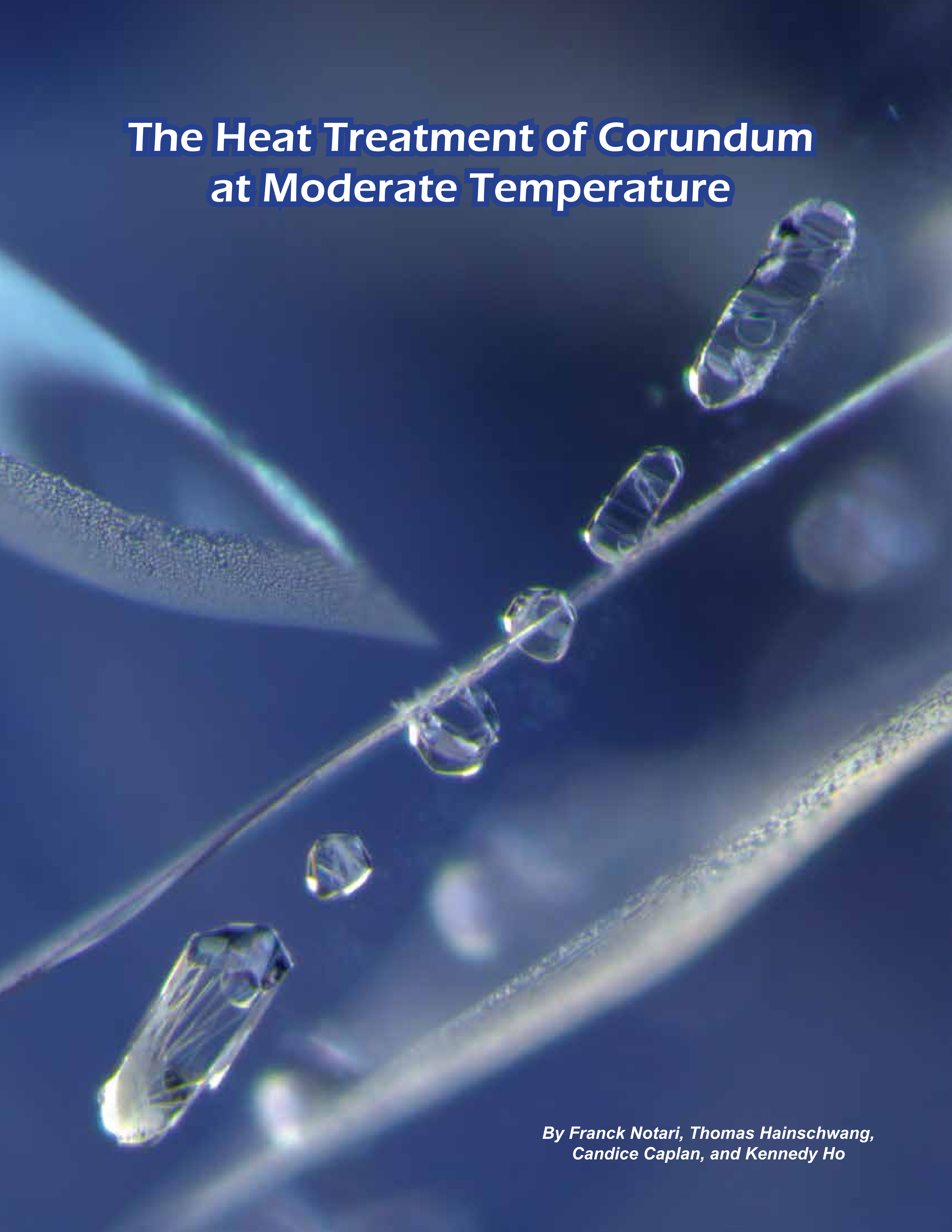
The Heat Treatment of Corundum at Moderate Temperature



By Franck Notari, Thomas Hainschwang, Candice Caplan, and Kennedy Ho

History

The thermal treatment of minerals has been part of humanity's history for millennia. The first established indications of this treatment, applied to siliceous rocks, were found in the Indus Valley and Mesopotamia, among others. They were dated to about 16,000 years ago, which corresponds to the late Pleistocene[1] a period known as Tarentian[2]. At that time, heat treatment was associated with the shaping of stone tools because it facilitated the final shaping by pressure.

It is likely that the color change of certain mineral substances appeared fortuitously, especially by the accidental mixing of chalcedony [containing hematite: Fe_2O_3, or goethite: α-$Fe_3O(OH)$] to siliceous rocks used in workshops producing tools. The sometimes significant change in color and translucency of the heated chalcedony having attracted the attention of artisans, it is reasonable to assume that the colors obtained—brown to orange, approaching the red hue rarely encountered in surface rocks—must have been appreciated by the men of that epoch.

Realizing that heat-treating certain rocks gave them beautiful colors probably led these early people to isolate them, ultimately giving birth to their use as ornamental "gems" for the making of ornaments, offerings, etc.

The oldest bibliographical reference mentioning the heat treatment of corundum (ruby) is in the book: *Al-Jawāhir wa ma Shabhala* (*Gems and the Likes*), about 850-870 AD, written by al-Kindi (Abū Yūsuf Yāqūb bin Ishāq ibn as-Sabbah ibn Ōmran ibn Ismāil al-Kindi[3], a great Hellenizing Arab philosopher and scientist (801 - 873 AD) (Figure 1).

Figure 1. Representation of al-Kindi in a Syrian post stamp of 1994.

Opposite page: Unheated blue sapphire from Sri Lanka, with multiphase inclusion: liquid/gaseous CO_2, diaspore and graphite.

Figure 2: This manuscript, posterior to ca. 1250 AD, reproduces (pp. 94-101) some passages from al-Kindi's book *Kitab khawas al-jawāhir*.

In his book, al-Kindi describes in a detailed manner the heat treatment applied to rubies:

Irāqi traders possessing the dark kind, desire that it should fetch a higher price. They heat it in a crucible of the Sogdian[4] bole and the roasting process results in its becoming lighter. All the orifices between the two crucibles are thoroughly plugged and the stones are heated in the crucibles, which are specifically designed for heating gems. This process of heating is continued for a period sufficient to melt a mithqāl[5] of gold (a.n.: 1064°C). A poultice is applied to the stones for cooling them. The stone finally crystallizes as a clear and transparent gem, and fetches a higher price. This practice is applied when the stone is rendered free from all kinds of concavities and orifices. A poultice of the bole from the mine from where the stone is obtained is then applied. This bole is admixed with ground clay kneaded with clarified butter and dried. It is then heated on firewood, the jewelers being fully aware of the length of time for the heating process. In the event, heating is carried on for an hour at the minimum and twenty-four hours at the maximum followed by cooling. The stone is roasted again in case it does not clarify. As for the mine from where the ruby is brought, it is said that it is situated in the recess of the island of Serāndīb[6] at a place known as Naghz. It is mined from the mountains of that island as well. In the Indian language Serāndīb is Sanklādīp. Dīp is the generic name for an island. When I pounder upon the name it appears to me that the name designates a cluster of islands, that is, a mother of islands surrounded by several isles.[In Al-Bīrūnī's book, kitāb al-jamāhir fi ma'rifat al-jawāhir, Said H.M., 1989.]

[1]About 126,000 to 11,700 years ago.

[2]Pleistocene subseries, not recognized in international stratigraphic nomenclature. = Magdalenian, that is to say 17,000 to 12,000 years before the present (1950).

[3]Known in Latin as Alkindus.

[4]From "Sogdia," an ancient Iranian civilization, with Samarkand as its capital, existing from the 6th century BC to the 11th century AD.

[5]A mithqāl was a mass unit equivalent to 4.5 grams, used to weigh precious metals.

[6]The ancient name of Sri Lanka.

Figure 3. The traditional corundum heat treatment carried out in Ceylon (Sri Lanka) in 1995.

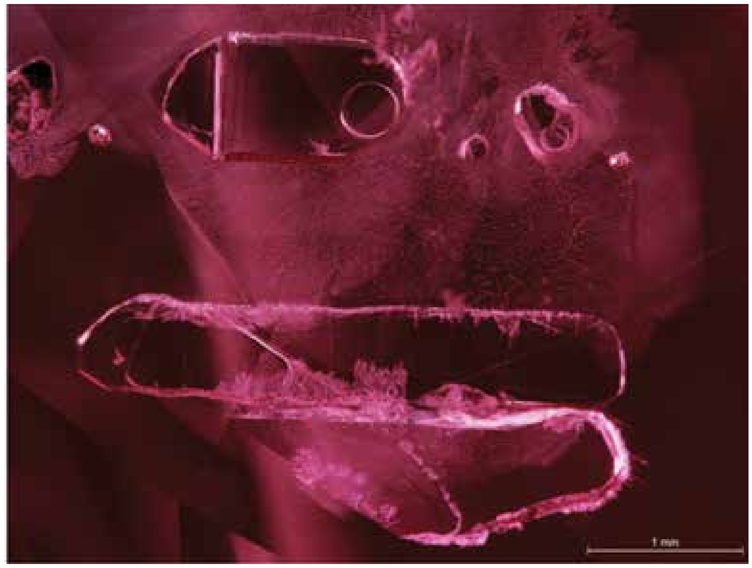


Figure 4. In corundum, the multiphase inclusions frequently contain liquid/gaseous hydrogen sulphide (H_2S, usually mixed with CO_2 and COS). Here with whitish crystals of boehmite and diaspore, AlO(OH).

Al-Kindi is certainly the scientist who most studied gemstones at that time. He wrote several books on the subject, often very detailed and precise. Among others, one can also mention *Kitab khawas al-jawāhir* (*The Book on the Properties of Precious Gems*), about 840-860 AD, frequently cited later. (Figure 2).

This shows that heat treatment for aesthetic purposes—simple or associating chemical compounds, applied to gems (in the broad sense)—is several millennia old. To the best of knowledge, it was first applied to ornamental "gems" (considered as precious at that time) and later to what we today call "precious" gems, the most emblematic being rubies and sapphires.

Traditional Heat Treatment of Corundum

It is thought that the heat treatment of sapphires and rubies appeared in Ceylon (*Serandib* at that time) at least 1,500 to 1,800 years ago. At the time, this treatment made it empirically possible to heat the sapphires and rubies in an oxidizing or reducing environment, at temperatures (at the time) typically from ≈ 900 to ≈ 1,100°C, but which could be raised to ≈ 1,200 to 1,300°C.

The equipment consists of the use of a terracotta pot, containing incandescent charcoal, fanned with the help of a tube in which a "burner" blows on the embers. The heating could last several hours with several "burners" taking turns. In Ceylon, this technique is called *Batā kubalā*[7] (phonetic) (Figure 3).

Heating in an oxidizing medium was achieved by placing the gem directly on the embers. The air (ambient as well as the one blown by the "burner"), including ≈ 21% oxygen in the form of O_2, is thus sufficient to oxidize the chromogenic elements generating an unwanted sub-hue.

The other major component of the air is nitrogen (≈ 78%), in the form of N_2, which is neutral in this context. Under these conditions, a ruby of metamorphic origin with a purple sub-hue must be heated for a few hours with the resulting purer red hue by iron oxidation, transforming the Fe^{2+} to Fe^{3+}. This will eliminate the intervalent charge transfer effect for which Fe^{2+} is needed (rather a molecular orbital, because the atoms do not see their valence really modified: $Fe^{2+} \leftrightarrow Ti^{4+} \leftrightarrow 3O^{2-}$), which generates a broad absorption around 565 nm (± 50 nm).

Hydrogen present in the stone, especially in the form of alumina hydrates that will release hydrogen (by de-hydroxylation) at a temperature as low as ≈ 450°C and to a lesser extent in the air, in the form of H_2O, which is cracked as early as ≈ 900°C to release H_2 hydrogen and O_2 oxygen ($2H_2O \rightarrow 2H_2 + O_2$) or ($H_2O \rightarrow H_2 + ½\ O_2$), will also participate in the oxidation process. Indeed, having an ^{e}A[8] of 0.75 eV, the hydrogen can engage its electron to form hydrides[9] with the present metal elements (i.e. TiH_2 from 300 to 500°C)[10].

Note that these hydrides can be naturally present in unheated corundum, for example, as liquid hydrogen sulfide (H_2S)[11] in rubies and sapphires, usually mixed with other gases (Figure 4).

For heating in a reducing environment, the gem is placed in a ball of dried vegetal material, and then placed on embers without stirring them. The combustion is thus slow and finally produces a thick coating very rich in carbon around the gem. The set with the stone is then placed into the embers, which are then fanned.

The gem is heated in the presence of nitrogen, oxygen, hydrogen and carbon. In a simplified way, nitrogen having a negative electronic affinity (^{e}A) (≈ -1.48 eV) is not involved in the process. But oxygen and carbon have positive affinities (^{e}A = ≈ 1.46 eV and ≈ 1.26 eV respectively) and, in these conditions, will initially form carbon monoxide (CO), and then carbon dioxide (CO_2). The formation of these two gases, especially CO, generates a reducing environment. As in the case mentioned above, the hydrogen present in the stone will intervene in the process.

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[7] In English: "Blow Pipe."

[8] Electronic affinity.

[9] *Stricto sensu:* the anion hydrogen, H^-.

[10] At atmospheric pressure.

[11] Usually mixed with CO_2 and COS.

Modern Heat Treatment

More recently (in the 1970s; controversial date), modern technology made it possible to apply heat treatment to rubies and sapphires with very precise control of the conditions, allowing extreme temperatures up to 1600 to 1700°C during long periods of time with various environments (gases or flux), and with or without the addition of chemical elements. This permits the treatment of corundum in a wide variety of conditions, the details of which are beyond the scope of this article, but which go well beyond the so-called "traditional" heat treatment (Figure 5).

Side Effects of Both Methods

When applied to corundum, the so-called "traditional" treatment essentially consists of modifying a hue, either by developing or reducing it at temperatures between ≈ 900 and ≈ 1200°C without the use of flux. It is important to point out that this is only an enhancement *stricto sensu*.

Side effects on the gem and its inclusions are moderate. The corundum matrix is not significantly modified, and the inclusions remain for the most part recognizable by their facies[12], often generating usually discoid fractures by a process of dilatation (Figure 6). Examples for this phenomenon are the cavities containing liquid CO_2 or zircons in the process of metamictization[13]. These fractures are, empty of any substances generated by the process as for the naturally induced fractures (Figure 6).

Modern methods of simple heating or with the addition of chemical compounds, allow not only to reduce or increase a color (with a greater amplitude), but also the actual creation of a new integral color (i.e. creating blue sapphires from non-blue "Geudas"[14] (Figure 7). Added to that, heating may improve the transparency of corundum—generally in

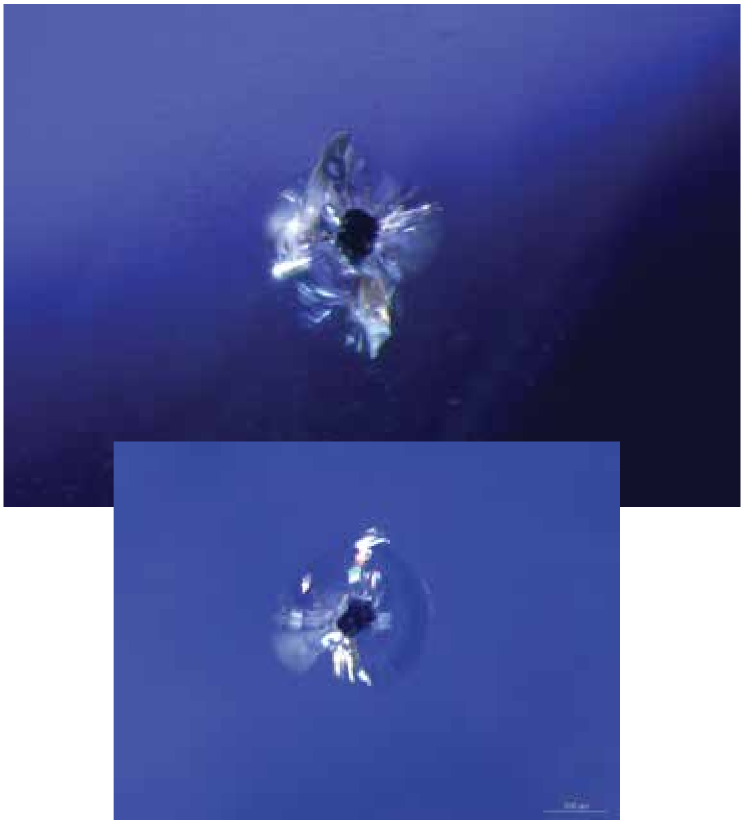

Figure 6. U-thorianite inclusions in blue sapphires. Top: In an unheated blue sapphire from Mogok (here the cracks are induced by metamictization). Below: In a blue sapphire heat-treated traditionally (blow pipe), exhibiting a discoid fracture induced by the heat.

[12]From Latin which means "aspect."

[13]Progressive destruction of the crystalline structure of a mineral, usually due to the presence of radioactive compounds.

[14]Corundum that appears grayish and often semi-transparent due to rutile (TiO_2) inclusions.

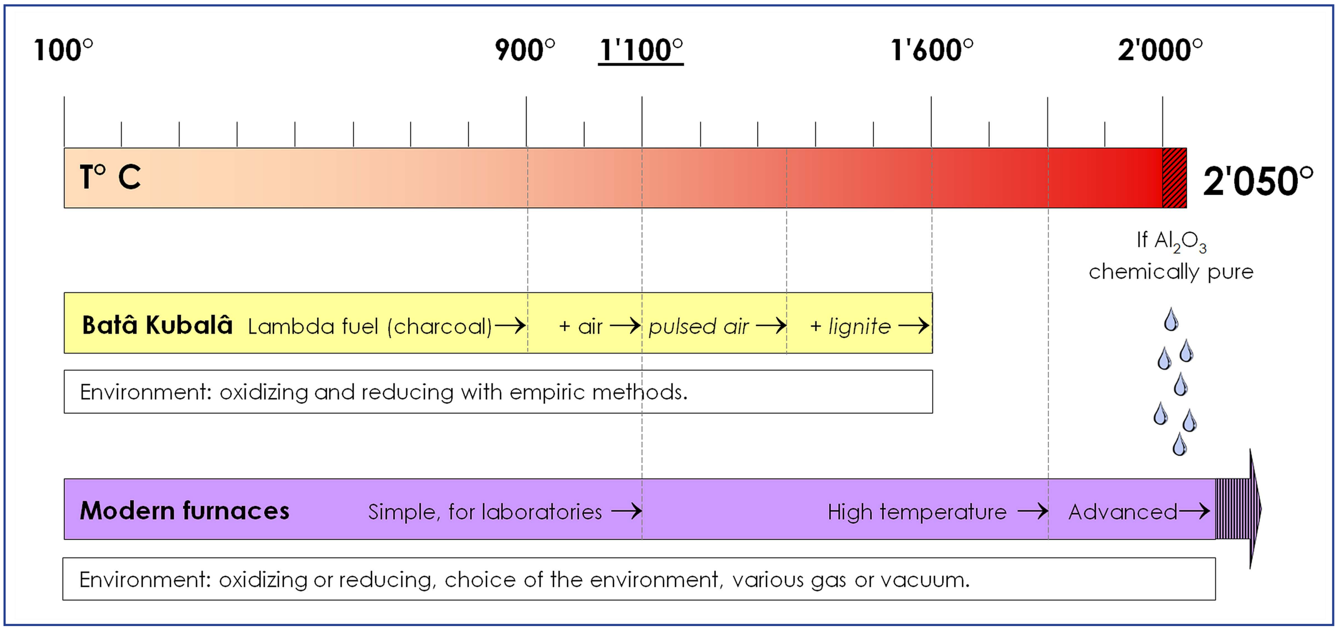

Figure 5. Comparative scale of resistance of corundum to temperature with the efficiency domains of the two equipments (traditional and modern) allowing the heat treatment. Note the theoretical limit of 1,100°C which corresponds approximately to the temperature of the "Blow pipe."

rubies—by dissolving all or part of the inclusions present and via the healing of cracks.

Figure 7. Example of color creation: An oval gray and opaque "Geuda" sapphire was faceted and then cut in two parts. One half was heat treated at high temperature (right); it became blue and transparent. (Photo: Coralie Nacht)

Ignoring treatments involving the diffusion of chromogenic elements or the fracture and cavity filling with high refractive index glasses, modern heating methods—when applied using fluids (flux)—generate several phenomena.

Among others, here are three examples.

- *The first concern* is the improvement of transparency that occurs mainly for rubies since, at the high temperature used, the flux will partially dissolve the corundum. During the cooling process, the flux will saturate and subsequently crystallize corundum in the open cracks, leaving a veil consisting of synthetic corundum and/or glass; besides, cavities of various shapes (bubbles, channels, etc.) are formed that generally contain essentially gas and that are covered with a thin layer of vitreous substance on the inner wall of the cavities (Figure 8). This phenomenon must thus be regarded as being part of the concept of corundum synthesis by the action of man.

In the emblematic case of rubies, healed cracks thus may have cavities in which the crack, initially present and widened by the melting, is filled by synthetic ruby. This synthetic ruby can sometimes occur in an automorphic habitus if it is formed in a crack or on a facet more or less parallel to the *c* plane of the crystal, which is the favorable growth orientation (Figure 9).

In addition to the formation of synthetic corundum, other more exotic species can be formed synthetically, like dendritic crystals of what is, for the moment, considered to be spinel (probably from iron-rich hercynite[15]) that it is frequently found in heat-treated yellow sapphires (Figure 10).

It is not uncommon to observe unidentified crystallizations on the subsurface of sapphires and rubies, generated by heat treatment in a flux (Figure 11), but they are often removed by re-polishing. This is quite commonly encountered in beryllium-diffused corundum. When these processes occur, it is important to emphasize that on this scale, the addition of synthetic material to a natural material is not technically detectable (demonstrable) by laboratories, although by reasoning we understand and explain it simply by microscopic observation.

- *The second concern* is the ability of glassy substances to penetrate into the corundum, sometimes resulting in the diffusion of the chromophores present in the vitreous substance into the corundum lattice. When flux is used during the high temperature treatment, it will penetrate into the gem, not only through open fissures, but also through Rose channels[16] and within associated polysynthetic twin planes, whenever present (Figure 12). This is why corundum, which has been heated using flux and does not exhibit any healed cracks, will nevertheless nearly always contain glassy substances as long as it contains Rose channels and/or polysynthetic twin planes. As long as no color changes resulting from the addition of chromogenic elements are noticeable, it is virtually impossible for any laboratory to detect these fillings. Therefore, as long as a stone does not show indications of conventional flux-healed fractures, there will be no mention of the presence of these vitreous substances on a gem testing report.

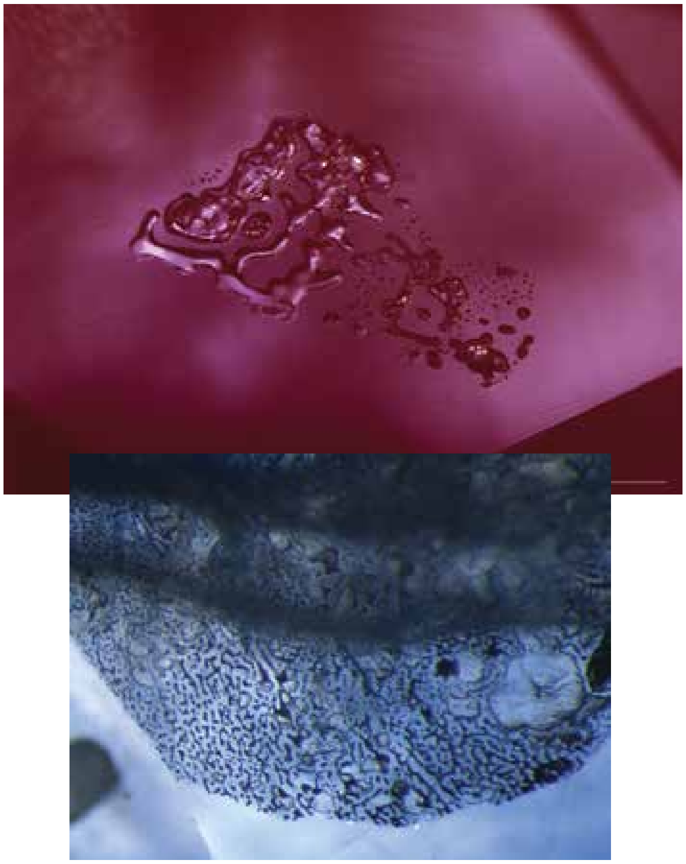

Figure 8. (Top) Healed cracks with residual cavities containing mainly gas with a film of vitreous substance on the inner wall. (Bottom) Healed fissure in a blue sapphire, containing flux residues with a high concentration of chromogenic elements, giving a black appearance.

[15]Hercynite: a member of the spinel group, with formula: $Fe_2{+}Al_2O_4$.

[16]Channels oriented at the junction of the planes r, r' and r'' of rhombohedrum.

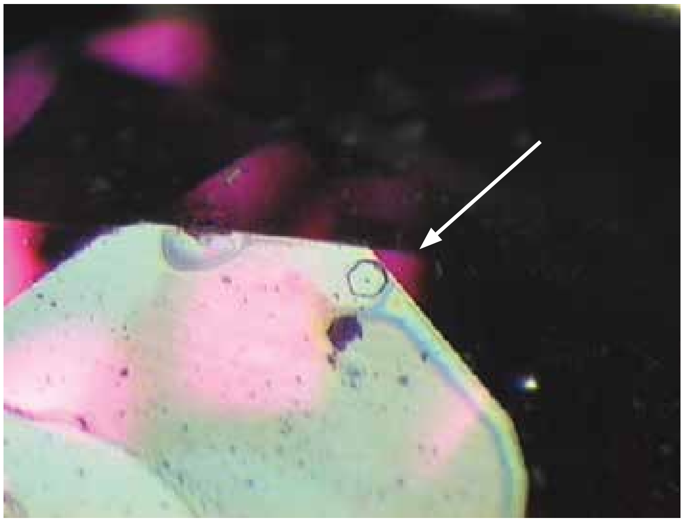

Figure 9. Automorphic synthetic corundum crystal that formed on the surface of a ruby treated at high temperature in a fluid environment.

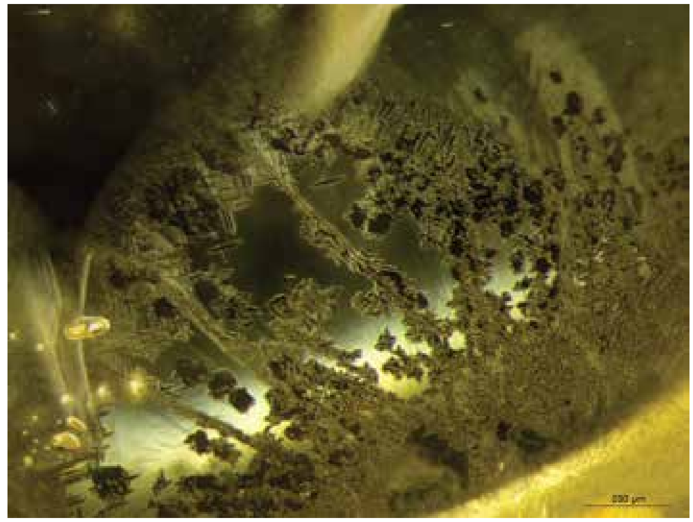

Figure 10. Spinel-like synthetic crystals (probably hercynite) in a fracture of a heated yellow sapphire.

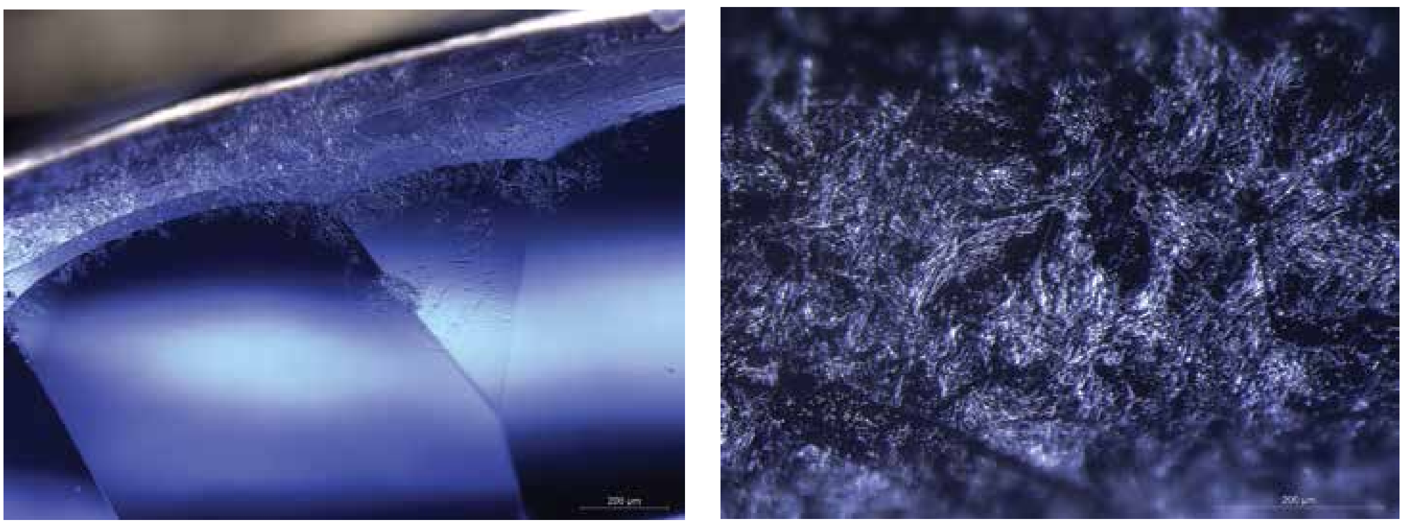

Figure 11. Unidentified crystallizations on the subsurface of sapphires treated at high temperature, here without diffusion of light elements.

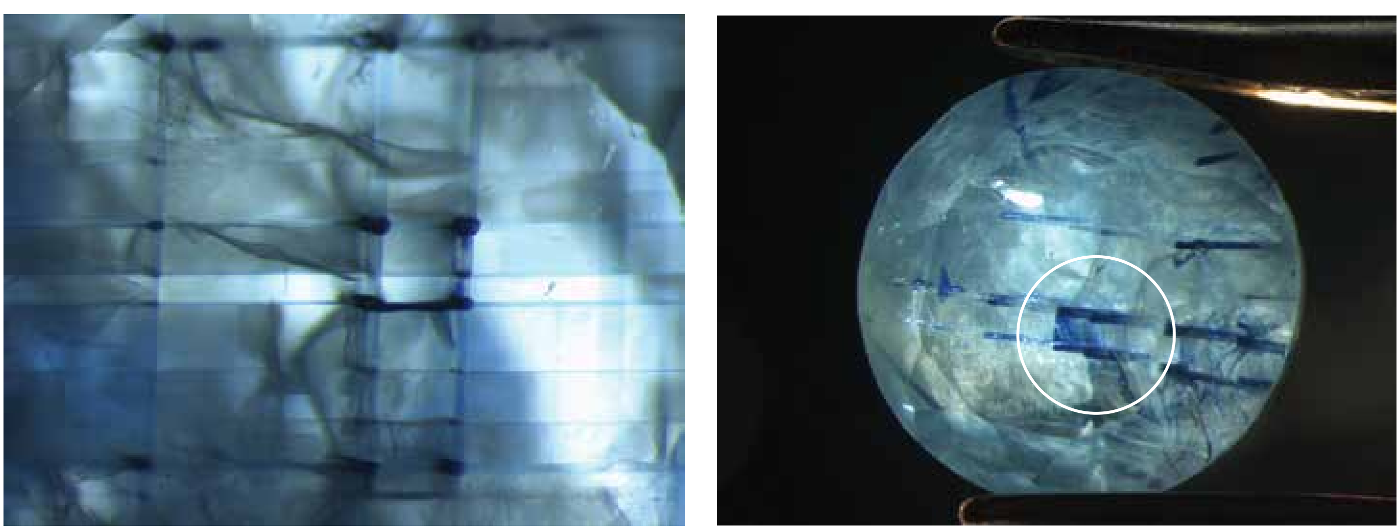

Figure 12. The propagation of vitreous substances through Rose channels and along polysynthetic twin planes. Highlighted by a white circle is the area where a chromophore-containing substance has penetrated between two channels along a twin plane.

- *The third phenomenon* concerns the modification of inclusions belonging to other mineral species.

As an example, gemologists are familiar with the white rounded inclusions modified by heat, known as "snowballs."

These are often inclusions of urano-pyrochlore [(U,-Ca,Ce)$_2$(Nb,Ta)2O$_6$(OH,F)] or urano-thorianite [(U,Th)O$_2$] that were melted and modified by the high temperature. When such inclusions are observed, only a white layer corresponding to the miscibility zone containing chemical rearrangements between the inclusion compounds and the corundum matrix can be seen (Figure 13); that is to say, compounds that are not clearly identified and are of a totally artificial (and synthetic) nature.

Another example of remarkable modifications of inclusions concerns zircon (Wang W. et al., 2006). Some deposits, particularly the one in Ilakaka, Madagascar, produce sapphire, which almost always contain large amounts of zircon. When these stones are heated at high temperature, the zircons ($ZrSiO_4$) are ultimately transformed into two immiscible liquids, one consisting of silica, and the other of zirconium oxide, according to: [ZrSiO4 + high T°] → [SiO_2 + ZrO_2] (Figure 14). Generally, high temperature treatments dramatically change the appearance and sometimes the composition of the inclusions present in corundum, and some are even destroyed by the process if they get in direct contact with the flux.

Furthermore, the formation of vitreous substances occurs that extends from an inclusion into the newly formed discoid fracture and that causes the healing of the fracture, via the production of artificial and synthetic compounds, during cooling process (Figure 15).

Figure 13 (Three images). "Snowballs" which show the zone of miscibility of chemical rearrangements between the inclusion compounds and those of the corundum.

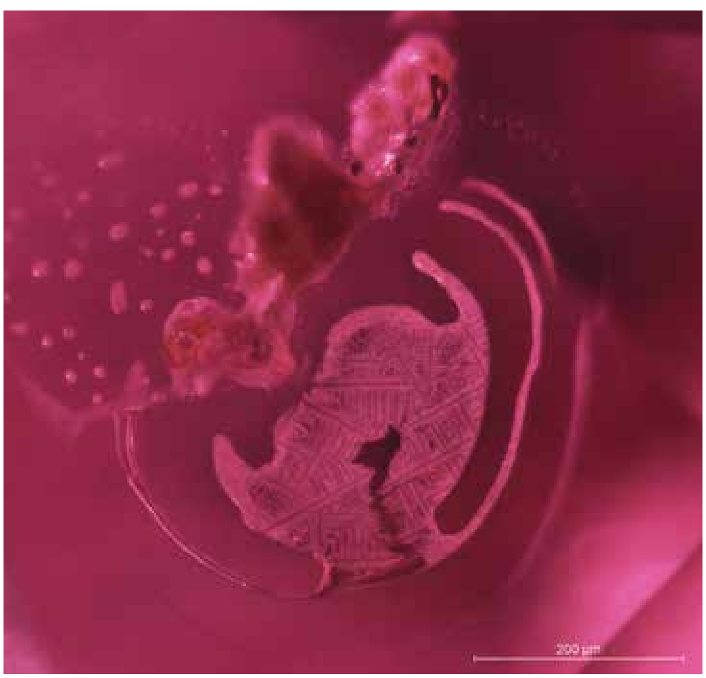

Figure 14. Dissociated zircon ($ZrSiO_4$) after heat treatment at high temperature. Up: melted silica (SiO_2); below: zirconium oxide (ZrO_2).

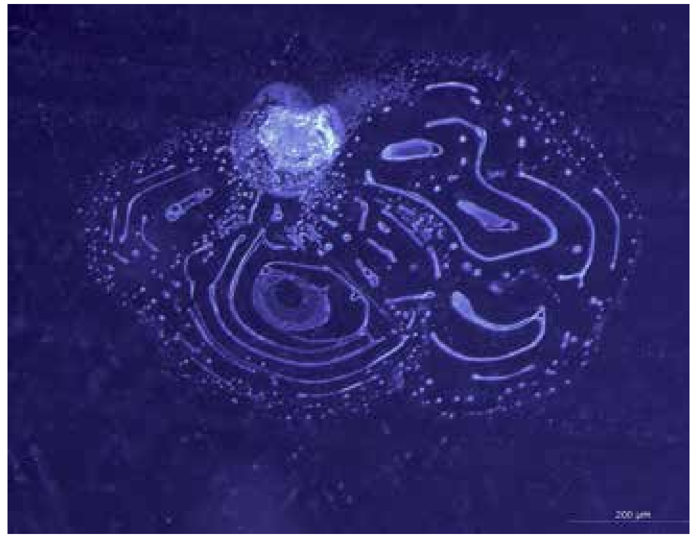

Figure 15 (Three images). Discoid fractures healed during cooling, with formation of synthetic and artificial compounds. (Micrographs courtesy of Patthamaporn Sukkasem)

Discussion

These few examples nicely demonstrate that high-temperature heat treatment—usually associated with a fluid (flux) environment—dramatically alters corundum. This alteration includes both the modification or creation of colors, and the modifications of inclusions that involve the creation of different types of artificial/synthetic compounds, generally made up of the constituents of the host gem. Finally, when these heat treatments are performed in flux, vitreous residues are very frequently present in the gems.

For these reasons, it seems necessary and appropriate to differentiate lower temperature and high-temperature heat treatments in the wording on the gem testing reports, since the effect of the treatments is very drastically different from one to the other.

In absolute terms, it can be considered that corundum treated traditionally (at lower temperature) should have a higher value than those treated at high temperature, with or without flux, since the modifications induced are less severe at lower temperature than at high temperature. Comparing the starting material of heat treated stones of identical appearance, the vast majority of the traditionally (lower temperature) treated corundum had a far better color and/or transparency than the great majority of those treated at high temperature.

Taking into consideration the respective intrinsic nature of the treated corundum (i.e. the very likely original appearance prior to treatment) with the two treatment methods, we have created an arbitrary scale on the Y-axis (from 0 to 10) using relative units of "quality/value." These are two criteria intimately linked used to compare their intrinsic nature and of course their real market value.

Currently, the description of the heat treatment on gemological reports uses the same wording for both and does not indicate importance of the treatment. As it is obvious that high temperature heat treatment is much more severe than traditional heat treatment at lower temperature, we thus consider it insufficient and inappropriate to put all heat-treated corundum into the same nomenclature.

We therefore propose two different wordings: "Indication of thermal treatment" (+ TE, TE1, TE2, etc.) and "Indication of thermal treatment at moderate temperature" (+ MTE) (Figures 16 and 17).

If it is necessary to locate this rank on the scale proposed by the LMHC (Laboratory Manual Harmonization Committee), which has done very good work in harmonizing the terminology on the gemological reports of its members (CGL, CISGEM, DSEF, GIA, GIT, Gübelin Gem Lab, SSEF), we could propose a position between the two current grades "No indications of heating" and "Indications of heating" (no residues) (Figure 18).

This proposed new grade concerns rubies and sapphires showing:

- Moderate analytical indications of heat treatment (FTIR, Imaging under various UV excitation, etc.).

- No indications of significant structural changes of inclusions by microscopic observation.

- No indication of presence of vitreous substances or during the heat treatment.

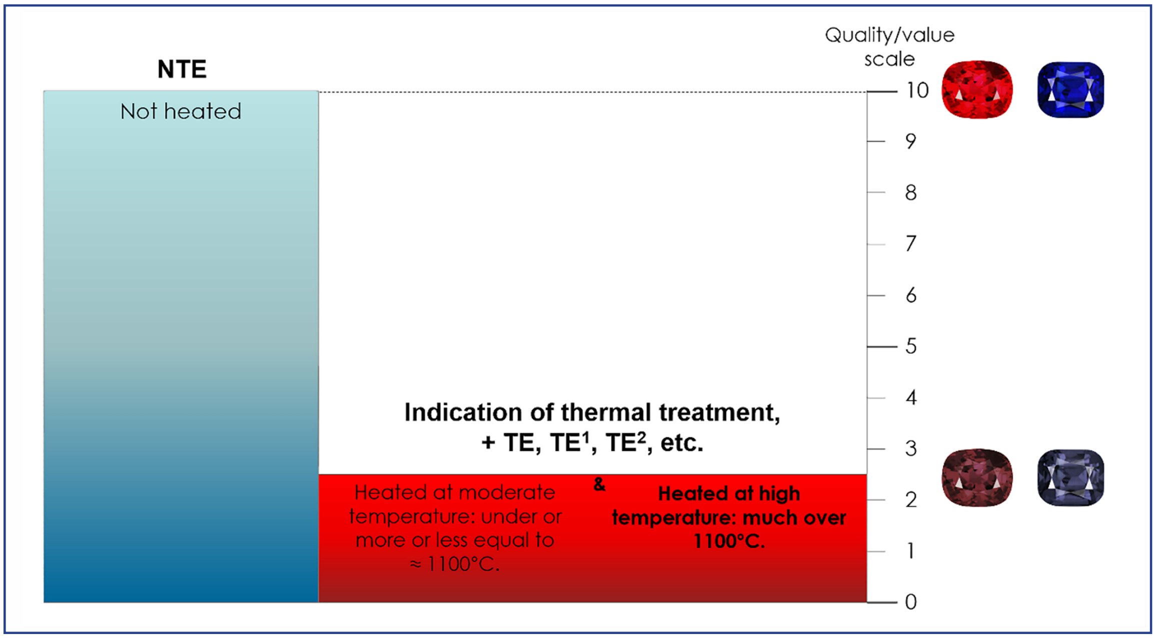

Figure 16. Relative scale "quality/value" of the two types of treatments resulting from the common wording disclosure of heat treatment. The gems are either unheated or heated with or without glassy substances, at high or low temperature.

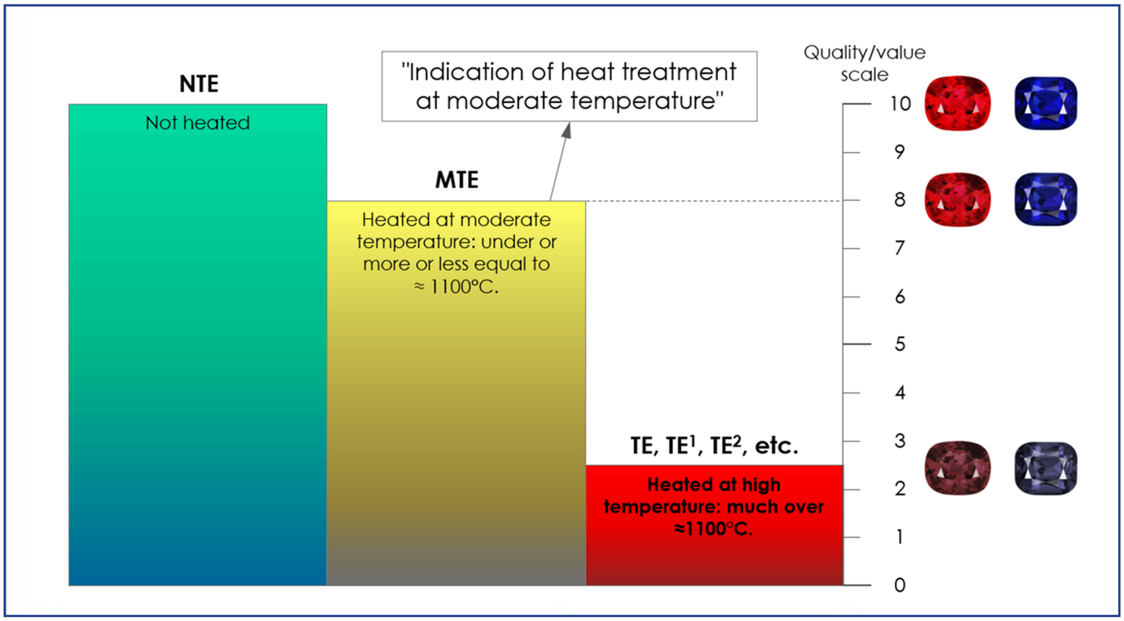

Figure 17. Relative scale "quality/value" of the two types of treatments with two different wording for the disclosure of the heat treatment. The gems are either unheated or heated at moderate temperature in a dry environment, either heated at high temperature (with or without vitreous substances).

Condition →	No indications of heating	Indications of heating (no residue)	Indications of heating with residues in fissures				
Report Alpha numeric →	NTE	TE	TE1	TE2	TE3	TE4	TE5
Report Text →	No indications of heating	Indications of heating	Minor residue in fissures		Moderate residue in fissures		Significant residue in fissures

Condition →	Indications of heating with residues in cavities		
Report Alpha numeric→	C1	C2	C3
Report Text→	Minor Residue in cavities	Moderate Residue in cavities	Significant Residue in cavities

No indications of heating	Indications of heating with minor modifications (without residues)	Indications of heating (no residue)
NTE	MTE	TE
No indications of heating	Indications of heating at moderate temperature	Indications of heating

Figure 18. Position of the proposed new grade on the LMHC table (LMHC Information Sheet #1, Corundum with residues from the heating process present in healed fissures and/or cavities).

The laboratories GGTL Laboratories Switzerland and Liechtenstein, as well as the laboratory of the Asian Institute of Gemological Science, founding members of GemAlliance, decided to propose a new mention disclosing the heat treatment at moderate temperature: *Indications of heat treatment at moderate temperature, MTE.*

Obviously, it is not possible to determine this for all rubies and sapphires because, for certain cases, the detection of the heat treatment can be somewhat problematic, depending on the chemistry of the stones concomitant to the absence of inclusions. Nevertheless, the majority of the stones submitted to a well-equipped laboratory with experienced technicians, gemologists and scientists can be categorized according to the proposed scale.

Looking at the enormous difference of the effects of the two types of heat treatment conditions, we consider this to be a relevant factor for the gem market, which would permit assessing a different/higher value to a traditionally heated corundum than to one that has been treated at very high temperature.

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References

Bacchi, E. (2013). *Al-Bīrūnī's Canon Masudicus: Arabic sources for the issue of the Persian intercalations*. Ph.D in History.

Carra de Vaux, B., 1921, *Les Penseurs de l'Islam*, 5 vols. Geuthner, Paris.

Grobon C., 2003, *La cornaline en* Égypte *Ancienne—une approche gemmologique*, Mémoire de Master en Egyptologie, Faculté des Lettres, Université de Genève. 85p (+ annexe 37p).

Said H.M., 1989, Abu-'r-Raiḥān Muḥammad Ibn-Aḥmad al-Bīrūnī. (≈ 1042-1045), English translation of *kitAb al-jamAhir fi ma'rifat al-jawAhir (The Book Most Comprehensive in Knowledge on Precious Stones):* Al-Beruni's Book *on Mineralogy*. Pakistan Hijra Council, Islamabad, Pakistan, 354 p.

Suter, H. et alii, 1920-21, Beiträge zur Geschichte der Naturwissenschaften. LX. Über al Bîrûnî und seine Schriften, in: *Sonderabdruck aus den Sitzungsberichten der physikalisch-medizinischen Sozietät in Erlangen* Bd. 52.53 (1920-21), Erlagen, pp. 55-96.

Wang, W., Scarratt, K., Emmett, J. L., Breeding, C. M., & Douthit, T. R. (2006). The effects of heat treatment on zircon inclusions in Madagascar sapphires. *Gems & Gemology*, 42(2), 134.

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