HEAT TREATING THE SAPPHIRES OF ROCK CREEK, MONTANA

By John L. Emmett and Troy R. Douthit

Renewed interest in large-scale commercial mining of Montana sapphires motivated a detailed study of the heat treatment of sapphire from the Rock Creek deposit. During the course of this systematic study, over 75,000 stones were processed. It was found that approximately 65%–70% of the pale blue, pale green, and near-colorless sapphire could be converted to well-saturated blue and yellow colors. Some improvement in clarity was noted as well. Yellow hues were easily developed by heating in oxidizing atmospheres and were relatively insensitive to time and temperature. Blue hues were developed by processing in reducing atmospheres. The relatively high iron content of Rock Creek material restricts the range of reducing conditions that can be used to achieve optimal coloration because of hercynite precipitation in the sapphire.

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The sapphire deposits of Rock Creek, Montana, have been known since the late 1890s. In fact, from 1906 to 1943 they were mined almost continuously to provide corundum for industrial applications. While most sapphires from this deposit are of gem clarity, the hues in which they typically occur—pale blue, pale green, pink, pale yellow, or near colorless—are not commercially desirable. Although natural blue, yellow, and pink sapphires with good color saturation are found at Rock Creek, the quantities are too small to justify commercial mining for these gems alone (figure 1).

In principle, heat treatment can improve color, clarity, or both in sapphire (Nassau, 1981, 1984; Themelis, 1992), and for many years now sapphires from various localities have been successfully enhanced in this fashion. Rock Creek sapphires have been heat treated locally and in Asia since at least 1977, but the results have been highly variable (G. Billings, pers. comm., 1993). As part of their overall evaluation of the commercial viability of the Rock Creek deposits, Skalkaho Grazing Inc. retained the authors to undertake a detailed, systematic study of the response of this material to heat treatment. This article presents quantitative as well as qualitative results of our efforts to develop optimal heat-treatment processes for the Rock Creek sapphires (figure 2). It also provides an explanation of various aspects of the physical processes involved in sapphire heat treatment.

HISTORY AND BACKGROUND

Sapphire was discovered in Montana in 1865. George F. Kunz (1894) attributes the discovery to Ed Collins, a gold miner who was working on one of the gravel benches, or "bars," just above the Missouri River near Helena. By 1895,

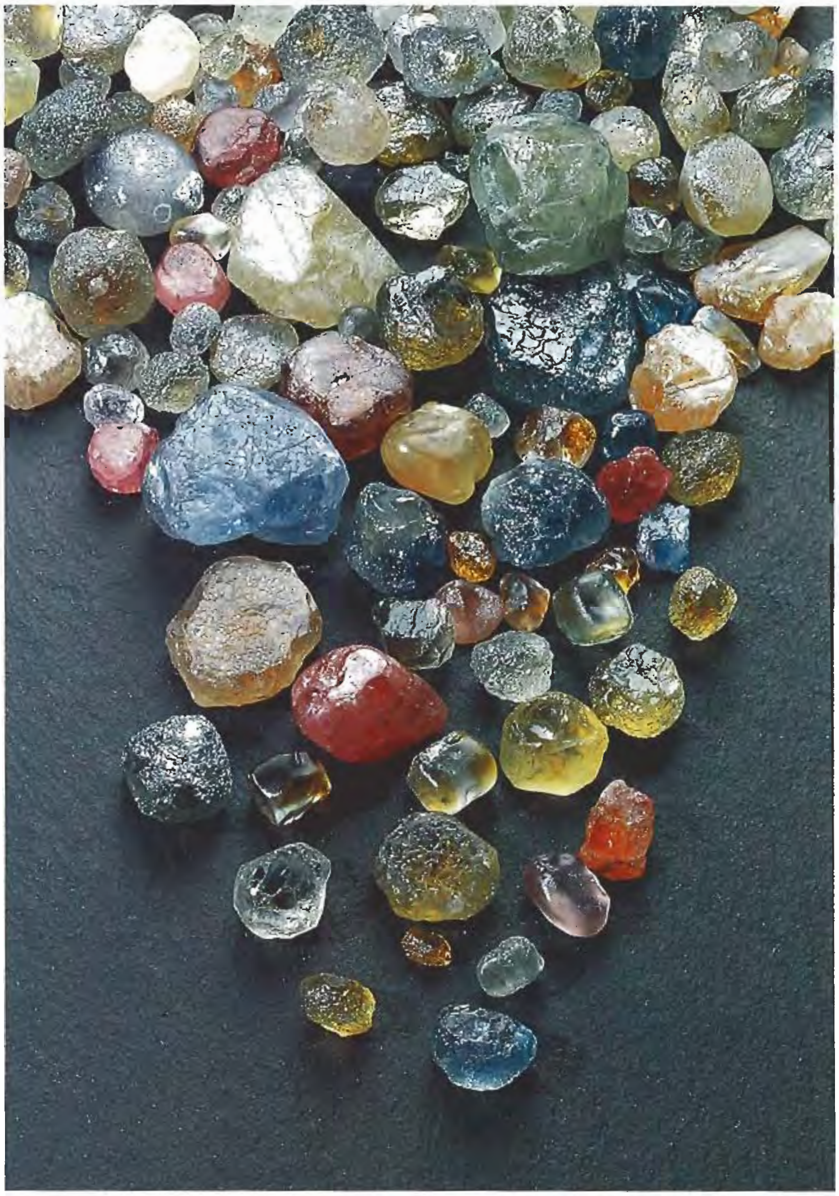


Figure 1. These rough sapphires were assembled from material mined at Rock Creek to show both the size range (here, 0.5–15 ct) and color range from this Montana deposit. Note that the largest —and the well-saturated—stones featured here represent a very small percentage of the total production. Photo © GIA and Tino Hammid.

the relentless search for gold in Montana had resulted in the discovery of most of the significant deposits of sapphire that had sufficient clarity to be classed as gem material. Of the many deposits discovered, four have been mined on a more or less substantial basis: Rock Creek, Dry Cottonwood Creek, Yogo Gulch, and the gravel bars of the Missouri River, most notably Eldorado Bar (figure 3). Detailed accounts of these deposits, including some fascinating historical material, are contained in Pratt (1906), Clabaugh (1952), Sinkankas (1959), and Voynick (1987). At Rock Creek, Dry Cottonwood Creek, and the Missouri River bars, all of the sapphires found to date have been in secondary, or placer, deposits. Although the sapphires from these three deposits are similar in color—primarily near colorless, pale green, pale blue, pale yellow, pink, and orange—they differ from one deposit to the next in such characteristics as size, dominant crystal morphology, and quantitative trace-element composition. Historically, stones from these three deposits have been sold primarily for industrial purposes: the manufacture of wire-drawing dies, watch bearings, and other precision instrument bearings. Only a negligible portion of these sapphires have been sold for jewelry use because of the pale, rather uninteresting natural colors.

Rock Creek is unique in that it was the only placer deposit in Montana rich enough to be mined for sapphire alone in the years from discovery to

Figure 2. The 3.08-ct sapphire in this ring illustrates the depth of color achieved in the larger Rock Creek sapphires with heat treatment. Photo © GIA and Tino Hammid.

World War II (Clabaugh, 1952). The main mining area is located in Granite County, about 16 miles (26 km) southwest of Philipsburg, in and along two tributary gulches on the north side of West Fork Rock Creek (again, see figure 3). The westernmost gulch is known as Anaconda Gulch; Sapphire Gulch, called Myers Gulch before the onset of sapphire mining, lies about 1^1/2 miles to the east. Sapphire has also been found in most of the smaller gulches that drain into the Anaconda and Sapphire gulches and in the long meadow along West Fork Rock Creek extending eastward from the mouth of Anaconda Gulch. Farther north, sapphire has been found in the Quartz and Cornish gulches as well. Sapphire has not been reported south of West Fork Rock Creek.

Enormous quantities of sapphire have been mined from Rock Creek. We were able to review mining records for 10 years of production during the period 1906–1923, which show cumulative shipments to customers of 38 metric tons from the Anaconda and Sapphire gulches alone (J. Higgins, pers. comm., 1993). Records for specific weekly shipments in 1907 reveal an average of 1,000 pounds (455 kg) per week. This number is even more impressive when one notes that the material shipped was deemed sufficiently clean and fracture free to be used for precision industrial applications. Rock Creek continued to produce and ship large quantities of sapphires until 1943. Shipping documents from 1936, for example, show substantial sales to such concerns as Diamond Tool Company of New York; Industrial Jewel Company of Waltham, Massachusetts; Eugene Deshusses of Geneva, Switzerland; and General Electric Company of West Lyons, Massachusetts (J. Higgins, pers. comm., 1993).

The mining of sapphire in Montana for industrial applications was effectively terminated by the development of large-scale production capabilities for synthetic sapphire, most notably by Union Carbide in the U.S. and Hrand Djevahirdjian in Switzerland. Using the Verneuil flame-fusion growth process, these companies produced a very uniform, high-quality synthetic sapphire, in volume, at such low cost that the industrial use of natural crystals was quickly abandoned. Since 1943, there has been little interest in commercially mining the Rock Creek deposits. A portion of the deposit, known as the Gem Mountain Sapphire Mine, has been operated for many years as a fee digging area for hobbyists and individual gem miners, and it is now operated as a fascinating tourist attraction where individuals can screen sapphires from sapphire-bearing ore mined by the operators.

Skalkaho Grazing owns the portion of the deposit that encompasses the long meadow at the mouths of the Anaconda and Sapphire gulches, and it is this area that the company is evaluating to determine the economic feasibility of large-scale gem mining. During the summers of 1972 and 1973, the Day Mining Company drilled and assayed the portion of this meadow that is at the mouth of Anaconda Gulch. In addition to the drill core samples, they mined a large ore sample of approximately 3700 cubic yards which yielded 47 ct per cubic yard, or a total of approximately 35 kg (J. Higgins, pers. comm., 1993). These and subsequent studies conservatively calculated a recoverable reserve over 25 million carats for the portion studied. Since only the portion of the long meadow adjacent to the mouth of Anaconda Gulch was sampled, it is probable that the total sapphire recoverable from the whole meadow substantially exceeds this figure. However, after careful study of the sapphire sample, including cutting and appraisal of the stones, the

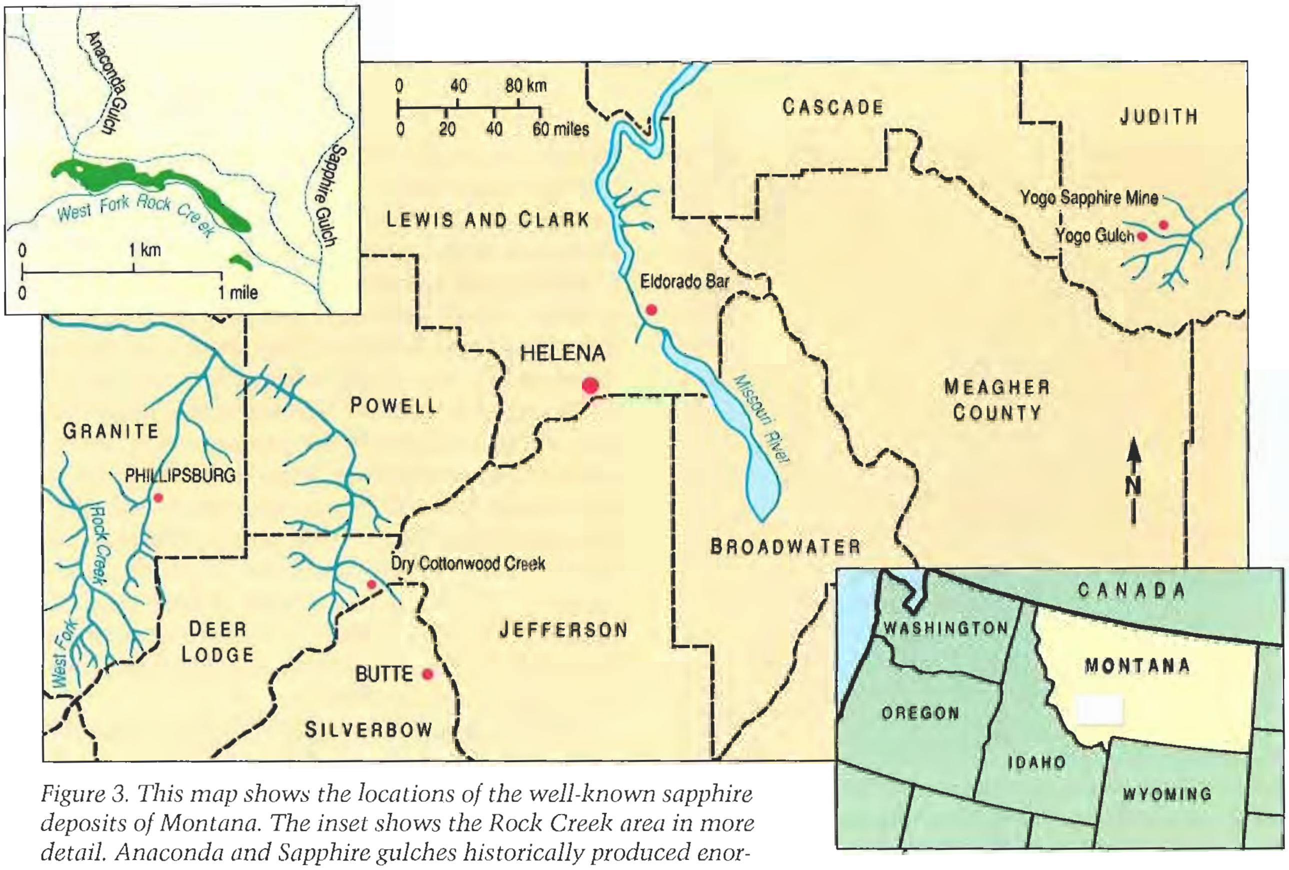


Figure 3. This map shows the locations of the well-known sapphire deposits of Montana. The inset shows the Rock Creek area in more detail. Anaconda and Sapphire gulches historically produced enormous quantities of sapphire. The meadow region along West Fork Rock Creek at the mouths of the Anaconda and Sapphire gulches was never mined commercially. The sapphire discussed in this article is from the meadow property. Artwork by Carol Silver.

Day Mining Company decided not to develop the deposit because the yield of commercially valuable colors was too low to be economic. Note, though, that commercial heat treatment was in its infancy in the early 1970s, and was not being applied to Montana sapphires.

DESCRIPTION OF THE ROCK CREEK SAPPHIRES

Sapphires found at Rock Creek range up to about 15–20 ct, although stones over 10 ct are found only occasionally. The early production records referred to previously (10 years in the period 1906–1923) indicate that crystals seldom exceed 6 ct (8.4 mm), with almost 75% in the range 0.1–2.2 ct (2.2–6.5 mm; see figure 4). These stones are typically near colorless, pale blue, pale green, pink, and pale yellow. Some show both pale yellow and pale green or blue in the same stone; these are locally referred to as "pintos." A few stones in highly saturated hues are also recovered. The approximately 35 kg recovered by Day Mining Company was graded for hue as shown in figure 5. Day Mining concluded that only 8% had sufficient color saturation to be marketable as gems. Therefore, 92% of the stones recovered are near colorless or of pale hue.

The best characteristic of Rock Creek sapphire is its clarity: Most stones, as mined, are sufficiently transparent and free of fractures and large inclusions to be faceted (see, e.g., figure 6). While a large proportion (90%) of the stones have at least some inclusions (fine rutile needles or silk), only 5%–10% of these stones contain enough inclusions to substantially reduce visual clarity. These rutile inclusions can be dissolved by heat treatment both to increase clarity and induce a blue coloration.

A small portion of Rock Creek sapphire crystals show sharp and distinct crystal faces. On the great majority of crystals, however, the faces are abraded or corroded, giving an overall appearance of rough, almost spherical pebbles. Careful examination reveals that the original crystals are hexagonal cylinders or modified hexagonal cylinders. Thus, they usually show both the unit prism $\{11\bar{2}0\}$ and the basal pinacoid $\{000\bar{1}\}$. These forms are often

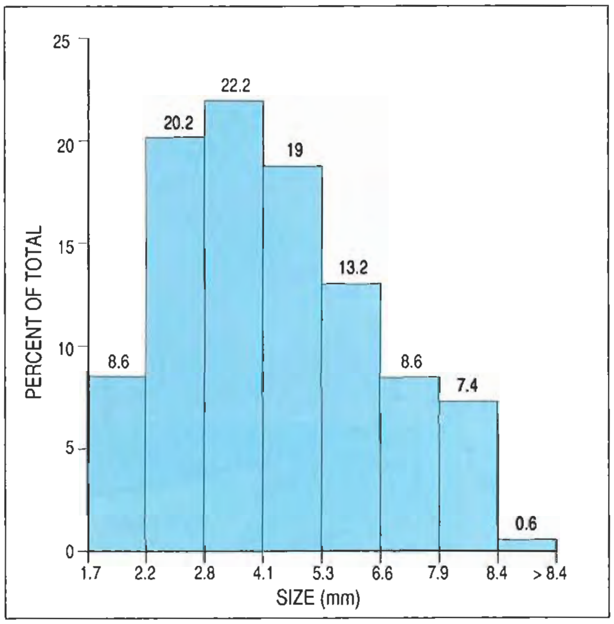


Figure 4. Rock Creek sapphires over 8.4 mm (about 6 ct) make up only 0.6% of mine-run material. The vast majority range from 2.2 to 7.9 mm (0.1 to 2.2 ct). This histogram of sapphire size was assembled from production records for 10 years of mine operation within the period 1906–1923; it represents a total of 38 metric tons of rough sapphire shipped from the Anaconda and Sapphire gulches, as graded through square-aperture screens. For example, the 22.2% bar represents those stones retained on a sieve with holes 2.8 mm square and passed through a sieve with 4.1-mm holes. Data courtesy of J. Higgins.

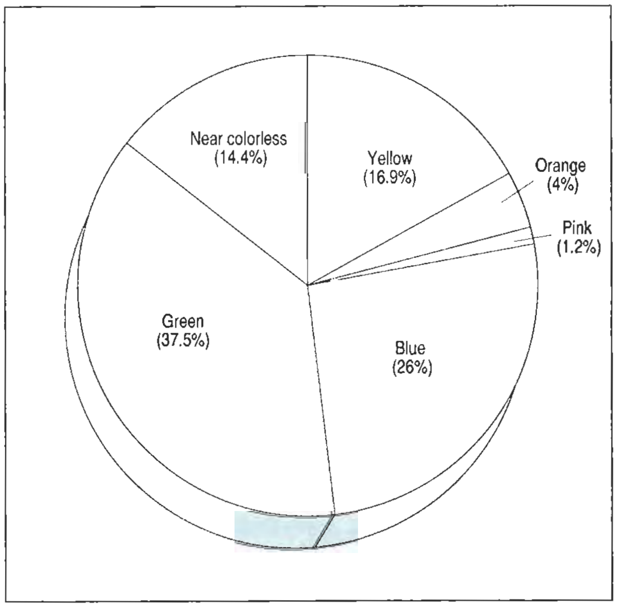
modified by the unit rhombohedron [$10\bar{1}1$] and the second order pyramid [$22\bar{4}3$]. While a small percentage of the crystals occur as thin hexagonal plates or long prisms, most appear as slightly flattened spheres in which the c-axis is about 0.7 to 0.8 times as long as the a-axis—well suited to the faceting of standard round brilliants.

EFFECTS OF HEAT TREATMENT ON CLARITY AND COLOR

Clarity Enhancement. It is the scattering of light, rather than the absorption or direct transmission of light, that is responsible for a lack of clarity in normally transparent gem materials. Anything in the gem (like a fracture or an inclusion) with an index of refraction different from that of the host material will scatter light by reflecting it off its surfaces, thus reducing the clarity of the host. In general, heating to high temperatures alone will not improve the clarity of a stone that has multiple fractures, as it will not close and seal a significant portion of the fractures. However, heating the stone to a high temperature for 10–20 hours does usually produce enough solid-state diffusion bonding to partially heal some fractures. This process strengthens the stone so that it can subsequently be cut without disintegration. Note that fracture filling is often part of the heat-treatment process, with borax or other boron compounds being used. However, the use of such fracture-filling materials is not part of the work described in this article. On rare occasions, iron-stained fractures in sapphire may become somewhat less visible if heat treated at high temperatures (1800°C), because at such temperatures iron oxides decompose and vaporize out of the fracture (Sata, 1984).

More commonly, sapphire crystals contain very large numbers of microcrystals of another mineral (Gübelin and Koivula, 1986) that are often so small (0.5–20 μm) and so numerous that they appear as a cloud or haziness to the unaided eye, substantially

Figure 5. This chart is adapted from color grading done by Day Mining Company on a large sample of sapphires obtained at Rock Creek in 1972. With the exception of the fractions marked orange and pink, the colors are quite pale on the average. Day Mining Company determined that 8% of the total material had sufficient color saturation to be marketable as gems. Data courtesy of J. Higgins.



reducing the clarity of the host gem. In many cases, when the stone is heated to high temperatures, the microcrystals will dissolve back into the sapphire and remain in solid solution as the stone cools rapidly (relative to geologic processes), thus substantially improving the clarity. It is worth noting at this point that it is not necessary to melt the microcrystals to dissolve the material back into the sapphire. Since diffusion into solid sapphire is the limiting diffusion rate, it does not matter, temperatures being equal, whether the inclusion is solid or liquid. Rutile, for example, has a melting point of about 1830°C, yet rutile needles 1–5 μm in diameter will dissolve rapidly into sapphire at 1600°C. In this case, a combination of the finite solubility of TiO_2 in sapphire at 1600°C and the unusually high diffusion rate of Ti^{4+} determines the apparent rate of dissolution.

In the specific case of Rock Creek sapphire, as noted above, we find that the great majority of the stones as mined possess unusually high clarity. However, stones that appear somewhat brown or green usually contain a small amount of exsolved rutile as fine needles (Bratton, 1971; Phillips et al., 1980) and another phase of small (5 μm), compact, euhedral crystals of an as-yet-unidentified material. While the rutile needles easily dissolve into the sapphire, the unidentified crystals do not. Since the quantities of these unidentified microcrystals are very small relative to the rutile needles, heat treatment that dissolves the rutile produces extraordinarily high clarity in the sapphire. Natural-color Rock Creek stones with highly saturated colors, if they are heat treated at all, are processed solely to dissolve the rutile.

Color Enhancement. To understand the color transformations that can be induced by various heat-treatment processes, it is necessary first to understand the origins of color in sapphire. Inasmuch as there are at least seven causes of the yellow coloration alone (Nassau and Valente, 1987), in this article we will address only those agents that are directly responsible for the coloration of the Rock Creek material.

Absolutely pure sapphire is composed only of aluminum and oxygen (Al_2O_3). Such material has a transparency range from approximately 160 nm in the far ultraviolet to 5500 nm in the infrared region of the spectrum. Thus, pure sapphire is colorless. All color in sapphire is the result of impurities (other elements) or other point defects in the crystal (Kröger, 1984; Fritsch and Rossman, 1987, 1988). These other point defects can be, for example, missing atoms (a vacancy in the lattice), additional (interstitial) atoms, or charge carriers such as extra electrons.

Figure 6. Although all of these natural-color Rock Creek sapphires (0.32–1.04 ct) exhibit high clarity and consequently are quite bright, only the rare, more saturated, blue stone would find a ready market. Photo © GIA and Tino Hammid.

Heat treatment can induce chemical reaction among the existing impurities and other point defects in sapphire, thus producing entirely different absorption spectra and corresponding transformations in color. Specifically, heat treatment can potentially induce any or all of the following processes:

1. Change the valence state of an impurity, thus changing the absorption spectrum
2. Induce isolated impurities to form pairs that absorb differently from the unpaired impurities
3. Dissolve exsolved minerals, which can bring new impurities into solution, adding new absorptions
4. Exsolve or precipitate impurities out of solution, thus changing the combination of absorbing impurities in solution

For an understanding of the terminology and techniques of heat treatment discussed here, see box A, on thermochemistry.

BOX A: THERMOCHEMISTRY

In the discussion of sapphire heat treatment, we use the terms *oxygen partial pressure* and *hydrogen partial pressure* to describe the atmosphere inside the furnace. *Oxygen partial pressure* simply means that portion of the total gas pressure that is attributable to oxygen. For example, the oxygen partial pressure of air is 0.2 atmospheres (atm), since oxygen makes up about 20% of the air. At high temperatures, both the valence state of the impurities and the concentrations and types of other point defects in oxide crystals (such as sapphire) can be changed by changing the oxygen partial pressure, thus changing color. The point defects with which we are most concerned are missing oxygen or aluminum atoms (vacancies), extra oxygen or aluminum atoms (interstitial atoms), or extra electrons or holes. As the oxygen partial pressure is raised, oxygen vacancies decrease and oxygen interstitials increase. Likewise, aluminum interstitials decrease and aluminum vacancies increase. Since all of these responses to the change of oxygen partial pressure are initiated at the surface of the crystal, how is the inside of the crystal changed? Some of these point defects are highly mobile at high temperatures and can move in or out of a crystal by diffusion. Oxygen does not really diffuse in or out of the sapphire crystal as the diffusion rate is far too slow. Rather, the effect of oxidation or reduction on color, in response to changes in the oxygen partial pressure, is achieved by diffusion of these much more rapidly moving point defects (Dutt and Kröger, 1975).

The hydrogen partial pressure in the furnace is also important, because hydrogen atoms are so small that they can diffuse rapidly into sapphire and participate in solid-state chemical reactions. Other typical furnace gases, such as N_2, CO, CO_2, H_2O, etc., do not diffuse into sapphire to any significant degree because their atoms are relatively large.

How are furnace atmospheres controlled? Sapphire is often heat treated in furnaces that burn natural gas, propane, oil, or charcoal with air and/or oxygen. The stones are exposed to an atmosphere made up of the high-temperature combustion gases. For example, if the furnace burns natural gas, which is mostly methane, with oxygen, the combustion reaction is essentially

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

As written, the formula indicates that there is exactly enough oxygen to burn all of the methane to water vapor and CO_2 (methane/oxygen ratio = 0.5); thus we have a neutral flame. If we have more than enough oxygen, excess oxygen appears in the combustion gases. If we have insufficient oxygen to complete combustion, both carbon monoxide (CO) and hydrogen (H_2) exist in the combustion gases, and the oxygen partial pressure (pO_2) is very low. Figure A-1 shows the partial composition of the furnace gases at 1700°C as the methane/oxygen ratio is varied from oxidizing to reducing. Thus, by changing the ratio of methane and oxygen fed in to fire the furnace, both the oxygen and hydrogen partial pressures of the combustion gases making up the furnace atmosphere can be controlled over a wide range, but not independently. However, the furnace temperature is somewhat dependent on the methane/oxygen ratio of the gas firing the furnace. For example, if the ratio is very high or very low, one usually cannot maintain the furnace at the high temperature desired. Electrically heated furnaces can provide any furnace atmosphere independent of temperature, as described in the article.

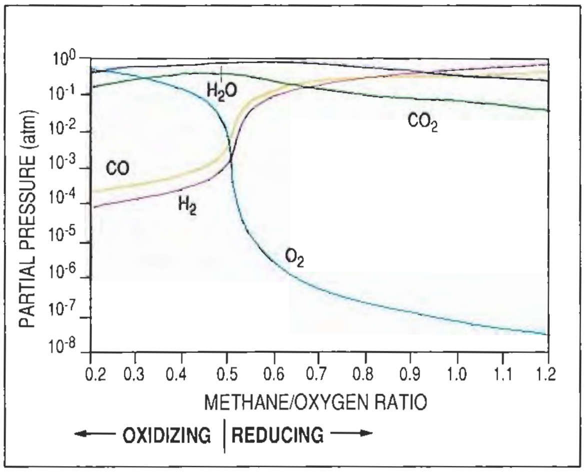


Figure A-1. This chart shows the partial pressures of the major products of combustion of methane and oxygen at 1700°C. Oxygen partial pressure is controlled by manipulating the methane/oxygen ratio of the gases fed in to fire the furnace. Note that hydrogen partial pressure increases rapidly as the reducing regime is entered. Thus, reductions in furnaces burning hydrocarbon fuels with oxygen or air are always done in the presence of hydrogen, which strongly participates in the solid-state chemical reactions in sapphire. (At low oxygen partial pressures and high temperatures, O_2 is largely dissociated into oxygen atoms. To simplify presentation, we have plotted the oxygen partial pressure equal to $pO_2 + {}^1/_2\, pO$.)

In other heat-treatment approaches, stones are packed in charcoal or sugar in partially sealed crucibles to create reducing atmospheres (Nassau, 1984; Themelis, 1992). While the charcoal or sugar exists, the oxygen partial pressure is very low. In fact, it is lower than is optimal for high iron-content sapphire. In the presence of carbon, the oxygen partial pressures at 1300°C and 1800°C must be less than 10^{-16} atm and 10^{-14} atm, respectively. What is generally not recognized about these types of reductions is the important role of hydrogen. In temperate climates, dry charcoal usually contains 8%–12% water. As the temperature is raised, water is driven off but it is also split by the water-gas reaction with carbon as follows:

$$C + H_2O \longrightarrow CO + H_2$$

This creates an atmosphere that has almost equal amounts of carbon monoxide and hydrogen. Thus, reductions conducted in a charcoal environment are usually accomplished more by hydrogen than by equilibration with the extremely low oxygen partial pressure defined by excess carbon. A related situation exists with sugar, starch, or other organic materials. Sucrose sugar, for example, is approximately $C_{12}H_{22}O_{11}$. When heated to high temperatures, it decomposes, creating an atmosphere with almost equal amounts of carbon monoxide and hydrogen. Under such conditions, the oxygen partial pressure is low but, again, reductions are usually driven by hydrogen.

Hercynite precipitation ($Fe^{2+}Al_2O_4$) constrains reduction conditions in high iron-content sapphire such as the Rock Creek material. Figure A-2, adapted from Meyers et al. (1980), shows the phase diagram of iron oxides and Al_2O_3 at 1500°C. High oxygen partial pressures are referred to as "oxidizing conditions"; low oxygen partial pressures as "reducing conditions." A "deeper reduction" means that we have lowered the oxygen partial pressure, for example, from 10^{-6} atm to 10^{-7} atm. At high oxygen partial pressures (very top of diagram), iron remains in the sapphire in solid solution (within the sapphire crystal structure) up to rather high concentrations. As the oxygen partial pressure is reduced, iron spinel (hercynite) precipitates out of the corundum phase. As the oxygen partial pressure is further reduced, metallic iron precipitates. Excellent identification and imagery of the phases associated with these processes are presented in the paper by Moon and Phillips (1991). Thus, hercynite precipitation limits the depth of reduction that can be used to treat high iron-content sapphire.

Temperature-time profiles for heat-treatment processes are usually determined more by the desire to achieve longevity in the muffle tubes and heating elements of the furnace than by any special requirement of Rock Creek sapphires. At 1700°C, the diffusion of point defects responding to changes in oxygen partial pressure, hydrogen diffusion, and rutile dissolution require less than one hour to equilibrate in a 15-ct stone. Thus, one hour at this temperature is quite sufficient. The high resistance of sapphire to thermal shock–induced fracture would allow heating to 1700°C in one hour or less, and cooling at a similar rate. However, furnace components may deteriorate rapidly under such conditions, so the rise and fall portions of the heat-treatment cycle are determined more by economic decisions than by thermo-chemical ones.

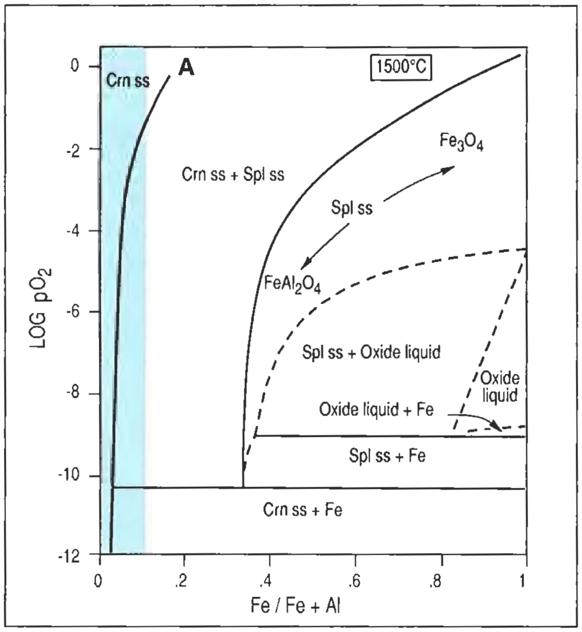


Figure A-2. The phase diagram of aluminum oxide and iron oxides is shown at 1500°C as a function of composition and oxygen partial pressure (Meyers et al., 1980). The vertical axis is the oxygen partial pressure in the furnace atmosphere. For example, –4 means that the oxygen partial pressure is 10^{-4} atm. For gem sapphire, we are interested in only the far left (blue shaded) portion of the chart. A typical Rock Creek sapphire would correspond to about 0.025 on the horizontal axis. At high oxygen partial pressure, above the phase separation boundary (marked A), iron remains in solid solution in sapphires. As the oxygen partial pressure is lowered below the phase separation boundary, iron begins to precipitate as hercynite ($Fe^{2+}Al_2O_4$) particles, and then as metallic iron particles. Hydrogen in the reducing atmosphere shifts the phase separation boundary to the left. Key: Crn ss = sapphire solid solution, Spl ss = spinel solid solution, Fe = metallic iron. (Figure reproduced with permission of its authors and The American Ceramic Society.)

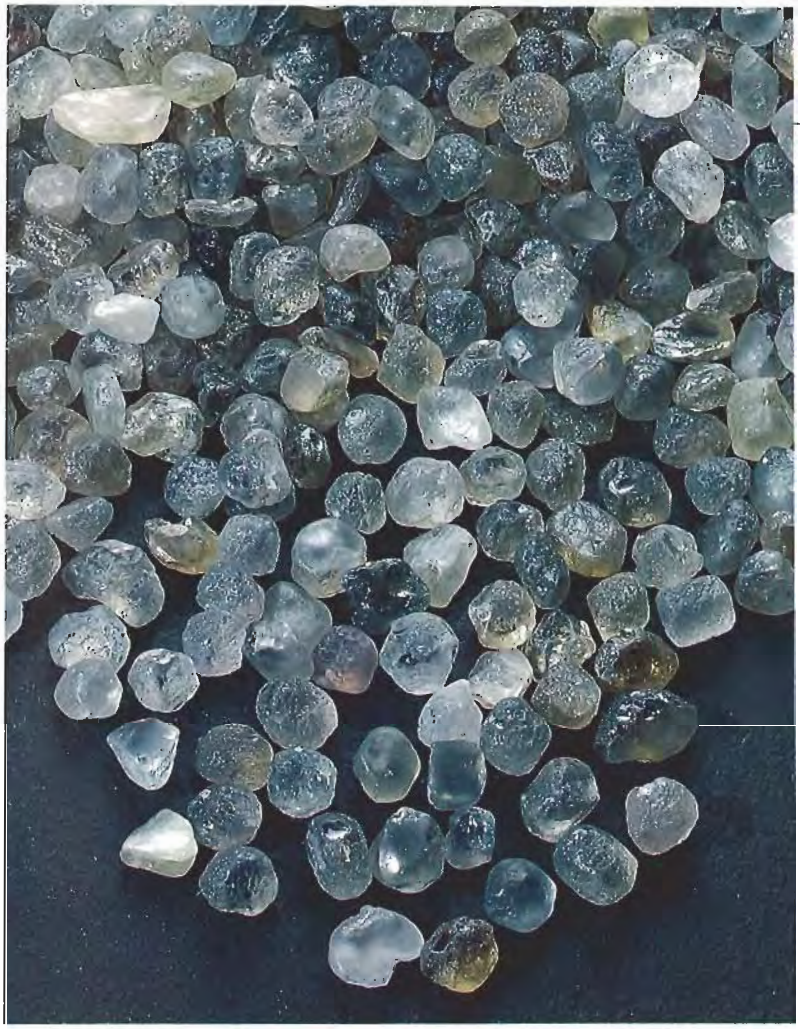


Figure 7. This sample of rough Rock Creek sapphire has been graded for size (average 4.5 mm), but the near-colorless, pale green, and pale blue colors are typical of the great majority of Rock Creek sapphires. The heat-treatment experiments focused on this color range of material and produced the heat-treated rough and faceted stones illustrated in this article. Photo © GIA and Tino Hammid.

As with almost all chemical reactions, heat increases the reaction rate. Thus, the heat of heat treatment is applied to achieve reaction rates that are rapid enough to be useful. In principle, a specific solid-state chemical reaction in sapphire can be achieved at 1600°C or at 1750°C, with treatment for different lengths of time. In practice, temperatures are chosen between 1300°C and 1900°C for the convenience of the treater or to optimize a specific chemical reaction over other competing reactions.

Far more important than the temperature is the atmosphere to which the stones are exposed inside the furnace. Since sapphire is an oxide, at high temperature its point-defect structure and the valence states of dissolved impurities are quite sensitive to the oxygen partial pressure of the furnace atmosphere (Kröger and Vink, 1956; Kröger, 1974). Low oxygen partial pressures promote the reduction of impurity ions, such as the partial reduction of Fe^{3+} to Fe^{2+}. High oxygen partial pressures drive the reaction in the other direction, that is, Fe^{2+} to Fe^{3+}. The hydrogen partial pressure in the furnace atmosphere is another important variable. Among the chemically reactive gases, only hydrogen atoms are small enough to diffuse rapidly into a sapphire crystal and actually take part in solid-state chemical reactions (El-Aiat and Kröger, 1982; Norby, 1990). Some chemical reactions in solid oxides—including, for example, sapphire and zircon, which require reduction (i.e., of the valence of a particular ion)—will not proceed without hydrogen regardless of how low an oxygen partial pressure is maintained. Thus, the major variables available to the heat treater to manipulate the color of sapphire are the oxygen partial pressure, the hydrogen partial pressure, the temperature, and the time held at that temperature. The temperature and time held at temperature are of far less importance than the oxygen and hydrogen partial pressures, as time and temperature are chosen only to assure that a desired chemical reaction goes to completion. However, it is the oxygen and hydrogen partial pressures that determine what type of chemical reaction proceeds and thus whether a Rock Creek sapphire, for example, changes to yellow or blue.

MATERIALS AND METHODS

For this study, Skalkaho Grazing supplied us with 15.7 kg of rough sapphire. These stones were a portion of the smaller rough of a 110-kg lot separated by Skalkaho Grazing in 1989 from ore mined in the meadow at Rock Creek in 1982 (J. Higgins, pers. comm., 1993). They were partially color graded by Skalkaho Grazing and could be characterized as pale blue, pale green, and near colorless; thus, they represented the corresponding hue groups of figure 5 but with highly saturated stones removed—that is, about 75% of the mine-run material. The stones were not separated by hues but were thoroughly mixed so that any sample from the lot contained all the hues described. We graded these stones for size through circular-hole diamond sieves and found a very narrow size distribution which averaged 4.5 mm (0.73 ct). In the experiments described below, where individual lots of rough stones were processed, every effort was made to ensure that each small experimental group was fully representative of the entire lot. Figure 7 shows a typical sample of this material. It is an accurate representation of the entire lot in both size and color of the individual stones.

In addition to the material described above, Skalkaho Grazing also supplied small quantities (10–30 grams) of rough stones from yellow and pink hue groups of figure 5. These stones were used primarily for spectroscopic studies. The large quantities of this material necessary for heat-treatment process development were not available at the time.

To determine the most effective heat-treatment conditions—temperature, time at temperature, and the composition of the furnace atmosphere (as discussed above)—we conducted more than 115 separate experiments. For each experiment, we used a fresh 50-gram lot (~340 pieces) of the rough Rock Creek sapphire previously described. When more critical comparisons of two different heat-treatment conditions were required, we increased the lot sizes to 100 grams (~680 pieces), 200 grams (~1,360 pieces), or 400 grams (~2,720 pieces) to ensure valid results. We made color assessments both visually and with a spectrophotometer. For the visual assessments, we not only sorted each heat-treated lot on a light box containing 5,000K fluorescent lamps, but we also made comparisons by viewing several different lots on the light box at the same time. We used the spectrophotometer both to make precise color determinations and to determine accurately the differences in the absorption spectra after heat treatment. Because the spectrophotometer requires samples with parallel polished surfaces to yield quantitatively comparable results, we had individual sapphires ground and polished on two sides to produce wafers from 0.6 to 2.0 mm thick. Five hundred such wafers were prepared for spectroscopy, chemical analysis, and inclusion studies.

Since natural gemstones are rarely as spatially uniform in color as liquids or glasses, special precautions must be taken to ensure reproducible measurements if accurate comparisons of before-and-after heat-treatment spectra are to be made. To accomplish this, we had an individual mold mounted on an aluminum plate constructed for each individual wafer. The wafer could be removed from this mounting and replaced repeatedly with high positional accuracy. A special kinematic mount was installed in the sample compartment of the spectrophotometer to hold the aluminum plates accurately in the measuring light beam, which was truncated to a rectangular cross section of 1.5 × 2.25 mm. The resulting spectra represent an average of the absorption coefficient over the 1.5 × 2.25 mm area of the sample and through the sample thickness.

We recorded the absorption spectra with an Hitachi U-2000 scanning spectrophotometer, at a wavelength resolution of 2 nm. The spectrophotometer was controlled, data were archived, and color calculations were performed by a Gateway 486 66MHz personal computer, using Spectra Calc software from Galactic Industries Corporation. A wafer of high-purity single-crystal synthetic sapphire, similar in size and thickness to the natural-sapphire wafer samples, was run before each sample to assure a correct baseline and to eliminate the effects of surface reflectivity. Using these techniques, we recorded 112 spectra on 60 different wafers of Rock Creek sapphire.

It is well known that sapphire is pleochroic; that is, different colors will be observed by viewing light that has passed through a crystal in different directions (Webster, 1983). In general, different absorption spectra will be recorded depending on whether the light propagating in the crystal has its polarization parallel or perpendicular to the c-axis of the crystal. Thus, a complete description of the absorption of light in sapphire requires two spectra. For clarity in presentation in this article, we illustrate only the spectrum in which the polarization of the light is perpendicular to the c-axis. This corresponds to the color observed viewing along the c-axis of the crystal with either polarized light or natural, unpolarized light.

To aid in the identification of the spectral features and to determine the possibilities for improvement by heat treatment, we obtained partial chemical analyses on the Rock Creek sapphires. These analyses were performed by Steve Novak of Evans East, Plainsboro, New Jersey, using secondary ion mass spectroscopy (SIMS). Since, with the exception of iron, the relevant impurities have concentrations in the range of a few to a few hundred parts per million atomic (ppma), SIMS was chosen for its sensitivity to low concentrations and for the availability of some ion-implant standards in sapphire. In all, 36 SIMS analyses were conducted on 25 samples of Rock Creek sapphire.

For research work, as well as for routine processing of ruby and sapphire from various localities, we use electrically heated furnaces manufactured by Thermal Technology, Inc. of Santa Rosa, California. The type 1000A series of furnaces (figure 8) use graphite heating elements and graphite insu-

Figure 8. The Crystal Research heat-treatment experiments were conducted using a Thermal Technology Group 1000A graphite hot zone furnaces identical to this one. The cylindrical device to the right is the furnace itself. The furnace body, muffle tube extensions, and end plates are water cooled, which is why this 2200°C-capable furnace is so compact. The equipment rack to the left contains a 20-kw power supply, a programmable temperature controller, and the gas flow controls. Photo courtesy of Thermal Technology, Inc.

lation, and can achieve temperatures far above the melting point of pure sapphire (2052°C). The heating element and insulation are enclosed in a water-cooled metal shell that forms the outside surface of the furnace. Nitrogen gas flows through the furnace body over the hot graphite to prevent combustion with the oxygen in the atmosphere. The furnace separates the heating element from the sapphires with a muffle tube assembly. The muffle tube is made from high-purity Al_2O_3 ceramic. The sapphires to be treated are placed inside the muffle tube, where any type of process gas can flow continuously over the stones. High-purity commercial cylinder gases are used. The flow is controlled by pressure regulators and flow meters of the ball and tube type. Thus, any type of atmosphere from pure oxygen to pure hydrogen or carbon monoxide can be used at any temperature below the collapse point of the ceramic tube (realistically, about 1950°C). Because the furnace is heated by electricity and not by the combustion of hydrocarbon fuels, highly reducing conditions can also be achieved without hydrogen in the furnace atmosphere. Temperature control is maintained with a type-C thermocouple connected to a Eurotherm Model 818P microprocessor temperature controller. Accurate temperature measurement of the sapphires is achieved by embedding a ceramic black-body cavity in the sapphires which is viewed with an optical pyrometer through a quartz window in the furnace body (McGee, 1988).

RESULTS

Yellow in Rock Creek Sapphire. Iron is probably the most common impurity in sapphire. Iron oxide, Fe_2O_3, is structurally similar to aluminum oxide (sapphire). The iron in Fe_2O_3 is Fe^{3+} and can substitute for the Al^{3+} of sapphire. Up to approximately 5 atomic % (at.%) iron can be incorporated in sapphire at geologic temperatures. This relatively high solubility of iron, combined with the fact that it is ubiquitous within the earth's crust, virtually assures that any natural sapphire contains some iron.

In the Rock Creek sapphires, iron is the dominant impurity. Measured concentrations of iron range from 0.2 at.% to 1.4 at.%, with 0.7 at.% being typical (see table 1). The concentration of iron in Rock Creek sapphires is typically 100 times that of other impurity elements. Figure 9 shows the optical absorption spectrum of a pale yellow sapphire in which iron is the only color-producing impurity. This spectrum has several major features. First, there are three relatively narrow absorption bands centered at 377, 388, and 450 nm, and three broad bands centered at 540, 700, and 1050 nm. The bands at 388, 540, 700, and 1050 nm are assigned to the single Fe^{3+} ion, whereas the bands at 377 and 450 nm are assigned to Fe^{3+}-Fe^{3+} ion pairs (Ferguson and Fielding, 1971, 1972; Krebs and Maisch, 1971). By pairs, we mean two Fe^{3+} ions that are close enough together in the lattice that they act as a single specie in absorbing light. Only those absorption bands in the visible region of the spectrum (450, 540, 700 nm) cause color. Since the single Fe^{3+} ion bands at 540 and 700 nm are very weak in sapphire with iron concentrations typical of Rock Creek (see table 1), they have little impact on the color of these stones. Thus, for a sapphire containing iron as the only color-causing impurity, the Fe^{3+}-Fe^{3+} pair absorption band at 450 nm is the primary cause of color. This is the absorption feature often seen when observing sapphire with a handheld spectroscope (Liddicoat, 1981).

Since the probability that two Fe^{3+} ions are close together in the lattice increases approximately as the square of the Fe^{3+} concentration, the strength of the 450-nm absorption also increases approximately as the square of the Fe^{3+} concentration. Thus, the 450-nm absorption band is a sensitive indicator of the amount of Fe^{3+} in the crystal. However, the absorption strength of the 450-nm band, per ion pair, is not high in sapphire nor is the band wide. Thus, this band produces only a pale yellow coloration in sapphire with iron concentrations typical of Rock Creek. The yellow color produced by iron alone is a clean, almost pure yellow that does not tend toward orange. The color coordinates of the sapphire in figure 9 are shown in table 2. Iron as Fe^{3+} in Rock Creek sapphire can also contribute to green when combined with other color-producing impurities (discussed below).

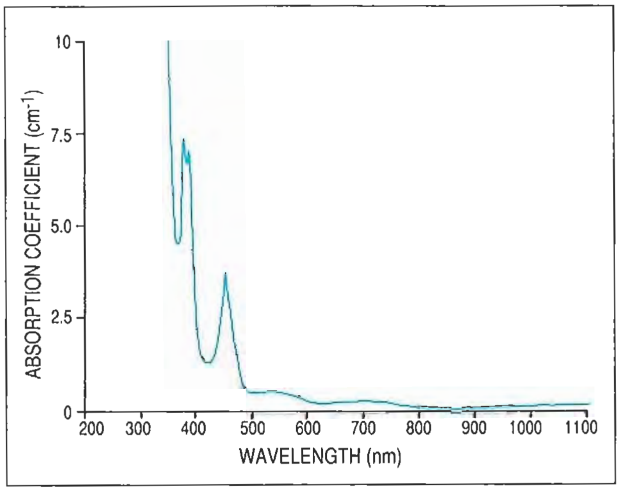


Figure 9. Iron causes the pale yellow coloration of some sapphires, primarily by absorption from Fe^{3+}-Fe^{3+} pairs, as evident in this absorption spectrum. The narrow peak at 388 nm and the broad bands at 540, 700, and centered at 1050 nm are assigned to Fe^{3+}, while the narrow peaks at 377 and 450 nm are assigned to Fe^{3+}-Fe^{3+} pairs (Krebs, 1971; Ferguson, 1971, 1972); see table 2.

Can heat treatment dramatically alter the color of Rock Creek sapphire colored by iron alone? Only to a limited degree. Heating in an oxidizing atmosphere simply assures that all of the iron is present

TABLE 1. Partial chemical analyses of Rock Creek sapphire.[a]

Sample no.	Color	Na	Mg	Si	K	Ca	Ti	Cr	Fe	Ga
313	Near colorless	0.0110	32.0	25.0	0.0060	0.470	42.0	1.60	0.670	13.0
323	Near colorless	0.1700	42.0	54.0	0.0180	0.600	42.0	3.70	0.670	12.0
324	Pale blue	0.1200	27.0	27.0	0.0650	0.910	32.0	1.80	1.180	14.0
331	Pale blue	0.0069	26.0	23.0	0.0032	0.370	32.0	15.00	0.810	13.0
337	Pale green	0.0044	55.0	37.0	0.0069	0.850	60.0	8.20	1.290	17.0
344	Pale green	0.0250	47.0	55.0	0.0190	0.630	55.0	0.85	1.090	12.0
345	Pale green	0.0012	36.0	26.0	0.0017	0.460	54.0	0.20	0.810	12.0
352	Pale green	0.0046	41.0	23.0	0.0025	0.560	54.0	6.60	0.920	12.0
309	Pale blue	0.0460	89.0	29.0	0.0140	0.500	80.0	1.30	0.730	8.7
310	Pale blue	0.0130	61.0	23.0	0.0210	0.290	61.0	5.30	0.790	6.6
319	Pale blue	0.0060	89.0	28.0	0.0063	0.390	71.0	26.00	0.710	8.4
320	Pale blue	0.0140	61.0	45.0	0.0110	0.310	59.0	24.00	1.400	9.0
321	Pale blue	0.0087	48.0	23.0	0.0065	0.240	41.0	4.60	0.850	8.1
351	Pale green	0.0028	48.0	18.0	0.0040	0.220	43.0	20.00	0.770	6.7
423	Yellow spot	0.0046	22.0	11.0	0.0011	0.190	11.0	12.00	0.280	5.9
423	Colorless area	0.0021	16.0	13.0	0.0004	0.130	15.0	11.00	0.300	5.9

[a] *These analyses were performed by Steve Novak of Evans East, Plainsboro, NJ, by secondary ion mass spectroscopy (SIMS). SIMS was chosen because it was important to have accurate measurements in the range of a few to few hundred parts per million atomic (ppma) range to compare quantitatively with the absorption spectra. The data are presented in ppma except for iron, which is in the units of atomic percent (i.e., parts per hundred).*

as Fe^{3+}, producing the "pure" pale yellow color just discussed. Heating in a moderately reducing atmosphere converts a small portion of the Fe^{3+} to Fe^{2+}. Yet detailed studies of this process have shown that, even in highly reducing atmospheres, the ratio of Fe^{2+} to Fe^{3+} rarely exceeds 10^{-3} (Koripella and Kröger, 1986)—and absorptions of Fe^{2+} alone in small concentrations have little impact on color. However, if the total iron concentration is high enough, a strong wide absorption band centered at about 875 nm appears as a result of reduction that has been ascribed to Fe^{2+}-Fe^{3+} pairs (Ferguson and Fielding, 1971, 1972). While detailed proof of this assignment is lacking, the arguments for it appear reasonable. The short-wavelength tail of this band provides some absorption in the 650–750 nm region, giving a bluish or greenish cast to an otherwise yellow stone. If the stone is heated in a much more strongly reducing atmosphere, microcrystals of hercynite (iron spinel, $FeAl_2O_4$) precipitate (Meyers et al., 1980; Moon and Phillips, 1991; see thermochemistry box A). These microcrystals add a gray hue and reduce clarity (see, e.g., figure 10). Further reduction leads to the precipitation of both hercynite and metallic iron, eventually producing total opacity and a reflective black exterior.

Figure 10. Overreduction of high-iron sapphire, such as that from Rock Creek, leads to hercynite precipitation; this makes the material, like the sample shown, a translucent gray. Prior to heat treatment, this wafer (5 mm in diameter and 0.34 mm thick) was colorless and transparent. Photo © John L. Emmett.

We have seen that iron, in concentrations typical of those seen in Rock Creek sapphires, produces only a pale yellow; yet there are many Rock Creek stones with a strong orangy yellow color (see figure 1), which is usually limited to the central region of the crystal. Figure 11 shows a wafer cut from such a natural-color crystal. To understand the origin of this coloration, we measured the absorption spectrum through both the yellow area and the colorless portion of this stone (see figure 12). To compare these absorption spectra, we simply subtracted the

TABLE 2. Color coordinates in C. I. E. L*, a*, b* space as related to the absorption spectra.[a]

Sample no.	Color	Figure no.	Illuminant A	Illuminant D65
S191AR	Medium yellowish green	18	79.3, −4.8, 7.8	79.7, −9.7, 10.5
S213AR	Pale yellow	9	93.6, 2.2, 29.1	92.7, −7.2, 31.3
S229AR	Medium blue	17	63.1, −1.5, −27.6	64.7, 3.2, −25.2
S389	Light blue	24, curve A	34.1, −8.3, −16.2	35.8, −7.1, −12.7
S389	Light blue with some gray	24, curve B	28.2, −7.4, −13.5	29.7, −6.8, −10.3
S454	Pale greenish brown	19 and 20 (curve A)	34.4, 5.2, 14.4	33.6, 0.0, 15.0
S454	Medium blue	20 (curve B) and 21	24.4, −7.7, −28.1	26.7, 0.1, −24.7
S462	Strong orangy yellow	11 and 12, on yellow spot	77.8, 39.7, 106.7	71.2, 35.8, 101.2

[a]To relate color to the absorption spectra, the color coordinates for the various spectra are presented here. The color system chosen is the C.I.E. L, a*, b*. Two light source types or illuminants were used. C.I.E. illuminant A represents incandescent light; illuminant D65 is one representation of natural daylight. Comparing the color coordinates for the two illuminates allows one to judge the amount of color change under different illumination. The color coordinates were calculated for a 2° observer, and for light making a single pass through a 4-mm-thick sapphire in all cases. For understanding of these color coordinates and conversion to other color coordinate systems, see Billmeyer and Saltzman (1981).*

Figure 11. This 0.9-mm-thick wafer was cut and polished from a natural unheated Rock Creek sapphire to illustrate the presence of yellow in only a portion of the stone, a feature that is relatively common in material from this locality. Photo © John L. Emmett.

spectrum of the colorless area from that obtained through the yellow area (figure 13).

From this differential spectrum, two important conclusions can be drawn. First, the Fe^{3+} concentration in the central yellow spot is essentially the same as in the colorless area of the stone. That is, subtraction of the colorless-area spectrum from that of the yellow spot almost completely eliminates all the Fe^{3+} absorption features at 377, 388, and 450 nm. Thus, Fe^{3+} is not responsible for the strong yellow coloration. Second, the strong broad absorption band that starts at 600 nm and extends through the blue and violet portion of the differential spectrum is responsible for the strong yellow coloration. While not completely understood, it appears to be associated with impurity-initiated point defects in the sapphire crystal (Kvapil et al., 1973; Mohapatra and Kröger, 1977; DuVarney et al., 1985; Boiko et al., 1987). If a divalent impurity such as magnesium (Mg^{2+}) replaces aluminum (Al^{3+}) in the sapphire lattice, there is a point defect created at the site which has insufficient charge. Such point defects are often referred to as color centers (see, e.g., Fritsch and Rossman, 1988). When sapphire is heat treated under highly oxidizing conditions, a hole (the opposite of an electron) is created in the lattice which has an effective electrical charge of +1. This hole combines with the Mg^{2+}, providing the +3 charge required at that lattice site. Therefore, the strong broad band in figure 13 appears to be the optical absorption associated with this Mg^{2+}-hole pair. Since the yellow area is usually in the center of the crystal, it appears that the chemical environment must have changed during the growth of these sapphires. Chemical analyses carried out on these stones indicate that the yellow coloration forms in those portions of the crystal where the concentration of magnesium substantially exceeds the con-

Figure 12. These are the absorption spectra of the sapphire sample shown in figure 11: (A) measured through the colorless area of the stone; (B) measured through the yellow area.

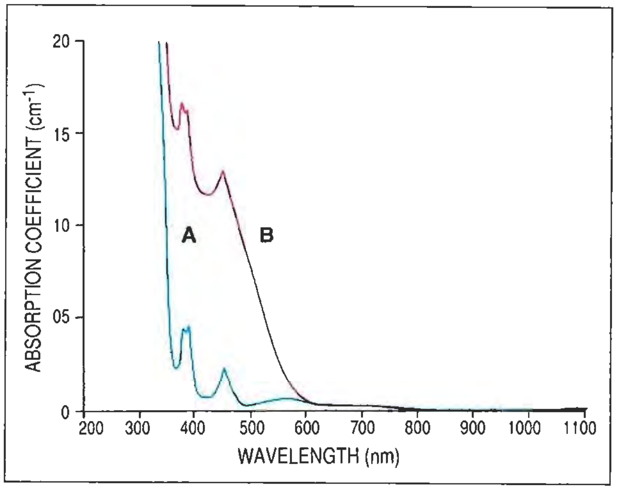
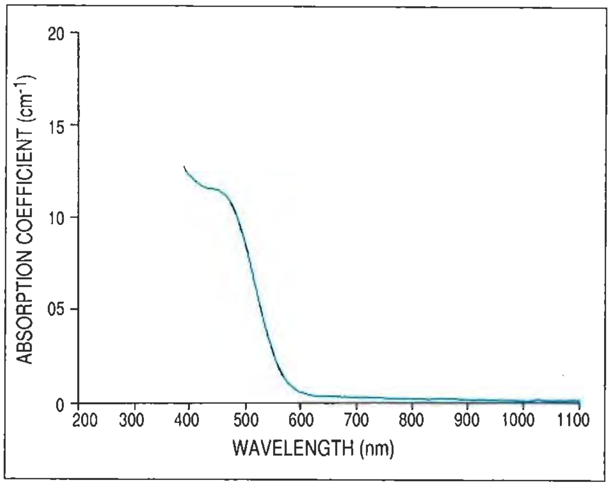


Figure 13. This absorption spectrum is the differential (B–A) of the two spectra shown in figure 12. Since the narrow absorption peaks of iron at 377, 388, and 450 nm are completely missing from this spectrum, it can be concluded that the iron concentrations in the colorless and yellow areas of the stone are identical. Thus, the yellow coloration does not result from iron.



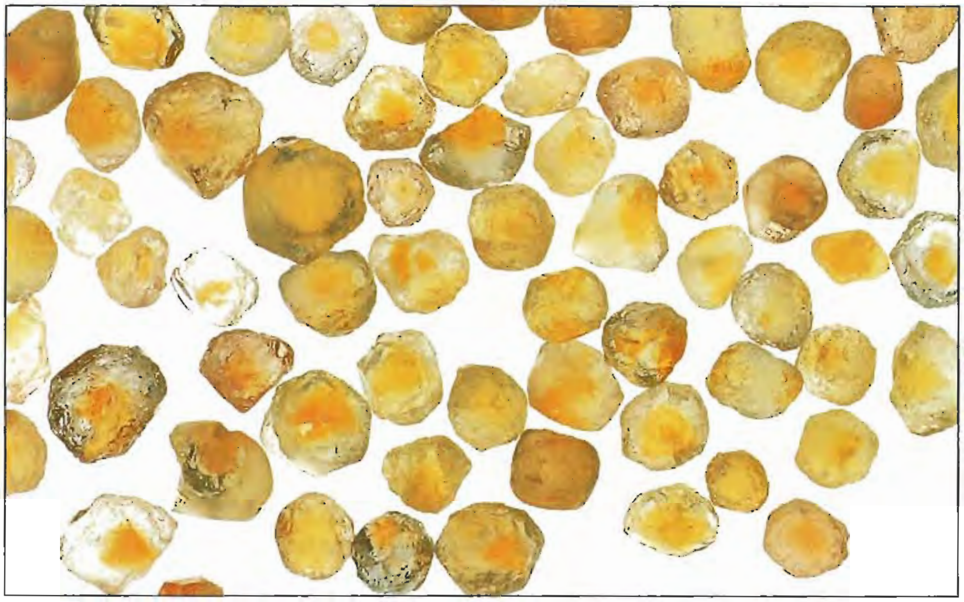


Figure 14. The yellow coloration of these stones was produced by heating the near-colorless, pale blue, and pale green material of figure 7 to 1200°C in a highly oxidizing atmosphere. Note the localization of the coloration in the crystals. The yield of such yellows from the material in figure 7 is 15%–20%. Photo © John L. Emmett.

centration of titanium (see table 1).

The interaction in a crystal of point defects and impurities is rarely as simple as single isolated centers like the Mg^{2+}-hole pair. It is quite possible that the absorption spectrum of this point defect is modified by association with the major impurities, or by the formation of point defect clusters (Koripella and Kröger, 1986). To understand the origin of this coloration more fully, we have studied the absorption spectrum of high-purity, single-crystal synthetic sapphire intentionally doped with magnesium and heat treated under highly oxidizing conditions. In this material, we observed absorption spectra that are nearly identical to that in figure 13. This point defect, or color center, cannot be bleached in oxidizing atmospheres up to 1850°C. However, the strength of the absorption is greatly reduced by heating to 1500°C at lower oxygen partial pressures ($pO_2 = 10^{-4}$ atm; Mohapatra and Kröger, 1977). Differential spectra, recorded through the yellow areas of natural stones equilibrated at two different oxygen partial pressures ($pO_2 = 1$ atm and $pO_2 = 10^{-3}$ atm), again yield absorption spectra nearly identical to that in figure 13.

The strong orangy yellow coloration produced by this point defect is very different from the pale pure yellow of iron-produced coloration. These different yellow colors are compared in table 2, where color coordinates are calculated for both the iron-colored sapphire of figure 9 and the point-defect-colored area of the stone in figure 11.

Since the strength of the yellow coloration is sensitive to one of the main variables (oxygen partial pressure) under a heat treater's control, this coloration can be enhanced or reduced. Good blue stones from Rock Creek often exhibit yellow centers. The yellow center is easily removed by heating the stones under slightly reducing conditions. We have found also that heat treating a sample of our near-colorless, pale blue, and pale green stones at 1200°C in a pure oxygen atmosphere will produce some highly saturated yellow stones (figures 14 and 15). Just as in the natural-color stone, the yellow coloration is usually confined to the central region of the crystal. Thus it appears that this heat-treatment process simply raises the equilibrated oxygen partial pressure for those Rock Creek stones that were equilibrated at a lower partial pressure in nature. For a 400-gram lot of our experimental Rock Creek sapphire described previously, 60–80 grams, or approximately 400 to 545 stones, were judged to have sufficient color saturation in a large enough region of the crystal to cut commercially valuable gems. Thus, the yield of good yellow stones from the pale-hued study material found at Rock Creek is about 15%–20%.

Pink and Orange in Rock Creek Sapphires. It is well known that chromium, as Cr^{3+}, is responsible for pink sapphire and (in greater concentrations) deep red ruby. In addition, the valence state of chromium—and thus the depth of color—in sapphire cannot be changed by heat treatment. Therefore, heat treatment cannot produce a more intense pink or red in the significant quantities of pale pink sapphire produced at Rock Creek. However, it can produce a pinkish orange, or "padparadscha," color, as well as orangy yellow and

Figure 15. These stones were cut from heat-treated sapphires like those shown in figure 14. Note the high clarity and broad range of color saturations. Photo © GIA and Tino Hammid.

bright orange (figure 16), by inducing the yellow coloration previously discussed into the pink stones. At the present time, we do not have good quantitative yield statistics on these colors, as sufficient quantities of pale pink stones are not yet available for testing.

Blue and Green in Rock Creek Sapphires. If sapphire contained only a small amount of Fe^{2+}, or only Ti^{4+}, it would remain colorless. However, when both Fe^{2+} and Ti^{4+} are present at the same time and are on neighboring lattice sites, an intense blue is created (Townsend, 1968; figure 17). This type of absorption is caused by intervalence charge transfer (Burns, 1981; Nassau, 1983; Fritsch and Rossman, 1988).

Since neither Fe^{2+} nor Ti^{4+} is easily incorporated into sapphire, most natural sapphire is not blue. In fact, the solubility of Ti^{4+} in sapphire is so low at normal temperatures that the majority of the titanium in natural sapphire is exsolved as titanium-containing microcrystals. Thus, much natural sapphire with both iron and titanium, and the sapphire of Rock Creek in particular, contains the iron as dissolved Fe^{3+} and most of the Ti^{4+} as exsolved TiO_2 microcrystals. Under certain conditions, Fe^{2+} and Ti^{4+} can enter sapphire at the same time and their solubility together is greater than the solubility of either alone (Roy and Coble, 1968; Ikuma and Gordon, 1983). This enhanced solubility results from mutual charge compensation—that is, one Ti^{4+} ion plus one Fe^{2+} ion have a total charge of +6, which equals that of the two Al^{3+} ions they replace. Thus, the incorporation of these two impurities as pairs during crystal growth does not require formation of substantial point defects.

Figure 16. When yellow coloration from heat treatment like that used on the stones in figure 14 is induced in pale pink stones that contain a low concentration of chromium, this range of colors is produced. While the percentage of pale pink stones from the deposit that can achieve these colors is not high, the number of stones is still very large. Photo © GIA and Tino Hammid.

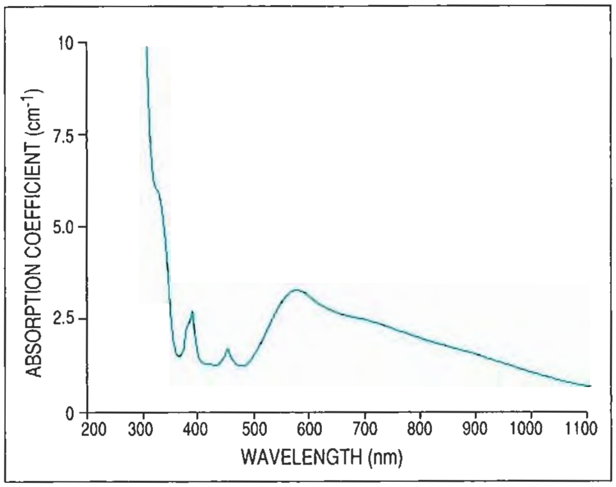


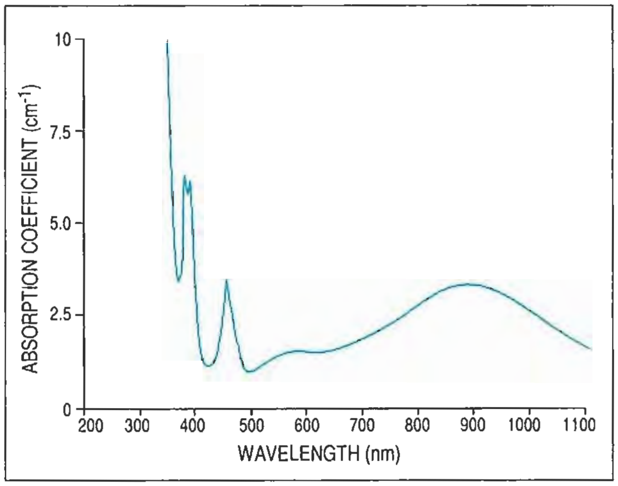
Figure 17. The natural-color stone from which this spectrum was taken is blue because the Fe^{2+}-Ti^{4+} pair absorptions centered at 575 nm (yellow) and 700 nm (deep red; here, overwhelming the weak Fe^{3+} absorption) are much stronger than the absorption at 450 nm. Compare this spectrum with those in figures 9 (yellow sapphire) and 18 (green).

The pale green coloration predominant in Rock Creek sapphire is a combination of Fe^{3+}-Fe^{3+} yellow with a small amount of Fe^{2+}-Ti^{4+} blue. A comparison of the visible-range absorption spectrum of a green sapphire (figure 18) with the spectra of blue (figure 17) and yellow (figure 9) sapphires reveals that the only significant difference in the visible regions of these spectra is the relative ratio of the 450-nm absorption to the 575-nm absorption. Thus, where the 450-nm absorption is much stronger than the 575-nm absorption, the stone appears yellow. As the relative strength of the 575-nm absorption (or concentration of Fe^{2+}-Ti^{4+} pairs) increases, the color goes from yellow to green. With further increases in the relative strength of the 575-nm absorption, the stone appears blue.

With the foregoing information as background, we can interpret the very pale green hue of the majority of Rock Creek sapphires and determine the possibilities for converting these stones to a marketable blue. The low concentration of the Fe^{3+}-Fe^{3+} ion pairs absorbing at 450 nm, combined with a very low concentration of Fe^{2+}-Ti^{4+} pairs absorbing at 575 nm and 700 nm, is consistent with the low concentration of titanium in solution indicated in table 1. Production of a deep blue color in these stones requires the introduction of more titanium into solution in the crystal as Ti^{4+}. It has been suggested that natural sapphire contains titanium as Ti^{3+} (see, e.g., Schmetzer and Bank, 1981) which, thus, could be a potential source of Ti^{4+} by heat treatment. However, this cannot be so. In sapphire, Ti^{3+} is a very strong reducing agent or electron donor and Fe^{3+} is an electron acceptor (Dutt and Kröger, 1975; Mohapatra and Kröger, 1977). Thus, Fe^{3+}+Ti^{3+} would become Fe^{2+}+Ti^{4+} (iron would gain one electron while titanium would lose one) during growth at any reasonable temperature. Other sapphire impurities, such as magnesium, are also electron acceptors (Mohapatra and Kröger, 1977). In sapphire when such electron-acceptor impurities far exceed titanium in concentration, Ti^{3+} will not exist to any significant degree and neither will heat treatment convert Ti^{4+} to Ti^{3+}. Indeed, we have yet to observe the well-known Ti^{3+} absorption spectrum in any natural-color or heat-treated natural sapphire (Ti^{3+} can be produced in very high-purity synthetic sapphire where it is the dominant impurity and is processed under extremely reducing conditions; Lacovara et al., 1985).

The only potential source of Ti^{4+} remaining in these natural sapphires are the microcrystals of rutile. To evaluate this possibility, we had wafers of Rock Creek sapphire cut and polished, perpendicular to the c-axis, as previously described (figure 19). Examination of several hundred of these wafers revealed that more than 90% of the sapphires contain rutile needles, identified by their morphology

Figure 18. The natural-color sapphire (S191AR) from which this spectrum was taken is green because the absorptions in the yellow and red region of the spectrum begin to modify the predominantly yellow coloration produced by the 450-nm absorption. Compare this spectrum with those in figures 9 (yellow sapphire) and 17 (blue).



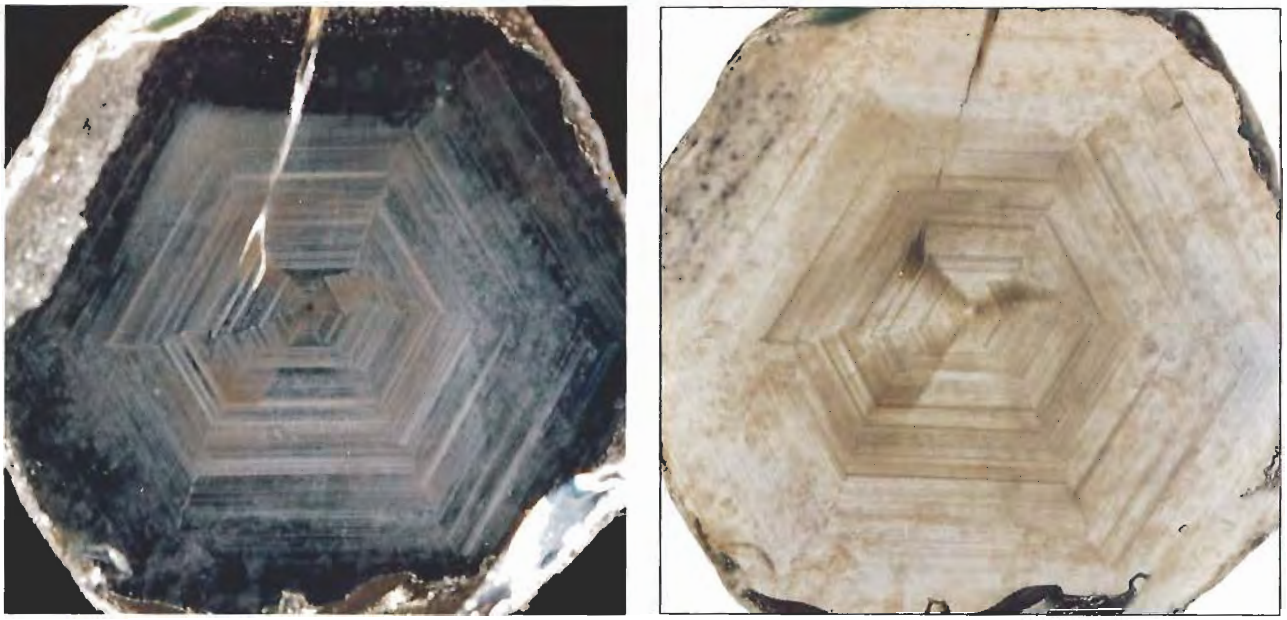
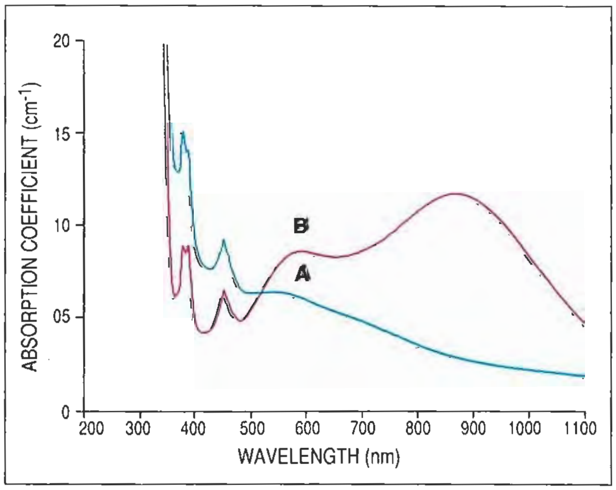


Figure 19. More than 90% of Rock Creek sapphires have been found to contain rutile, as evident in this 1.76-mm-thick wafer viewed with darkfield illumination (left). Only the heaviest rutile concentrations are easily seen without darkfield illumination (right). Photo © John L. Emmett.

and orientation (Phillips et al., 1980), but that the concentration varies widely. Where sufficient concentration exists, the color can be improved by heating the stones first in either an oxidizing or a neutral atmosphere to dissolve the rutile, placing titanium in solid solution as Ti^{4+}, and then continuing to heat them in a reducing atmosphere to reduce some of the Fe^{3+} to Fe^{2+}. The Fe^{2+} reacts with the Ti^{4+}, forming Fe^{2+}-Ti^{4+} pairs, and thus the blue coloration. The actual process is slightly more complex, as the dissolution of rutile in sapphire also forces the reduction of some Fe^{3+} to Fe^{2+} independent of the external oxygen partial pressure, but the basic concept remains the same. Note in figure 20 that the Fe^{2+}-Ti^{4+} pair absorptions are substantially greater in the rutile-containing sapphire heat treated in a strongly reducing atmosphere (spectrum B) than in the natural-color stone (spectrum A). Spectrum B also features a strong, wide absorption band centered at 875 nm—attributed to Fe^{2+}-Fe^{3+} pairs—as a result of reduction. These spectra are very typical for stones that contain substantial quantities of rutile microcrystals. Color coordinates for these spectra are also given in table 2.

As illustrated in figure 21, the blue color induced in the stone by heat treatment is localized to the regions of original rutile deposition. This is because the diffusion of titanium in sapphire is slow compared to the relatively short time (1–10 hours) used for heat treatment. Figure 22 shows a group of the blue stones that resulted from heat treating the near-colorless, pale blue, and pale green Rock Creek material. These stones have been treated by the process described at 1650°C in a reducing atmosphere that contains some hydrogen. The wide range of blue color saturation achieved mirrors the

Figure 20. These spectra show the aborption characteristics before (A) and after (B) heat treatment of the sapphire wafer of figures 19 and 21, respectively. The stone became blue because heat treatment substantially increased the absorption in the yellow to red region of the spectrum, while it substantially reduced the absorption in the violet, blue, and green regions. Compare the color coordinates of these spectra in table 2.



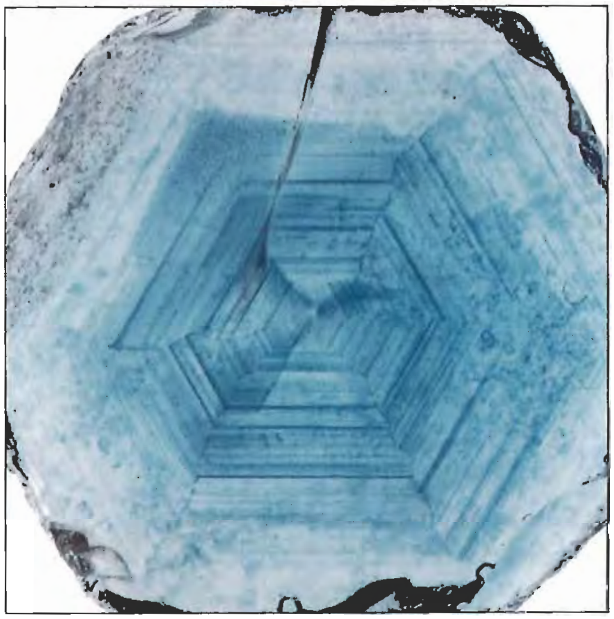


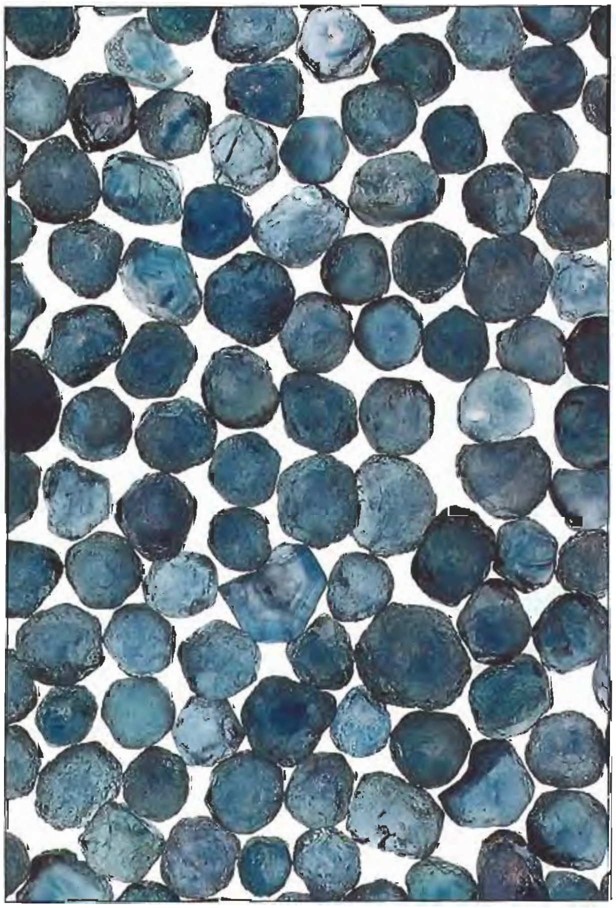
Figure 21. After heat treatment for rutile dissolution and reduction, blue was produced in the sapphire wafer shown in figure 19 by the formation of Fe^{2+}*-*Ti^{4+} *pairs in the sapphire. Although iron is uniformly distributed throughout the crystal, the rutile providing* Ti^{4+} *is very localized, producing a blue pattern that matches the original rutile deposition pattern. Photo © John L. Emmett.*

wide range of rutile concentration in the natural stones. However, the color range shown in figure 22 is 50% of the heat-treated lot. Processing a 400-gram batch of the sample stones yielded about 200 grams, or approximately 1,360 stones similar to those in figure 22. An additional 5-kg lot of the same starting material processed in this fashion gave similar yields. Although the blue coloration produced in the Rock Creek sapphire by this process is not spatially uniform, attractive stones can be faceted (figure 23).

We also investigated whether the color of the lighter blue stones in figure 22 could be deepened by treatment in a more reducing atmosphere. The answer in this case was no. The stones in figure 22 were reduced in an oxygen partial pressure that was found to be optimal for this material. There is an optimum because, while the goal is to create enough Fe^{2+} to form pairs with all of the Ti^{4+}, excess Fe^{2+} (which results when the stone is overreduced) will precipitate out as hercynite microcrystals, adding a gray component to the color. The spectra in figure 24 show the results with optimal processing (A) and slightly deeper reduction (B), with the difference (C) nearly constant across the visible spectrum and thus simply the addition of gray. The color coordinates of the stone for these two processing conditions are given in table 2. Similar spectra have been recorded on 15 wafers, which exhibit a wide range of initial rutile concentrations. It is the relatively high concentration of iron in Rock Creek sapphire, and the associated hercynite precipitation during reduction, that makes optimization of the heat treatment more difficult for this material than for low-iron-concentration material such as the geuda from Sri Lanka.

Since the production by heat treatment of good

Figure 22. These rough blue sapphires were produced by heat treating the pale material shown in figure 7. The wide range of color saturation mirrors the wide range of rutile concentration. The yield of the material shown here from the near-colorless, pale blue, and pale green material of figure 7 is 50%. Photo © John L. Emmett.



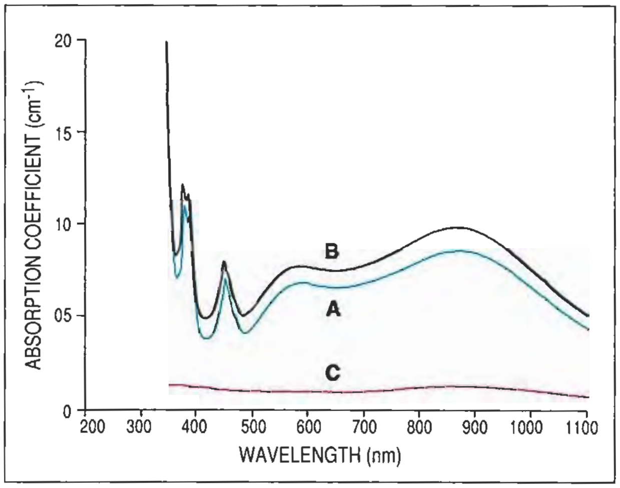
blue stones requires a high titanium concentration, and the production of good yellow stones requires a low titanium concentration, these two groups are produced almost independently from the near-colorless, pale blue, and pale green Rock Creek sapphires. Thus, the total yield of commercially valuable stones from this material is 65%–70%. Note also that the colors produced are stable to both light and heat.

Figure 23. The faceted blue sapphires pictured are cut from material like that shown in figure 22. These stones are representative of the color range and clarity that is produced by heat treating the pale green and blue stones shown in figure 7. Photo © GIA and Tino Hammid.

EVIDENCE OF HEAT TREATMENT IN ROCK CREEK SAPPHIRE

TiO_2 occurs in Rock Creek sapphire not only as fine needles, but also as compact euhedral crystals 25 µm to 1 mm in size (but typically 25–250 µm). These inclusions are protogenetic; that is, they formed elsewhere, were transported to the growing surface of the sapphire crystal, and were enclosed by subsequent sapphire crystal growth. Rutile has a higher thermal expansion coefficient than sapphire. Consequently, if an embedded rutile crystal is large enough, it will fracture the sapphire at high temperature. We have observed two types of phenomena related to these inclusions following heat treatment. First, if the crystal is small, fracture does not occur and the inclusion begins to dissolve into the sapphire, creating the familiar blue halo around the inclusion (Koivula and Kammerling, 1988). Second, if the rutile crystal is large, it creates a small plate-like fracture in the sapphire. Titanium oxides rapidly coat the internal surfaces of the fracture and begin diffusing into the bulk of the sapphire. As the titanium diffuses into the sapphire, it reacts with the iron dissolved therein, creating an intense blue coloration. As the sapphire is cooled, the fracture closes almost completely. Thus, it does not reflect light from internal sapphire-air interfaces. What remains in the stone is a deeply colored flat blue disk (figure 25).

Figure 24. These spectra show what happens if a Rock Creek sapphire is overreduced. Spectrum A is of a stone optimally reduced for its iron concentration. Spectrum B is of the same stone processed to a greater reduction. Subtracting A from B shows the absorption difference, spectrum C, which is almost constant across the visible portion of the spectrum and, thus, only contributes gray to the color of the stone. Compare the color coordinates of these spectra in table 2.



Because the difference in the coefficient of thermal expansion between rutile and sapphire is not large, this fracturing process is quite sensitive to temperature. At 1400°C only large rutile crystals create fractures, but as the temperature is increased, successively smaller crystals create fractures. Fractures around solid inclusions are a common occurrence in natural unheated Rock Creek sap-

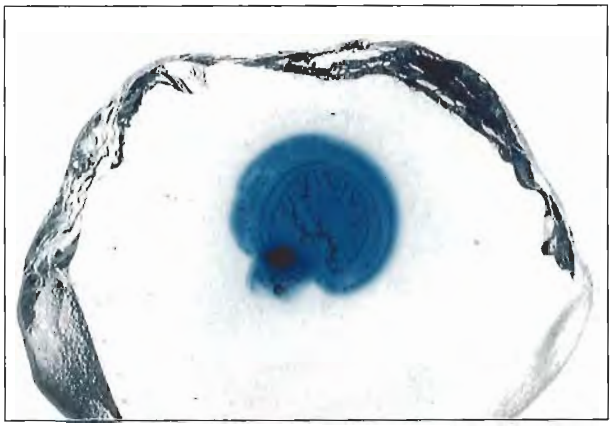


Figure 25. This Rock Creek sapphire shows a compact euhedral rutile crystal that is approximately 300 µm in diameter. When heated, this inclusion expanded more than the sapphire host, resulting in a large plate-like fracture. The titanium oxides then rapidly coated the internal surfaces of the fracture and begun diffusing into the bulk of the sapphire, producing the blue coloration. On cooling, the fracture almost completely closed, eliminating the reflective interfaces usually seen in such fractures surrounding inclusions. Photo © John L. Emmett.

phires, but blue halos around inclusions or blue staining of fracture surfaces are a clear indication of heat treatment.

Two-phase (liquid and gas) inclusions are also observed occasionally in Rock Creek sapphires. During heat treatment, the heated liquid creates enormous pressure, causing a localized "fingerprint" fracture, which can be observed after cool-down to be partially liquid filled.

The incorporation of hydrogen into sapphire is another effect that merits discussion. When sapphire is heated in an atmosphere containing hydrogen, some hydrogen diffuses into the stone and a portion of the H atoms will ionize into an electron and a proton. The proton is a positive point charge that is infinitesimal compared to any other positive ion. As a consequence, it will sink into the electron cloud around an oxygen ion. This creates an OH^- molecular ion in the sapphire crystal that can be detected by infrared spectroscopy at 3310 cm^{-1} (3021 nm; Eigenmann and Günthard, 1971). In the limited set of measurements conducted thus far, we have not seen this absorption feature in any natural unheated sapphire. This subject deserves additional study. If it could be shown that natural sapphire never exhibits this absorption feature, then presence of this feature in blue sapphire would provide additional proof of heat treatment.

While we have not made an exhaustive comparison between natural Rock Creek sapphires of highly saturated coloration, and similar appearing heat-treated stones, we can provide several observations that may be of value to gemologists in the detection of heat treatment.

Blue Sapphires. Observation of the deep blue discs described above, or inclusions with blue halos, is certain evidence of heat treatment. If a blue pattern tied to an original rutile deposition pattern of partial hexagonal structure as shown in figure 21 is observed, it also is almost certain evidence of heat treatment. We have not observed such patterns in any of the several hundred natural wafers we have studied. Finally, we should note that highly saturated blue non-heat-treated Rock Creek stones are quite rare. Thus, the burden of proof should be on the claim that the stone is not heat treated.

Yellow Sapphires. Proof of heat treatment in these stones is far more difficult. The heat-treated point-defect-colored yellow stones without any inclusions are identical in every way we have examined to the natural point-defect-colored yellow stones. Proof of heat treatment comes from effects of heat, such as those that may be observed on inclusions contained within the stone.

We have not studied enough pink and orange stones to make any definitive comments regarding the detection of heat treatment.

CONCLUSION

Heat treatment of Rock Creek sapphire can produce high yields of commercially viable yellow and blue stones. The formation of strong yellow colors in highly oxidizing atmospheres, previously thought to be due to Fe^{3+} absorption, has been shown instead to be the result of a broad absorption band beginning at 600 nm and extending to the shortest visible wavelengths. We suggest that this may be caused by divalent ion-hole pairs or color centers in the crystal. The production of blue proceeds by the well-known mechanism of rutile dissolution in the presence of dissolved iron, followed by reduction of a portion of the iron. However, the relatively high iron content of Rock Creek sapphire constrains the acceptable reduction conditions to a rather narrow range because of hercynite precipitation.

The heat-treatment processes that have been developed for the pale blue, pale green, and near-colorless material yield 65%–70% of marketable yellow and blue sapphires. Excluding the small quantities of orange and "hot pink" sapphire that come from the deposit, the heat-treated material is of substantially higher gem quality in terms of color and clarity than the best of the natural material. The heat-treatment processes have now been tested at batch sizes from 50 grams to 1.5 kg and have proved to be viable, reproducible, commercial processes. Given that the colors studied represent about 75% of the estimated yield of 25 million carats in the assayed portion of the meadow property, the yield of cut stones can be estimated as approximately 3–5 million carats depending on the minimum stone size cut. This estimate excludes any yield from the remaining 25% of other colors in the deposit, significant quantities of which were not available for testing at the time this study was initiated.

Authors' Caution to the Reader. *Reducing gases are, by their very definition, highly explosive when mixed with air or oxygen. Combining this hazard with the high temperatures used during heat treatment poses many substantial risks. We strongly encourage all who would experiment in this field to seek support from people trained in the disciplines of high-temperature chemistry.*

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