THE IDENTIFICATION OF BLUE DIFFUSION-TREATED SAPPHIRES

By Robert E. Kane, Robert C. Kammerling, John I. Koivula, James E. Shigley, and Emmanuel Fritsch

Blue diffusion-treated sapphires are becoming more prevalent than ever before. The diffusion technique, which involves the addition of color-causing chemicals during heat treatment, results in a thin layer of color at the surface of colorless or light-colored sapphire. The color was found to be stable to routine cleaning procedures; however, it may be partially or completely removed if the stone is repolished or recut. Recently, significant quantities of so-called "deep" diffusion-treated sapphires have entered the market. This article documents the properties of these and other blue diffusion-treated sapphires, and presents means of identifying this method using simple gemological tests.

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The heat treatment of pale, colorless, or milky white "geuda" sapphires to produce attractive blue stones has been practiced for a number of decades. These stones have become a staple in today's international gem markets. A different but related color-enhancement technique that emerged in the late 1970s and early 1980s is now also becoming prevalent in the trade: diffusion treatment (see figure 1). This process involves the diffusion at very high temperatures (1700°C and higher) of color-causing transition elements such as iron, titanium, chromium, or nickel (depending on the color desired) into a region that extends just below the surface of the otherwise colorless or very light colored corundum (Carr and Nisevich, 1975). The result is a thin color layer at and just below the surface of the gemstone (see figure 2). This layer may be partially or completely removed if the stone is repolished or recut. It is commonly used on corundum that does not respond to standard heat treatment. Unlike some treatment methods, the diffusion treatment of sapphires does not have any parallel in nature. As Nassau (1981) stated, "the results of diffusion treatment . . . remind one more of Lechleitner synthetic emerald overgrowth on a natural beryl than of heated aquamarine."

Since 1979, numerous brief reports of diffusion-treated corundum have been published (Crowningshield, 1979a and b, 1980; Brauner, 1981; Crowningshield and Nassau, 1981, 1982; Fryer et al., 1981, 1982a and b; Graziani et al., 1981; Leone and Cumo, 1981; Mai, 1981; Nassau, 1981, 1982; Herzberg, 1981; Scarratt, 1981, 1983; Hänni, 1982; Read, 1982; "New CIBJO guidelines given to sapphire description," 1983; Hughes, 1987; Ohguchi, 1983a and b; Kammerling et al., 1990a; Koivula and Kammerling, 1990).

Although relatively little corundum treated in this manner was seen in the mid- to late 1980s, it appears to have become quite prevalent in the international gem markets in recent months. In late 1989, several blue diffusion-treated sapphires (and samples of starting mate-

Figure 1. These blue sapphires (0.67–2.85 ct) have all been diffusion treated, reportedly by a process that produces an unusually deep layer of color at and just under the surface of the stone. Courtesy of Gem Source; photo by Shane F. McClure.

rial) were donated to GIA by Karla and Bob Brom, of The Rainbow Collection, Honolulu, Hawaii (figure 3). They report (pers. comm., 1990) that they have received 500 ct of faceted and cabochon-cut material from a scientist in Bangkok, Thailand, who purports to use a complex treatment process involving eight to 10 separate heating periods of 40 hours each.

More recently, at the 1990 Tucson Show, significant quantities of faceted blue diffusion-treated sapphires were offered for sale by Gem Source, of Las Vegas, Nevada, and Bangkok, Thailand (again, see figure 1). According to a promotional flier provided by the vendor, these blue sapphires had been subjected to "new techniques resulting in much deeper penetration of the metal ions. The penetration is so deep that many stones treated with this method are entirely recut, with a weight loss of over 10%, yet they retain a fine color." According to a report in *Jewellery News Asia* ("New colour diffusion for sapphires," 1990), the vendor claims that about 25,000 ct of this material have been treated and repolished, with 12,500 ct currently in the world market. Trade sources and our own observations at Tucson indicate that a number of vendors are now selling diffusion-treated blue sapphires.

Another point of interest not previously mentioned in the literature is the experimentation in Bangkok, Thailand, with diffusion treatment that involves not only iron and titanium, but also other color-causing impurities such as cobalt. We had an opportunity to examine a number of these stones as well.

To better understand the different types of diffusion-treated stones on the market, the pro-

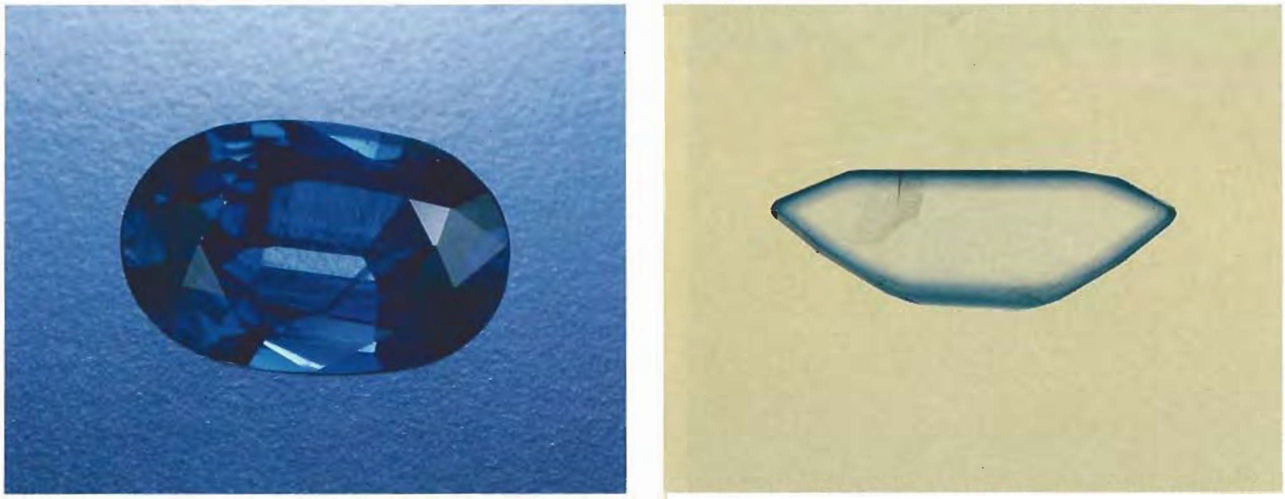


Figure 2. The color of a blue diffusion-treated sapphire is confined to a shallow layer that has been produced by diffusing chemicals into the surface of a fashioned gem. The 1.45-ct stone on the left was supplied by Gem Source, and is marketed as a "deep" diffusion-treated sapphire. A 1.3-mm-thick section was sawed from the center of this stone. The polished section (right) reveals the near-colorless natural sapphire core and the induced blue surface layer, which is approximately 0.4 mm deep. Photos by Shane F. McClure.

cesses used, the best means of identification, and the durability of these stones in various cleaning and repair situations, we performed a variety of tests and experiments on a number of blue diffusion-treated sapphires. The following report reviews the history of this enhancement, discusses the results of our research, and presents simple techniques that can be used to readily identify natural fashioned sapphires that have been treated in this manner.

Although some references will be made to the (apparently experimental) cobalt-doped material, the article will focus an iron-titanium diffusion, which appears to be most common.

HISTORY OF DIFFUSION TREATMENT AND DISCLOSURE PRACTICES

History. The diffusion treatment of colorless or very light colored corundum to produce blue sapphire is the application of U.S. Patent No. 3,897,529—"Altering the Appearance of Corundum Crystals"—issued on July 29, 1975, to Carr and Nisevich of Union Carbide Corp. Union Carbide's Japanese patent on this same process (No. 115998) was issued on November 6, 1975. In these patents, this particular treatment process was described in detail combined with a process intended for inducing or improving asterism in synthetic rubies and sapphires (which was patented in 1949 by Burdick and Glenn, also of Union

Figure 3. In Fall 1989, we received this group of blue sapphires which had been treated in Bangkok. The faceted stones (1.21–2.22 ct) may represent yet another commercial source of diffusion-treated corundum in the 1990s. The rough pieces (2.85–5.46 ct) represent heat-treated material that did not produce satisfactory results—the type commonly used as the "starting" material for diffusion treatment. Stones courtesy of the Rainbow Collection; photo by Shane F. McClure.

Figure 4. In the early 1980s, a gem dealer in Bangkok supplied six different heat-treating operations with light-colored Montana sapphire rough (as seen in the center of this photo). Five lots of the heat-treated sapphires were returned with little or no improvement in color. The sixth operation, however, returned intensely colored blue sapphires to the dealer (as seen here on either side of the original light-colored rough). Subsequent cutting revealed that the blue color was confined to a thin superficial layer: The sapphires had been diffusion treated. The largest piece weighs 0.75 ct. Photo by Shane F. McClure.

Carbide). Carr and Nisevich later described this treatment procedure as a separate process (1976 and 1977). When the Linde division of Union Carbide ceased production of synthetic star corundum, all four of these patents were assigned to Astrid Corp. of Hong Kong, which had acquired Linde's stock of synthetic star rubies and star sapphires (Nassau, 1981). Astrid Corp., a member of the Golay Buchel group, produced diffusion-treated sapphires in Bangkok until the early 1980s (D. Biddle, pers. comm., 1990).

However, it appears that diffusion treatment is being practiced by other firms. In late 1984, a Bangkok gem dealer reported to one of the authors (R. Kane) that he had given very light colored sapphire rough from Montana to six different persons involved in the heat treatment of corundum in Thailand. Five of the heat treaters returned the treated sapphires with very little or no apparent improvement in color. The sixth person, however, presented the Bangkok dealer with the intensely colored blue sapphire rough shown on either side of the untreated material in figure 4. Elated over the apparently successful heat treatment, the Bangkok dealer began organizing the purchase of large quantities of Montana sapphire rough. When he cut a portion of the treated rough, however, he discovered that the blue color was confined to a very thin area near the surface (R. K. Stevenson, pers. comm., 1984). In June of 1990, Bob Crowningshield of the East Coast GIA Gem Trade Laboratory reported seeing another lot of diffusion-treated Montana sapphire rough that was being marketed as heat-treated material.

Disclosure Practices. Although there is no worldwide agreement concerning disclosure practices for the heat treatment of blue sapphire, there is general consensus in the trade that disclosure of diffusion-treated corundum is essential because the added color is confined to a surface layer. Consequently, while the terminology may vary, corundum treated in this manner is nearly always described as synthetically or artificially colored. For example, the GIA Gem Trade Laboratory issues the following conclusion on identification reports:

> DIFFUSION-TREATED NATURAL SAPPHIRE
>
> Note: The color of this stone is confined to a shallow surface layer that has been produced by diffusing chemicals into the surface by heat treatment.

THE DIFFUSION MECHANISM

The color in blue sapphire is due to Fe^{2+}-O-Ti^{4+} charge transfer, influenced by $Fe^{2+} \rightarrow Fe^{3+}$ charge transfer and Fe^{3+} absorptions (Smith and Strens, 1976; Schmetzer, 1987). Diffusion treatment first brings the necessary iron and titanium coloring agents into contact with the stone's surface. The stone is then heated, sometimes to just below its melting point, causing the corundum lattice to expand and allowing the thermally energized transition metal ions to migrate into a layer at the surface, resulting in a near-surface concentration of color.

Generally speaking, the higher the temperature maintained and the longer the time used for the heating step, the greater the depth of color penetration will be. In this regard, the possible difference between so-called "deep" diffusion treatment and earlier diffusion-treated stones may be in a higher temperature being reached and/or maintained. It may also be in the use of more than one heating stage in the treatment procedure. J. Bergman reports (pers. comm., 1990) that the Gem Source stones undergo multiple heatings; that is, after the stones are cooled, they are usually reheated several times. As mentioned above, a similar process was claimed by the Bangkok supplier of the Rainbow Collection stones. Bergman also reports that their process can require treating over the course of two months for some stones.

The Diffusion Treatment Process. Classically, colorless or light-colored fashioned corundum is first embedded in a powder that consists of a major amount of aluminum oxide, a minor amount of titanium oxide, and a lesser amount of iron oxide, which has been placed in an alumina crucible (figure 5). The crucible is then subjected to extended heating in a furnace. Carr and Nisevich (1975) reported that the heating time can vary from two to 200 hours. The elevated temperature will usually range from about 1600°C to about 1850°C, with 1700°C to 1800°C preferred. At temperatures below 1600°C, the process becomes uneconomically slow; at excessively high temperatures, the surface of the sapphire may be damaged (Carr and Nisevich, 1975). In practice, the surface of the corundum usually does become "pockmarked" and show some melting (figures 6 and 7), which indicates that the higher temperatures have been used. The light repolishing required may result in the complete removal of the diffused color from the girdle and/or some facets. Figure 8 illustrates the appearance of sapphires at various stages in diffusion treatment; again, see figure 2 for an illustration of the color penetration. J. Bergman reports a recovery rate of only 60% for the diffusion-treatment process Gem Source uses, because many of the stones are severely damaged by the high temperatures used ("New colour diffusion for sapphires," 1990).

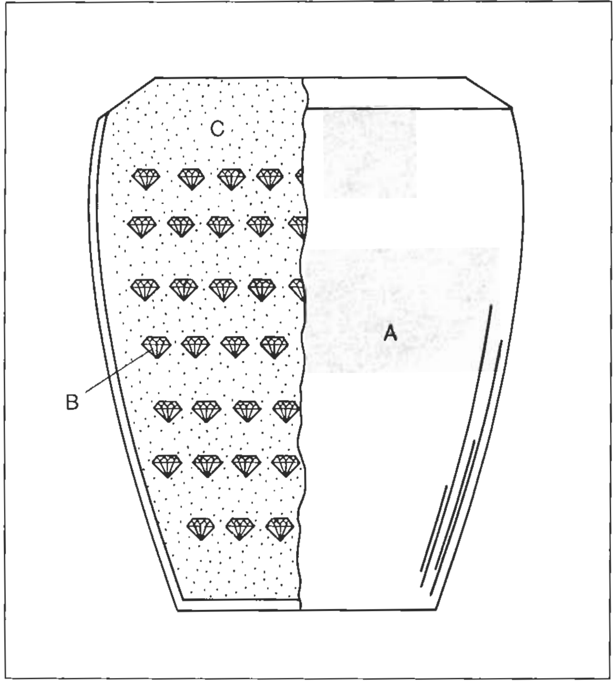


Figure 5. To produce moderate to deep blue coloration by diffusion treatment, the colorless or light-colored corundum (B) is placed in a crucible (A) while its entire surface is in contact with a powder (C) comprising a major amount of aluminum oxide and minor amounts of titanium and iron oxides. The crucible is then exposed to extended heating at very high temperatures (1700°C to near the melting point of corundum, 2050°C). Adapted from U.S. Patent 3,897,529.

The thickness of the treated zone (before repolishing) would logically depend on the length and number of heatings and the temperature attained, as mentioned above. To determine the thickness of the diffusion color layer after repolishing, we sectioned and polished three blue diffusion-treated sapphires representing both early (Astrid Corp.) and more recent (Rainbow Collection and Gem Source) production (figure 9, top).

The polished sections revealed that most of the treated zones consisted of two different levels of color (figure 9, bottom), both of which we measured at the table edge on all stones. The blue diffusion layer of the Astrid Corp. material measured 0.20 mm in total depth; the top portion of this was a darker 0.07-mm primary layer. The blue diffusion layer of the Rainbow Collection stone measured approximately 0.15 mm in total depth, of which 0.03 mm was a darker primary layer. The blue diffusion layer of the Gem Source stone measured a total depth of 0.42 mm; the darker primary surface layer in this stone was 0.12 mm. In

Figure 6. Partially reflected light reveals the rough, sintered surface on this unrepolished 3.37-ct diffusion-treated sapphire. Courtesy of Gem Source; photo by Shane F. McClure.

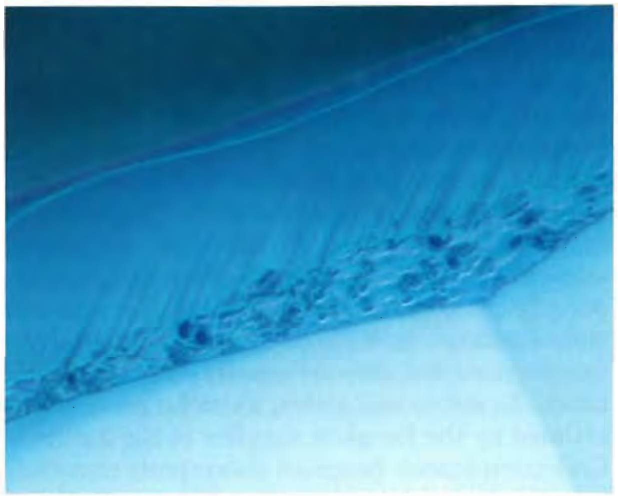


Figure 7. "Light" repolishing of a diffusion-treated stone often produces a "double girdle" and may leave a melted or sintered surface, which is evidence of the very high temperatures used. Photomicrograph by Robert E. Kane; darkfield illumination, magnified 25×.

this instance, the color layer in the Gem Source sample was twice as deep as in one comparison stone and almost three times as deep as in the other.

For additional comparison, we sectioned and measured a Gem Source diffusion-treated sapphire that had not been repolished. This section showed a dark blue layer that measured approximately 0.10 mm at the table edge. In contrast to the finished Gem Source section (figure 9), the "rough" piece did not show an obvious secondary layer. J. Bergman (pers. comm., 1990) reported that this sample had not completed the multiple-heatings procedure because of fracturing early in the process. The fact that the limited heating produced only a single layer suggests that the multiple layers are produced by multiple stages of the diffusion process, as was reported (see above) for both the Gem Source and Rainbow Collection stones.

Figure 8. These three stones (1.10–3.37 ct) represent the various stages involved in producing diffusion-treated blue sapphires: Left, the starting material is a faceted colorless (or light-colored) sapphire; center, the use of chemicals and extreme heat produces a dark blue stone with rough, corroded, and "pock-marked" surfaces; right, repolishing produces a finished blue diffusion-treated sapphire. Courtesy of Gem Source; photo by Shane F. McClure.

It is important to note that the measurements provided here can vary significantly because of several different factors: (1) temperature and length of heating, as well as number of heatings; (2) extent of repolishing; (3) preparation of the sample for measuring (if the large "face" on the polished section is not perpendicular to the table, the true thickness of the treated zone will be exaggerated); and (4) variation in measurements from one side of a particular section to the other.

Although any of several colors can be induced by this process (Carr and Nisevich, 1975; see table 1), blue diffusion-treated sapphires are the most prevalent on the market at the present time. It is interesting to note, however, that the first diffusion-treated sapphire seen in the GIA Gem Trade

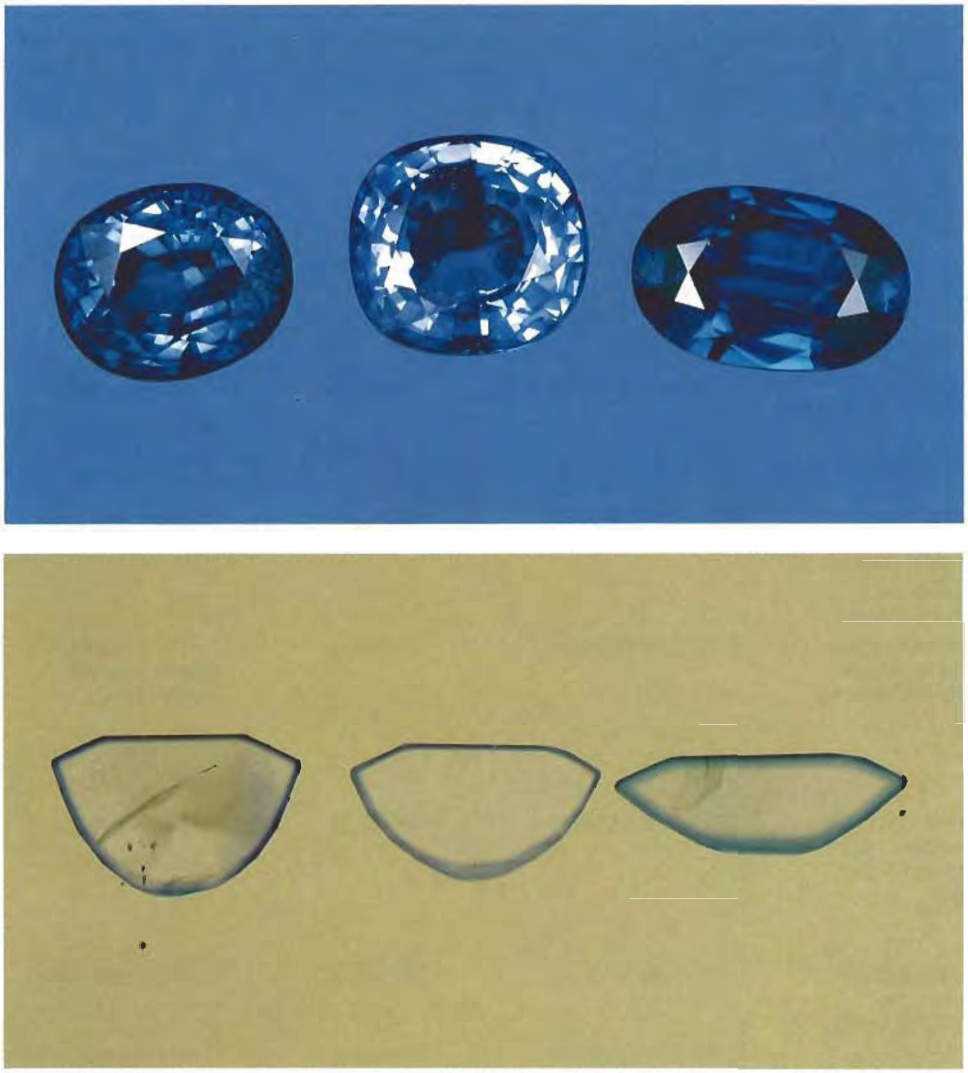


Figure 9. To determine the thickness of the diffusion color layer after repolishing, three representative samples were selected (top): left, 2.24 ct, from the Astrid Corp.; center, 2.22 ct, from the Rainbow Collection; and, right, 1.45 ct, from Gem Source. All show a dark outlining of blue around the girdle that is common in diffusion-treated stones. The three samples were sawed down the center and polished, producing sections about 1.3 mm thick. As seen here (bottom), immersed in methylene iodide over diffused transmitted light, the color layer ranged from 0.15 to 0.42 mm thick. Note the two layers of color in the stones. In this limited sample, the color layers are thicker in the "deep" diffusion-treated stone on the far right. Photos by Shane F. McClure.

Laboratory was red-orange (Crowningshield, 1979).

IDENTIFICATION OF BLUE DIFFUSION-TREATED SAPPHIRES

Materials and Methods. To establish identifying features of blue diffusion-treated sapphires, we examined 40 stones, ranging from 0.63 to 5.46 ct: nine faceted samples obtained from Astrid Corp. in 1981; 11 (five faceted and three cabochon-cut diffusion-treated stones, plus three rough heat-treated stones that were allegedly the starting material for the diffusion-treated stones) obtained from the Rainbow Collection in late 1989; 14 (one faceted untreated colorless sapphire plus two faceted [not repolished] and 11 faceted [repolished] diffusion-treated stones) obtained from Gem Source in February 1990; and six "rough" preforms that had been diffusion treated in Thailand using various oxides including iron, titanium, and cobalt. We also referred to numerous stones examined in the GIA Gem Trade Laboratory over the past 10 years to draw our conclusions.

The study material was subjected to standard gemological testing procedures (refractive index, specific gravity, pleochroism, absorption spectra as viewed through both prism and diffraction-grating spectroscopes, reaction to ultraviolet radiation, microscopy using various types of illumination, and immersion). Specific samples were also subjected to high-resolution spectrometry analysis of the ultraviolet-visible and near-infrared portions of the spectrum; microprobe analysis; and energy-dispersive X-ray fluorescence spectrometry (EDXRF) analysis. The results for the Astrid Corp., Rainbow Collection, and Gem Source stones—all of which were diffusion treated with iron and titanium—are presented below. The results for the

TABLE 1. Examples of diffusion-treated corundum experiments cited in United States Patent 3,897,529, July 29, 1975, titled "Altering the Appearance of Corundum Crystals," by R. R. Carr and S. D. Nisevich of the Union Carbide Corporation.

Starting color of corundum	Powdered addition agents (in wt.%)	Temperature and length of heating	Heating environment	Resulting appearance and color
1. Reddish purple sapphire and ruby with low color saturation or nonuniform color	6% chromium oxide, 24% titanium oxide, and 70% alumina	1750°C for 96 hours	Oxidizing	Uniform "ruby red"
2. Yellow sapphire with nonuniform color or too high or too low a color saturation	3%–6% chromium oxide, 24% titanium oxide, and the remainder alumina	1750°C for 48 hours	Oxidizing	Uniform "salmon pink"
3. Yellow sapphire with nonuniform color or too low a color saturation	2.5% nickel oxide, 3.5% chromium oxide, 15% titanium oxide, and the remainder alumina	1750°C for 96 hours	Oxidizing	Uniform light gray-green
4. Pink sapphire with nonuniform color, black sapphire with nonuniform color, and white sapphire with nonuniform color	22% titanium oxide and the remainder alumina (no coloring agent)	1750°C for 96 hours	Oxidizing	Uniform color (pink, black, or white, respectively)
5. Milky white sapphire with nonuniform color or undesirable color such as grayish tinge	6% chromium oxide, 22% titanium oxide, and the remainder alumina	1750°C for 96 hours	Oxidizing	Uniform pink
6. Pale blue sapphire with nonuniform color	10%–15% titanium oxide and the remainder alumina	1750°C for 96 hours	Reducing	Uniform pale blue
7. Deep blue sapphire with nonuniform color	0.1%–0.5% ferric oxide, 12%–18% titanium oxide, and the remainder alumina	1750°C for 30 hours	Reducing	Uniform deep blue

stones into which cobalt was incorporated, which are not commonly seen commercially, are presented in the accompanying box.

Most of the gemological properties of the iron and titanium–doped blue diffusion-treated sapphires studied overlap those of unheated and heat-treated blue natural sapphires. Visual examination of immersed stones reveals easily detectable identifying characteristics of surface-diffused coloration.

Visual Appearance and Optical and Physical Properties. The refractive indices, birefringence, and specific gravity of diffusion-treated stones do not differ significantly from those of natural-color and heat-treated stones. Furthermore, the pleochroism is consistent with that of natural-color and heat-treated blue sapphires of comparable depth of color even though the color is concentrated in a shallow surface layer. This indicates that the diffusion layer is crystalline, not amorphous. In addition, the fashioned diffusion-treated sapphires studied varied from blue to violetish blue in moderate to very dark tone, which overlaps the colors seen in both natural and heat-treated sapphires.

However, when we examined these diffusion-treated sapphires with the unaided eye in sunlight or overhead artificial illumination, we observed in many of them a "watery" appearance, that is, a decrease in transparency that was not caused by visible inclusions. This is probably a result of the concentrated diffusion of color-causing impurities

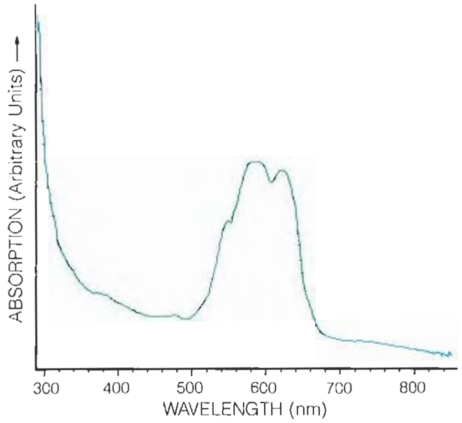
EXPERIMENTAL(?) COBALT-DOPED BLUE DIFFUSION-TREATED SAPPHIRES FROM BANGKOK

In the course of this study, we also examined six blue diffusion-treated sapphire "preforms" that were reported to contain varying amounts of cobalt. The samples were obtained by one of the authors (R. Kane) in Bangkok, where they reportedly were treated, in 1984.

The U.V.–visible absorption spectrum of a cobalt-doped blue diffusion-treated sapphire is illustrated in the accompanying figure for random orientation. The color is mainly caused by three intense merging absorption bands with apparent maxima at about 550, 590, and 620 nm. Minor absorptions are present at about 375, 388, 410, 450, and 479 nm.

These bands correspond to those attributed to cobalt in synthetic blue spinels by Anderson and Payne (1937) and Webster (1983), and in natural blue spinel by Shigley and Stockton (1984). Therefore, we interpret this spectrum as being due to Co^{2+}. Because these absorption bands are not naturally occurring in sapphire, when observed in corundum they can be considered diagnostic of cobalt diffusion treatment.

It is interesting to note that the diffusion process introduces cobalt in the corundum lattice as Co^{2+}, although this element is incorporated as Co^{3+} in Co-doped synthetic sapphires. Co^{2+} has never been reported in the spectrum of natural sapphire.



In this U.V.–visible absorption spectrum of a cobalt-doped blue diffusion-treated sapphire, the three merging bands between 500 and 700 nm are due to Co^{2+}.

The cobalt-doped diffusion-treated sapphires were also examined through a Chelsea color filter while illuminated by intense transmitted light. Through the filter the stones appeared a moderate patchy to intense uniform red, the intensity and distribution of the filter color correlating with the depth and distribution of blue color of the stones. The reaction is consistent with that of cobalt-doped synthetic blue spinel of similar color.

into the surface of the sapphire. Also, a dark outline of blue could be seen around the girdle in a number of stones (again, see figure 9, top).

Absorption Spectra. The absorption spectra (400 nm to 700 nm) of all the treated sapphires were examined through both a Beck prism spectroscope mounted on a GIA GEM Instruments spectroscope unit and a GIA GEM DISCAN diffraction-grating spectroscope. Five of the Astrid stones and one of the Gem Source stones exhibited a weak absorption band at 455 nm, while four of the Gem Source stones, one of which was the colorless "starting material" stone, exhibited a fluorescent line at 693 nm; none of the other stones examined showed any lines or bands. All of these features are consistent with those seen in natural-color or heated sapphires from various localities. Thus, spectra observed through a hand-held type of spectroscope do not provide a means of identifying blue diffusion-treated sapphires.

Ultraviolet Fluorescence. The reactions of the sample stones to long- and short-wave U.V. radiation were found to overlap those of natural-color and/or heat-treated blue sapphires from various localities. In this regard, it is interesting to note that many heat-treated blue sapphires exhibit a chalky whitish blue to green fluorescence when exposed to short-wave U.V. radiation, whereas natural-color blue sapphires do not exhibit this characteristic reaction (Crowningshield and Nassau, 1981). Despite the extreme heat used in the process, some of the blue diffusion-treated sapphires did not fluoresce to short-wave U.V. radiation. This was the case for all but one of the Astrid Corp. stones and for one of the Rainbow Collection samples. It is possible that the dominance of iron as a coloring agent in these stones (see discussion of chemistry below) quenches any fluorescence that may otherwise have been induced by heat.

One of the Astrid stones, however, showed a small, chalky patch of moderate yellowish green

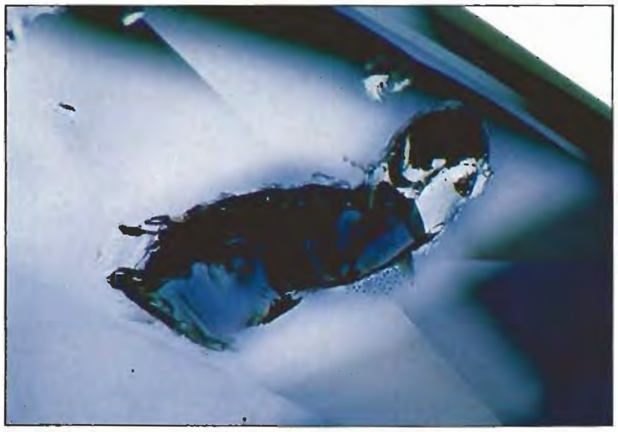


Figure 10. Dark concentrations, or "bleeding," of color are often seen in and around surface-reaching breaks and cavities in blue diffusion-treated sapphires. Photomicrograph by Robert E. Kane; diffused illumination, magnified 30×.

fluorescence when exposed to short-wave U.V. radiation; eight of the Rainbow Collection stones and 12 of the stones from Gem Source fluoresced a moderate chalky yellowish green, and one of the Rainbow Collection stones fluoresced a strong bluish white, also to short-wave U.V.

In addition, one of the Rainbow Collection stones fluoresced a strong orange to long-wave U.V. and a weak orange to short-wave U.V.; one of the Gem Source diffusion-treated stones fluoresced a weak pinkish orange to long-wave U.V. and a chalky yellowish green to short-wave U.V. A strong pinkish orange fluorescence to long-wave U.V. and very weak pinkish orange to short-wave U.V. has been noted in the past for some natural, untreated Sri Lankan sapphires, both colorless and blue. The combination of a pinkish orange reaction to long-wave, and a chalky yellowish green reaction to short-wave, U.V. would be consistent with some heat-treated Sri Lankan sapphires, although it would not separate those that had been diffusion treated.

In general, then, U.V. fluorescence reaction does not provide diagnostic information for the identification of diffusion treatment.

Magnification. While magnification alone is usually not sufficient to identify that a stone has been diffusion treated, it will provide clues to the fact that the stone has been heated in some fashion.

The evidence of treatment at high temperatures that is seen in sapphires with magnification includes: stress fractures surrounding inclusions; melted crystals; partially absorbed and dot-like rutile "silk"; blotchy color banding or diffused zoning; and pockmarked surfaces (see, e.g., Kammerling et al., 1990b). These features are frequently seen in diffusion-treated sapphires, but they provide proof only of high-temperature treatment. Of particular use in the identification of diffusion treatment is the "bleeding" of color in and around surface-reaching pits and fractures (figure 10), which is a localized reaction to the diffusion process.

Immersion. The most effective means of detecting a diffusion-treated stone is its appearance when immersed in methylene iodide and examined in diffused transmitted light; this simple procedure is described and illustrated in figure 11. When examined in this fashion, all of the diffusion-treated stones studied (figure 12) showed one or both of the following:

1. Greater relief, as indicated by a concentration of color along facet junctions and around the girdle (figure 13).
2. Localization and blotchiness of color caused by a combination of uneven diffusion and light repolishing (figure 14); the girdle and some facets may have the diffused color completely removed (figure 15).

Blue sapphires not treated in this manner will show low relief in methylene iodide; the facet junctions generally are not easily visible (see left view in figure 16). Note, however, that abraded facet junctions may have high relief when immersed. To illustrate this effect, we selected two virtually identical flame-fusion synthetic blue sapphires and held one as a control sample while the other was polished for approximately 48 hours in a vibratory tumbler with Linde A as an abrasive. Figure 17 shows the two stones immersed in methylene iodide; although the effect was exaggerated for the purpose of this research, the greater relief of a stone with abraded facet functions (e.g., with an appearance similar to that of the stone on the left in figure 17) could cause some confusion for the gemologist.

The two stones in figure 18 are also potentially misleading. The 5.40-ct Montana sapphire on the left has an additional tiny flat facet at the junction of most of the pavilion facets (where ordinarily

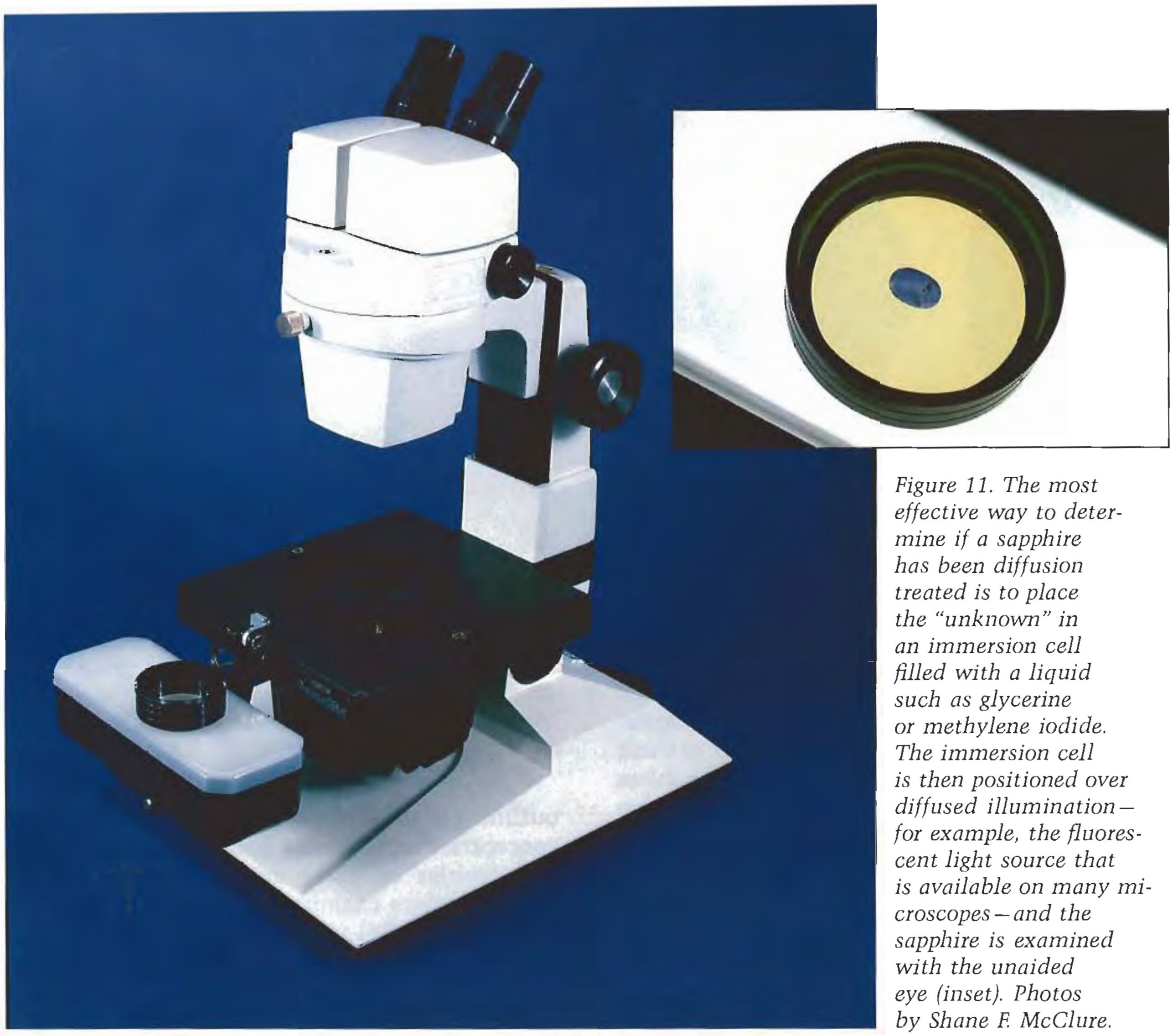


Figure 11. The most effective way to determine if a sapphire has been diffusion treated is to place the "unknown" in an immersion cell filled with a liquid such as glycerine or methylene iodide. The immersion cell is then positioned over diffused illumination—for example, the fluorescent light source that is available on many microscopes—and the sapphire is examined with the unaided eye (inset). Photos by Shane F. McClure.

Figure 12. Immersed in methylene iodide over transmitted diffused illumination, this selection of diffusion-treated sapphires, from various "manufacturers," reveals the characteristic identifying features. These include: greater relief due to color concentrations at facet junctions, blotchiness of the diffused color layer, and areas without color. Photo by Shane F. McClure.

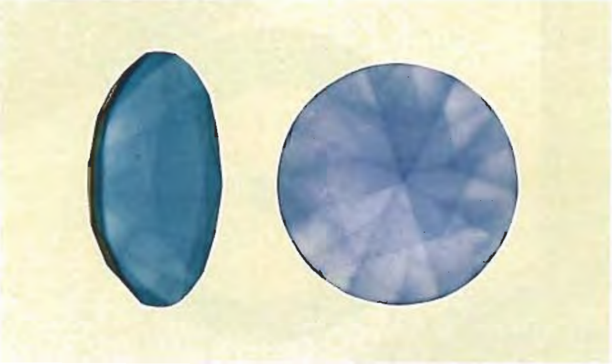


Figure 13. Proof of diffusion treatment in a faceted blue sapphire is provided by concentrations of color along facet junctions and/ or the girdle. Photo by Shane F. McClure.

Figure 14. In addition to high relief and color concentrations at facet junctions, immersion may also reveal a blotchiness of the diffused color layer caused by a combination of uneven diffusion and light repolishing. Photo by Shane F. McClure.

there would be a sharp edge). This created a subtle blue outlining of these facet junctions when the stone was immersed and examined over diffused illumination. The 1.77-ct Kashmir sapphire on the right has abraded facet junctions. Neither of these stones was diffusion treated. Many blue sapphires also show strong growth and color zoning (figure 19), but their appearance is still significantly different from that of diffusion-treated stones.

Detecting diffusion treatment in cabochons may be considerably more difficult, as they lack the many sharp junctions on which color concentrates in their faceted counterparts. On the three cabochons the authors examined for this report, the one diagnostic feature noted was a dark color outlining of the girdle edge (figure 20). Deep color concentrations have also been observed in cracks and cavities on these and other cabochon-cut stones we have examined.

Because methylene iodide is somewhat toxic to breathe (particularly for extended periods of time)

Figure 15. Heavy repolishing of a badly melted or sintered diffusion-treated sapphire can result in the removal of the diffused color from the girdle and some facets. Note that immersion reveals this effect on all sides of the girdle. Photomicrograph by Robert E. Kane; transmitted diffused illumination, magnified 15×.

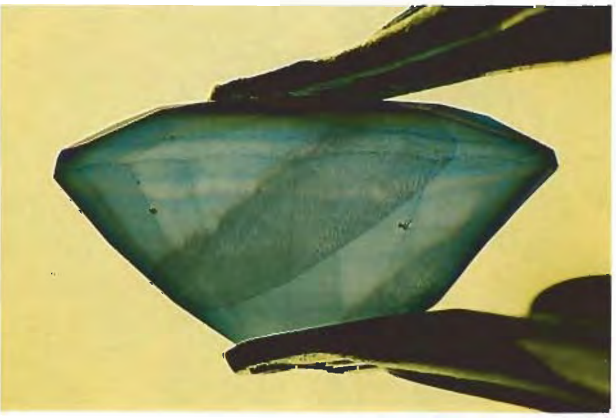
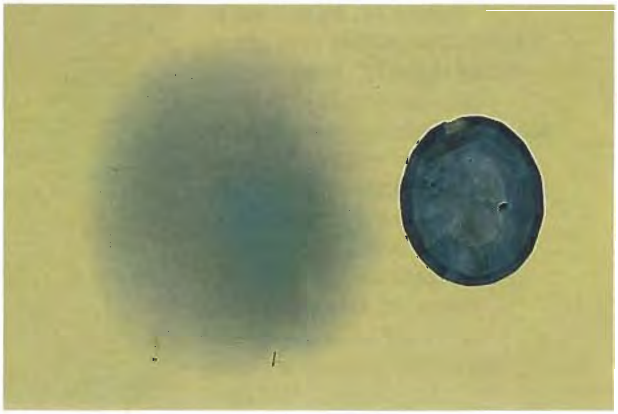


Figure 16. A natural blue sapphire (left) is shown here next to a diffusion-treated sapphire (right), both immersed in methylene iodide over diffused transmitted illumination. With immersion, the natural sapphire on the left has low relief and does not show any facet junctions. In contrast, the diffusion-treated stone has much greater relief, as exemplified by a blue outlining of facet junctions. Photo by Shane F. McClure.



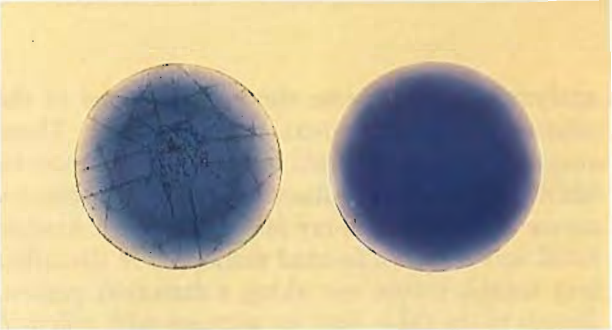


Figure 17. To illustrate how abraded facet junctions on a non-diffusion-treated sapphire could cause confusion—i.e., high relief—we selected two virtually identical flame-fusion synthetic blue sapphires. One was held as a control sample (right) and the other was tumble polished to intentionally abrade the facet junctions. The tumble-polished stone (left) now shows high relief of facet junctions with immersion. Photo by Shane F. McClure.

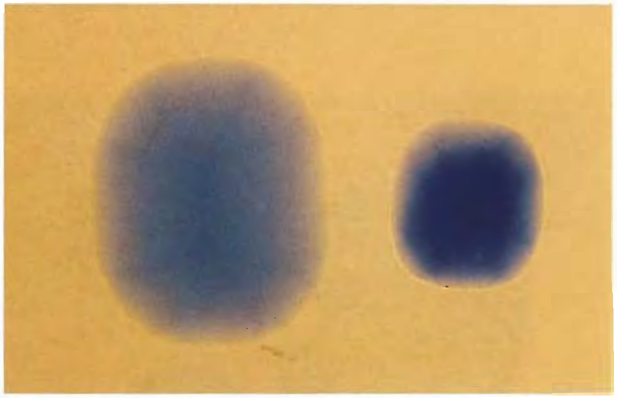


Figure 18. On occasion, natural untreated sapphires may exhibit confusing features when examined with immersion over diffused illumination. The 5.40-ct Yogo Gulch, Montana, sapphire (left; courtesy of Rogers Jewelers, Great Falls, Montana) possessed a tiny flat facet at the junction of most of the pavilion facets. This created a subtle blue outlining of these facet junctions. The 1.77-ct untreated Kashmir sapphire (right) shows a higher relief caused by abraded facet junctions. Photo by Shane F. McClure.

or if absorbed through the skin, we experimented with different immersion media. We selected three stones, one each from Astrid Corp., the Rainbow Collection, and Gem Source (again, see figure 9). We placed the three stones table-down in an immersion cell over diffused (through white translucent plastic) transmitted illumination in: (A) air (R.I. 1.00), (B) water (R.I. 1.33), (C) glycerine (R.I. 1.47), and (D) pure methylene iodide (R.I. 1.75; Weast et al., 1988). Figure 21 shows the appearance produced by each medium. In some cases, diffused illumination in air is sufficient to identify a diffusion-treated sapphire; in others, immersion in methylene iodide is necessary (the closeness in R.I. helps accentuate treatment features). We found that glycerine, which is colorless and quite innocuous, provided an excellent immersion fluid for routine testing. Although it is quite viscous, it cleans off easily with a tissue and water. We also experimented with several other immersion fluids and found that satisfactory results were achieved

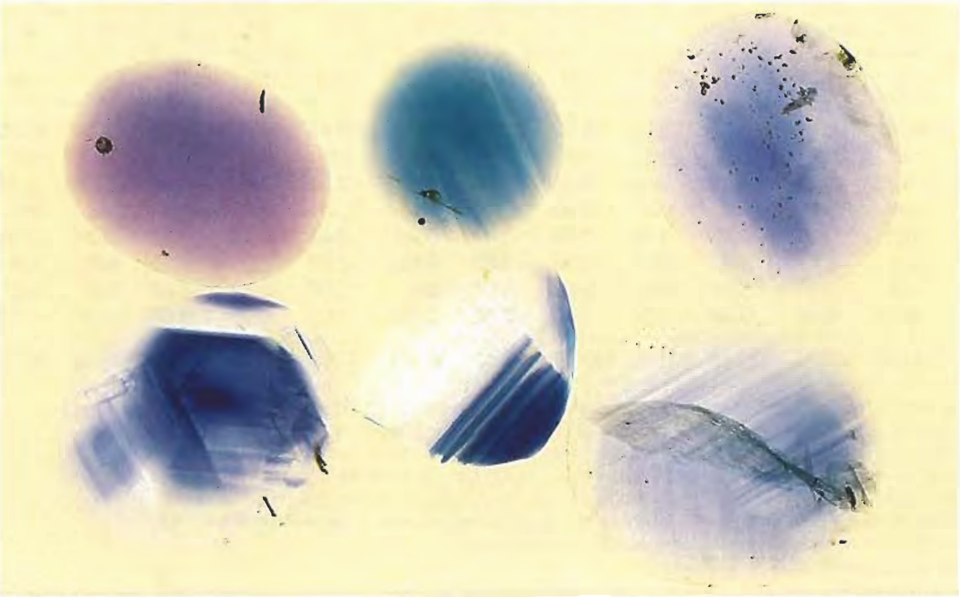


Figure 19. With immersion, non-diffusion-treated blue sapphires can show a variety of appearances, such as color zoning and inclusions. These stones are still easily identifiable by their lack of features typical of diffusion-treated sapphires. Photo by Shane F. McClure.

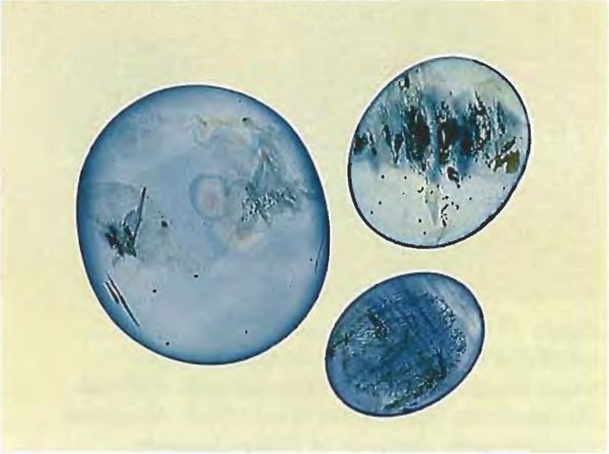


Figure 20. Cabochon-cut blue diffusion-treated sapphires show a characteristic dark blue outlining of the girdle. They may also show "bleeding" (concentrations) of color in surface-reaching breaks. If mounted in a bezel setting, particularly one that is closed backed, cabochon-cut sapphires treated in this manner could, indeed, be difficult to identify. Photo by Shane F. McClure.

with many and, in particular, with oils such as sesame oil.

Chemical and Spectral Data. Five representative blue diffusion-treated sapphires were chemically analyzed to investigate the compositions of the interior and surface areas of each sample. These analyses were performed by electron microprobe (JEOL 733) and X-ray fluorescence (XRF) spectrometry (a TRACOR X-ray Spectrace 5000). Sample R302 was left as a faceted stone, while the other four samples were cut along a direction perpendicular to the table into flat sections with polished parallel sides. This permitted microprobe analysis of both the near-surface region affected by the diffusion treatment process, as well as the unaffected interior portion of each sample.

The electron microprobe was used to obtain quantitative analyses of each sample (table 2). The faceted sapphire, R302, was analyzed at three separate locations on the table. The other four samples, in the form of polished sections, were analyzed at several locations—one near the surface of the table, and three or four further locations at progressively greater depths into the stone. The elements Ca, Cr, Co, Ni, Ga, and Cu were found to be below or near the detection limit of the instrument (approximately 0.01 wt.% oxide), and to display no particular distribution patterns. For Fe and Ti, however, a distinct pattern was noted with both elements increasing in concentration (between two- and 10-fold) from the interior to the surface (where diffusion occurred), as shown in figure 22. The plot of findings in figure 22 also

TABLE 2. Chemical analyses of five blue diffusion-treated sapphires.[a]

		R302 (Gem Source)				R296 (Gem Source)					R293 (Gem Source)				
	Analysis no.	1	2	3	Average	1	2	3	4	5	1	2	3	4	5
Wt.% oxide	Depth[b]	0	0	0	0	>200	170	120	70	~20	>200	150	110	70	~20
Al_2O_3		99.37	98.69	98.96	99.01	100.07	99.73	99.62	99.37	98.64	99.44	98.99	99.23	98.59	98.50
CaO		bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.01	bdl
TiO_2		0.22	0.24	0.23	0.23	0.03	0.14	0.15	0.20	0.19	0.03	0.08	0.12	0.16	0.23
Cr_2O_3		0.01	bdl	bdl	bdl	bdl	bdl	0.03	0.01	bdl	0.01	bdl	bdl	bdl	bdl
FeO		0.87	0.82	0.81	0.83	0.10	0.19	0.25	0.42	0.49	0.09	0.06	0.18	0.41	0.99
CoO		0.01	0.02	bdl	0.01	bdl	bdl	0.02	0.03	0.03	0.02	bdl	bdl	bdl	bdl
NiO		0.05	bdl	bdl	0.01	0.01	bdl	bdl	0.07	bdl	0.03	0.02	0.02	bdl	bdl
CuO		0.07	bdl	0.04	0.03	0.04	0.04	0.02	0.02	0.02	0.02	0.02	0.05	0.02	0.01
Total		100.60	99.77	100.07	100.12	100.25	100.10	100.09	100.12	99.37	99.64	99.17	99.60	99.19	99.73

[a] *Electron microprobe analyses were performed on a JEOL 733 microprobe operating at a beam accelerating potential of 15 kV, a current of 35 nA, and spot size of between 10 and 25 μ. Entries indicated by "bdl" were below the detection limits of the instrument (less than 0.01 wt.% oxide). The data were corrected using the program CITZAF (Armstrong, 1988). Analyst: Paul Carpenter, California Institute of Technology. Specimen R302 was analyzed at three distinct locations on the table of the faceted stone; these three analyses are shown along with an average analysis. The other four samples consisted of polished sections cut perpendicular to the table of the faceted stone. Each was analyzed at various locations below the surface of the table in order to document changes in trace-element chemistry with increasing distance into the sample. At each of these locations, one analysis was performed.*

[b] *Depth = Approximate depth below the surface of the table (in microns).*

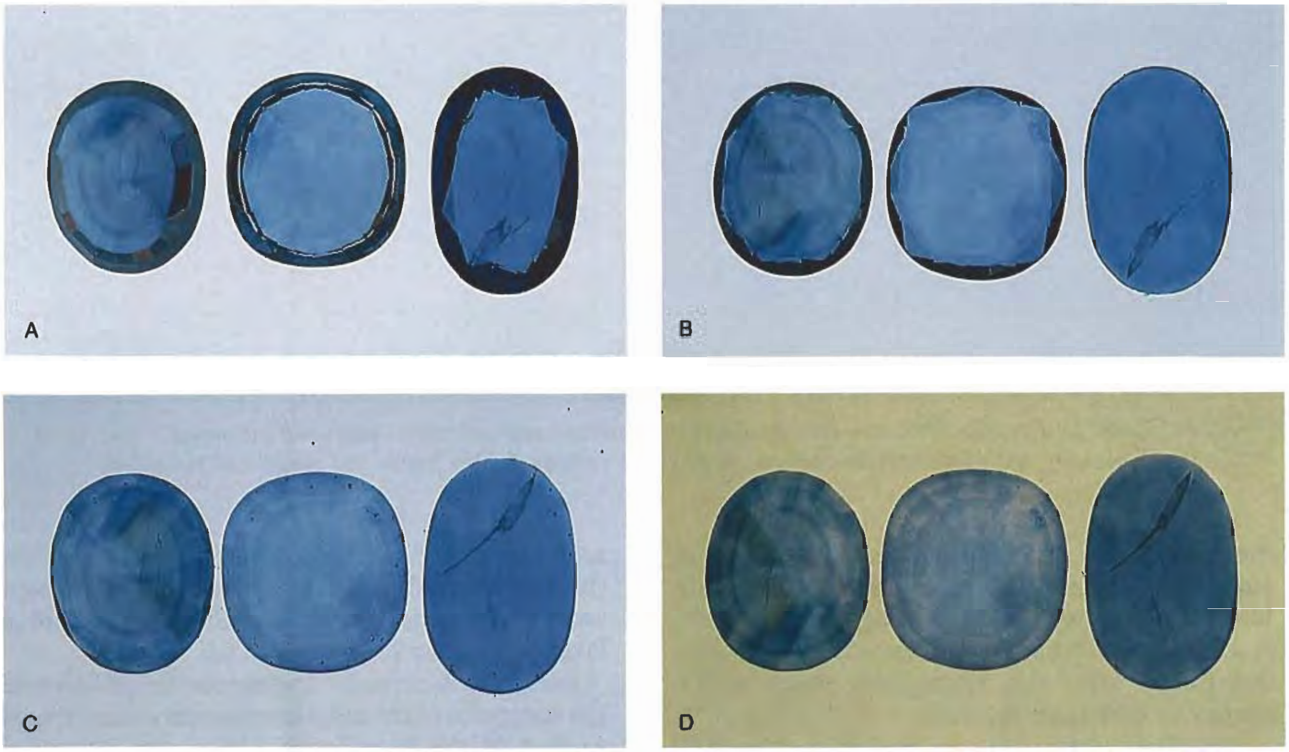


Figure 21. These photos illustrate the differences observed when blue diffusion-treated sapphires are immersed in different media and viewed with the unaided eye. The stones are, from left to right: 2.24 ct from the Astrid Corp., 2.22 ct from the Rainbow Collection, and 1.45 ct from Gem Source. The stones are placed table down in an immersion cell over diffused transmitted illumination in (A) air (R.I. 1.00); (B) water (R.I. 1.33); (C) glycerine (R.I. 1.47); and (D) pure methylene iodide (R.I. 1.75). In some stones, the identifying features may be visible in air or while immersed in water; in others, methylene iodide is necessary. Glycerine was found to be excellent for routine testing. Note that even with different orientations, key features are evident. Photos by Shane F. McClure.

R294 (Rainbow Collection)				R295 (Astrid Corp.)		
1	2	3	4	1	2	3
150	110	70	~20	400	200	~20
99.46	99.87	99.05	98.41	100.54	100.52	99.76
0.02	bdl	0.01	0.02	bdl	0.01	bdl
0.05	0.12	0.15	0.22	0.03	0.04	0.17
0.01	bdl	0.01	bdl	bdl	bdl	bdl
0.02	0.02	0.01	0.08	0.05	0.03	0.14
bdl	bdl	0.06	bdl	bdl	0.01	0.02
0.04	0.04	0.01	0.02	0.04	0.02	bdl
bdl	0.02	0.03	0.03	0.05	bdl	0.05
99.60	100.07	99.33	98.78	100.71	100.63	100.14

suggests that diffusion of iron and titanium into these sapphires resulted in these elements being distributed (at progressively lower concentrations) to depths as great as approximately 200 microns below the surface. This gives some idea of how deep into the sapphires these coloring agents were able to diffuse during treatment. It is interesting to note, too, that among these five stones, which were randomly selected from the full suite of stones available for study, there did appear to be a greater depth of diffusion in the three from Gem Source. Because of the small size of this sample, however, we cannot draw firm conclusions in this regard. Chromium was occasionally detected in each sample at levels that would have no significant influence on color, but would allow resolution of a fluorescent line at 693 nm through the hand-held spectroscope.

Qualitative XRF analyses (more sensitive to low concentrations than the microprobe) of both the inner (near-colorless) and outer (diffusion-treated) surfaces of the sawn, polished sections confirmed

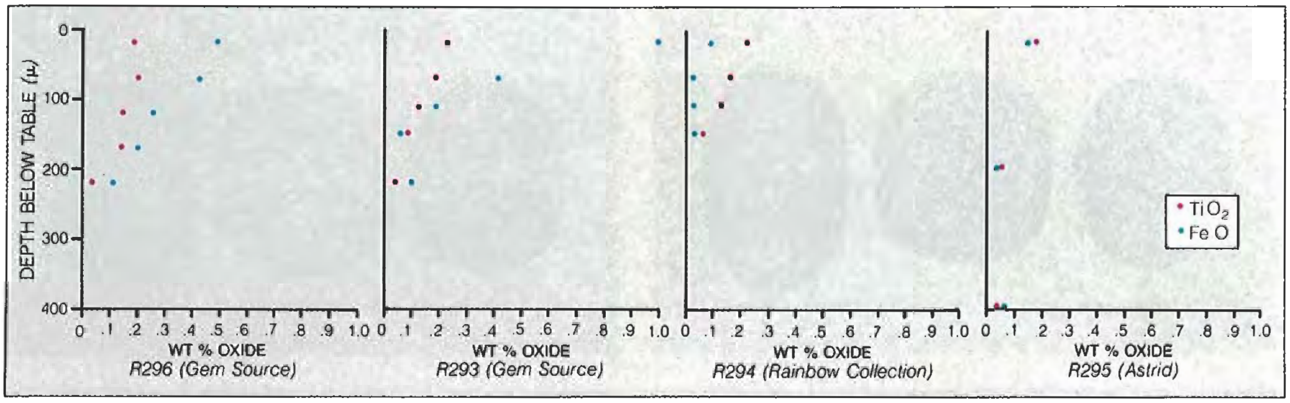
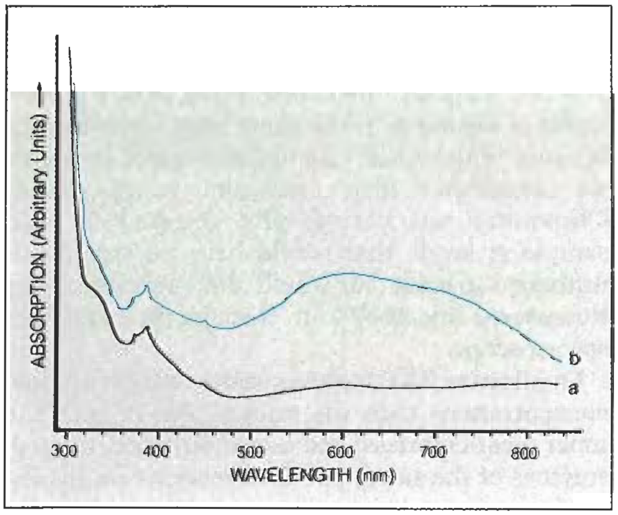


Figure 22. These four graphs illustrate the changes in iron (blue) and titanium (red) content noted in the study samples with microprobe analysis of areas at various depths below the surface of the table.

the presence in each sample of Al, Ca, and Ga, along with the transition elements Fe, Ti, and Cr. In addition, Cu was noted in samples R295, R294, and R293, and Ni was noted in R293. The diffusion-treated layer was consistently richer in titanium and iron than the core.

The ultraviolet/visible absorption spectra of all five samples were measured at room temperature using a Pye Unicam 8800 spectrophotometer, at a resolution of 0.5 nm. The spectra were run through the center of the polished slabs, in order to document the absorption in the untreated part of the sapphire (see figure 23, spectrum a), and then through one of the other two pieces left by sectioning, to document absorption in the superficial blue layer (see figure 23, spectrum b).

Figure 23. These U.V.–visible absorption spectra were taken in a central colorless part (spectrum a), and in the outer blue region (spectrum b), of a diffusion-treated blue sapphire in the same random optic orientation. The features at 335, 375, 390, and 450 are attributed to Fe^{3+}, and the broad bands at 560 and 700 nm are attributed to Fe^{2+}-O-Ti^{4+} charge transfer.



Spectrum b actually represents the addition of the spectrum of the colorless portion of the crystal to that of the blue layer. The major difference between spectra a and b is two broad bands with maxima around 560 and 700 nm, which have been interpreted to be the result of Fe^{2+}-0-Ti^{4+} charge transfer (Ferguson and Fielding, 1971). The sharper bands at about 375, 390, and 450 nm are due to Fe^{3+} (Lehmann and Harder, 1970), and the broader band at about 335 nm could be due to either isolated Fe^{3+} ions (Lehmann and Harder, 1970) or exchange coupled pairs of the same ions (Ferguson and Fielding, 1971). The spectra of the diffusion-treated sapphires we studied are identical to those of natural blue sapphires from Mogok, Burma (Schmetzer, 1987) or Sri Lanka (Schmetzer and Kiefert, 1990). This confirms the statement made earlier that absorption spectra are not diagnostic indicators of this kind of diffusion treatment.

DURABILITY AND STABILITY OF THE TREATMENT

One of the first questions most jewelers and gemologists ask about a gemstone enhancement is how well it holds up to routine wear, jewelry cleaning, and repair procedures. Therefore, we conducted a number of tests on three faceted diffusion-treated sapphires in order to determine the durability and stability of this treatment under a wide range of conditions to which sapphires might routinely be subjected. The stones used were (1) a 1.23-ct mixed-cut pear shape from Gem Source, (2) a 1.21-ct oval mixed cut from the Rainbow Collection, and (3) a 0.75-ct oval mixed cut from Astrid Corp. To test this material under

TABLE 3. Durability and stability of the treatment in diffusion-treated sapphires.[a]

Test	Procedure	Result
Ultrasonic cleaning	Placed in ultrasonic cleaner containing a solution (10%) of commercial jewelry cleaner (BRC) and water for 47 minutes on the high setting at a maximum temperature of 68°C:	
	[b]Placed in stainless steel wire basket and suspended in solution	No effect on treatment
	[c]Placed in plastic cup half-filled with concentrated jewelry cleaner	No effect on treatment
	[d,e]Hung from wire in cleaning solution	No effect on treatment
Steam cleaning	[b,c,d,e]Used two steam cleaners with pressure maintained between 35 and 80 psi, stones placed one-half to one inch from nozzle for approximately 15 minutes	No effect on treatment
Boiling in detergent solution	[b,c,d,e]Stones boiled in solution of dishwashing liquid and water for 25 minutes	No effect on treatment
Heat and chemicals from jewelry repair	[b]Set in 14K gold cast head; one prong tip removed by sawing; stone and mounting fire-coated with boric acid/methyl alcohol solution and prong retipped with 14K yellow gold ball and 14K yellow gold hard solder (flow point approximately 750°C) and green flux	Moderate surface etching in vicinity of new prong[h]
	[b]Remaining three prong tips sawed off and retipped, care taken to minimize contact of flux with stone's surface	Minor surface etching in vicinity of new prongs[h]
	[d,e]One prong tip removed by sawing; stone and mounting fire-coated with boric acid/methyl alcohol solution and prong retipped with 14K yellow gold ball and 14K yellow gold hard solder (flow point approximately 750°C) and green flux	Moderate surface etching in vicinity of new prong[h]
	[d,e]Prong tips built up with 18K hard white gold solder (flow point approximately 768°C), care taken to minimize contact of solder with stone's surface	Moderate to severe etching, especially on stone's table[h]
	[c]Set in 14K gold cast head; four prong tips removed by sawing; stone and mounting fire-coated with boric acid/methyl alcohol solution and prongs retipped with 14K yellow-gold ball and 14K yellow-gold hard solder (flow point approximately 750°C) and green flux, care taken to minimize contact of flux with stone's surface	Minor surface etching in vicinity of new prongs[h]
Rhodium electroplating	[b,c,d,f]Stones and mountings cleaned, then flash rhodium electroplated for five minutes at 6 volts, then 10–15 seconds at average of 3 volts; two-step plating procedure repeated for all three stones, followed by second cleaning	No additional changes noted in stones' surfaces
Low temperature/thermal shock	[b,c,d,g]Stones dropped into cup containing liquid nitrogen, cooled to −185°C	No additional changes noted in stones' surfaces

[a] *All tests performed by GIA Jewelry Manufacturing Arts staff members with exception of low temperature/thermal shock which was performed by the authors.*

[b] *1.23-ct pear-shaped mixed cut from Gem Source.*

[c] *1.21-ct oval mixed cut obtained from the Rainbow Collection.*

[d] *0.75-ct oval mixed cut purchased from the Astrid Corporation.*

[e] *0.75-ct oval mixed cut (same as stone "d" above) mounted in used six-prong 14K white gold oval setting and attached to a ring shank before this test was performed.*

[f] *All three stones in mountings when this test was performed.*

[g] *All three stones removed from mountings before this test was performed.*

[h] *Surface etching may result in stone requiring repolishing; repolishing may partially or completely remove diffusion-induced color layer. This would be expected with any corundum—treated or untreated natural or synthetic—when so exposed to borax-containing chemicals.*

the greatest number of circumstances, the 0.75-ct stone was mounted in a used six-prong 14K white gold oval setting attached to a ring shank before the durability testing began.

Table 3 outlines the tests used and the results observed. Neither ultrasonic or steam cleaning nor boiling in a detergent solution appeared to have any effect on the treated stones, which were examined with magnification both before and after the cleaning procedure.

To test the response of the sample stones to stress received during such jewelry repair procedures as the retipping of prongs, we also had the other two test stones mounted but in 14K yellow gold cast heads. One prong tip was removed by sawing on all three of the stone-set mountings, and the prongs were retipped following the procedures described in table 3. Eventually, all four prongs were sawed off and retipped on the 1.23-ct pear shape. As would be expected with any corundum, the use of borax-containing chemicals (both firecoat and flux) contributed to moderate surface etching of the diffusion-treated sapphires. We did find, though, that the retipping of prongs with 14K gold solder produced only minor etching when care was taken to minimize the contact of the borax-containing flux with the surface of the stone. However, when one of the prong tips was built up with 18K gold, even though care was taken to avoid contact of the flux with the stone's surface, the higher temperatures required by the higher melting point of 18K (versus 14K) solder resulted in moderate to severe etching, especially on the surface of the table, as would happen with any corundum. If etching is severe enough, the stone might have to be repolished. Inasmuch as the color of a diffusion-treated sapphire is confined to a thin surface layer, such repolishing might lighten or totally remove the diffused color.

The best way to avoid this potential problem is to unmount the stone before retipping. Should the decision be made to retip prongs with the stone in place, however, a cotton swab dipped in alcohol should be used to carefully remove the firecoat from the stone before heat is applied (M. Allbritton, pers. comm., 1990). Although another option might be to use a non-borax-containing soldering flux, the only one we know to be available, a fluoride-based flux, is more toxic than borax-based fluxes and thus is not widely used (M. Allbritton, pers. comm., 1990).

When the three mounted diffusion-treated sapphires were subjected to rhodium electroplating, magnification revealed no additional changes in the appearance of the stones' surfaces.

As a final step in durability testing, the three treated sapphires were unmounted and then checked for their reaction to low temperatures and thermal shock by instantaneously lowering the temperature of each to −185°C by means of immersion in liquid nitrogen. The stones were then removed from the nitrogen bath and allowed to return to room temperature. This procedure tested not only the effects of extreme cold but, in the rapid way the cooling was performed, it also subjected the stones to extreme thermal shock. Again, though, there were no additional signs of damage.

Since the origin of the blue color in diffusion-treated sapphire is identical to that in natural-color blue sapphire, the diffusion-induced color can be considered to be as stable as that of natural blue sapphire.

CONCLUSION

The fact that more blue diffusion-treated sapphires have entered the gem market than ever before has increased the need for awareness on the part of the gemologist. With this procedure, color-causing chemicals are diffused into the surface of a stone by high-temperature heat treatment for extended periods of time, as long as a week or more. Apparently, by using higher temperatures, longer periods of heating, and/or multiple heatings, a deeper diffusion layer can be produced. This was evident in the one polished Gem Source stone in which we actually measured the diffusion layer and in the three Gem Source stones that were chemically analyzed. Even so, although the surface color layer produced by diffusion is stable to routine cleaning procedures, the shallowness of the layer makes it susceptible to partial or complete removal if the stone is subsequently repolished or recut.

Diffusion treatment can best be detected by examination of the stone while it is immersed in a liquid such as glycerine or methylene iodide over diffused transmitted illumination. In most cases, the unaided eye is more effective than magnification.

The 1975 Union Carbide patent listed numerous examples of the colors that could be produced in corundum with diffusion treatment, including red and orange. We have been told by Karla Brom (pers. comm., 1990) that diffusion-treated rubies and "padparadscha" sapphires have already been produced in Bangkok on a limited experimental basis; a red-orange diffusion-treated sapphire was examined by Bob Crowningshield at the GIA Gem Trade Laboratory in 1979. Inasmuch as large quantities of blue diffusion-treated sapphires—from a variety of treaters—are now being sold in the gem market, it is possible that the trade will also begin to see other colors of diffusion-treated corundum in the not-too-distant future. If procedures similar to those described above are used to produce these other colors, it is likely that they, too, will be readily identifiable.

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