

Henry A. Hänni

## 個人簡歷

9. Jan. 1945 born in Basel, Switzerland

1976 Diploma in Gemmology (FGA) London

1980 dissertation in mineralogy, doctoral thesis on beryl from Swiss Alps.

1980 gemmologist and scientific staff at SSEF,

SSEF Swiss Gemmological Institute, the Swiss gem trade lab.

1990 director of the SSEF Swiss Gemmological Institute in Basel.

1996 professor for gemmology at Basel University

regular teaching and supervising university students

1998 member of IMA International Mineralogical Society,

gemstone section, delegate for Switzerland

Publications over 100 papers on gemstones and pearls, analytical

techniques, detection of gemstone treatments, in English, German and French

numerous talks and education courses in various countries

1945年1月9日 生於瑞士巴索

1976年 FGA

1980年 礦物學論文，博士論文為瑞士阿爾卑斯山的綠柱石

1980年 瑞士寶石研究所（SSEF）及瑞士寶石鑑定室的科學家及寶石學家

1990年 巴索瑞士寶石研究所的主任

1996年 巴索大學寶石學的教授，負責一般教學及大學生管理工作。

1998年 國際礦物協會IMA會員，寶石組，瑞士代表。

發表超過100篇以上的寶石及珍珠分析技巧，檢測寶石的處理。並以英文、德文及法文

發表，在各國發表無數的評論和教育課程。

# Observations on treated ruby and sapphire

Prof. Dr. H. A. Hänni, SSEF Swiss Gemmological Institute, Basel, Switzerland

The occurrence of natural ruby and sapphire does not consist only of high quality stones alone. Top quality is rare and a necessity exists to enhance the medium and lower quality volume of stones, which is much more important volume wise. When we discuss the improvement of quality we could first define what quality means. Size, weight, colour, transparency and mechanical stability are important quality factors. Many stones are found to be small, with an unpleasant colour, not transparent or brittle due to many fractures. The small size can only be improved by adding synthetic corundum and using the small natural bit as a seed (as done earlier e. g. by Chatham). Recent treatments concentrate more on enhancing the colour, transparency and mechanical stability. In the following I try to give you an overview on techniques of treatment and also on characteristics of identification.

## Increasing transparency

Fractured stones are often treated with colourless oil, wax or sometimes resin. The organic fissure filling media will be absorbed by the fractures and replace the air that was in the gaps before. By this treatment the fissures become barely visible. Fissure filling may also be performed with inorganic fillers, mainly glass. To bring glass into the fractures, a heat treatment is necessary. It depends of the kind of treatment temperature and additive what temperature is necessary. We have encountered fillings from lead glass that flows at lower temperatures (ca. 700 °C). The appearance of lead glass filled fissures is easy to recognise and quite characteristic. The fissure planes contain gas bubbles and the glassy fillings produces bluish to orange flashes under magnification (Fig. 1). We think that there is no difference in the value of a stone, whether it is fracture filled with epoxy, borate glass or lead glass. It should there not be pressure on the laboratories to identify what the composition of the filler would be. Such stones are any way in the category of treated (fracture filled) stones.

A high heating often leads to a clarification of a stone that is cloudy by fine rutile inclusions (Fig. 2). The thermal treatment, when performed at temperatures over about 1200°C, will usually leave clear traces on fissures and on included minerals. For the trade it is important to know whether a ruby or sapphire is heated or not. The laboratory must thus identify heating and put on the test report. Not always a heating is clearly identifiable, especially when low temperature was used. Often IR spectra and laser tomography furnish valuable information for a decision.

## Adding colour

Some material is found colourless or light in tone. When such stones contain a regular pattern of fissures, these can be stained in attractive colours. Impregnation of fissured corundum is often done with red or blue dye. A similar procedure is also used to provide a



stronger colour to emeralds (see Indian joban oil). Such dyeing is performed with the dye dissolved in oily substances (Fig. 3). This means that the colour is not permanent and may run out of the fissures. Identification is easily done with an acetone wetted cotton swab that will immediately show the dyeing.

More permanent addition of colour is possible by diffusion treatment. At high temperature, usually 1800°C, colour-giving elements that are brought on the surface of pre-cut stones will travel through the surface into the stones. So far elements such as Ti, Cr and Be were successfully diffused into corundum. Ti enables the blue colour provided that bivalent iron is sufficiently in the stone. This process was frequently applied in the mid 1980's. The diffusion of Cr produces pink to red corundum. Because of the large size of the Cr ion, the penetration is not deep although considerable time may be offered. The identification is possible in diffused light or in immersion: the layer of blue or red colour only affects a thin layer of a few tenths of a millimetre. Facetted edges appear saturated and the girdle area is also deeper in colour. The small size of Be on the other hand allows a deep penetration, 3mm stones were found to be completely coloured without showing a rim. Be is providing a yellow colour component. The diffused new colour can overlay an already existing colour, pink sapphires may end up as orange ones after a Be diffusion (Fig. 4). One should, however, not forget that there are older heated yellow sapphires, characteristically produced around 1985, whose colour is due to the oxidising heat treatment alone, no diffusion from outside is involved.

Today the identification of Be is no longer a problem, as it was at when the application of Be-diffusion was new. Analytical instruments (LA-ICPMS, SIMS, GEM-LIBS) are sensitive enough to identify low level Be concentrations in an almost destruction free process (Fig. 5).

Rumours are around that also blue sapphires would be treated with beryllium. The small number of stones tested for Be did not give a clear image. Probably Switzerland is not the place where many treated stones turn around. The Sri Lankan sapphires with colourless rims (Fig. 6) were free of Be, and we concluded that a malfunction of the furnace was the reason for the effect. Of course small amounts of Be might also come from Be polluted furnaces that were used before for yellow and orange sapphires by Be diffusion. Some typical inclusions consisting in small whitish rings do not yet prove that they occur always together with a Be diffusion treatment (Fig. 7).

#### **Modifying colour**

When a blue sapphire is too light or even milky and white, a heating in reducing atmosphere may create a blue colour. At high temperature, usually 1800°C, possible inclusions of rutile TiO<sub>2</sub> are dissolved and the Ti may now act as a colour-giving element together with Fe (Fig. 8). This process is well described by Nassau (1981) and Hughes (1997). It may be called an internal diffusion since the chromophore elements are contained in the stone and move during the treatment to form effective chromophore pairs. Another process of diffusion may also create asterism when Ti is allowed to form rutile needles. The precipitation may

occur between 1300 and usually 1400°C and the resulting dense pattern of needles in three dimensions creates a 6-rayed star on a cabochon-cut stone.

Colour modifications are a regular treatment with pink sapphires and rubies. Here we may have a problem of identification because some changes of colour are possible at quite low temperature (from 800°C on). Usually the pink or red colour of the natural stone has a bluish shade, which represents a sapphire component. This blue colour component can be destroyed with an oxidising heat treatment. The same treatment is also used to lighten up some blue sapphires that are too dark. During heat treatments the stones are commonly coated with borax, to prevent chipping, as some treaters say. Heating with additives brings us to the next category of treatments.

#### **Fissures filled with glassy substances**

Today the large majority of rubies is heated and contains artificial residues from the treatment (Fig. 9). When borax is used to heat ruby or sapphire, at elevated temperature the sodium borate will transform into a melt whose character is very aggressive. The melt does dissolve silicate minerals, oxides and also the surface of corundum. The originally pure borax melt enriches its chemistry by the digested minerals that may accidentally be encountered on the surface or in cracks and fissures. When it gets a high amount of alumina due to corrosion of corundum surface, this amount of alumina will to a great extent be ex-solved upon cooling. It is this amount of exsolved alumina that makes an artificial healing of fissures possible. Many heat-treated rubies have fissures which are partly re-crystallised and healed by the described process. Some of the former borax melt is locked in the partly healed fissures as a so-called glassy residue (Fig. 9). With a scanning electron microscope such changes in the structure can be studied and the material can be analysed (Fig. 10). This foreign material in the gemstone is not much appreciated, and on test reports it must be mentioned. A number of gemmological laboratories of high standard have got an agreement of how to express the treatment situation. Harmonisation is achieved about the different degrees of foreign material in a stone. On a report, the treatment situation might be described in the following way: Indications of heating with minor residues in fissures. There may be an alphanumeric or text description for the amount of residues: TE1 - TE5, or minor - moderate - significant (Fig. 11). The details are written down in the Laboratory manual of the harmonisation committee that includes the major gemmological laboratories AGTA, CISEGEM, GAAJ, GIA-GTL, GIT, Gübelin Gem Lab, and SSEF.

It becomes clear that many stones are not simply heated because with the same heating process a number of changes can happen. The application of borax allows the healing of the fissure, increasing the mechanical stability (by re-crystallisation of the fissures). The heat may shift the colour to a better end and also dissolve turbid areas in a stone. That means that in the gemmological laboratory, when we observe signs of heating, we check also for diffusion treatment and glassy residues. A few times we have encountered heat-treated synthetic stones that contained healing fissures with glassy residue. The Verneuil synthetic stones were quench-crackled and the fissures re-crystallised with borax flux to imitate natural heated stones!



## References

- Emmett, J. & Douthit, T.R. (1993) Heat treating sapphires of Rock Creek, Montana, *Gems & Gemology*, Vol. 29, 4, Winter, 250-272.
- Emmett, J. (1999) Fluxes and the heat treatment of ruby and sapphire, *G&G*, Fall, 90-92
- Europäisches Patentamt (2001): Glass composition and method of filling microcavities in natural minerals. EP 1 069 087 A1
- Günther, D., Bleiner, D., Guillong, M., Hattendorf, B. & Horn, I. (2001) Access to isotopic and elemental composition and their distribution in solid materials by laser ablation inductively coupled mass spectrometry. *Chimia*, 55, 778-782.
- Häger, T. (2001) High Temperature Treatment of Natural Corundum. Proc. Intl. Workshop on Material Characterization by Solid State Spectroscopy: The Minerals of Vietnam, Hanoi, April 4 - 10.
- Hänni, H. A. (1982): Characteristics of heat-treated and diffusion-treated corundums. *Swiss Watch and Jewelry Journal* No. 5/82, 573-577.
- Hänni, H. A. (1992): Identification of fissure-treated gemstones. - *J. Gemm.* 23, 4, 201-205
- Hänni, H. A. (1993): Identification of fissure-treated gemstones. - *J. Gemmol. Assoc. of Hong Kong*, Vol. XV, 29-33.
- Hänni, H. A. (1998) Short notes on some gemstone treatments. *J. Gemmol. Assoc. Hong Kong*, 20, 44-52
- Hänni, H. A., & Krzemnicki, M. S. (2004): a new analytical instrument to analyse beryllium in orange sapphires. *J. Gemmol. Assoc. Hong Kong*, XXV, 93-95.
- Hänni, H. A., & Krzemnicki, M. S. (2004): a new analytical instrument to analyse beryllium in orange sapphires. *J. Gemmol. Assoc. Hong Kong*, XXV, 93-95.
- Hughes, R. W. (1984) Surface repaired rubies. *Austral. Gemmol.* 15, 8, 279-280.
- Hughes, R. W. (1997) *Ruby & Sapphire*, RWH Publishing, Boulder, CO, USA
- Johnson, M. L. & McClure, S. (2000) An investigation of fracture fillers in Mong Hsu rubies. *Gem Trade Lab Notes*, *Gems & Gemology*, Fall, XXXVI, 257-259.
- Kane, R. E. (1984) Natural rubies with glass filled cavities. *Gems & Gemology*, 20, 4, 187-199.
- Krzemnicki, S. M., Hänni, H. A. & Walter, R. A. (2004). A new method for detecting Be-diffusion treated sapphires: Laser-induced breakdown spectroscopy (LIBS). *Gems & Gemology*, Winter, 2 - 10.
- Nassau, K. (1981) Heat treating ruby and sapphire: Technical aspects. *Gems & Gemology*, 17, 3, 121-131
- Nassau, K. (1984) *Gemstone Enhancement*. (Introducing fingerprints in synthetic ruby, p. 41/42 & 117), Butterworths, second edition,
- Peretti, A. (1995) Rubies from Mong Hsu, spring, *Gems & Gemology*, 2-26
- Peretti, A. & Günther, D. (2002) The color enhancement of fancy sapphires with a new heat treatment technique (part A): Inducing colour zoning by internal migration of color centres. *Contributions to gemology*, 1, May 2002

- Scarratt et al. (1984) Glass filling in sapphire, J. Gemmol. 20, 4, 203-207
  - Schmetzer, K., Bosshart, G. & Hänni, H. A. (1983) Naturally colored and treated yellow and orange-brown sapphires. J. Gemmol. GB, XVIII, 7, 607-621.
  - Shida, J. (1999) Laser Tomography: A new powerful method to identify natural, synthetic and treated stones. Case study of corundum. J. Gemmol. Soc. Japan, 20, 79-98
  - SSEF (1998) Standards and Applications for Diamond Report, Gemstone Report, Test Report, SSEF Swiss Gemmological Institute, Editor.
  - Themelis, T. (1992) The heat treatment of ruby and sapphire. Gemlab Inc., Houston TX
- Address of the author: Prof. Dr. H. A. Hänni, SSEF Swiss Gemmological Institute, Falknerstrasse 9, CH - 4001 Basel, Switzerland
- e-mail : gemlab@ssef.ch

### Figure captions



圖一  
鉛玻璃填充紅寶常有著氣泡和紫藍色閃光。  
由於是低溫的處理，鈦針狀物將是完整的。  
(照片提供H. A Hänni, SSEF)

Fig. 1

A lead glass filled ruby with characteristic gas bubbles and purplishblue flashes. Due to the low treatment temperature, rutile needles would be found intact.

Photo © H. A. Hänni, SSEF



圖二  
來自緬甸莫谷的熱處理紅寶，當中的鈦絲狀物早就被溶解，以使得寶石更透明。點狀的線指出原來存在有鈦針狀物。  
(放大約30倍照片，提供H. A Hänni, SSEF)

Fig. 2

A heated Ruby from Mogok, Burma, where the rutile silk has been dissolved in order to make the stone more transparent. Dotted lines indicate the former presence of rutile needles. Magn. approx. 30x, Photo © H. A. Hänni, SSEF





圖三  
有機染料易於被溶劑如丙酮鑑別出來，在這顆刻面的珠子裂隙中被填充著紅色的油。  
(照片提供H. A Hänni, SSEF)

Fig. 3  
Organic dyes are easily identified with a solvent like acetone.  
In this faceted bead all fractures were filled with red oil. Photo © H. A .Hänni, SSEF



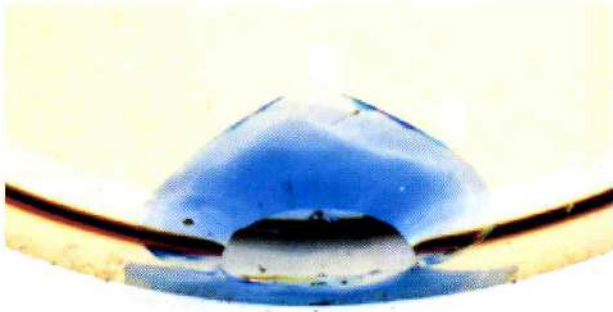
圖四  
鉍擴散處理的淡粉紅剛玉，和新的黃色的加入比重液中顯示黃色邊緣。  
(照片提供H. A Hänni, SSEF)

Fig. 4  
Beryllium diffusion treated light pink sapphires with new yellow colour added in immersion showing yellow rim. Photo © H. A .Hänni, SSEF



圖五  
SSEF Gem LIBS系統用來分析低量鉍元素集中在切割好的寶石上。分析作用常在寶石腰部進行。  
(照片提供H. A Hänni, SSEF)

Fig. 5  
The SSEF GemLIBS system to analyse low beryllium concentrations on cut stones.  
Analyses are usually performed on the girdle. Photo © H. A. Hänni, SSEF

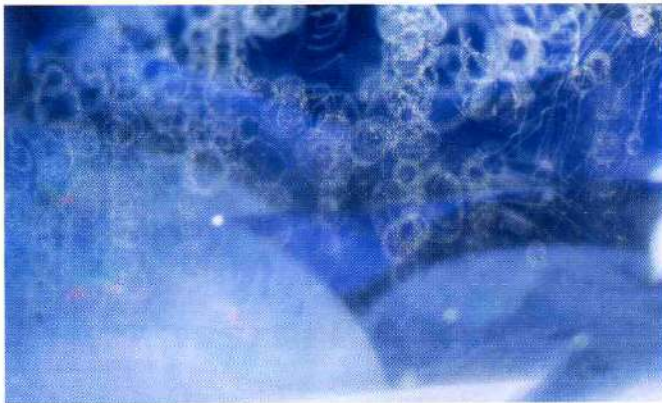


圖六

來自斯里蘭卡熱處理藍寶有著一無色的邊緣平行於刻面表面。去色作用有可能是由於後氧化作用，在其過程中，後來以LA ICPMS證實並無Be的存在。（照片提供H. A Hänni, SSEF）

Fig.6

Heat-treated blue sapphire from Sri Lanka with a colourless rim parallel to the faceted surface. The de-colourisation is most probably due to a late oxygen wave in the process. The absence of beryllium has been proved by LA ICPMS. Photo © H. A. Hänni, SSEF



圖七

如灰塵造成的圈圈及軌跡圖形，被視為是藍寶石鉍擴散處理的訊號。（GAJJ Tokyo提供）

Fig.7

A pattern of dust rings and dust tracks, which is regarded as a signal that the blue sapphire might have been Be diffused. Picture courtesy GAJJ Tokyo



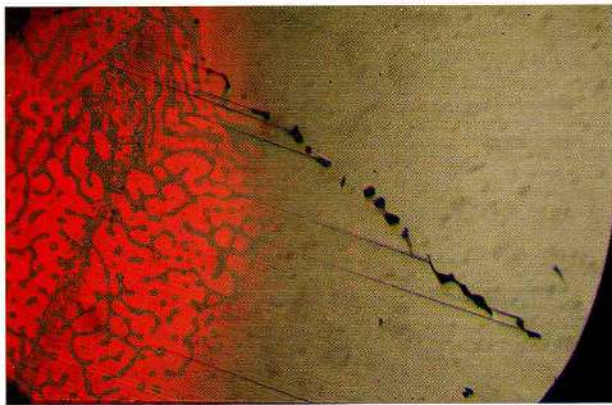
圖八

熱處理藍寶和原來是二氧化鈦的針狀物，現在成線狀的白點。內部鈦的擴散，造成藍色雲狀物，致色的鐵鈦成對形成了。（大約30倍，照片提供H. A Hänni, SSEF）

Fig.8

Heat treated sapphire with ex-rutile needles, now lines of white spots. The internal diffusion of Ti creates blue clouds where coloring Fe/Ti pairs were formed. Magn. approx. 30x, Photo © H. A. Hänni, SSEF



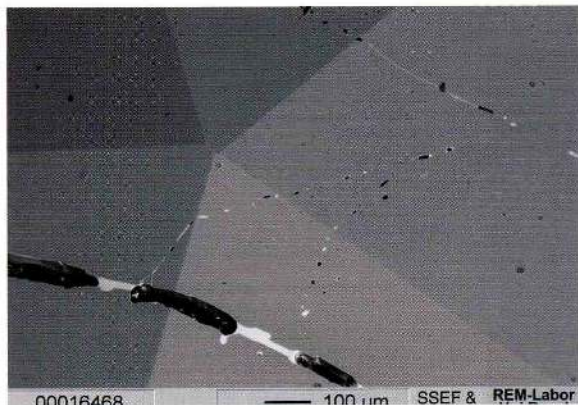


圖九

這圖片顯示出圖一紅寶中部分的構造。充填裂隙到達寶石表面，在原先裂隙侵入表面（大概20倍）之前，比較大的空洞是可看見的。  
（照片提供H. A. Hänni, SSEF）

Fig. 9

The pictures show part of the structures from the ruby of Fig. 1. Where the healed fissure reaches the surface, relatively coarse voids are visible before the former fissure dips under the surface (approx. 20x). Photo © H. A. Hänni, SSEF

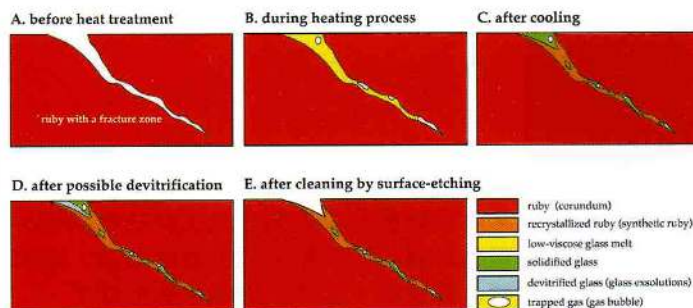


圖十

熱處理紅寶（灰色）和玻璃助熔劑殘餘（亮）及氣體和縮小氣泡（黑色）。原先的裂紋仍然清晰可見，同時在玻璃殘餘之間形成新的（合成）剛玉。掃描電子顯微鏡的圖片，圖片的寬度大約1.5mm。  
（巴索大學電子顯微鏡實驗室）

Fig. 10

Scanning electron microscopic (SEM) picture of a heat-treated ruby (grey) with glassy flux residues (bright) and gas and shrinking bubbles (black). The traces of the former fissures are clearly visible, also the newly formed portions of (synthetic) corundum between the glassy residues. Width of the picture is approx. 1.5 mm. Picture © SEM Laboratory of Basel University.

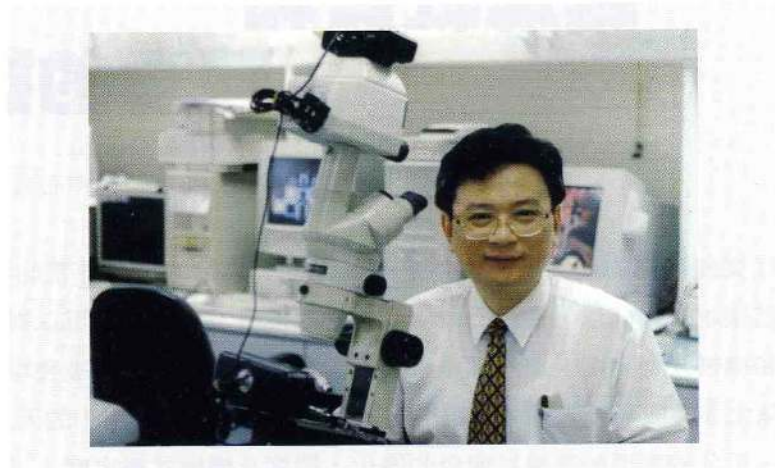


圖十一

圖示裂隙充填紅寶熱處理在助熔劑協助下產生的過程。這合併處理的目標是在迫使裂隙癒合，除了造成很小部分的合成紅寶外，玻璃質助熔劑的殘留物，和最後脫玻化作用產物落入在寶石中。  
（圖片提供SSEF）

Fig. 11

Diagram displaying the processes occurring with flux assisted heat treatment of fissured ruby. Main target of the combined treatment is the forced healing of the fissures. Besides of the creation of minute portions of synthetic ruby small residues of glassy flux and eventually devitrification products are trapped in the stones. © SSEF



吳舜田

## 個人簡歷

吳舜田，中國文化大學地質系畢業，美國愛荷華州立大學地質研究所深造，並至GIA取得G.G資格。曾擔任南非持有鑽石公司市場及鑑定部經理，負責遠東區銷售業務。並曾擔任GIA校友會會長，高雄寶石礦物研究學會創會長。目前為高雄國際寶石鑑定研習中心負責人，並曾任教於中國文化大學地質系及輔仁大學流行設計系。也為經濟部、財政部相關單位授課培育有關人員。

其重要著作有「實用鑽石分級學」、「世界重要寶石產業資源系統之建立」、「寶石礦物學實習」、「鑽石鑑定分級實習」、「珠寶奇緣」等。迄今發表的寶石相關文章已百餘篇，國外知名刊物如GIA的Gem & Gemology 及法國寶石協會的專刊都曾登載其文章。更值得一提的是曾和Prof. Hänni及袁心強院長一起發表「藍玉髓的玻璃模仿品」於英國皇家寶石協會的Journal of Gemology。

包括中華民國寶石協會、台灣金銀珠寶同業協會、台北市、台南市、高雄縣等商業同業公會都聘吳老師為顧問以肯定他的專業及對寶石業的貢獻。