7977	1807.4	94.9237	79	50.1642	51.1429	38.665
C3-14#	15	43.6429	22.0409	24	20.3693	85.4	72.3577	33.1667	15.356	74.3571	57.6338	184.556	160.841	293.733	62.1959	36	22	38.8	35.8631
reduced	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-15#	15	129.583	69.7095	2030.8	2365.25	131.167	51.2003	N/A	N/A	245.933	94.1562	215.5	112.594	9357.4	169.693	78.5	23.5	102	58.0345
C1-16#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C2-15#	15	24	15.107	38.5	23.3577	112.4	66.3343	18.7143	14.3896	285.5	71.5419	176.143	100.278	9190.93	317.631	43.1111	28.6878	41.4444	45.3753
C2-16#	30	39.4783	19.1104	34.4	25.0208	97.5	51.8097	9.27273	7.26249	70.7857	29.862	210.179	98.7591	8854.37	1073.94	34.5	17.801	44.2	23.0657
C3-15#	15	44.2	23.6677	45.75	26.729	54.875	57.2635	28.3571	21.1984	92	24.6928	164.308	81.0217	520.867	109.426	47.3333	29.586	31.375	26.528
C3-16#	15	31	21.3542	36.8182	32.9678	91.7143	76.7495	23.5385	19.2098	95.1333	31.5845	142.091	82.2949	385.867	79.9574	25.7143	19.6521	69.625	49.338

EPMA data for Exp 4

Exp5																			
Not heat treated	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-17	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-18	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-19	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-20	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C2-17	15	43.6923	25.5866	32.0833	17.1097	134.2	72.5407	28.4	13.403	47.1429	21.4605	206.5	136.67	9131.07	170.911	48.75	44.4543	65.8571	43.3834
C2-18	15	41	23.2348	43.9167	22.71	103.167	68.9261	12.1429	12.62	72.5	34.8379	203.929	160.678	7556.8	109.827	33.7778	20.7995	45.8571	30.6288
C2-19	15	37.5455	18.9226	70.3	23.3626	156.8	122.995	24.625	17.93	103.6	172.405	222.429	109.018	9089.87	183.976	69.3333	42.6302	51.8571	35.2519
C2-20	15	38.3333	27.2234	26.7143	21.9038	91.4	69.038	23.1667	14.0643	69.9286	31.8242	203.5	126.749	9129.4	158.279	33.8182	28.2676	28.5	22.5832
C3-17	15	48	25.2982	27.1818	21.9247	129	68.7812	33.2308	16.0487	94.5333	36.2452	160.5	105.528	337.533	67.5464	44.125	30.9897	45.9	45.866
C3-18	1	88	0	13	0	129	0	N/A	N/A	88	0	73	0	783	0	N/A	N/A	21	0
C3-19	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C3-20	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
oxidized	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-17#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-18#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C2-17#	15	47.8571	24.1302	45.1538	20.8506	99.5714	28.58	14.1667	8.82075	98.2	18.6876	196.769	99.3643	9147.2	102.35	60	24.4663	27.7143	19.5792
C2-18#	15	32.3636	13.7858	22.8	18.7553	60.2222	54.3196	7.4	3.2	53.6429	23.4417	236	169.585	7510.73	154.921	56.25	27.9631	54	43.3186
C3-17#	15	31.8571	24.3159	29	12.6265	79.5455	52.4341	24.2727	21.5537	82.4	30.3596	153.333	91.5772	308.6	41.4243	18.5	6.68954	42.2857	40.7491
C3-18#	15	36.9	17.7282	37.6429	17.6012	123.714	62.2844	42.0769	18.7184	64.9333	26.5794	143	98.2612	759.8	85.928	52.7778	42.7103	64.5	46.9622
reduced	n	Ca	s	Ti	s	Zn	s	Mg	s	Si	s	Ga	s	Fe	s	Mn	s	Cr	s
C1-19#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C1-20#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C2-19#	15	36.3077	21.0069	39.6154	19.3293	141.333	94.4602	13.1429	10.4119	53	27.9157	196.923	142.762	8876.93	489.42	41.4286	17.5325	73.5	36.4314
C2-20#	15	42.3846	23.7537	60.1667	32.0984	86.9	41.9892	15.1667	9.85591	72.0667	42.1718	218.308	113.576	8593.8	1687.83	34.5	31.8002	59.1429	26.6267
C3-19#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
C3-20#	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

EPMA data for Exp 5