THE HEAT AND DIFFUSION TREATMENT OF NATURAL AND SYNTHETIC SAPPHIRES

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INTRODUCTION

The subject of heat treatment of corundum has been touched upon only lightly in the gem literature. Although rumours that purplish rubies could be improved by heating were circulated more than thirty years ago, the commercial heating of blue sapphire has become so important that it can no longer be dismissed.

One of the first references that we can find is in an article 'Fakes & Frauds, Caveat Emptor' by J. H. Oughton in the *Australian Gemmologist*, Vol. 11 (4), 91, p.17, November 1971. In this article he refers to a single 'fraud' in which very silky Australian sapphires were presumably heated in a liquid; this was supposedly drawn into hollow tubes which appeared as silk and greatly improved the transparency of the stone. Later, he theorized, the liquid evaporated and the silk became visible again. This account seems to be that of an isolated case since we have not heard reliable reports that heated stones revert. Since the silk in Australian sapphire is caused by rutile needles rather than by hollow tubes, it is doubtful that this is an accurate report. However, a note by the same author in the November 1974 issue of the *Australian Gemmologist* (Vol. 12, p.117) seems to be on the track: here he states that a great deal of inky Australian sapphire is exported for treatment and that he has found no means to detect such treatment.

Also, in 1971 E. A. Jobbins described the 'Heat Treatment of Pale Blue Sapphire from Malawi' in Vol. 12, p.342 of the *Journal of Gemmology*. Evidently this experiment was conducted with the goal of darkening the colour under the assumption that this occurs when blue-green beryls are heated to turn them blue, when in fact the yellow component is merely bleached and the blue aquamarine remains (K. Nassau, *Gems & Gemology*, Vol. 16, p.343, Fall 1980).

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In recent months the GIA-GTL, Inc. has come to realize that the equating of blue sapphires and aquamarines in the matter of heat treating is highly misleading. First, the heat-treatment of many heated blue sapphires is detectable and, secondly, the potential value differences are great. Moreover, insidious additional treatments are being practised so that the sapphire problem is far from clear cut.

Information on the behaviour of ruby and sapphire on heat treatment is known from the manufacture of the synthetic material (K. Nassau, *Gems Made by Man,* Chilton, 1980) and from other technological studies. Based on such knowedge we can define the nine types of treatment of Table 1. The changes of the first five treatments can penetrate completely throughout a stone, but the effect of the next four is confined to the surface of a stone and is easily lost on repolishing. Several of the processes can occur simultaneously, depending on the condition used. More detail will be given in a forthcoming report (K. Nassau, to be submitted to *Gems & Gemology*).

There are also many hearsay reports, some of which are obviously unreasonable, and all of which should be taken with a heavy sprinkling of salt until confirmed by hard evidence. Thus the 4000 °C heat treatment reported to G. Tombs (*Z.Dt.Gemmol.*

TABLE 1.
Heat Treatments used on Sapphires and Rubies*

TREATMENT	RESULT
A. Heating only:	
1. Medium temperature	Develops potential asterism
2. High temperature, rapid cooling	Removes silk and asterism
3. Reducing heating	Develops potential blue colour
4. Oxidizing heating	Diminishes blue colour
5. Extended heating	Diminishes Verneuil banding and strain
B. Heating under unknown conditions:	
6. ?	Introduces fingerprint inclusions
C. Heating plus surface diffusion of impurities:	
7. Adding TiO_2	Produces asterism †
8. Adding TiO_2 and/or Fe_2O_3	Produces blue colour †
9. Adding Cr_2O_3, NiO, etc.	Produces other colours †

*Treatments 1 to 4 correspond to processes also occurring in nature; treatments 5 and 6 are used on synthetic material; treatments 7 to 9 do not correspond to natural processes, can be detected and, accordingly, it would seem that their use should be disclosed.

† Effect is limited to a region near the surface.

Ges., Vol. 29, p.79, 1980) is even above the melting point, while the 1000 °F reported to E. Sasaki (ibid., p.66) is as unreasonably low.

Simple Heat Treatment and Identifying Characteristics

In the mid 70s we began to hear that Thai dealers were appearing in Colombo, Sri Lanka, in search of a type of milky white corundum that has become known as 'Geuda stone' (possibly the name of a mine). It was rumoured that back in Bangkok this material was heated to produce quite acceptable clear blue faceted stones. This treatment is presumably a combination of treatments 2 and 3 of Table 1. GIA-GTL, Inc. received a sample of Geuda sapphire from New York dealer Alan Caplan in 1977 (Figure 1). For a short time in about 1976, parcels of heated blue sapphire were offered in New York as treated sapphires for considerably less than untreated stones. Buyers were wary until it was discovered that no positive proof of heat treatment was forthcoming. Gradually the trade here and abroad began to equate the heating of sapphires with the heat treatment of aquamarine, for which no tests exist. Geuda stones have been discussed by H. S. Gunaratne in this *Journal,* (January 1981, Vol. 17, p.292.).

Looking back twenty-five to thirty years at the tests on which we used to rely for distinguishing natural blue sapphires from synthetics, it now appears that most heated Ceylon sapphires do have indentifying characteristics. For one thing, we rarely ever encountered a natural blue sapphire with the dull, chalky green fluorescence we see in a large percentage of heat treated stones. At the same time, we do not see the iron absorption line at approximately 4500 Å in the spectroscope in most heated stones. Under magnification we frequently see internal stress fractures (Figure 2) around single crystal inclusions and in areas where there had been fingerprint inclusions. Also, cross-hatched colour-banding (Figure 3) and areas of rutile needles reduced to Kashmir-like colour-zoning were never seen in the past, while the then common rutile silk is no longer seen now. Cut stones that are heated need to be repolished and evidence of this takes the form of pock-marked facets or girdles not completely retouched (Figure 4). Also the girdles may have many planes unlike a normal girdle (Figure 5).

FIG. 1. Geuda sapphire.

FIG. 2. Internal stress fractures around single-crystal inclusions in heat-treated natural sapphire.

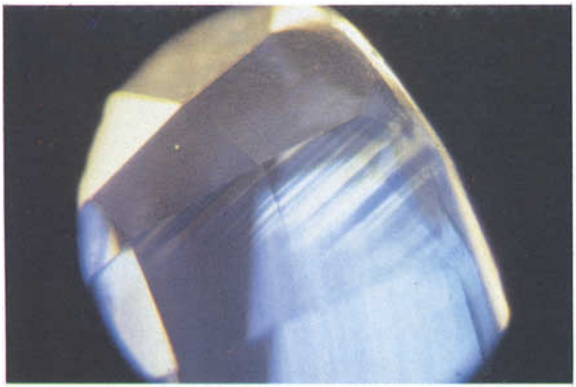

FIG. 3. Cross-hatched colour-banding in heat-treated natural sapphire.

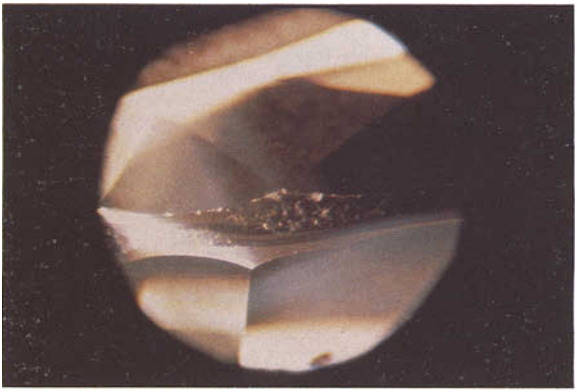

FIG. 4. Pock-marks in incompletely retouched girdle of cut stone after heat treatment.

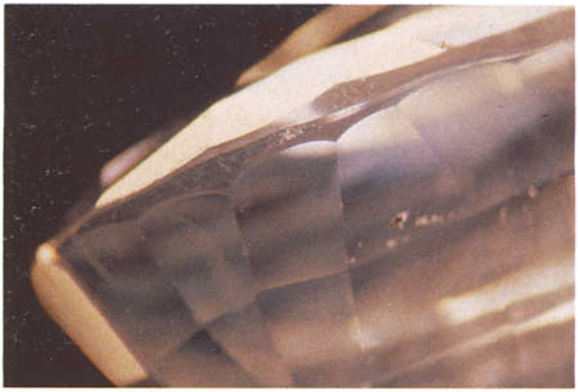

FIG. 5. Girdle of cut stone after heat treatment, having many planes (unlike normal girdle).

Rumours that yellow colour in natural sapphires is being produced through heat treatment by a laboratory in the U.S.A. have persisted since early 1980. The GIA-GTL, Inc. has had occasion to test several orange-yellow to yellow-orange natural sapphires (*Gems & Gemology,* Summer 1980, Vol. 16, p.320.) which did not have a characteristic fluorescence or an iron absorption. Failing to secure permission to conduct a simple fade test in direct sunlight, the reports indicated that the origin of the colour is unknown, but if it were due to irradiation, as all gemmologists know, the colour will fade. We have now had an opportunity to fade-test some beautiful orange-yellow sapphires which did not fade and were claimed to be a product of this new lab.

In view of the fact that the colour is unnaturally intense and the fact that the colour is due to treatment, the Labs indicate this on reports. This would appear to be a case of discrimination, since so many blue sapphires have their colour and appearance enhanced by heating and the Labs do not at present mention it. The reason, of course, is that tests for blue sapphires are not conclusive in many cases. If a yellow to orange sapphire had no diagnostic inclusions, it would be necessary to do a careful Plato test to separate it from a Verneuil synthetic.

The development of potential asterism by employing heating as in process 1 of Table 1 where nature did not complete the process, has been used on an experimental basis for a long time.

Lightening of a deep blue colour by process 4 of Table 1 has been reported; this may lead to green or yellow sapphire if an underlying yellow colour is also present. This process is probably used on the pale and/or milky Ceylon and Australian rough reportedly heat-treated to produce yellow to orange sapphire (although, if it turned colourless, irradiation could then have been used to produce a yellow to orange, which is, however, not commercially acceptable as the colour is not stable to light or heat). Similarly produced may be the heated Australian sapphires, presumably lightened from the very dark blue and reported to have a pronounced green dichroic direction. Purple sapphire could be converted to ruby by this treatment.

Much less is known about the heating of rubies. It is felt by many experienced dealers that a great percentage of Thai rubies have been improved in colour by heating. At one time such stones were said to be from a new mine. The old purplish to brownish typical Thai ruby has virtually disappeared from the market, suggesting that it now reaches the market enhanced by heat. The red ruby coloration is not affected by heat, but undesirable modifiers such as blue can be removed.

Even less is known about the prevalence of heating cloudy Burma rubies to increase transparency and improve colour. It is rumoured that it may require several heatings to accomplish the desired results and there is considerable risk of damage involved.

SURFACE DIFFUSED SAPPHIRES AND IDENTIFYING CHARACTERISTICS

In the fall of 1979 we reported in *Gems & Gemology* (Vol. 16, p.194) the testing of a red-orange natural sapphire in which most of the colour lay on the surface (Figure 6) with some facets lacking colour entirely. We deduced that it seemed to be an example of colour diffusion using process 9 of Table 1. This process is among those outlined in U.S. patent 3,897,529 issued to R. R. Carr and S. D. Nisevich of the Union Carbide Corporation in 1975 and can produce a full range of diffusion colours from orange to red to pink. At that time we did not anticipate seeing the same process used with blue sapphires. However, in September of 1980 in the New York lab we encountered the first of an avalanche of such blue, diffusion-enhanced stones, clearly made by process 8 of Table 1. Their detection is simple if they are unset and can be immersed in methylene iodide. It is usually not necessary to use the microscope if a clear immersion cell is available. The stone and cell are held a few inches above a white paper so that the splotchiness of colour caused by unequal repolishing of the facets is revealed (Figure 7). Because the raw material may be heavily colour-zoned and the diffused surface colour evens out the appearance, the Gem Trade Laboratory simply states on reports for these stones—'Natural Sapphire, Wt. . Note: Color has been surface enhanced by an artificial diffusion process'.

In May, 1981 we encountered our first heavily zoned stones in which colour seemed to be concentrated at facet junctions (Figure 8). Such zoned rough is reported to be typical of the Ootu Mine in Sri Lanka. The explanation has to be that the stones were diffused in the preform stage, possibly after unsuccessful heat-treating attempts. It resulted in some of the most handsome blue treated stones we have seen. This type of diffused colour treatment is not recognizable without immersion and might be impossible to detect in a mounting. At the same time we encountered our first example of a colour-diffused cabochon. The colour has been removed from an area around the girdle (Figure 9) reminding us of the faceted stone in Figure 22 in the Spring 1981 issue of *Gems & Gemology,* Vol. 27, p.46). Most of the surface-diffused stones we have seen do not fluoresce under short UV. None of the twenty cabochons in the necklace (Figure 10) from which this stone was removed for testing

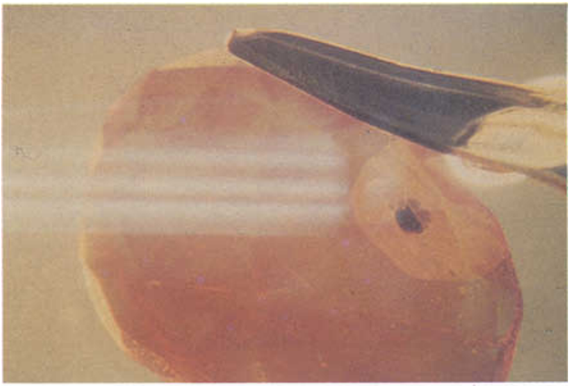

FIG. 6. Red-orange sapphire with most of the colour on the surface.

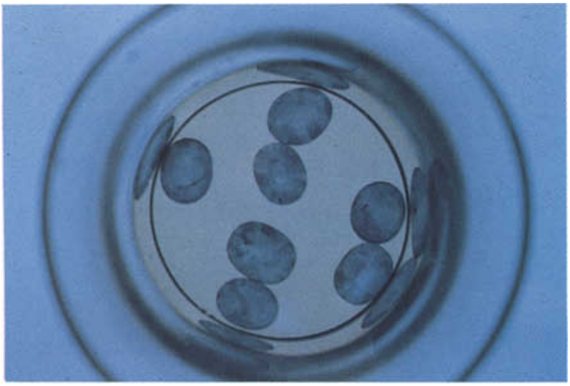

FIG. 7. Splotchiness of colour in diffusion-enhanced sapphires.

FIG. 8. Colour apparently concentrated at facet junctions in a heavily zoned stone.

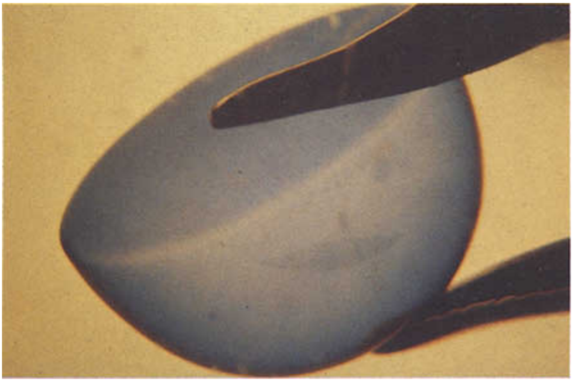

FIG. 9. Colour-diffused cabochon sapphire, with colour removed from an area around the girdle.

FIG. 10. Necklace from which colour-diffused cabochon sapphire in Figure 9 was removed.

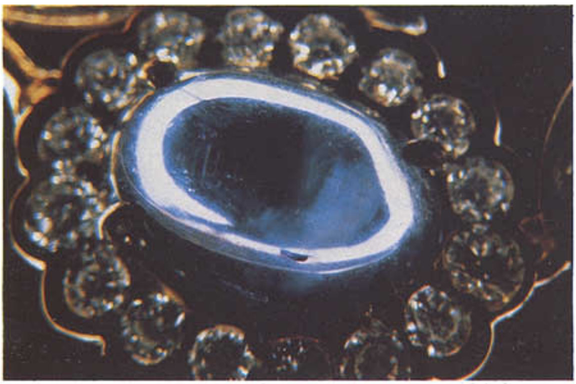

FIG. 11. 'Bleeding' inward of colour in colour-diffused cabochon sapphire.

was recognized as diffused when first observed in the setting. Then we noted a clue in a few of the stones which indicated diffused treatment: this was the 'bleeding' inward of colour from open pits, fissures, and fractures (Figure 11). We examined some of our own faceted diffused stones and noted the same features.

Many experienced dealers feel they can recognize both diffused and heat treated blue sapphires by a certain watery appearance or thinness of colour. Perhaps compared with older Burma, Ceylon, and Australian stones this is a factor, but, if the heated or diffused stone was originally heavily colour-zoned, this characteristic is not evident.

We and others have reported the lack of success in securing eyewitness accounts of the actual heating process. We have had reports that heating is done with crucibles (Figures 6 and 7 of Summer 1980 issue of *Gems & Gemology,* Vol. 16, p.318) packed into 55-gallon drums serving as ovens. But we have also heard that sophisticated furnaces and platinum crucibles are used. In fact, one dealer claimed he was present when such an oven exploded in the next room while visiting a supplier in Bangkok.

Asterism can be added by a surface diffusion step as described in U.S. Patent 2,690,630 issued to W. G. Eversole and J. N. Burdick of Union Carbide and Carbon (Linde) in 1954 and also in the Carr and Nisevich patent. This is process 6 of Table 1 but only seems to have been used experimentally. It was not until 1968 that the GIA-GTL, Inc. in New York was shown some of these stones (Figure 12). Since they were never available commercially, we had not seen any since that time until May, 1981 as this manuscript was being prepared.

Three star sapphires (Figure 13) were submitted to the Los Angeles Gem Trade Lab and subsequently forwarded to the New York Lab for study. They were reported to have been a recent purchase in Bangkok. Like the stones we first examined in 1968, the individual star-causing needles are extremely fine and the star unnaturally sharp. The colour of two of the stones is 'not right' and 'bleeding' of colour around pits and fractures indicated colour diffusion (Figure 14), while the fine needles indicate the induced asterism. Two stones showed weak greenish fluorescence under short UV and all showed a weak iron line at 4500Å in the spectroscope. The third stone is a pleasing blue, but the star is 'too

FIG. 12. Asterism added by a surface diffusion step (process 7, Table 1).

FIG. 13. Three star-sapphires with induced asterism. These stars are sharper than they appear in the photograph.

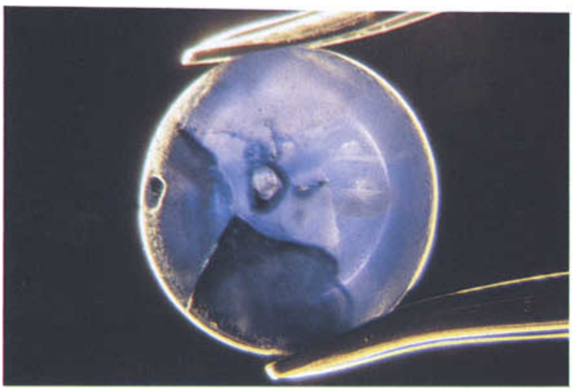

FIG. 14. 'Bleeding' of colour around pits and fractures indicates colour- diffusion.

sharp'. All three stones exhibited iridescent internal fractures. Possibly, such flawed material is not suitable for faceting, hence it is relegated to being processed as star material.

CHANGES IN INTERNAL STRUCTURE (TREATED VERNEUIL SYNTHETICS)

Dealers have tried to secure information on heat treatments for us, for which we are most grateful. One dealer's Bangkok supplier, after many requests, finally sent him three parcels of sapphires purported to be three stages in the heating process. We were delighted to see some heavily colour-zoned preformed 'Ootu' stones before heating, some evenly coloured similar shape preforms presumably heated and some quite beautiful cut stones. However, upon testing the three lots, only the unheated preforms were natural sapphires. The rest were heated Verneuil synthetics, most with induced fingerprint inclusions (Figure 15)! One report states that the heating of Verneuil synthetics (which improves the appearance considerably) is not done in Bangkok, but in California, Japan, and Switzerland. The donor of the crucibles mentioned in the Summer 1980 issue of *Gems & Gemology,* Vol. 16, p.315, says that heating of Verneuil synthetics with induced fingerprint inclusions is carried out in Bangkok. To the jeweller gemmologist who must identify them, it really makes no difference where the treatment is performed. We have noted that a positive Plato test is more difficult to secure since the heating eases some of the strain in the crystal structure in addition to improving the colour immensely. However, we doubt that repeated heating of natural banded sapphires finally causes the bands to curve, as several Bangkok dealers have mentioned in defence of their heat treated Verneuil synthetics!

We have encountered Verneuil synthetic rubies and pink sapphires containing induced fingerprint inclusions (Figure 16). It would seem logical to anticipate similar deceptions with all colours of synthetic corundum. The pink synthetic sapphire shown here was beautifully 'native' cut. It had fingerprint inclusions and repeated twinning lines. However, it also had tiny gas bubbles and characteristic chalky green over red fluorescence under short UV. The diminishing of the curved growth lines of Verneuil rubies and sapphires is process 5 of Table 1, while the unknown process involved in producing fingerprint inclusions is process 6 of Table 1.

FIG. 15. Induced fingerprint inclusion in heated Verneuil synthetic sapphire.

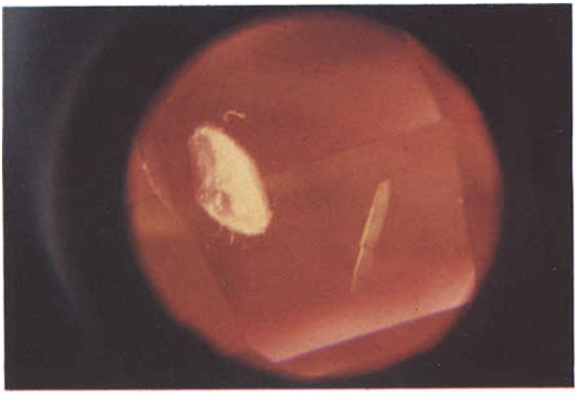

FIG. 16. Induced fingerprint inclusion in Verneuil synthetic pink sapphire.

Summary

The jeweller gemmologist today is confronted with a wide variety of treatments and processes which have complicated the task of identifying many colours of sapphire. A blue or yellow faceted stone that appears to be a sapphire may with careful testing be identified as any one of the following: a natural, unheated stone; a synthetic stone; a simply heat-treated natural stone (lightened or darkened); a heat-treated synthetic stone (with or without induced

fingerprints); a natural sapphire with surface colour diffused either when the stone was preformed or finished; an irradiated yellow to orange fading sapphire. When one considers the imminent commercial appearance in the market of flux-grown synthetic blue sapphires to say nothing of garnet and glass doublets and natural/synthetic sapphire doublets, the comparison with heating beryl to produce aquamarine is indeed inappropriate.

Only by becoming aware of all the possible treatments used on corundum can one know for what specific signs to be alert. Unlike the heat-treatment used on aquamarine, it is often possible to detect the heat or diffusion treatments in sapphire.

If diffusion has been used, the effects are limited to a very thin skin at the surface of the stone and can accidentally be removed if recutting becomes necessary. This has become a definite problem for dealers world wide as well as in Bangkok.

Aside from unusual inclusions seen in heated Burma rubies such as rutile needles that have been incompletely absorbed, the evidence of heat treatment is scant.

The first four treatments of Table 1, correspond to processes also occurring in nature. The reason why some of those can be recognized lies in the rapidity of these treatments: since geological periods of time are not available, it is necessary to use somewhat higher temperatures than nature uses and this sometimes leaves evidence in the stones. The last four treatments do not correspond to natural processes and are identifiable; accordingly, it would seem that disclosure of their use is essential.

As a last point, it is clear that corundum from different localities can show considerable variation in its reaction to these treatments.

[*Manuscript received 4th July, 1981.*]