CARBON DIOXIDE FLUID INCLUSIONS AS PROOF OF NATURAL-COLORED CORUNDUM

By John I. Koivula

The question of how to identify natural-colored from heat-treated corundum has long puzzled the gemological community. One important clue is now provided by carbon dioxide fluid inclusions. Because such inclusions cannot survive heat treatment, their existence intact and unruptured in rubies and sapphires is conclusive proof that no heat treatment has occurred.

ABOUT THE AUTHOR

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The photomicrographs in figures 2, 3, and 4 were taken by the author.

Until the mid-1970s, when the practice of high-temperature treatment of corundum became widespread, liquid and gaseous carbon dioxide (CO_2) fluid inclusions were commonly observed in Sri Lankan rubies and sapphires. In fact, the author has studied well over a hundred pieces of geuda (untreated) corundum with these inclusions. Traditionally, these inclusions have been useful in establishing the natural origin of their host (Gübelin and Koivula, 1986). With the prevalence of heat treatment, however, they have taken on additional significance: Because carbon dioxide fluid inclusions cannot survive the temperatures required to alter color in corundum, their presence provides conclusive proof that the color also is natural.

HISTORICAL BACKGROUND

Sir David Brewster, a Scottish physicist, first discovered CO_2 fluid inclusions while examining sapphires and other single-crystal gem materials with the microscope. The year was 1823. Although he did not identify the liquid as carbon dioxide, he made note of his discovery and reported on this "remarkable new fluid found in the cavities of rocks" (Brewster, 1823). He observed that this strange new fluid was often found in the presence of water, although the two were immiscible (would not mix). The liquid had a refractive index less than that of water and a coefficient of thermal expansion approximately 30 times that shown by water. The fluid was also nonwetting and would ball up like elemental mercury rather than flow over and coat the interior walls of a negative crystal cavity.

Since Brewster's discovery, the study of CO_2 fluid inclusions has continued. With infrared absorption spectrometry (passing an infrared beam though a thin parallel-windowed plate of a gem), inclusion investigators have identified five separate forms of closely related carbon-oxygen compounds which may occur in fluid inclusions (Roedder, 1972). Three of these are found in solution with

Figure 1. The 1.84-ct Sri Lankan blue sapphire used in the experiment. Photo © Tino Hammid.

water: H_2CO_3, HCO_3^{-1} and CO_3^{-2}. The remaining two, liquid and gaseous CO_2, are the ones of primary interest to gemologists concerned with the identification of heat-treated rubies and sapphires.

THE EXPLOSIVE NATURE OF CO_2

As indicated by the following statement taken from a letter written by Sir David Brewster to Sir Walter Scott in 1835, Brewster had, through continued experimentation, become aware of the explosive potential of CO_2 fluid inclusions when heated:

> When the gem which contains the highly expansive fluid is strong, and the cavity not near the surface, heat may be applied to it without danger, but in the course of my experiments on this subject, the mineral has often burst with a tremendous explosion, and in one case wounded me on the brow.

It is this explosive potential of CO_2 fluid inclusions (Koivula, 1980, 1980–1981) that makes their presence excellent positive proof that the host rubies and sapphires have not undergone heat treatment.

Although Brewster was not referring to temperatures anywhere near as high as those required to effect a color change in corundum, it is nonetheless surprising how little heat is required to actually explode (shatter) a gem containing one or more of these fluid inclusions. Brewster's statement regarding the application of heat "without danger" when the inclusion is "not near the surface" holds true for some gem corundums heated to temperatures of only 250°C to 400°C (depending on the size of the host gem, and the size, shape, and position of the CO_2 fluid inclusion within the gem). It is not true, as discovered experimentally by the author, for gems heated above 400°C. Because of this "explosive fatality," heat treaters of Sri Lankan rubies and sapphires commonly trim away areas of the rough that contain inclusions, or partially saw, or even drill, into the inclusions.

If the CO_2 inclusions are completely removed, then the gem has an excellent chance of surviving the 1500°C-plus temperatures required to alter color in corundum. If they are not removed, the inclusion will explode and the gem will be badly damaged or completely destroyed. In either case, these inclusions will no longer exist.

EXPERIMENTAL CONSIDERATIONS

Liquid carbon dioxide has a critical temperature of 31.2°C (88.2°F). Above this temperature inclusions containing the liquid form of CO_2 homogenize into a uniform high-pressure fluid; as the temperature is increased above the critical point, pressure also rises drastically.

When we consider that crystals containing CO_2 inclusions form under great pressure at considerable depth within the earth, it becomes apparent that if such crystals are now at the earth's surface, then the compensating pressure of the rock that once surrounded them is removed. Yet the inclusions are still at their original high pressure of formation. So at room temperature we now have corundum crystals containing fluid inclusions with high outward pressure (1000 psi or more) that have only external atmospheric pressure (instead of tons of rock) to compensate.

If we further aggravate this volatile situation by faceting, preforming, or trimming the stone and bring the inclusions closer to the surface (i.e., by cutting away layers of protective crystalline corundum that lend structural integrity to the crystal) we have dramatically increased the chances for a pressure burst. It is easy to see, then, why stones containing CO_2 inclusions do not survive the application of heat energy.

EMPIRICAL PROOF

To dramatically prove this point, the author selected a 1.84-ct untreated blue Sri Lankan sapphire with a tiny, intact carbon dioxide fluid inclusion just beneath the table surface (figure 1).

When the host sapphire was held below the critical temperature of 31.2°C (88.2°F), both the liquid and gaseous CO_2 phases were visible within the negative crystal (figure 2). Just a slight warming above the critical temperature by the heat generated from the microscope lamp caused the meniscus around the bubble to disappear (figure 3).

In the name of science, this gem was placed on a ceramic tile in an electric muffle furnace and the temperature was gradually increased. A popping sound was heard when the temperature gauge on the furnace indicated just 270°C. At this point, the furnace was turned off and allowed to cool.

The stone was inspected. The CO_2 fluid inclusion had exploded, blown a shard out of the table, and left behind a crater (figure 4).

CONCLUSION

Many gem dealers today feel compelled to heat treat virtually every piece of corundum. Fine gems in no real need of treatment are subjected to the furnace with the hope that a few extra dollars can be cooked from them. Even gems that originally entered the market years before heat treatment became popular are being burned for "improvement." And little by little, inclusions that once gave natural, unadulterated gems uniqueness are disappearing. The heat treater's furnace is acting as

Figure 2. Negative crystal filled with liquid and gaseous carbon dioxide as observed below the critical temperature. Dark-field illumination, magnified 50×.

Figure 3. The same CO_2-filled negative crystal as in figure 2 but just above the critical temperature (31.2°C) for carbon dioxide. Dark-field illumination, magnified 50×.

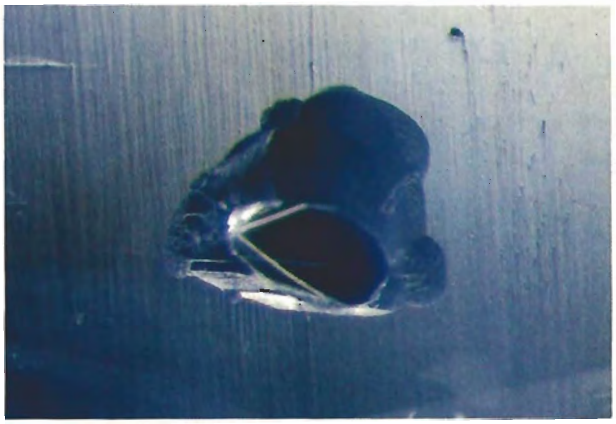

Figure 4. The same negative crystal as shown in figures 2 and 3 but after exploding. The gem was heated to only 270°C. Dark-field and shadowed oblique illumination, magnified 50×.

a gem-blender, slowly homogenizing the corundum population and making the relatively common appear rare to the uneducated.

As a consequence, very few CO_2 fluid inclusions in corundum have been seen in the GIA Gem Trade Laboratory during the last few years (R. Crowningshield, pers. comm.). Mr. Crowningshield's observation concerning the Gem Trade Laboratory is an important one. The more prevalent heat treatment has become, the fewer of these inclusions are seen. Carbon dioxide fluid inclusions will not survive heat treatment. Therefore, an unruptured carbon dioxide fluid inclusion in a ruby or sapphire is absolute proof that the gem is natural and has not been heat treated.

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