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Gem corundum deposits in Vietnam

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Abstract: Since 1983, gem-quality rubies have been recovered from the Luc Yen and Quy Chau mining areas in northern Vietnam. Since 1991, 'basaltic'-type blue-green-yellow ('BGY') sapphires have been mined in southern Vietnam. This article briefly reviews the history and geology of these different areas and shows the importance of marble and basalt-type deposits. Other types of corundum occurrences are found in amphibolite, pegmatite, gneiss and metasomatite. The gemmological, chemical and isotopic characteristics of these different types of corundum are described.

The most notable features of rubies contained in marbles are that many crystals have blue colour zones, and inclusions of rutile, anhydrite and salts. The primary fluid inclusions are composed of carbon dioxide and hydrogen sulphide with native sulphur and diaspore daughter minerals. Sapphires from placers in basalts are characterized by inclusions of columbite, pyrochlore and baddeleyite. The trace element contents of corundums allow distinction of rubies in marbles from sapphires in basalts and metamorphic rocks. Rubies have high chromium ($0.54 < \text{Cr}_2\text{O}_3 < 0.66$ wt.%) and low iron ($0.01 < \text{FeO} < 0.07$ wt.%) contents. The geological origin of Vietnam corundums can be clearly determined from the isotopic composition of their structural oxygen, i.e. $\delta^{18}\text{O} = 21.0 \pm 0.9\text{‰}$ for rubies in marbles and $\delta^{18}\text{O} = 6.6 \pm 0.4\text{‰}$ for sapphires in basalts.



Figure 1: (a) Gem-quality rubies from the Quy Chau deposit in Vietnam. The samples range from 1.36 to 6.21 ct. (b) Two stars rubies from Tan Huong deposit (13.67 and 15.86 ct, respectively). Photographs by Pham Van Long.

Introduction

Gem corundums have been known in Vietnam since 1983. During the last ten years, Vietnam has become a significant ruby and sapphire-producing country in south-east Asia (Figure 1).

In this paper, the term ruby is used for Cr-bearing corundum including pink and purple coloured crystals.

Development of the gem industry is due to the important programme of geological field mapping maintained by the Vietnamese government. These geological investigations resulted in the first discovery of rubies in marbles and in the development of prospecting programmes leading to the discovery of corundum-bearing placer deposits. At the same time, thousands of local peasants searched for ruby and sapphire and in 1991, alluvial sapphires related to basalts were found in Southern Vietnam. Scientific investigations of the genesis of these deposits led to several publications (Kane *et al.*, 1991; Dao *et al.*, 1996; Dao and Delaigue 2000, 2001; Garnier *et al.*, 2002; Pham Van, 1999, 2002) and international workshops (Hofmeister *et al.*, 2001). The aim of this paper is to present a detailed review of the main types of gem corundum deposits in Vietnam within their geological framework. Their gemmological and mineralogical properties are compared with the intention of finding features which would allow one to identify Vietnamese corundums after removal from their geological environment.

Discovery of gem corundum in Vietnam

Rubies and sapphires have been found and mined in many places in Vietnam (Figure 2). Rubies and blue sapphires are now exploited in the northern part of the country, respectively



Figure 2: Map of Vietnam showing the location of basalt-hosted and other types of gem-corundum sources. There are more details of areas indicated in Figures 3 and 8.

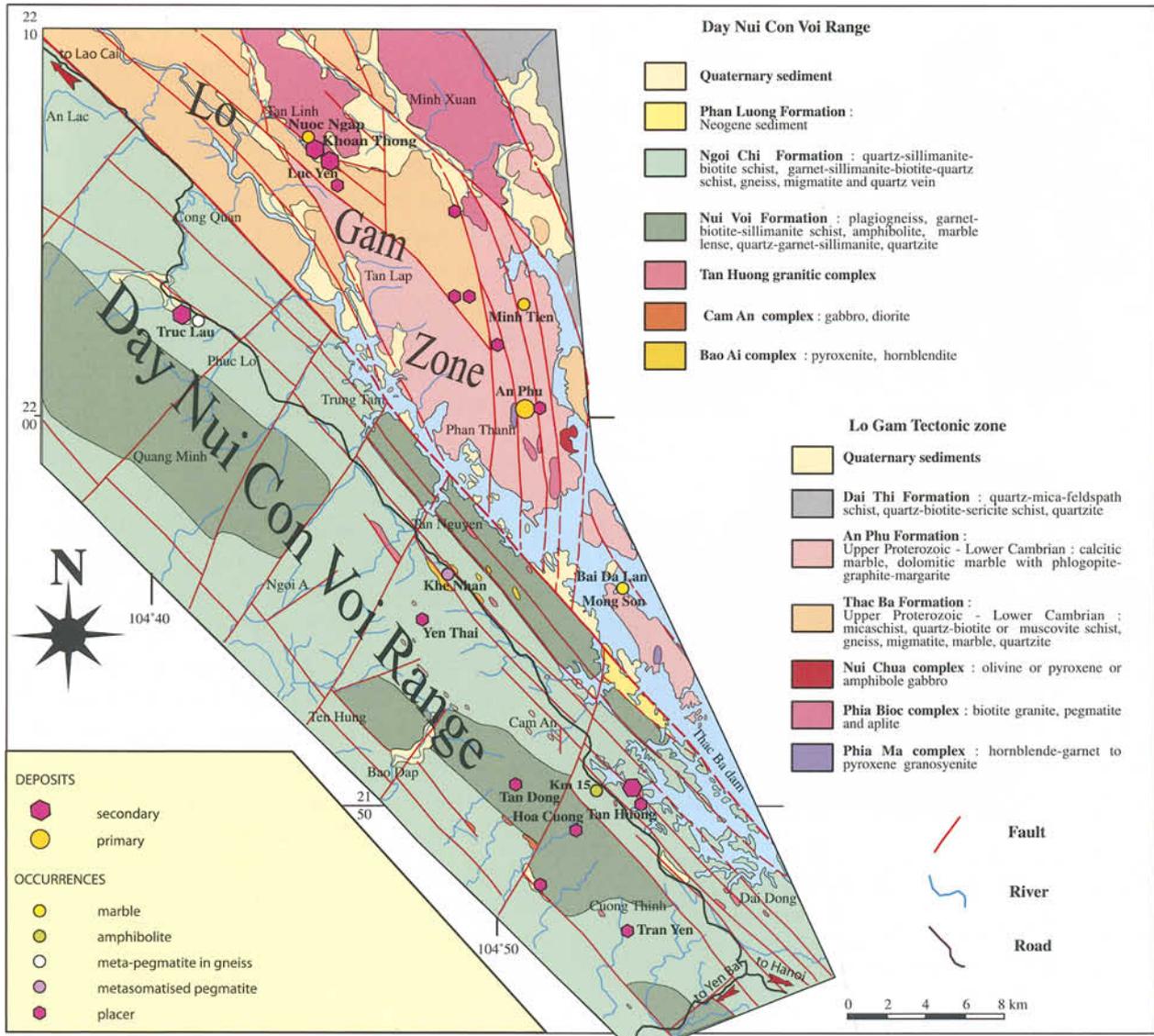


Figure 3: Geological map showing the major tectonic domains of the Red River shear zone with locations of the main corundum occurrences and deposits (adapted from Phan Trong and Hoàng Quang, 1997).

in the Yen Bai province from the Luc Yen and Yen Bai mining districts and in the Nghe An province from the Quy Chau deposits. In southern Vietnam, the corundums commonly include blue-green-yellow sapphires called 'BGY'-sapphires by Sutherland *et al.* (1998a), which are now exploited in the Dak Nong and Binh Thuan deposits in the Dak Lak and Lam Dong provinces respectively.

In 1983, ruby was discovered by a geologist during field mapping in the An Phu area (Luc Yen district), 270 km north of Hanoi (Figure 3). This corundum occurrence was investigated in detail and mining started in 1987. In March 1988, Vinagemco

(Vietnam gemstones company) was set up by the Vietnamese Government to control the mining activity. In the same year, Vinagemco and Boonsing-Hang Mining Company from Thailand established a joint-venture with the aim of mining the Khoan Thong placer (Figure 3). From November 1989 to March 1990, the company recovered about 244 kg of gem-quality corundums. Almost all the production was cut and traded in Bangkok.

From 1990 to 1994, thousands of independent miners swarmed over the area and some new gem-quality corundum occurrences were found in places such as Minh Tien, Nuoc Ngap, Hin Om, Khau

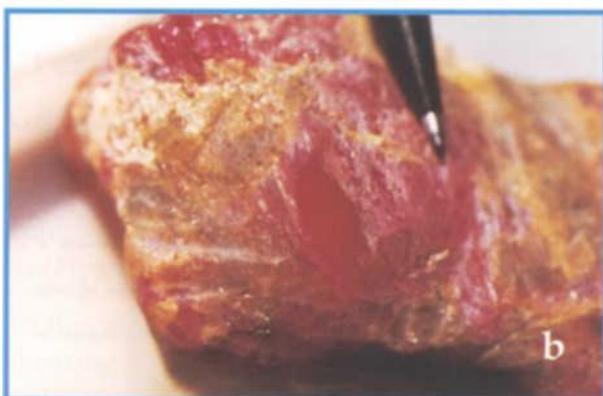


Figure 4: (a) Tan Huong ruby rough and one cabochon cut from ruby found in the Tan Huong placer located on the Day Nui Con Voi metamorphic range (northern Vietnam). (b) Ruby boulder from Tan Huong placer mine. Photographed in 1998 by Gaston Giuliani.

Nghiem, Vang Sao, May Thuong and May Ha (Figure 3). At the same time rubies, sapphires and other minerals already sorted in placers were found, and with corundum crystals from the marbles, were brought to the gemstone market in Luc Yen.

Between 1994 and 1995, rubies were discovered in the Tan Huong and Truc Lau areas (Figure 3). These two mines are now directly managed by the Yen Bai Gem and Gold Company. Boulders of corundum up to 1 kg with zones of gem quality ruby are common in these placers (Figure 4a, b). In April 1997, two huge ruby crystals were found in the placer of Tan Huong with weights respectively of 2.58 and 1.96 kg. These two stones of very high quality have been declared State treasure and can be displayed but not sold.

The Quy Chau mining district is located about 120 km north-west of the city of Vinh (Nghe An Province), about 300 km south of Hanoi (Figure 2). In 1988, rubies and blue sapphires were discovered in concentrates from alluvial deposits. Between 1989 and 1990, 10,000 miners migrated to the region from all over Vietnam. The illegal mining activities were outside the control of the Nghe An People's Committee and hundreds of people died when, in July 1990, there was a collapse in the Ho Ty mine (Billion hill mine, Figure 5a).

In addition to the monthly auctions of the rubies held by the provincial government, thousands of carats of rough rubies of high gem-quality have been sold to Thai traders. In an auction in 1996, a 56 ct rough ruby was sold for US \$562,000. In 1996, the management of the Quy Chau deposits was taken over by the Nghe An Gem and Gold Company. Since then, hundreds of kg of rubies have been recovered. Production was first displayed for auction on September 15, 2001, and since July 2002, weekly auctions have been held at the head office in Hanoi of the Vietnam National Gem and Gold Corporation (which organized the sale of gems mined by the Nghe An Gem and Gold Company).

Since 1991, 'BGY' sapphires have been found in many places in southern Vietnam. The first discovery occurred in Dak Nong (Dak Lak province) and the second in Di Linh (Lam Dong province). Very dark blue sapphires have been found also in Ham Thuan (Binh Thuan province). These sapphires range from transparent to translucent or opaque, but the percentage of transparent gem quality material has been very low. From 1992 to 1995, the mine was exploited by local peasants and hundreds of kg of sapphires were illegally mined and sold. In 1996, the Tay Nguyen Gem and Gold Company was created to manage the mining of the deposits. The company carried out a detailed investigation and the mine opened in 1997. Although thousands of kilograms of sapphires were mined, they were mostly of very low gem quality and the mining activities in Tay Nguyen ceased finally in 2000.

Figure 5: The Quy Chau mining area. (a) View of the famous Billion hill mine which became a lake after the end of its exploitation in July 1990. (b) The Doi San placer in 1998. (c) View of the new dressing plant in October 2001. (d) The ruby-free skarn in Quy Chau consisting of alternating bands of green calc-silicates and brown to black phlogopite in marble.



Materials and methods

The corundums used for this study were purchased by the authors during different field seasons at the mine sites and consist of faceted and rough rubies and sapphires. Optical properties of the samples were obtained by standard gemmological methods. Internal features were examined with a gemmological microscope, a Hitachi 2500 scanning electron microprobe (SEM) and the inclusion compositions obtained by energy-dispersive spectrometry (EDS). Rubies and sapphires from different geological environments and covering the full colour range of the samples were analysed by a CAMECA Camebax SX 50 electron microprobe with wavelength-dispersive spectrometers (WDS). The operating conditions of the electron microprobe were: an accelerating voltage of 10 kV, beam current of 10 nA, collection time of 10 s for major elements, and 20 kV, 100 nA, 30 s respectively for trace elements. The 'BGY' sapphires were also analysed by a semi-quantitative EDXRF method using a spectrace 5000 EDXRF system (Stern, 1984). The compositions of selected fluid inclusions and solid inclusions were obtained using a Labram Jobin-Yvon Raman microspectrometer. The excitation radiation was the 514.5 nm line of an Ar-ion laser (2020 Spectra-physics) that delivered 10-20 mW at the sample surface. The oxygen isotopic composition of rubies and sapphires was analysed following a modification of the laser-fluorination technique described by Sharp (1990).



Gem corundum deposits

Two main types of gem-corundum deposits are found in Vietnam: rubies and sapphires in metamorphic rocks (northern Vietnam) and 'BGY'-sapphires in basalts (southern Vietnam).

Corundum in northern Vietnam

The Yen Bai and Luc Yen mining districts

1. The primary corundum occurrences of Yen Bai occur within the high-grade metamorphic gneisses forming the Day Nui Con Voi range (*Figure 3*), which extends to the southeast from the Ailao Shan in Yunnan (China). This range is bounded by lateral strike-slip faults forming the major Cenozoic geological discontinuity in East Asia known as the Ailao Shan-Red River shear zone.

The Day Nui Con Voi range is composed of high-grade metamorphic rocks with sillimanite-biotite-garnet gneisses, mica schists with local successions of marbles and amphibolites. The deformation occurred under amphibolite facies conditions (pressure = 4-6.5 kbar and temperature = 600-750°C, Phan Trong *et al.*, 1998; Leloup *et al.*, 2001). Corundum occurs (A) as grey to blue sapphires in garnet-sillimanite-mica schists and gneisses containing leucosome and leucocratic granitoid dykes (Truc Lau gneisses and Khe Nhan metapegmatite); (B) in amphibolites transformed by metasomatism into biotite schists with some layers containing centimetre-sized grey to dark-grey sapphires (north of Tan Huong mine, Km 15 occurrence; *Figure 3*); (C) as rubies in large marble boudins intergrown with



Figure 6: (a) Partial view of the Khoan Thong placer worked from 1989 to 1996 in the Luc Yen area. In the middle distance are karst hills showing the classical karst erosion patterns of marbles. (b) Part of the washing plant at the Tan Huong mine. (c) The primary Bai Da Lan ruby deposit hosted in marbles viewed from the Thac Ba dam. (d) Typical fresh section of banded marbles characterized by alternating bands of white and dark marble consisting of carbonates, phlogopite and graphite. All photographs by G. Giuliani in 1998.

Figure 7: Mineral features of gem corundum deposits in the Luc Yen mining district. (a) Ruby in a marble from the Min Thien mine. Calcite and phlogopite mica (dark brown) are the gangue minerals in the language of mining. Size of the corundum up to 1.5 cm. (b) Rubies at the gem market in Luc Yen town. These and rough crystals of coloured sapphires have been recovered from placers. The biggest crystal is around 4 cm long. (c) A 3 cm long crystal of ruby from Luc Yen associated with flakes of graphite (black) in a white marble. (d) Red spinel and green amphibole (pargasite) in marble from the primary An Phu ruby deposit. (e) A bipyramidal corundum from the gem market of Luc Yen. Photographs by G. Giuliani.



gneiss, mica schist and amphibole (Tan Huong drill cores). These marbles represent previous limestones interleaved with mudstones, which were sheared and metamorphosed during the tectonic activity along the Red River shear zone.

The gems occur in placer deposits along the shear zone such as at Tan Huong (Figure 6b) and Truc Lau. The paleoplacer of Truc Lau consists of 10 m of sediments overlying bedrock. The rubies and blue sapphires are contained in a gravel layer, 5 m thick, overlain by 3.5 m of Quaternary sediments and 1-1.5 m of soil. In 2002, up to two boulders (1-2 kg) of ruby were recovered every month in the paleoplacer. In the Tan Dong placer, assemblages of blue sapphire-margarite-plagioclase are the remnants of metasomatized pegmatites. Blue trapiche-like sapphires are found together with rubies and grey to pale blue sapphires in the placers of the Yen Bai area.

2. The ruby and sapphire deposits of Luc Yen occur in moderate-to-high temperature recrystallized marble units of Upper Proterozoic-Lower Cambrian age in the

eastern side of the Red River shear zone: the Lo Gam zone (Figure 3). Primary ruby occurs (A) as crystals disseminated within marbles (Figure 7c) with phlogopite (Figure 7a), dravite, margarite, pyrite, rutile, spinel, edenite, pargasite (Figure 7d) and graphite (Bai Da Lan, An Phu, Minh Tien, Nuoc Ngap, Luc Yen and Khoan Thong mines); (B) in veinlets associated with calcite, dravite, pyrite, margarite and phlogopite (An Phu mine); (C) in fissures with graphite, pyrite, phlogopite and margarite (Bai Da Lan mine, Figure 6c; Minh Tien region, Figure 6d). Gravels form placer deposits in karst topography (Figure 6a) and in alluvial fans in the Luc Yen valleys with blue, pale yellow and colourless sapphires, rubies and trapiche rubies (Figure 7b), and bipyramidal grey to brown sapphires (Figure 7e).

The Bâ Be sapphire occurrence

The Bâ Be sapphire occurrence is located in the Bac Kan province, 320 km north of Hanoi (Figure 3). It is close to the granite of Nui Chua and the gabbro-monzonite of Hoang Tri. The colourless to pale blue sapphire occurs in a pegmatite composed of quartz, K-feldspar and muscovite which intrudes schists and marbles.

The Quy Chau mining district

In this area, located 200 km south of the Red River shear zone, the Bu Khang dome (Figure 8) consists of a broad antiform of Paleozoic and Mesozoic sedimentary and meta-sedimentary rocks overlying a core of mica schists, granitoid rocks, paragneisses and orthogneisses (Jolivet *et al.*, 1999). The north-eastern part of the dome is limited by the major extensional Cenozoic shear zone of Quy Chau where the corundum deposits are located.

Rubies and blue sapphires have been mined since 1987 in the placer deposits of Doi Ty, Doi San, Mo Coi and Quy Hop (Figure 8). The corundums occur mainly in the Quy Chau area (A) as very rare (and non-economic) rubies disseminated in marbles associated with pyrite and graphite, and (B) in placers which form the economic deposits (Figures 5a, b, c). In the Doi San and Doi Ty area, granitic intrusions linked with the injection of

pegmatites are responsible for calcium-magnesium-rich skarns in the surrounding marbles, amphibolites, gneisses and mica schists (Figure 5d). Ruby has not been found in either the skarn or the pegmatite and its genesis remains unclear. Blue sapphire is very rare.

Corundum in southern Vietnam

In the Dak Nong area, sapphires are found in weathered residual soils lying above alkali basalt flows and also in placer deposits in the river and stream fans (Figure 9a). Generally, the alluvial corundums resemble megacrysts found *in situ* in the basalts, but in Dak Nong, 'BGY'-sapphires have not been found in the host rocks. Their colours range from dark blue, through blue, green to yellow and some are colourless. The crystals occur as broken fragments but remains of the original habits are often present. Prisms and bipyramidal crystals may be up to 15 mm long and 2-4 mm wide.

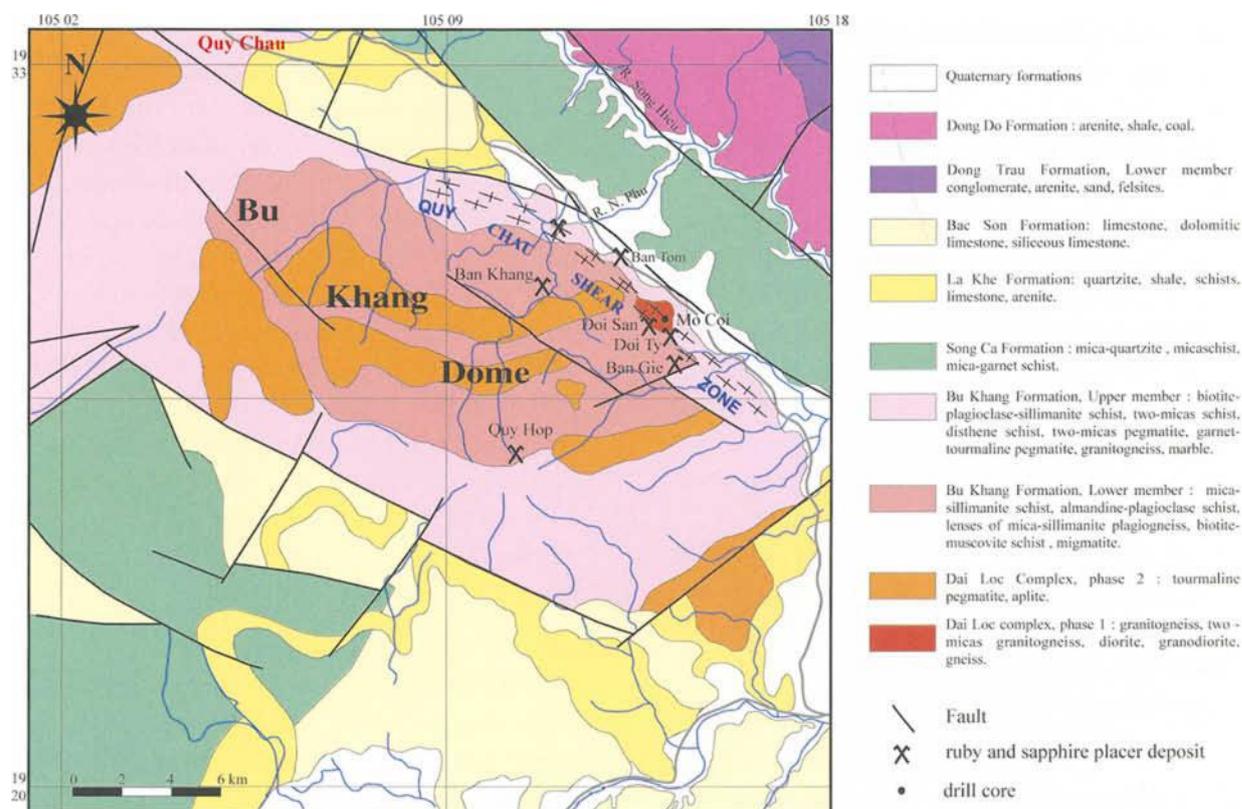


Figure 8: Geological map of the Bu Khang dome showing the location of the ruby and sapphire deposits of the Quy Chau and Quy Hop mining districts (map modified after Jolivet *et al.*, 1999).



Figure 9: The 'BGY'-sapphire deposits related to basalts in southern Vietnam. (a) View in 2001 of the Dak Nong placer deposit located in alluvial fans. (b) Corundum crystal found in alluvial soils above a basalt. (c) Alluvial corundum from the Bin Thuan area showing reflective surface attributed to high temperature corrosion which is indirect evidence of magma transport (small dots on the crystal surface). (d) Barrel-shaped habit of a deep-blue sapphire originating from the Binh Thuan area. Photographs by G. Giuliani.



In the Binh Thuan area, the sapphires have barrel-shaped habits (Figures 9b, d), and are blue to very dark blue. Some crystals show rounded glassy-looking margins indicating high-temperature corrosion, indirect evidence of transport in a magma (Figure 9c). In the Da Ban area (Binh Thuan province) megacrysts of dark-blue sapphires are sometimes found within alkali-basalts.



Gemmological properties

Optical characteristics

Colour: Corundums from the Quy Chau deposits range from moderate to high saturations of purplish red to purplish pink for ruby to blue for sapphire. In contrast, the corundums from the Yen Bai and Luc Yen deposits show all tones from red to pink (ruby), and grey to blue and colourless to pale yellow sapphire. The rubies from Luc Yen are usually less saturated than those from Quy Chau.

Corundum from southern Vietnam is commonly dark blue or greenish-blue and less commonly yellowish-blue. A small proportion of the corundums from the Binh Thuan deposit possess a very dark tone and yield deep blue cut stones.

Refractive index (RI): The RIs of rubies and sapphires were obtained in the Centre for Gem and Gold Research and Identification (VCCG) using a Gem Duplex II instrument and all results were in the range 1.762 to 1.770, birefringence 0.008, which are normal for corundum.

Specific gravity (SG): SGs were determined by the hydrostatic weighing method. The samples from Quy Chau (faceted and rough stones) gave values between 3.94 and 4.05; those from Luc Yen have values between 3.92 and 4.01. In both deposits, the SGs of the blue sapphires tend to be higher than those of red and pink rubies. Compared to the rubies and sapphires from Luc Yen and Quy Chau, most 'BGY'-sapphires from southern Vietnam gave SG values between 3.97 and 4.00 but some had SGs up to 4.08, which are exceptionally high for corundum.

UV luminescence: All the red and pink samples from Quy Chau and Luc Yen appeared red when exposed both to long-wave (366 nm) and short-wave (254 nm) ultraviolet radiation. The Quy Chau crystals tended to show stronger fluorescence than those from Luc Yen. Interestingly, some blue sapphires from Luc Yen (Khoan Thong area) also appeared red under both long- and short-wave ultraviolet radiation.

Internal characteristics

Twinning: The samples from Quy Chau and Luc Yen commonly show both lamellar and polysynthetic twinning.

Growth features: Straight and angular parallel growth features are quite common in rubies and sapphires from Luc Yen and Quy Chau. Other investigations (Kane *et al.*, 1991) have described a swirl-like growth effect that is common in Burmese rubies and coloured sapphires from Vietnam.

Colour zoning: Some samples in this study show colour zoning. The colour zones range in size from narrow to broad areas generally parallel to the largest flat face of the sample. In many samples, dot-like and band-like colour zones are present. These are easily seen by immersion in methylene iodide, and even a blue zone can be distinguished against a background of red and pink zones.

The sapphires from southern Vietnam usually show alternation of colour bands indicating consecutive growth layers of light blue, colourless, greenish-blue or yellowish-blue.

Solid inclusions: The different solid inclusions identified in Vietnamese corundums are listed in *Table I*. The most common mineral inclusions found in the Luc Yen and Quy Chau rubies are calcite, dolomite, rutile, diaspore and phlogopite. These minerals are also found in the marbles. SEM studies also confirmed the common occurrences of crystals of anhydrite and other salts (of Na-Cl; Ca-Cl; K-Cl). In contrast to the sapphires originating from basalts, rubies do not contain any columbite, ilmenite, pyrochlore or baddeleyite inclusions. In rubies, rutile is characteristically present as short needles and also as twinned plate-like crystals; less commonly, it appears as transparent orange brown or opaque crystals trapped along the growth zones. Zircons are found in corundums from both types of deposit and they have allowed indirect dating by the U/Pb method. The calculated ages of corundum formation are between 38 and 34 Ma for the Luc Yen and 34 to 27 Ma for the Quy Chau ruby deposits (Garnier *et al.*, 2002), and 6 to 1 Ma for the Dak Nong sapphires (Garnier *et al.*, 2004).

Fluid inclusions: Three main types of fluid inclusions were recognized in the rubies from Luc Yen and Quy Chau on the basis of their relative chronology (Hoàng Quang *et al.*, 1999; Giuliani *et al.*, 2003 a, b).

1. Type A fluid inclusions (primary) are 20 to 200 μm long and occur as isolated or oriented clusters from the core to the rim of the crystals (*Figures 10a, b*); they are best observed in longitudinal sections. Type A inclusions are commonly two-phase fluids (liquid and vapour carbon dioxide phases) but some are associated in a single growth zone with single phase carbon dioxide-rich inclusions. The volumetric fraction of the carbon dioxide-rich liquid in the carbon dioxide-rich phase shows degrees of filling (Flc) ranging between 60 and 100% (*Table II*).

These inclusions display two kinds of morphology: (i) euhedral negative crystals with polygonal or square outlines found in planes parallel to the basal pinacoid c (0001); (ii) flat or broad tubes, some with a cap of a mineral inclusion. Diaspore is found either

Table 1: Solid inclusions identified in Luc Yen and Quy Chau rubies from marbles and in sapphires from basaltic deposits.

Solid Inclusions	Luc Yen rubies	Quy Chau rubies	Basaltic sapphires
Anatase	2	2	
Andalusite		1	
Anhydrite	8	8	
Anorthite		1	
Apatite	6	6	1
Baddeleyite			1
Boehmite	6	6	
Brookite	2	2	
Calcite	6	6	
Columbite			5
Corundum	2	2	
Diaspore	2	2	
Dolomite	4	4	
Goethite			5
Graphite	2	2	
Halite	8	8	
Hematite	2		
Hercynite	2		
Ilmenite			5
Limonite	7	7	
Margarite	4	4	5
Monazite	7		
Muscovite	2	2	
Nepheline	7	7	
Nostrandite	6		
Phlogopite	6	6	
Plagioclase			5
Pyrite	4	4	
Pyrochlore			5
Pyrrhotite	6		
Rutile	6	8	
Titanite	7	7	
Na, Ca, K-Cl salts	8	8	
Spinel	1	1	
Tourmaline	2		
Zircon	2	2	1
Zoisite		2	

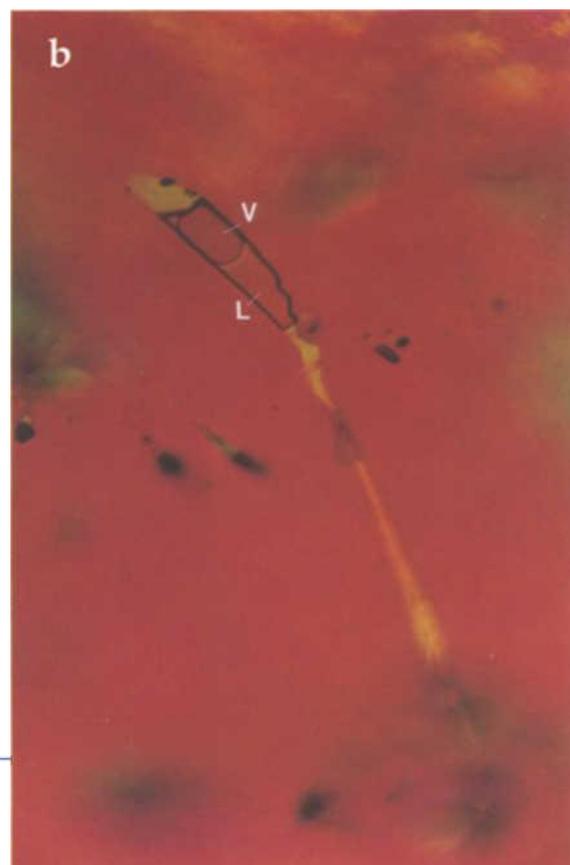
1: this study; 2: Pham Van (1999); 3: Pham Van (2002); 4: Hoang Quang *et al.* (1999); 5: Smith *et al.* (1995); 6: Kane *et al.* (1991); 7: Dao *et al.* (1996); Dao and Delaigue (2000, 2001); 8: Giuliani *et al.*, (2003 a, b)



2. Type B fluid inclusions (pseudo-secondary). These appear as small clusters or isolated in crystals and are mainly related to small intra-granular fractures. Planes of fluid inclusions are related to micro-cracks and subsequent fractures healed during crystal growth. At room temperature, Type B inclusions are single or two-phase (liquid and vapour carbon dioxide phases) with degree of filling (Flc) between 40 and 100%. Inclusions may range in size from 20 to 125 μm and display various shapes resembling negative crystals. Some of the negative crystals are capped by mineral inclusions (mainly calcite) at one end and contain calcite, rutile and daughter crystals of diaspore and native sulphur - all identified using Raman spectrometry.
3. Type C fluid inclusions (secondary). These occur along healed fracture planes which cross-cut several growth zones and show an elongated (Figure 10a) or rounded-morphology. Some inclusions are irregularly or crescent-shaped and they are interpreted as products of textural equilibration.

Figure 10: Photomicrographs of fluid inclusions in ruby from the Luc Yen area. (a) Isolated primary fluid inclusion (labelled I), 100 μm long, containing a liquid phase composed of CO_2 , H_2S and COS . Trail of secondary inclusions (labelled II) crosscutting the ruby crystal. (b) Primary two-phase fluid carbonic inclusion containing a liquid (L) and vapour (V). The size of the inclusion is 80 μm long. Crossed nicols. Photographs by G. Giuliani.

as very rare solid inclusions present in fractures or as isolated prismatic crystals with a length up to 15 μm . Also, diaspore occurs in the fluid-inclusion cavities as an invisible film, 2-3 μm thick, coating the wall of the whole inclusion cavity. The film was identified from its Raman lines at 331 and 448 cm^{-1} , respectively (Figure 11). Native sulphur is present at room temperature, as very rare vitreous globules in the inclusions but it is commonly nucleated from an invisible thin layer during laser irradiation. S_8 was identified from its characteristic Raman peaks at 220 and 462 cm^{-1} (Figure 11).



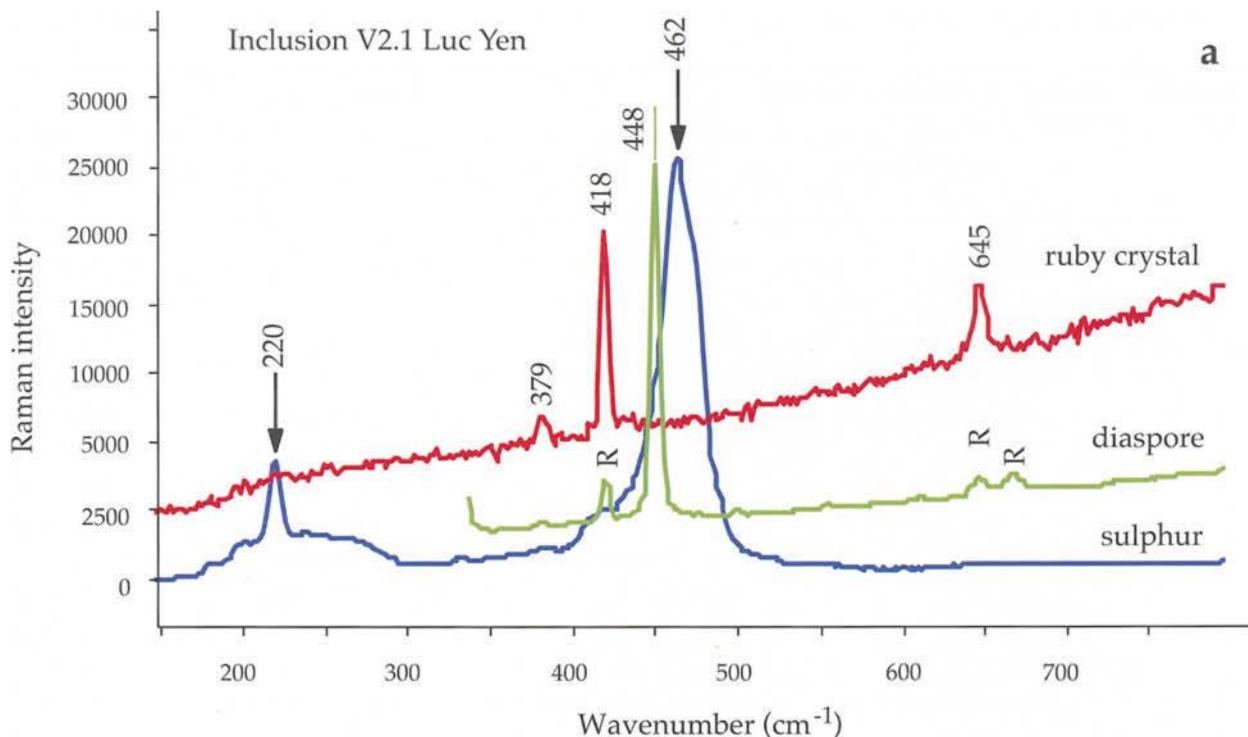


Figure 11: Raman spectra of the different phases analysed in fluid inclusion cavities in ruby. (a) Diaspore and amorphous sulphur detected in the same fluid inclusion (Luc Yen sample). The peaks of sulphur are obtained during irradiation of the liquid phase. The diaspore spectrum was obtained from the invisible diaspore film, 2-3 μm thick, which coats the wall of the fluid inclusions cavity. (b) Raman spectra of the volatile phase found in a primary fluid inclusion in a Quy Chau ruby. The components are CO_2 , H_2S , COS , S_8 and diaspore as found for the fluid inclusions in Luc Yen rubies. R denotes peaks due to the ruby matrix.

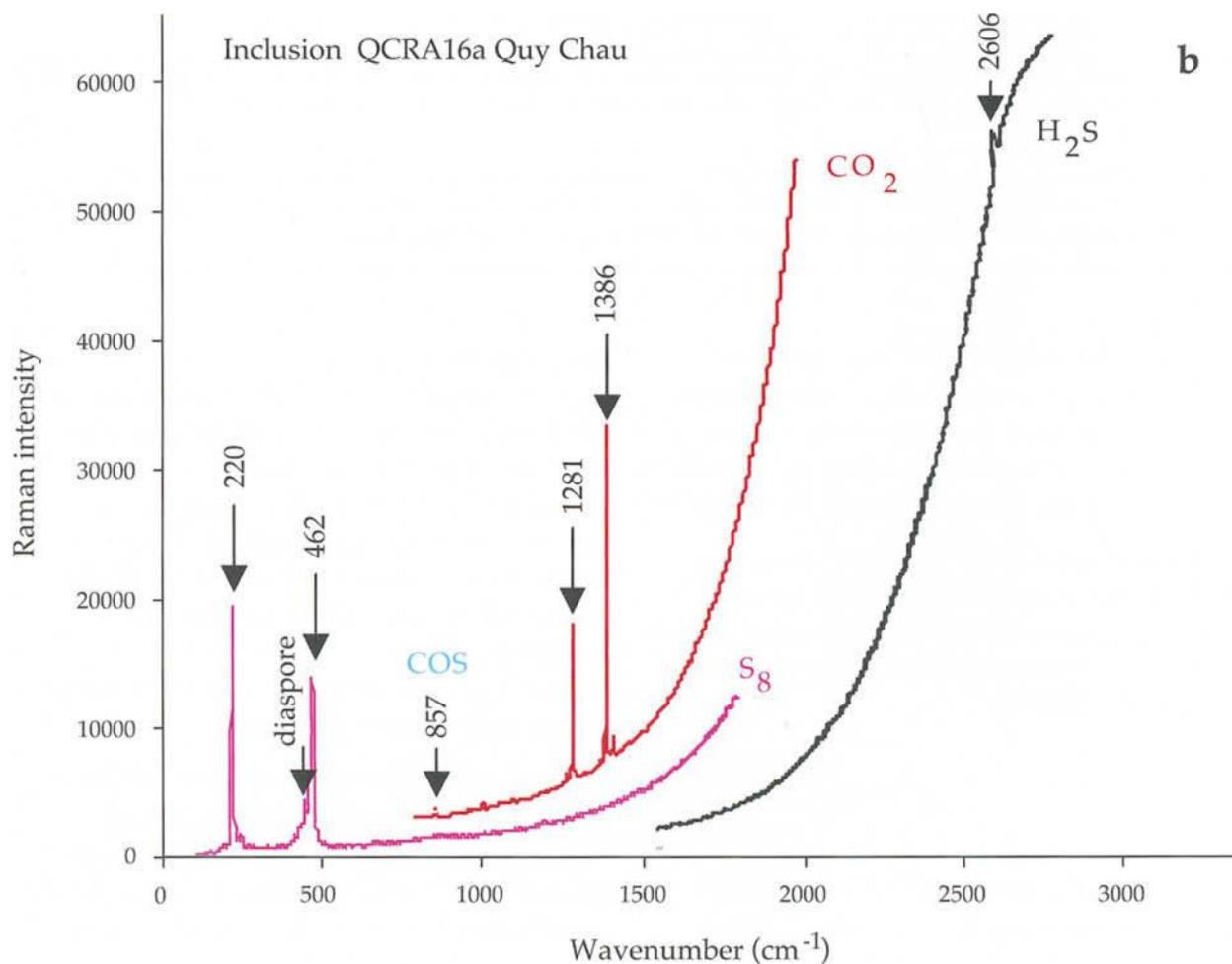


Table II: Microthermometric and Raman data for fluid inclusions in rubies from Luc Yen and Quy Chau.

Inclusion type	Sample number	Microthermometry			Raman data							
		Flc	TmCO ₂	ThCO ₂	CO ₂	H ₂ S	COS	native sulphur	diaspore	rutile	dolomite	calcite
Luc Yen ruby mines												
A	V.5.1	100	-61.3	16.5L	87.9	12.1	+	+				
A	V.5.1.1	100	-61.8	15.1L	90.4	9.6		+	+			
C	V.5.2	100	-61.0	13.9L	91.2	8.8	+	+	+			
A	V.1.1	100	-60.1	22.4L	93.8	6.2	+	+	+			
C	V.1.2	75	-59.7	29.3L	92.0	8.0	+	+				
A	V.1.4	90	-60.2	23.5L	93.3	6.7	+	+				
A	V.2.1	65	-62.0	33.9L	86.5	13.5	+	+	+			
B	V.3.2	100	-57.8	22.8L	+	+						
B	V.4.1	40	-62.6	28.8V	+	+		+	+			
A	LY399B-10	40	-64.3	36.4L	76.8	23.2	+	+	+			+
A	LY399A2	80	-63.7	26.7L	84.7	15.3	+		+		+	
A	LY399B-1	90	-65.0	31.8L	87.0	13.0	+	+	+			+
An Phu ruby mine												
C	V.6.2	85	-59.9	28.5L	96.1	3.9	+	+	+			
Knoan Thong ruby mine												
A	K.1.1	90	-59.9	30.9L	96.7	3.3	+					
Quy Chau ruby mine												
A	QCRA16a	70	-64.7	30.5L	88.5	11.5	+	+	+			
A	QCR2A-11a	60	-65.2	20.8L	85.5	14.5	+	+			+	
A	QCR2A-11b	60	-63.7	34.0L	90.9	9.1		+				
A	QCRB-2.1	80	-66.7	34.9L	90.8	9.2	+	+	+			

NB: Inclusion types A, B and C see text. Microthermometry Flc: volumetric fraction of CO₂ rich liquid in carbon-dioxide-rich phase. TmCO₂: melting temperature of CO₂ in °C. ThCO₂: homogenization temperature of CO₂; V vapour, L liquid.

Raman data compositions of CO₂ and H₂S in mol.%; + means presence detected. The mole fraction of each gas was calculated from the formula given by Dhamelincourt *et al.* (1979); the relative cross sections of Raman scattering are those given by Schrötter and Klöckner (1979), i.e. CO₂ = 1.5 and H₂S = 6.4.

Their size ranges from 10 to 100 µm. At room temperature, they contain one or two-phases and the volumetric fraction of the carbon dioxide-rich liquid in the carbon dioxide-rich phase is between 35 and 100%.

Raman analyses of the three types of fluid inclusion revealed that the carbon dioxide phase is always composed of major CO₂, with smaller amounts of H₂S and COS (Figure 11, Table II).

Geochemical properties

Chemical composition

Chemical analyses of 128 corundums from Vietnamese primary and secondary

occurrences are shown in Table III. The correlation diagram of (Cr₂O₃/Ga₂O₃) vs (Fe₂O₃/TiO₂) for corundums from the primary deposits from northern Vietnam is shown in Figure 12. This shows a clear separation of rubies in marbles from the coloured sapphires in gneiss, amphibolite and (meta-) pegmatite, with the one exception of the sapphires from the Khe Nhan pegmatite which fall within the field of the ruby-hosted marbles.

Corundums from the secondary deposits (placers) have clear chemical signatures. All the rubies and 'trapiche' rubies found in placers from northern Vietnam fall within the population field defined by marble-hosted

ruby. All the 'BGY' and colourless sapphires originating from Southern Vietnam and linked to placers in basalts define another distinct population (basaltic field) which is characterized by its very low chromium and gallium and high iron contents.

Chemical analyses obtained by the EDXRF method show that Dak Nong sapphires have higher gallium contents (0.03 to 0.045 wt%) and a wider range of Fe_2O_3 (0.65 to 2.4 wt%) than the other types of sapphire from basaltic areas in southern Vietnam, especially from Lam Dong Province (Figure 13). The chemical ratio $\text{Cr}_2\text{O}_3/\text{Ga}_2\text{O}_3$ vs $\text{Fe}_2\text{O}_3/\text{TiO}_2$ of the sapphires

match values recorded for 'basaltic' corundums by Sutherland *et al.* (1998a). Nevertheless, the wide variation of gallium content in the Dak Nong sapphires results in a correspondingly wide geochemical field (Figure 12).

The blue and colourless sapphires from Luc Yen and the blue (including the trapiche-like) sapphires from Yen Bai occupy a common field which partly overlaps the marble domain. Their field is defined by an $\text{Fe}_2\text{O}_3/\text{TiO}_2$ ratio around 1 and low concentrations of Cr_2O_3 and Ga_2O_3 . Although these sapphires were not observed in their parental rocks, they do not appear to originate

Table III: Electron microprobe analyses of rubies and sapphires from Vietnam.

Corundum from placers	Northern Vietnam						Southern Vietnam					
	Quy Chau ruby (n=40)		Luc Yen ruby (n=4)		Luc Yen colourless sapphires (n=16)		Dak Nong blue sapphire (n=14)		Dak Nong green sapphire (n=11)		Binh Thuan black sapphire (n=6)	
Wt%		σ		σ		σ		σ		σ		σ
TiO_2	0.03	0.03	0.01	0.00	0.13	0.17	0.04	0.05	0.02	0.01	0.04	0.04
Al_2O_3	99.28	0.72	99.76	0.84	99.81	0.46	99.14	0.74	99.11	0.47	98.14	0.24
Cr_2O_3	0.58	0.55	0.54	0.45	0.02	0.01	0.00	0.00	0.01	0.01	0.00	0.00
Fe_2O_3	0.07	0.07	0.01	0.00	0.15	0.16	1.35	0.34	1.19	0.39	1.86	0.19
V_2O_3	0.02	0.05	0.07	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ga_2O_3	0.01	0.00	0.01	0.02	0.01	0.00	0.03	0.01	0.03	0.00	0.03	0.00
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.01
Total	99.99	0.56	100.40	0.63	100.13	0.41	100.56	0.74	100.36	0.47	100.08	0.11
Corundum from primary deposits	Luc Yen		Yen Bai				Ba Be					
	Luc Yen marble		Tan Dong metapegmatite		Tan Hung amphibolite		Truc Lau pegmatite		Ba Be pegmatite			
Wt %	ruby	σ (n=29)	blue sapphire	σ (n=8)	blue sapphire	σ (n=7)	blue sapphire	σ (n=8)	blue sapphire	σ (n=4)		
TiO_2	0.02	0.01	0.19	0.18	0.00	0.00	0.01	0.00	0.00	0.00		
Al_2O_3	99.42	0.64	99.31	0.71	99.04	0.48	99.19	0.43	99.90	0.27		
Cr_2O_3	0.37	0.58	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00		
Fe_2O_3	0.02	0.01	0.67	0.15	0.94	0.07	1.31	0.06	0.44	0.01		
V_2O_3	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Ga_2O_3	0.01	0.01	0.03	0.00	0.01	0.00	0.02	0.00	0.02	0.00		
MgO	0.02	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Total	99.87	0.40	100.21	0.72	100.01	0.47	100.53	0.46	100.36	0.27		
NB: Zinc was also sought but below detection except for 0.02% ZnO in ruby from Luc Yen marble σ = one standard deviation; n = number of analyses.												

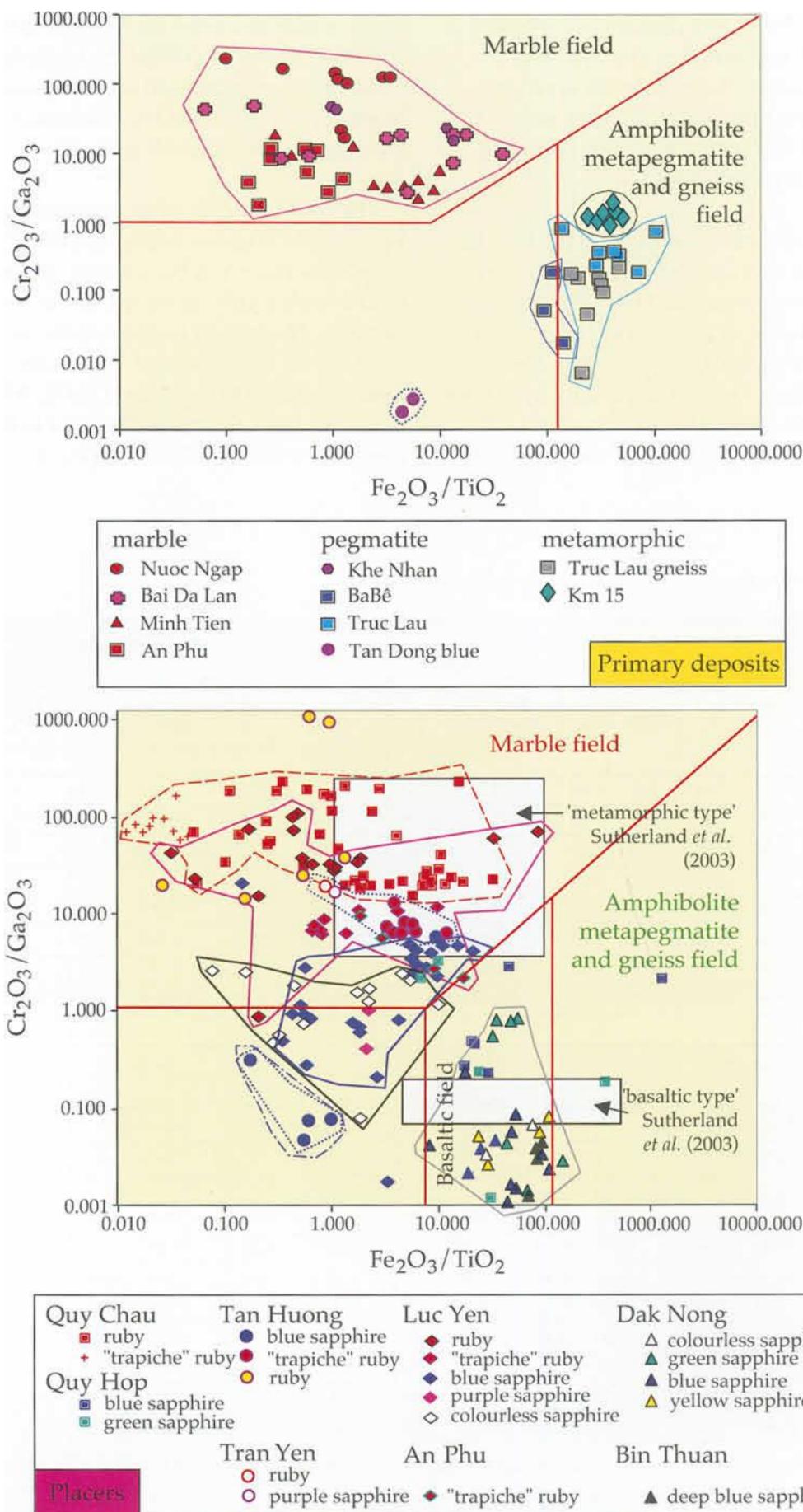


Figure 12: Correlation diagram of Cr_2O_3/Ga_2O_3 versus Fe_2O_3/TiO_2 for corundums from primary and secondary deposits in Vietnam. The fields of the metamorphic and basaltic types defined by Sutherland et al. (1998a, 2003) for the Eastern Australian and South East Asian corundums are shown for comparison.

from marbles, gneiss, amphibolite or pegmatite. Their origin is unclear but the presence of the primary Tan Dong blue sapphire in the same field could indicate that some of these blue sapphires could be related to metasomatic alteration of pegmatites or other metamorphic rocks (hydrothermal field?).

The Tran Yen rubies originated probably from marbles; but different Quy Hop sapphires from placers in the Bu Khang dome plot in the basaltic, gneiss, amphibolite and metapegmatite fields and could come from a range of sources.

Oxygen isotope geochemistry

The rubies from Luc Yen have oxygen isotopic compositions ($\delta^{18}\text{O}$, in ‰ versus SMOW) between 19.3 and 22.4‰ (average $\delta^{18}\text{O} = 21.0 \pm 0.9\text{‰}$, 8 samples) and are in the same range as those from Quy Chau (average $\delta^{18}\text{O} = 22.2 \pm 0.05\text{‰}$, 3 samples). The oxygen values of the rubies fall within the oxygen isotopic range defined for marbles from Luc Yen and Quy Chau. Thus, the isotopic composition of ruby is apparently buffered by

the host rock (Giuliani *et al.*, 2003b). In contrast, the oxygen isotopic compositions of the Dak Nong sapphires are quite different from the rubies whatever their colour may be (Figure 13). The oxygen isotopic compositions are between 6 and 6.9‰ (average $\delta^{18}\text{O} = 6.6 \pm 0.4\text{‰}$, $n=5$) and are outside the range of the associated alkali basalts ($4.9 < \delta^{18}\text{O} < 5.7\text{‰}$), but within the range of syenitic rocks (Garnier *et al.*, 2004).

Conclusions

Corundum is found in Vietnam in a number of different geological environments; these include amphibolite, gneiss, marble, basalt, pegmatite and metasomatized pegmatite. Of these, only two types of deposits are economically viable for gem production: marbles mined since 1983 in the Luc Yen, Yen Bai and Quy Chau districts, and basalts mined since 1991 in the Dak Lak, Lam Dong and Binh Thuan provinces. The appearance and characteristic features of the rubies and coloured sapphires from the Vietnamese gem deposits are generally related to their respective geological environments.

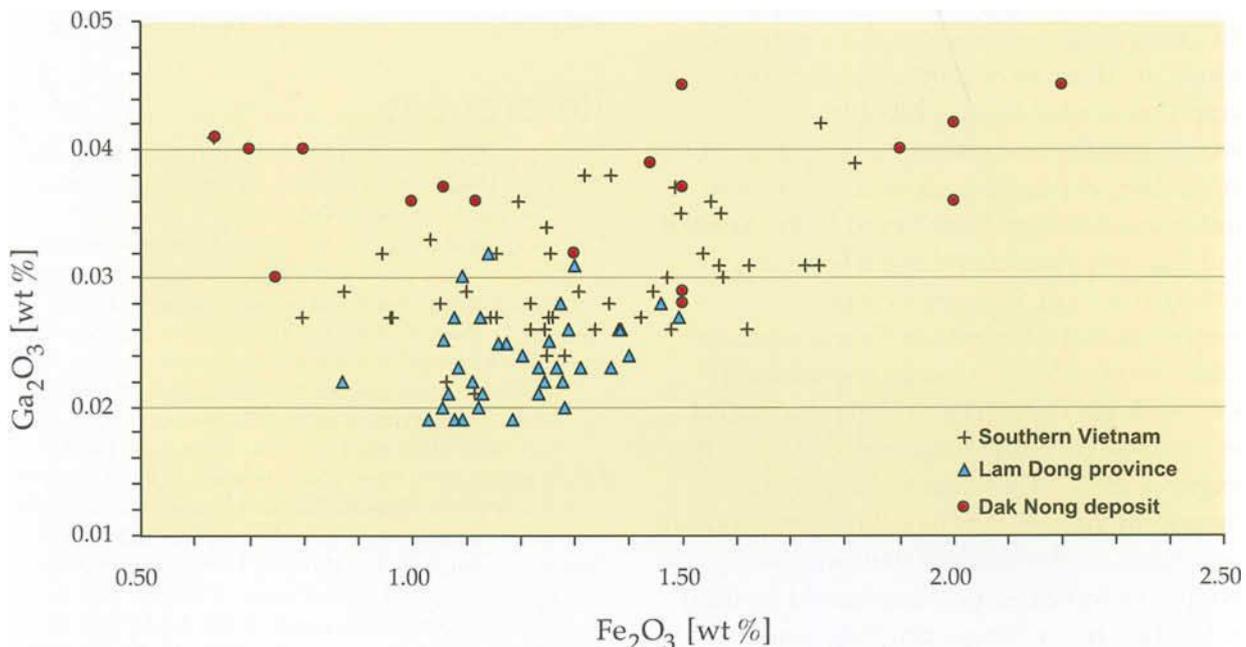


Figure 13: Chemical variation diagram showing wt% plots of gallium (Ga_2O_3) versus iron (Fe_2O_3) contents of corundums from alkali basalts in southern Vietnam. The red circles – sapphires from Dak Nong; blue triangles – sapphires from the Lam Dong province; black crosses – sapphires of unknown locality.

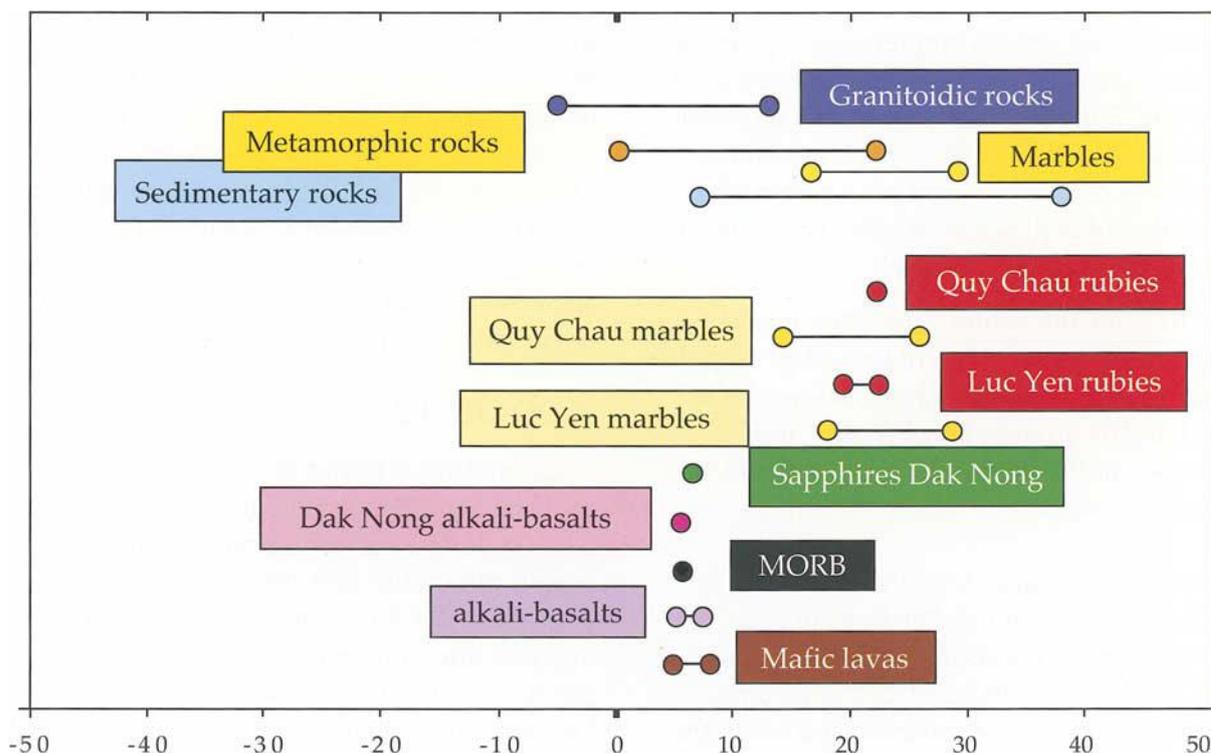


Figure 14: Oxygen isotopic composition of rubies from the Quy Chau and Luc Yen deposits versus 'BGY'-sapphires from Dak Long. The isotopic values of associated marbles and a range of basalts, sedimentary rocks and metamorphic rocks are shown for comparison (Hoefs, 1987).

Corundums exhibit consistent trace element variations which underline the diversity of their host-rocks. The $\text{Cr}_2\text{O}_3/\text{Ga}_2\text{O}_3$ versus $\text{Fe}_2\text{O}_3/\text{TiO}_2$ geochemical diagram divides the corundums into three main fields which are discrete or partly overlapping: sapphires hosted by amphibolite, metapegmatite and gneiss, basalts, and rubies in marbles. A fourth domain contains blue and colourless sapphires found in the Yen Bai and Luc Yen placers and these have an unknown origin. Oxygen isotopic composition studies which clearly separate rubies in marble from sapphires in basalt will, with the use of classical gemmological techniques, probably help in deciphering the origin of these sapphires. Rubies in marbles commonly have distinctive fluid composition signatures, and studies of their inclusions and oxygen isotopic compositions could be used in the future for 'fingerprinting' and determining the origin of rubies found in placers.

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- 15.30 *DTC* – Consumer Confidence in the Diamond Industry

Monday 6 September

- 11.00 *Martin Rapaport*. State of the Diamond Industry
- 13.00 *Vivienne Becker* – Jewellery Editor, *Harpers & Queen*. Our Jewellery World: Dreams, Themes and Inspirations
- 14.30 *Dr Christopher Corti* – World Gold Council. Special Colours of Gold: Purple, Black, Blue and Brown
- 15.30 *Michael Allchin* – Assay Master, Birmingham Assay Office. 'Behind the Scenes': a snap-shot of what's happening now in the jewellery market.

Tuesday 7 September

- 11.30 *Vivienne Becker* – Jewellery Editor, *Harpers & Queen*. Our Jewellery World: Dreams, Themes and Inspirations
- 13.00 *Wendi Mayerson* – GIA. GIA Gem Trade Lab Notes
- 14.30 *Doug Garrod* – Gem-A. Everything Included Part II
- 15.30 *Natalie Hacker and Ruth Donaldson* – Platinum Guild International. *Neill Swan* – Johnson Matthey Platinum Marketing. Selling Tools for Platinum

Wednesday 8 September

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The causes of colour in untreated, heat treated and diffusion treated orange and pinkish-orange sapphires – a review

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Abstract: Colours and the causes of colour in untreated, heat treated and beryllium diffusion treated sapphires in the yellow to red colour range are summarized. An overview of the major types of colour centres in sapphire is given. Properties of thermally unstable 'yellow' and 'orange' colour centres are compared with characteristic features of thermally stable 'orange' colour centres which are produced by high temperature heat treatment or by beryllium diffusion treatment. The models for understanding the formation of orange colour centres according to trace element contents of the samples as suggested by Häger and Emmett are described and discussed in detail. Both models are based on trace element ratios in the Mg-Fe-Ti and in the (Be+Mg)-Fe-Ti triangular diagrams. The causes of colour in untreated and heat treated padparadscha from Sri Lanka are compared with those of beryllium diffusion treated samples from Ilakaka, Madagascar, and from Songea, Tanzania. The great colour variability of untreated and treated samples is due to large variations of iron and chromium contents and to the concentration of colour centres.

Introduction

Since the appearance of orange sapphires 'enhanced' with a 'new heat treatment technique' on the market at the end of 2001 (see for example McClure *et al.*, 2002), the distinction of treated from untreated samples (Figure 1 a, b) as well as the definitive detection of the treatment technique applied has become

one of the major challenges for gemmological laboratories and scientists working in the gemmological field. Knowledge of the exact nature of the treatment technique and the mechanism of colour change or colour improvement are necessary for a correct nomenclature of treated samples.



Figure 1a: Untreated padparadscha from Sri Lanka of 3.09 ct (left) and Be-diffusion treated Ilakaka sapphire of 1.82 ct (right). (Photo by M. Glas)



Figure 1b: Sapphire of 1.28 ct (left) showing the colour typical of heat treated material from Sri Lanka and Be-diffusion treated Ilakaka sapphire of 1.70 ct (right). (Photo by M. Glas)

Many papers have been written containing a description of the history of this major issue and several public events such as panel discussions, related to the nomenclature problem have been held in 2002 and 2003. Summaries of the present knowledge about the new heat treatment technique and properties of treated samples are given by, for example, Coldham, 2002; Peretti and Günther, 2002; Wang and Green, 2002; Hänni, 2002; Hänni and Pettke, 2002; Fritsch *et al.*, 2003; and Emmett *et al.*, 2003.

Meanwhile, the new 'heat treatment technique' unquestionably involves a diffusion of beryllium from outside sources, e.g. from powdered chrysoberyl or from a beryllium-bearing melt, into the corundum lattice. Trace element analyses of the new type of treated sapphires reveal elevated amounts of beryllium, the highest amounts being detected in the rims of the samples. Samples of ruby or sapphire treated by this 'new heat treatment process' were first used in Thailand for ordinary heat treatment but either did not respond at all or became of unmarketable quality. Such types of corundum, e.g. purplish to purple material from Songea, Tanzania, and Ilakaka, Madagascar, are at least in part not convertible to bright ruby or bright pink sapphire by simple high temperature heat treatment.

To the knowledge of the present authors, diffusion treatment of corundum was first applied by Eversole and Burdick (1954) by introduction of titanium into the lattice of synthetic Verneuil-grown corundum; after subsequent heat treatment, this enabled formation of rutile needles and caused asterism in these samples. Later titanium was also diffused into natural corundum to develop or improve the desired blue colour of sapphires (Carr and Nisevich, 1975, 1976, 1977). The reaction mechanism of both processes is well understood (see Schmetzer and Glas, 2003).

However, the diffusion of beryllium into natural corundums causes internal reaction

and diffusion of Be and the already-present trace elements, mainly Mg, Ti, V, Cr, and Fe, as well as with the major chemical components of corundum, aluminium and oxygen. These processes are most probably very complex and not yet fully understood. In natural iron- and/or chromium-bearing corundums this reaction and diffusion mechanism caused the formation of an 'orange' colour centre with a broad absorption maximum in the visible range at about 460 to 470 nm combined with an additional ultraviolet absorption component. These absorption features are the major causes of colour change from, for example, pink to various shades of orange. A certain intensity of the 460 to 470 nm band in combination with the always present ultraviolet component is necessary for the desired colour change of natural sapphires. It is now generally accepted that without diffusion of beryllium from a solid or melt from outside into the corundum lattice, this absorption band would not be created with the intensity necessary for a distinct colour change or colour shift. Consequently, these stones should be called Be-diffusion treated sapphires.

Recent papers have focused on trace element determination of diffusion treated sapphires, and especially on beryllium analysis, and these have led to the first steps in understanding the mechanism of colour change by diffusion treatment (see, for example, Peretti and Günther, 2002; Hänni, 2002; Hänni and Pettke, 2002; Fritsch *et al.*, 2003; Emmett *et al.*, 2003; Peretti *et al.*, 2003; Pisutha-Arnond *et al.*, 2004). However, a general summary of present knowledge about various colour centres, which might influence sapphire colour, and of colour change by diffusion treatment, is not available in the gemmological literature.

A brief characterization of untreated padparadscha from Sri Lanka (the orangey-yellow, yellowish-orange, orange, pinkish-orange, rose orange, orange-pink, or reddish-orange sapphire variety –

to summarize some colour descriptions commonly used) and heat treated sapphires in the same colour range (treated without Be-diffusion) with respect to colour and its causes has been published by Notari (1996, 1997). In the latter paper, however, only general statements about the nature of 'colour centres' are found with no detailed comparison of properties of natural corundum with defects produced in doped synthetic corundum.

In gemmological literature generally there is not sufficient detail available about comparison of untreated and heat treated material from Sri Lanka with diffusion treated samples, especially according to the locality of origin of the untreated material. The present needs of the trade require recognition and distinction of untreated from diffusion treated material, and it is necessary to clearly characterize the types of untreated, heat treated and diffusion treated material available in the trade. The present paper tries to fill at least part of this gap and to contribute to resolving these problems.



Figure 2a: Sapphires with this colour originating from Sri Lanka are called padparadscha in the trade; in the upper row two untreated samples representing the pinkish-orange (left) and the yellowish-orange (right) padparadscha type are shown; in the lower row heat treated reddish-orange (left) and pinkish-orange sapphires (right) are shown; range of samples from 4.43 to 2.23 ct. (Photo by M. Glas)

Padparadscha and brownish-orange sapphire

The orangey-pink to pinkish-orange coloured corundum variety is called padparadscha in the trade. Natural padparadscha is considered to be the rarest sapphire variety. They originate from different mining areas in Sri Lanka, mainly from Ratnapura (G. Zoysa, pers. comm. 2003), but also from Elahera and Buttala (Gunawardene and Rupasinghe, 1986; Notari, 1996).

There is still an ongoing debate about the correct and appropriate definition of the term 'padparadscha' in the trade (*Figure 2a*). If we consider only colour, it is unquestionable that sapphires with a bright orangey-pink or pinkish-orange colour are called padparadscha and are considered as extremely fine samples (*Figure 2b*; see also Crowningshield, 1983; Kane, 1986; Gunawardene and Rupasinghe, 1986). There is, however, some discussion in the trade about the borderlines between padparadschas and yellow sapphires on the one side, and between padparadschas and rubies or pink sapphires on the other. Thus, the designation of individual padparadschas close to these borders might be handled differently in the trade and also by different gemmological laboratories.



Figure 2b: This untreated padparadscha of 9.05 ct has an extremely fine intense orange colour. (Photo by M. Glas)

Notari (1996, 1997) subdivided padparadschas from Sri Lanka into a more yellowish-orange to orange, sometimes pastel coloured type (which he called 'original' type) and a more orange to pinkish-orange type (which he called 'antique' type). According to their colour (see again *Figure 2 a, b*), both types may overlap. The more yellowish-orange to orange type of Notari is definitely not heat treated. The more orange to pinkish-orange type may have been heat treated at high temperatures (F. Notari, pers. comm., 2003). In other words: heat treated and non-heat treated samples with a specific pinkish-orange colour are known to exist. It is also possible to cause a shift of colour from yellowish-orange or orange stones towards pinkish-orange by very careful low temperature heat treatment (F. Notari, pers. comm., 2003).

According to G. Zoysa (pers. comm., 2003), somewhat milky-appearing Sri Lanka sapphires with a distinct pink or orange shade are used for high temperature heat treatment to obtain pinkish-orange or reddish-orange sapphires with a colour comparable to that of untreated padparadscha. F. Notari (pers. comm., 2003) mentioned that pale to medium pink sapphires with colour zoning consisting of colourless and pale pink areas are used for the high temperature heat treatment process.

Another way of defining padparadscha is by using its spectroscopic properties (Schmetzer and Bank, 1981; Schmetzer *et al.*, 1983). Absorption spectra of untreated padparadschas from Sri Lanka consist of an almost continuously increasing absorption from red to violet (similar to that of yellow sapphires due to 'yellow' colour centres) on which are superimposed the absorption bands of chromium. Upon heat treatment to about 500°C, the absorption of 'yellow' colour centres is normally removed and padparadschas turn pink or red, according to the chromium content of the sample (Schmetzer *et al.*, 1983). With careful heat treatment at low temperatures, the colour of

a sample may be shifted slightly from yellowish-orange towards pinkish-orange. This is understandable by removing only part of the 'yellow' colour centres present in untreated stones.

Upon heat treatment at high temperatures, a pinkish-orange padparadscha from Sri Lanka turned yellowish-orange (Kane, 1986). In this case, most probably, thermally unstable 'yellow' colour centres disappeared and more intense thermally stable 'orange' colour centres were formed, with some chromium being always present. Kane's description is consistent with numerous heat treatment experiments and spectroscopic investigations performed by one of the authors in the 1980s and 1990s (KS, unpublished data).



Figure 3: The colour of untreated brownish-orange sapphire from Ilakaka (left) occasionally resembles that of pinkish-orange untreated padparadscha from Sri Lanka (right), although the Ilakaka material is coloured by chromium and iron, and the colour of the Sri Lanka material is caused by 'yellow' and/or 'orange' colour centres and chromium; weight of samples are 1.20 and 1.66 ct. (Photo by M. Glas)

Sapphires with brownish-orange colours similar to those of untreated and heat treated padparadschas (*Figure 3*) have been known for several decades from Umba, Tanzania (Schmetzer and Bank, 1981; Gunawardene, 1984; Hänni, 1987; Notari, 1996, 1997; see also Schmetzer and Peretti, 1999) and have been called 'padparadscha' or 'African padparadscha' in the trade. Some brownish-orange sapphires from

Umba are coloured by high amounts of iron and chromium (Schmetzer *et al.*, 1983) and similar stones coloured by iron and chromium from Malawi have also been called 'padparadscha' (Henn *et al.*, 1990). Recently, samples from Ilakaka, Madagascar (see also Figure 16b), with this type of chromium-iron coloration have also been described by Schmetzer (1999). However, the colours in the brownish-orange sapphires from Tanzania (Umba), Malawi, and Madagascar (Ilakaka) have different causes and the present authors cannot support the designation of these samples as padparadschas.

Colour centres in corundum

Before discussing causes of colour in Be-diffusion treated sapphires, we have to summarize briefly the present knowledge about colour centres in natural and synthetic corundum.

Various colour centres in natural and synthetic corundum have been created by different types of irradiation and/or heat treatment in oxidizing or reducing atmospheres. An overview of the most prominent colour

Table I: Colour centres in corundum.

Type	Designation	Description	Absorption maximum (nm)	References
Anion defect centres	F	Oxygen vacancy with two trapped electrons	203-207	Evans and Stapelbroek, 1978; Crawford, 1984; Pogatshnik <i>et al.</i> , 1987; Chen <i>et al.</i> , 1991; Brock <i>et al.</i> , 2001
	F ⁺	Oxygen vacancy with one trapped electron	197-206; 225-230; 258	
	F ₂	Two oxygen vacancies with four trapped electrons	300-302	
	F ₂ ⁺	Two oxygen vacancies with three trapped electrons	355	
	F ₂ ²⁺	Two oxygen vacancies with two trapped electrons	450-459	
Cation defect centres	V ²⁻	Aluminium vacancy with hole trapped at an adjacent oxygen	403	Kvapil <i>et al.</i> , 1972, 1973; Govinda, 1976; Lee <i>et al.</i> , 1977; Lee and Crawford, 1977; Valbis and Itoh, 1991; Jacobs <i>et al.</i> , 1993
	V ⁻	Aluminium vacancy with two holes trapped at two adjacent oxygens	403	
	V _{OH} ⁻	Aluminium vacancy with hole trapped at an adjacent oxygen plus adjacent OH	420	
Magnesium related centres	Mg ⁰	Magnesium with hole trapped at an adjacent oxygen	See Table II	See Table II
	F _{Mg} ⁻	Oxygen vacancy with two trapped electrons adjacent to magnesium	170; 200; 280	Kulis <i>et al.</i> , 1979, 1981; Kortov <i>et al.</i> , 1985; Kotomin <i>et al.</i> , 1995 a, b; Brock <i>et al.</i> , 2001
	F _{Mg}	Oxygen vacancy with one trapped electron adjacent to magnesium	217; 247	

Table II: Colour centres in natural, treated and synthetic corundum which relate particularly to Mg and Be.

Dopant	Synthetic (s); Natural (n); Diffusion treated (d); Heat treated (h)	Absorption maximum (nm)*	Remarks	Reference
Mg + Mn	s	469 + uv component		Geschwind <i>et al.</i> , 1962
Cr + N	s	460, 370 shoulder	orange	Hoskins and Soffer, 1964
Mg	s		orange	Townsend and Hill, 1965
Mg + Ti	s, irradiated		brown	Cox, 1971
Mg	s	400-480 range	yellow to brown	Kvapil <i>et al.</i> , 1973
Mg	s	470, 380	orange	Sidorova <i>et al.</i> , 1973
Mg + Cr	s	470, 380	orange	
Mg	s	475, 260		Andreev <i>et al.</i> , 1976
Mg	s	468, 380	intense orange	Mohapatra and Kröger, 1977
Be + Cr	s		orange, all colours in the yellow to red range	Lor'yan and Rassvetaev, 1979
Orange colour centres, Mg + Cr + Fe	n/h	465 + uv component	orange-brown	Schmetzer <i>et al.</i> , 1983
Mg	s	480	greyish-purple	Wang <i>et al.</i> , 1983
Mg + Fe	s		yellow to brown	
Mg + Cr	s		orange	
Mg	s	495, 250, 217		Kortov <i>et al.</i> , 1985
Mg	s	460 + uv component	green	Boiko <i>et al.</i> , 1987
Mg	n/h	470 + uv component	yellowish-orange	Emmett and Douthit, 1993
Mg	s	496, 260	grey-purple	Tardio <i>et al.</i> , 2001
Mg	s	500	brownish-violet	Häger, 2001
Mg + Fe	s	470 + uv component		
Mg	n	Visible + uv range	brownish-orange,	Peretti and Günther, 2002
Mg	n/d	Visible + uv range	yellow, orange	
Mg	s	500	brownish-violet	Pisutha-Arnond <i>et al.</i> , 2002
Be	s/d	420	pale brown	
Mg + Fe	s	470 + uv component	yellow	
Be + Fe	n/d	470 + uv component	yellow	
Be + (Cr, Fe)	n/d	470 + uv component	pink orange	
Be + (Cr, Fe)	n/d	460 + uv component	yellow to orange	Hänni and Pettke, 2002
Be + (Cr, Fe)	n/d	470 + uv component		Fritsch <i>et al.</i> , 2003
Be	s/d	420	orangey-brown	Emmett <i>et al.</i> , 2003
Be + Cr	s/d	460, 380		
Be + (Cr, Fe)	n/d	460, 380	orange	
Be	s/d		brown	Peretti <i>et al.</i> , 2003
Be + Cr	s/d	470 + uv component	orange	
Be + (Cr, Fe)	s/d	470 + uv component	orange-red	
Be	s/d	420	pale brown	Pisutha-Arnond <i>et al.</i> , 2004
Be + (Fe, Mg)	n/d	460 + uv component	yellow	
Mg	s	500	brownish-violet	
	n	460 + uv component	yellow	
	n/h	460 + uv component	yellow	
Mg + Fe	s	460 + uv component	yellow	
Be + (Cr, Fe, Mg)	n/d	460 + uv component	orangey-yellow	

* from some papers the approximate positions of absorption maxima were taken from the spectra pictured; for the ultraviolet range, frequently only the presence of absorption bands is evident, but no specific position of the absorption maximum can be given.

centres is given in *Table I* with literature references. Physicists subdivide these colour centres into *anion defect centres* (related to oxygen vacancies) and *cation defect centres* (related to aluminium vacancies). Most of these colour centres reveal prominent absorption maxima in the ultraviolet, occasionally also in the violet part of the visible range (see also *Table I*). *Magnesium-related colour centres* reveal a hole trapped at an adjacent oxygen (trapped hole centres) or may be found adjacent to an oxygen vacancy. The latter, which are called F_{Mg}^- or F_{Mg} centres, reveal broad absorption maxima in the ultraviolet which may extend to the visible range (*Table I*).

Numerous papers have provided information about orange, yellow, brown or brownish-purple magnesium-related colour centres (*Table II*). The most prominent 'orange' colour centre is characterized by an absorption band at about 460 to 470 nm, which always is accompanied by a shoulder or second maximum at about 380 nm and/or an additional ultraviolet component without an exactly specified maximum. In beryllium diffusion treated sapphires, the 380 nm maximum is commonly hidden by an unspecified ultraviolet component and is only detected in difference spectra, i.e. in spectra in which the 'before' spectrum of the untreated samples is subtracted from the 'after' spectrum of the beryllium diffusion treated sapphire (Emmett *et al.*, 2003.). A spectrum of a sample showing the 460 to 470 nm absorption band alone, i.e. without an additional 380 nm band and/or without an additional ultraviolet component, has not yet been found.

The 460 to 470 nm absorption band can be produced by doping synthetic corundum feed material with Mg alone (Sidorova *et al.*, 1973; Andreev *et al.*, 1976; Mohapatra and Kröger, 1977; Boiko *et al.*, 1987) or with both Mg and Cr (Sidorova *et al.*, 1973), or with a combination of Mg and Fe (Wang *et al.*, 1983; Häger 2001; Pisutha-Arnond *et al.*, 2002, 2004). The absorption band in the 460 to 470 nm range is also typical for natural high temperature heat treated yellow to orange sapphires (Schmetzer

et al., 1983). The intensity of this colour centre is increased by heat treatment in an oxidizing atmosphere and reduced by heat treatment in a reducing atmosphere.

The exact nature of the 'orange' colour centre, also called a trapped hole centre (THC) in the literature, and the complex reaction forming this colour centre in natural sapphire is still debated although a simple model for the formation of an absorption band at 470 nm in synthetic orange corundum doped with magnesium or with chromium and magnesium has been known for a long time (Sidorova *et al.*, 1973; Andreev *et al.*, 1976; Mohapatra and Kröger, 1977). This model is based on an electron hole trapped for charge compensation at an oxygen adjacent to magnesium on aluminium lattice sites and may be described with the symbol $[Mg_{Al}^{2+}O^-]$. In the physics literature, the symbol $[Mg]^0$ is also commonly used, reflecting the electrical neutrality of this magnesium-oxygen-centre relative to the surrounding corundum lattice.

An absorption maximum is also produced in the range of the 'orange' colour centre by doping of corundum with magnesium and manganese (Geschwind *et al.*, 1962) or with chromium and nitrogen (Hoskins and Soffer, 1964). In these examples, Mn^{4+} is assumed to form the necessary charge compensation for Mg^{2+} , and, in the second case, Cr^{4+} is found to charge compensate for the N^{3-} present in oxygen sites.

Synthesis of corundum doped with Mg using extremely pure Fe- and Cr-free nutrient produces sapphire crystals which reveal an absorption maximum in the 480 to 500 nm range (Wang *et al.*, 1983; Kortov *et al.*, 1985; Tardio *et al.*, 2001; Häger 2001; Pisutha-Arnond *et al.*, 2002, 2004). Such sapphire samples are described as greyish-purple or brownish-violet. It was suggested, that, in contrast to these pure Mg-bearing sapphires, the 470 and 380 nm absorption bands mentioned above are due to Mg-related colour centres (trapped hole centres) combined with or needing some 'impurities' or traces of Fe and/or Cr to form Mg-Fe or Mg-Cr clusters.

This complex situation is duplicated by natural and synthetic Be-doped or Be-diffusion treated sapphires. As early as 1979, Lor'yan and Rassvetaev reported that the synthesis of sapphire doped with a combination of chromium and beryllium produces bright orange sapphires and, according to the Cr:Be ratio of the feed material, all colours intermediate between yellow and red may be produced.

Natural iron- and/or chromium-bearing corundum, which was diffusion treated with Be commercially in Thailand or in different laboratories in America and Europe for research purposes, also shows the absorption bands at 470 and 380 nm or an absorption band at about 470 nm and a strong ultraviolet absorption without an exactly specified maximum, i.e. spectra similar to 'impure' Mg-doped synthetic corundum (Peretti and Günther, 2002; Pisutha-Arnond *et al.*, 2002, 2004; Hänni and Pettke, 2002; Fritsch *et al.*, 2003; Emmett *et al.*, 2003). However, this situation is further complicated by Be-diffusion treated synthetic corundum, which was produced from Fe-free nutrient because it shows neither the 'pure' Mg absorption at 500 nm nor the 'impure' Be-related (Mg-Fe-Cr) cluster absorption bands at 470 and 380 nm, but an absorption maximum at about 420 nm (Pisutha-Arnond *et al.*, 2002, 2004; Emmett *et al.*, 2003).

It is evident from this complex situation that the nature of the 'orange' colour centre produced by Be-diffusion treatment and an exact reaction mechanism are not yet fully understood. A model for understanding the causes of colour and colour changes in Mg-, Fe- and Ti-bearing sapphires was developed by Häger (1992, 1993, 1996, 2001). His interpretation, based on heat treatment experiments in combination with absorption spectroscopy and trace element analysis, was described using an Mg-Fe-Ti triangle representing trace element contents in natural or synthetic sapphires (Figure 4a). This diagram represents natural or synthetic sapphires with relatively low iron contents, e.g. metamorphic sapphires, in which the

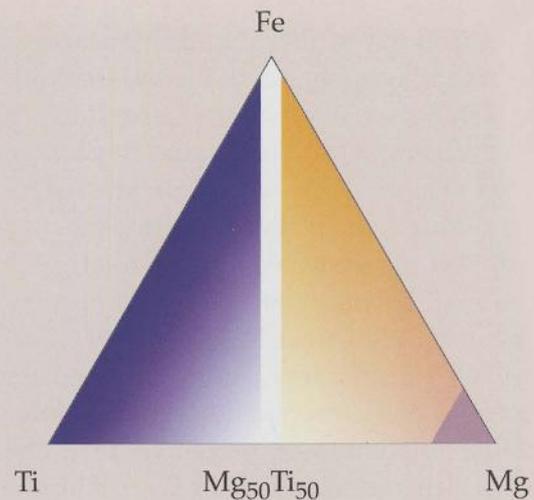


Figure 4a: This triangular Mg-Fe-Ti diagram for samples with low iron content (see text) illustrates a model for the development of colours in sapphires at 1850°C in an oxidizing environment. Samples on the Fe-Mg₅₀Ti₅₀ line, i.e. samples with equal atomic concentrations of magnesium and titanium are colourless; in samples right of this line, i.e. in samples with Mg > Ti, Mg-related colour centres are developed; in samples left of this line, i.e. in samples with Ti > Mg, the Fe²⁺/Ti⁴⁺ charge transfer absorption of blue sapphire is present; the special role of Mg-related colour centres in 'pure' iron-free corundum is indicated at the right corner; after Häger (2001).

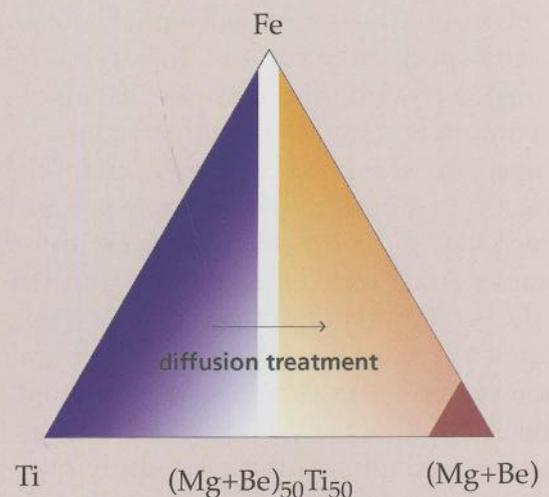


Figure 4b: Schematic model representing the colour development in beryllium diffusion treated sapphires adopted from the proposal of Emmett *et al.* (2003). In this triangular (Mg+Be)-Fe-Ti diagram, samples on the Fe-(Mg+Be)₅₀Ti₅₀ line, i.e. samples with equal atomic concentrations of (magnesium+beryllium) and titanium are colourless; in samples right of this line, i.e. in samples with (Mg+Be) > Ti, Mg-related 'orange' colour centres are developed; in samples left of this line, i.e. in samples with Ti > (Mg+Be), no orange colour centres are found; the special role of Be-related colour centres in 'pure' iron-free corundum is indicated at the right hand corner.

The beryllium diffusion treatment causes samples, which are left of the 'colourless' line, to shift to the right of this line and to develop 'orange' colour centres.

absorption bands of Fe^{3+} are weak and do not produce a yellow coloration. For simplicity, basaltic sapphires are not covered by this schematic diagram. It is summarized that all iron-bearing corundums with equal concentration of Mg and Ti atoms, i.e. all compositions that lie on the line $\text{Fe-Mg}_{50}\text{Ti}_{50}$, are colourless. This is understandable if one imagines complete charge compensation by Mg-Ti clusters or Mg-Ti interaction, with neither Mg-related hole centres nor Fe-Ti pairs (causing the blue sapphire colour) being formed.

All corundums with compositions right of this line, i.e. with $\text{Mg} > \text{Ti}$, reveal Mg-related colour centres and are yellow, orange or brownish-violet. Most samples left of the line $\text{Fe-Mg}_{50}\text{Ti}_{50}$, i.e. with $\text{Ti} > \text{Mg}$, are blue, which is caused by the presence of the $\text{Fe}^{2+}/\text{Ti}^{4+}$ charge transfer absorption bands in the red to green part of the visible range (for further details see Häger, 1996, 2001).

Emmett *et al.* (2003) adopted this model to explain the reaction mechanism and colour change caused by Be-diffusion into the corundum lattice (see also Hänni and Pettke, 2002; Fritsch *et al.*, 2003) but did not go on to use their chemical data to test this model and any of their consequent rules. If these rules and the general model prove to be correct, this theoretical approach should be supported by a correlation of colour, colour change reaction and chemical properties of treated and untreated samples.

Emmett's model (Figure 4b) describes the addition of Be to change the already existing trace element distribution by diffusion treatment, especially the Mg:Ti ratio to a new (Mg + Be):Ti ratio. By the addition of beryllium to the already-present trace elements, the ratios of some corundums are moved from left of the line $\text{Fe-Mg}_{50}\text{Ti}_{50}$ (representing colourless sapphires) to a trace element composition right of this line. Consequently, if - after Be-diffusion - the relationship is $(\text{Mg} + \text{Be}) > \text{Ti}$, the orange colour centre is developed and the desired colour change or colour improvement of the sample is achieved.

It may be assumed that Be acts as a charge compensator for Ti and, in this way, liberates Mg from this role. This 'free' Mg may form 'orange' Mg or (Mg-Fe) or (Mg-Cr) or (Mg-Fe-Cr) colour centres or clusters, i.e. Mg or (Mg-Fe) or (Mg-Cr) or (Mg-Fe-Cr) trapped hole centres with absorption maxima in the 470 and 380 nm and /or ultraviolet range. It may also be assumed that beryllium by itself can form orange Be or (Be-Fe) or (Be-Cr) or (Be-Fe-Cr) trapped hole centres with absorption maxima in the 470 and 380 nm and/or ultraviolet range (for further discussion see also Häger, 2001; Peretti and Günther, 2002; Hänni and Pettke, 2002; Pisutha-Arnond *et al.*, 2002, 2004; Fritsch *et al.*, 2003; Emmett *et al.*, 2003).

The chemical data presented in three recent publications (Peretti *et al.*, 2003; Pisutha-Arnond *et al.*, 2002, 2004) support the adoption of Häger's model by Emmett *et al.*, i.e. the application of the model describing the colour change of heat treated corundum (based on Mg contents) also to Be-diffusion treated corundum (based on Be + Mg contents). These authors (*op. cit.*) conclude from trace element analyses that a yellow or orange coloration is formed in samples with $(\text{Mg} + \text{Be}) > \text{Ti}$, and that no orange colour component is formed in rubies with $\text{Ti} > (\text{Mg} + \text{Be})$.

Within the rules described by Emmett *et al.* (2003), silicon is assumed to be effective in the corundum lattice and should therefore be added to titanium. The resulting conditions or rules are $(\text{Mg} + \text{Be}) > (\text{Ti} + \text{Si})$ for the formation of orange colour centres and an orange coloration. In contrast, sapphires with a trace element ratio of $(\text{Mg} + \text{Be}) < (\text{Ti} + \text{Si})$ should not show an orange coloration after diffusion treatment.

Peretti *et al.* (2003) outline specific analytical data from treated and untreated samples which are useful to check the silicon-related part of Emmett's model. These data indicate that silicon is heterogeneously distributed in the corundums and thus, the silicon contents measured might be due to minute inclusions and not to Si that is

Table III: Sources, colours and treatment history of corundums in this study.

Locality	Colour	Untreated	Heat treated	Beryllium diffusion treated
Sri Lanka	Yellow	16	14	
Sri Lanka	Yellowish-orange to orange	21	31	
Sri Lanka	Orange to pinkish-orange or reddish-orange	20	18	
Ilakaka, Madagascar	Pink, purplish-pink, purple, purplish-violet, violet	75	10	
Ilakaka, Madagascar	Yellowish-pink, yellowish-orange, brownish-orange, orange-brown, yellowish-brown	14		
Ilakaka, Madagascar	Yellowish-orange, orange, pinkish-orange, orangey-red, reddish-orange, brownish-orange			45
Songea, Tanzania	Colourless to red or pink, purplish-red, purple, violet (sometimes zoned with a colourless core)	22	10	
Songea, Tanzania	Colourless to yellowish-orange, orange, pinkish-orange, orangey-red, reddish-orange (sometimes zoned with a colourless core)			52

dispersed in the corundum lattice. In addition, a better correlation between the observed colour change by beryllium diffusion and the trace element composition was observed when the silicon content of the sapphires was completely neglected. According to the paper of Pisutha-Arnond *et al.* (2004), the role of silicon as described above is not proven at present and it is questionable if silicon is really present in the lattice of natural corundum in amounts capable of influencing any colour change by heat or diffusion treatment.

However, even with the data available now, it is still not clear how Be is involved in any of the recently designated 'orange' colour

centres, or in the possible (Be-Mg-Fe-Cr) clusters, or if the Be is only involved in a charge compensating mechanism for Ti. In other words: the difference between the orange colour centres creating the 470 nm absorption maximum and those colour centres with an absorption maximum at 420 nm, created by Be-diffusion in pure samples, is not completely understood. Furthermore, the role of bivalent and trivalent iron within this complex reaction system and its role as charge compensator for titanium in Be-, Mg-, Ti- and Fe-bearing, diffusion treated sapphires is not completely understood. Similar problems exist for chromium and a possible formation of Cr⁴⁺ as charge compensator for Mg²⁺ and/or Be²⁺.

Box I: Materials and methods

The sources, colours and treatment history of the 349 natural corundum samples examined in the present study are listed in *Table III*. All samples were highly transparent, gem quality rubies and sapphires ranging from about 0.2 ct to 9 ct in weight. With the exception of some slices polished on both sides (originating from Songea, Tanzania), only faceted samples were used for this research project.

The first lots of diffusion treated sapphires were obtained by one author (DS) during several visits to Bangkok and Chantaburi, Thailand, in 2002. According to the properties of the sapphires (see results) and the information given by the suppliers, these lots represented either Be-diffusion treated samples from Ilakaka, Madagascar, or from Songea, Tanzania. Further lots of Be-diffusion treated sapphires were obtained by colleagues of gemmological laboratories in Europe, USA and Thailand as well as from different European companies. Some of these lots – based on the properties of the samples – represented either Ilakaka or Songea material, some other lots were mixed and contained samples from both localities. A limited number of diffusion treated samples were excluded from the study, because the sapphires did not show the characteristic properties of one of these two localities mentioned or were – according to their characteristic features – definitely from other sources, e.g. from Sri Lanka.

The comparison of properties of Be-diffusion treated samples from Ilakaka and Songea with untreated natural sapphires from these localities is based on several lots of untreated Ilakaka material obtained by one of the authors (KS) from a German dealer soon after the locality was discovered (see Schmetzer, 1999). According to the colour and absorption spectra of the treated material, we used untreated Ilakaka samples in the pink to purple and the pink to orange-brown colour ranges for the present study, because samples from these ranges were submitted to Be-diffusion treatment. Knowing the properties of rubies from Vatomaniry, Madagascar, and of rubies and sapphires from Andilamena, Madagascar (see Schwarz and Schmetzer, 2001), this information was used to reject any corundum that was not from Ilakaka.

Untreated Songea material (see Schwarz, 2001) was obtained by one author (DS) in 1997 directly in the Tunduru-Songea mining area in southern Tanzania. From about 200 polished slices or faceted gem-stones of different colours available, 22 chromium-bearing samples were in the range red to purplish-red to colourless (zoned with colourless cores and red to purplish-red rims); these turn yellowish-orange, orange or reddish-orange after Be-diffusion treatment. From Ilakaka a number of heat treated pink sapphires were studied, and from Songea there were also heat treated rubies. The reader should be aware, however, that not only sapphire and ruby material from Ilakaka and Songea, which was first used for this new treatment, but corundum from many natural sources might be diffusion treated and released on the market (see, e.g., the summary of possible treatment results of ruby and sapphire material from worldwide sources presented by Themelis, 2003).

Untreated yellowish-orange, orange, pinkish-orange or reddish-orange Sri Lanka material, designated padparadscha in the trade, as well as untreated yellow sapphires were obtained from private collections as well as from old stock of different European companies. Heat treated yellow, yellowish-orange to orange (chromium-free) or orange to reddish-orange (chromium-bearing) samples of Sri Lankan origin were obtained from different companies who could establish from internal notes or personal knowledge, that these samples had been in stock for several years, at least before the turn of the millennium (i.e. before Be-diffusion treatment started). In this way, any diffusion treated material was excluded from this group of samples.

continued overleaf

Trace element contents of 152 samples were obtained by energy-dispersive X-ray fluorescence (EDXRF) spectroscopy. These analyses were performed with a Tracor Northern Spectrace 5000 system, using a program specially developed for trace element geochemistry of corundum. The samples for chemical analyses (Sri Lanka 26, Madagascar 84, Tanzania 42) were selected in order to cover the full range of colours seen in untreated, heat treated and diffusion treated material from all three sources. Although the non-destructive analytical technique applied is unable to detect the presence of light elements such as beryllium, EDXRF spectroscopy has become an important routine method for the characterization of rubies and sapphires, especially for origin determination.

Absorption spectra of all samples were recorded in the UV-visible-NIR range with both a Leitz-Unicam SP 800 UV-Vis spectrophotometer and a Perkin-Elmer Lambda 19 spectrophotometer.

Results

Chemical properties

General remarks

In the present paper, we describe iron and chromium contents which are the dominant transition elements which are the cause of colour. The analytical data are summarized in *Table IV*. Trace element contents were obtained from the tables of faceted samples or from polished surfaces of some sapphire or ruby slices. The X-ray beam incident to the samples covered an oval surface of about 2×1 mm. Consequently, the analytical data represent bulk chemical analyses and cannot discriminate fine variation of composition in colour zoned samples. Such information could be obtained by spot analyses using e.g. an electron microprobe.

The distribution of trace elements in corundums from the three sources studied do

not fall into different population areas related to whether they are untreated or heat treated (Sri Lanka) nor can untreated and diffusion treated samples from Madagascar and Tanzania be distinguished in this way. Thus, in order to avoid confusion, the analysed samples in *Table IV* are not subdivided into untreated or treated groups. A chromium-iron correlation diagram (*Figure 5*) also summarizes the analytical results.

Sri Lanka

The Sri Lankan padparadschas are located in a small population area near the lower left corner of the chromium-iron correlation diagram (*Figure 5*). This means that their iron- and chromium-contents are, in general,

Table IV: Chromium and iron contents of untreated and heat treated Sri Lankan padparadschas and yellowish orange sapphires, and of untreated and beryllium diffusion treated rubies and sapphires from Madagascar and Tanzania.

Wt.%	Sri Lanka (26 samples)	Ilakaka, Madagascar (84 samples)	Songea, Tanzania (42 samples)
Cr ₂ O ₃	bdl. – 0.11	0.02 – 0.21* 0.06 – 0.15**	0.11 – 0.53
Fe ₂ O ₃	0.03 – 0.25	0.05 – 1.95* 2.64 – 3.20**	1.04 – 1.80
bdl. = below detection limit. * 80 treated and untreated samples in different colours. ** 4 untreated samples with orange-brown or yellowish-brown colour.			

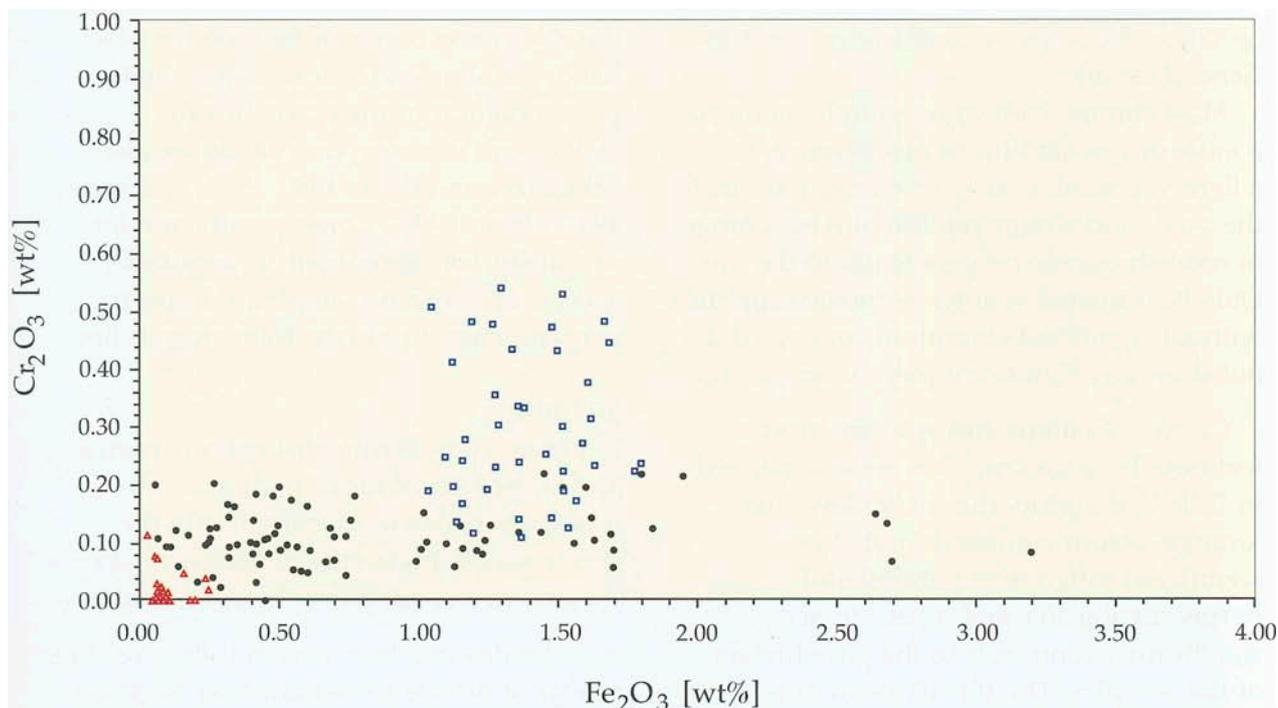


Figure 5: Graphical representation of iron and chromium contents determined for 152 samples from Sri Lanka, Madagascar and Tanzania by energy-dispersive X-ray fluorescence spectroscopy (EDXRF); red triangles represent heat treated and untreated samples from Sri Lanka, black circles represent untreated and diffusion-treated samples from Ilakaka, Madagascar, blue squares represent untreated and diffusion-treated samples from Songea, Tanzania (for further characterization of samples see Table III). It is evident, that the population fields for Sri Lanka and Madagascar samples partly overlap as do the population fields for Madagascar and Tanzania samples.

very low: Cr₂O₃ up to about 0.11 wt.% and Fe₂O₃ up to about 0.25 wt%. As mentioned above, the contents of Cr and Fe in the untreated and heat treated samples overlap and, thus, these samples are not subdivided into separate groups. These analytical results are consistent with data published by Notari (1997) for 11 padparadschas from Sri Lanka.

Ilakaka

The examined sapphires from the Ilakaka mining region in Madagascar display a wide range of iron content: most values from untreated and diffusion treated samples lie in a population field that covers the range 0.05 to 1.95 wt.% Fe₂O₃. Four untreated orange-brown or yellowish-brown samples contain even larger iron values of 2.64 to 3.20 wt.% Fe₂O₃. These samples revealed absorption spectra with Fe > Cr or Fe >> Cr, i.e. with stronger iron than chromium absorption

bands (see Figure 15). Compared to this large variation in iron contents, the chromium range is relatively small: the highest Cr₂O₃ values are 0.21 wt.% and some are as low as 0.02 wt.% Cr₂O₃.

Songea

The iron and chromium contents of untreated and diffusion treated rubies and sapphires from the Songea mining area in southern Tanzania lie in a well-defined population field. The iron concentration is always high (in the range of 1.04 to 1.80 wt.% Fe₂O₃) and chromium contents vary between 0.11 and 0.53 wt.% Cr₂O₃ (see also Schwarz, 2001).

Considering only iron and chromium contents, it is evident from Figure 5 that the population fields for Sri Lanka and Madagascar samples overlap, as do the population fields for Madagascar and Tanzania samples.

Spectroscopic properties and causes of colour

General remarks

Most chromium-bearing samples showed a more or less significant pleochroism, i.e. a light yellowish-orange or orange parallel to the *c*-axis and a more intense pinkish-orange or reddish-orange perpendicular to the *c*-axis. Only heat treated yellowish-orange sapphires without significant chromium contents did not show any significant pleochroic colours.

Causes of colour and spectroscopic features of orange sapphires are summarized in Table V; the properties of 'yellow' and 'orange' colour centres do not show significant differences parallel and perpendicular to *c* and, thus, do not significantly contribute to the pleochroism of the samples. The pleochroism of all chromium-bearing sapphires is caused by the significant differences in the intensity of chromium absorption bands parallel and perpendicular to *c* (Figure 6). If a blue sapphire component is present (mostly in untreated purplish and purplish-red sapphires from Ilakaka and Songea), the Fe²⁺/Ti⁴⁺ absorption also contributes to the pleochroism of the samples. The intensities of

the absorption bands of Fe³⁺, on the other hand, are almost identical parallel and perpendicular to the *c*-axis (for the assignment of absorption bands see also Schmetzer and Bank, 1980, 1981; Schmetzer 1987; Häger 1996). Consequently and for simplicity, we present only non-polarized spectra or, for some samples, the spectra perpendicular to *c* in the following section.

Sri Lanka

Before considering absorption spectra and causes of colour of padparadschas, it is appropriate to discuss briefly the spectroscopic properties of yellow to orange, chromium-free sapphires from Sri Lanka.

a. Untreated and heat treated yellow, yellowish-orange or orange (chromium-free) sapphires

Untreated yellow sapphires (Figure 7), in general, show a light yellow coloration, which is caused by colour centres. Yellow colour centres in corundum from Sri Lanka are normally unstable to heat treatment, and samples turn colourless after heating to temperatures in the range of 500 to 600°C (Schmetzer *et al.*, 1983; Nassau and Valente, 1987). The yellow coloration of heat treated,

Table V: Assignment of absorption maxima shown by orange sapphires.

Cause of colour	Maximum (nm)	Strength of peak according to polarization direction
Fe ³⁺	450 388 376	<i>c</i> ≈ ⊥ <i>c</i> <i>c</i> ≈ ⊥ <i>c</i> <i>c</i> ≈ ⊥ <i>c</i>
Cr ³⁺	693 556 ⊥ <i>c</i> ; 542 <i>c</i> 410 ⊥ <i>c</i> ; 397 <i>c</i>	Sharp line ⊥ <i>c</i> > <i>c</i> <i>c</i> > ⊥ <i>c</i>
Fe ²⁺ /Ti ⁴⁺	699 559	<i>c</i> ≈ ⊥ <i>c</i> ⊥ <i>c</i> > <i>c</i>
yellow colour centres	increasing absorption from red through violet to the ultraviolet (uv component)	<i>c</i> ≈ ⊥ <i>c</i>
orange colour centres	470 380 and/or increasing absorption from red through violet to the ultraviolet (uv component)	<i>c</i> ≈ ⊥ <i>c</i> <i>c</i> ≈ ⊥ <i>c</i>

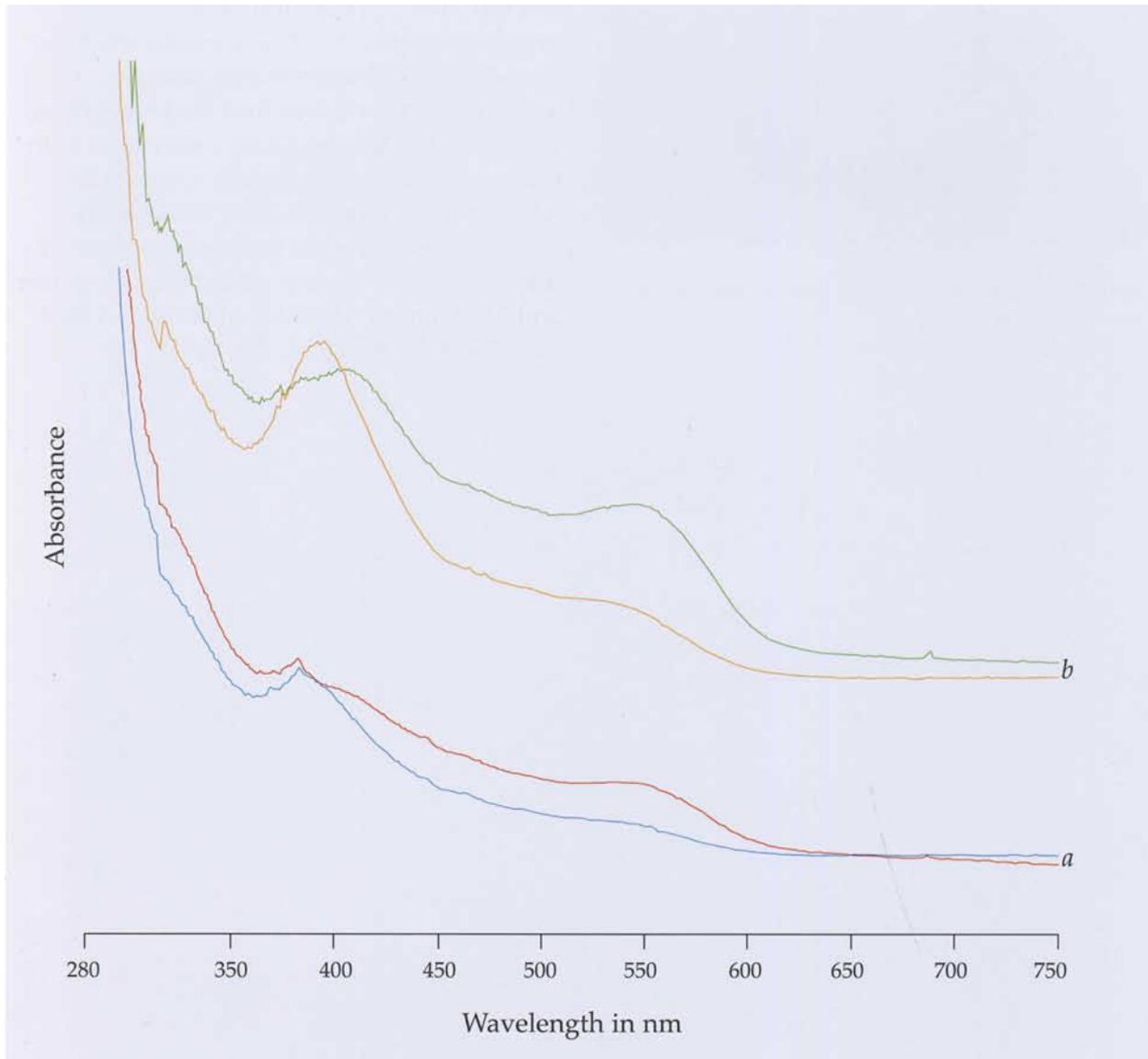


Figure 6: Polarized absorption spectra of an untreated yellowish-orange (a) and an untreated pinkish-orange (b) padparadscha from Sri Lanka; pleochroism of the samples is mainly due to differences in the chromium spectrum parallel (blue, yellow) and perpendicular (red, green) to the c-axis.

The label above all spectra shows the position of absorption maxima and their assignment, OCC = 'orange' colour centres.

colourless Sri Lanka sapphires is restored by exposure to various types of radiation, for example sunlight, UV light, X-ray or gamma-radiation (Nassau and Valente, 1987; for further details of the reaction of yellow Sri Lanka sapphires to various types of treatments the reader should refer to this detailed paper).

Absorption spectra of yellow Sri Lankan sapphires reveal an almost continuously increasing absorption from red to the violet part of the visible range, occasionally with small absorption bands of Fe^{3+} (Schmetzer and Bank, 1981; Schmetzer *et al.*, 1983). According to the low iron concentration (Table IV, Figure 5), the intensity of Fe^{3+} -



Figure 7: Untreated yellow sapphire from Sri Lanka of 5.97 ct. (Photo by M. Glas)

related absorption bands of such samples (see Table V), in general, is too small to influence the colour of the samples. An additional weak absorption band at about 470 nm may be present in a few yellow sapphires (Figure 8), i.e. at a position where the Mg-related absorption maximum of 'orange' colour centres may be present (see Table II). After a long search a specimen with these spectroscopic properties was found, which showed undisturbed three-phase inclusions, confirming that this sapphire was not heat treated (see Koivula, 1986; Schmetzer and Medenbach, 1988; De Maesschalck and Oen, 1989; Francis *et al.*, 2003).

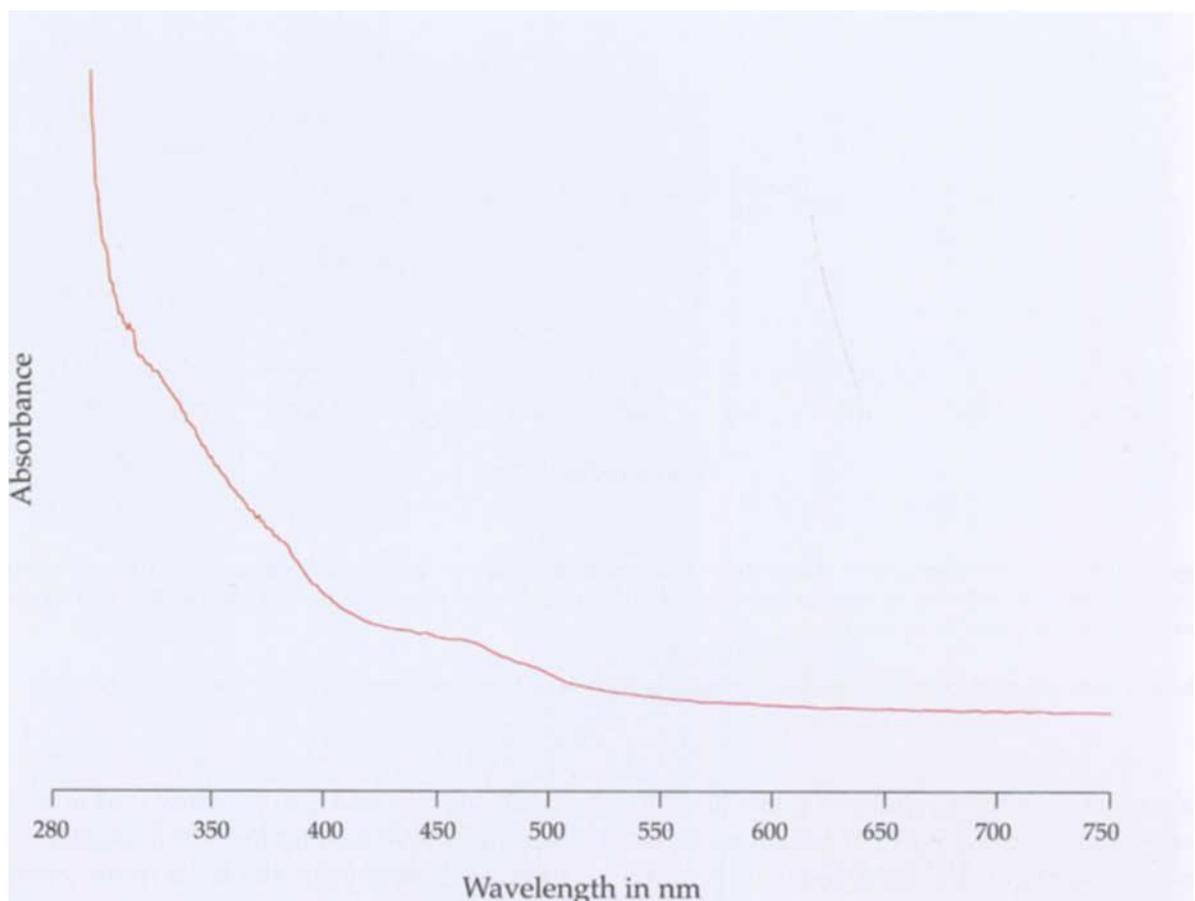


Figure 8: Absorption spectrum of untreated yellow sapphire from Sri Lanka; the spectrum shows an increasing absorption from the red to the violet part of the visible range; small iron bands as well as a weak absorption band due to 'orange' colour centres (OCC) are also present.

The 470 nm absorption and the always-present ultraviolet component can be produced or intensified by irradiation of originally colourless or pale yellow sapphires from Sri Lanka. The coloration of such orange irradiation-treated samples is unstable and the absorption band of the 'orange' colour centres can be removed by low temperature heat treatment and even in sunlight (see Schmetzer *et al.*, 1983; Pisutha-Arnond *et al.*, 2004).

Probably, the two spectroscopic features described above for yellow sapphires from Sri Lanka are independent of each other, but it is not yet possible to identify which may be the cause of colour in any one stone. Because almost all defect centres known in sapphires, whether or not related to Mg, reveal an absorption band in the ultraviolet or violet (see *Tables I and II*), the low energy tail of which extends into the visible range, an assignment to one of these centres is not possible at present. It is conceivable that the 470 nm absorption is caused by Mg-related 'orange' colour centres, but no further data exist to support this assignment. Further research, for example careful heat treatment experiments of untreated Sri Lankan samples combined with spectroscopic examination, is needed to resolve these problems.

Heat treated chromium-free yellow, yellowish-orange or orange sapphires (*Figure 9*) reveal an absorption spectrum consisting of two components, i.e. an absorption in the ultraviolet extending to the visible and small peaks or distinct shoulders in the 450-470 nm range (*Figure 10*); some of these spectra are also superimposed by weak Fe³⁺ bands at 450, 388 and 376 nm (see *Figure 10a*). According to the intensity of both components of this absorption spectrum, i.e. the maximum in the UV extending to the visible and the 470 nm band, these samples are yellow (weaker absorption) or become more or less yellowish-orange to almost orange (more intense absorption).

At present, it is not clear if the 380 nm maximum known from synthetic Mg-doped 'impure' sapphires is also present. It should be mentioned, however, that the 470 nm absorption is always accompanied by a strong UV component. Thus, if we speak about sapphires with thermally stable 'orange' colour centres, we have to consider the presence of the 470 nm absorption band together with the 380 nm maximum and/or a distinct UV component (see *Table II*). Both components of the spectrum of heat treated yellow to yellowish-orange sapphires might be independent of each other, or both might be caused by an orange, Mg-related colour centre. The maximum in the UV, however, might also be due to another defect with or without Mg (see *Table I*).

Upon radiation treatment of heat treated, chromium-free corundums of this type, 'orange' colour centres are produced and the 470 nm absorption band is intensified. These colour centres are unstable and can be removed by low temperature heat treatment (Schmetzer *et al.*, 1983), as described above for non-heat treated irradiated Sri Lankan sapphires.

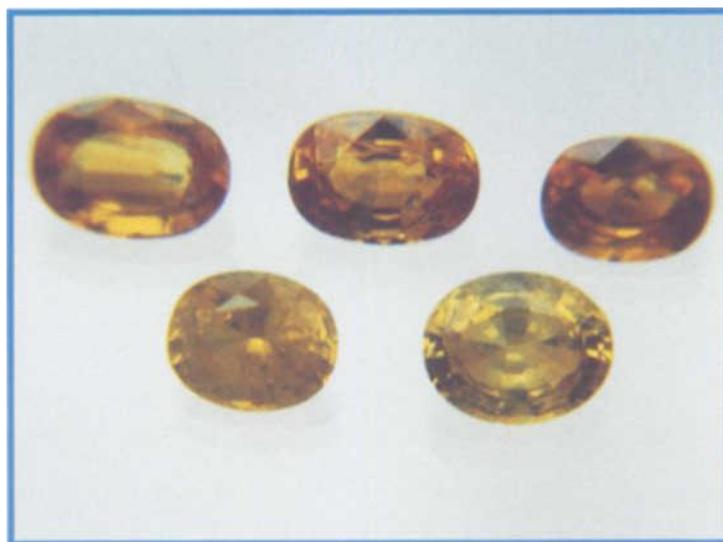


Figure 9: Heat treated yellow (lower row) and yellowish-orange (upper row) sapphires from Sri Lanka; range of samples from 1.59 to 2.33 ct. (Photo by M. Glas)

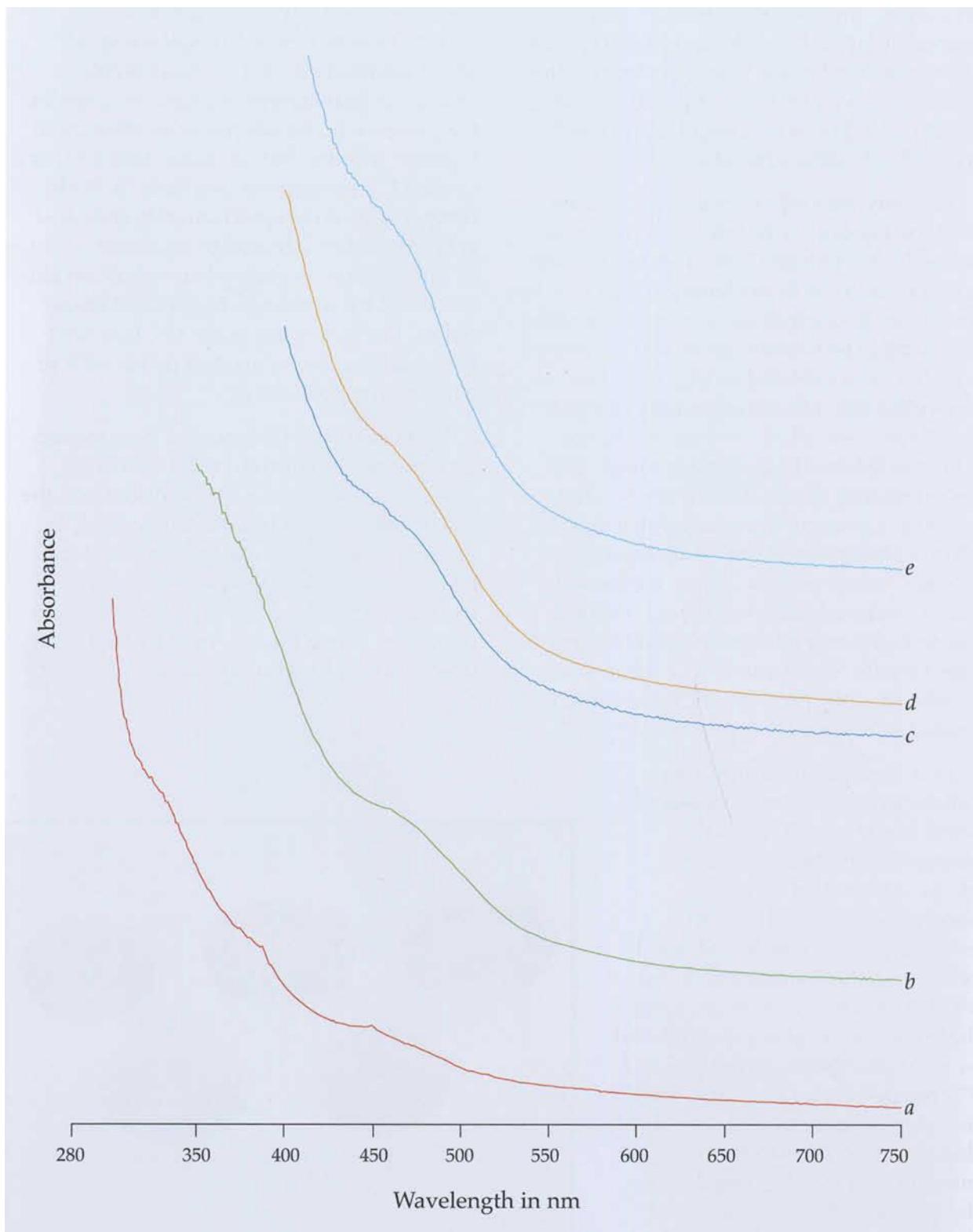


Figure 10: Absorption spectra of heat treated yellow and yellowish-orange sapphires from Sri Lanka; the spectra show increasing absorption from red to the violet part of the visible range on which is superimposed an absorption band of the 'orange' colour centre (OCC); with increasing intensity of both absorptions (a to e), the colour of the samples changes from yellow to yellowish-orange; weak absorption bands of Fe³⁺ are also present occasionally; spectra b to e are vertically displaced for clarity.

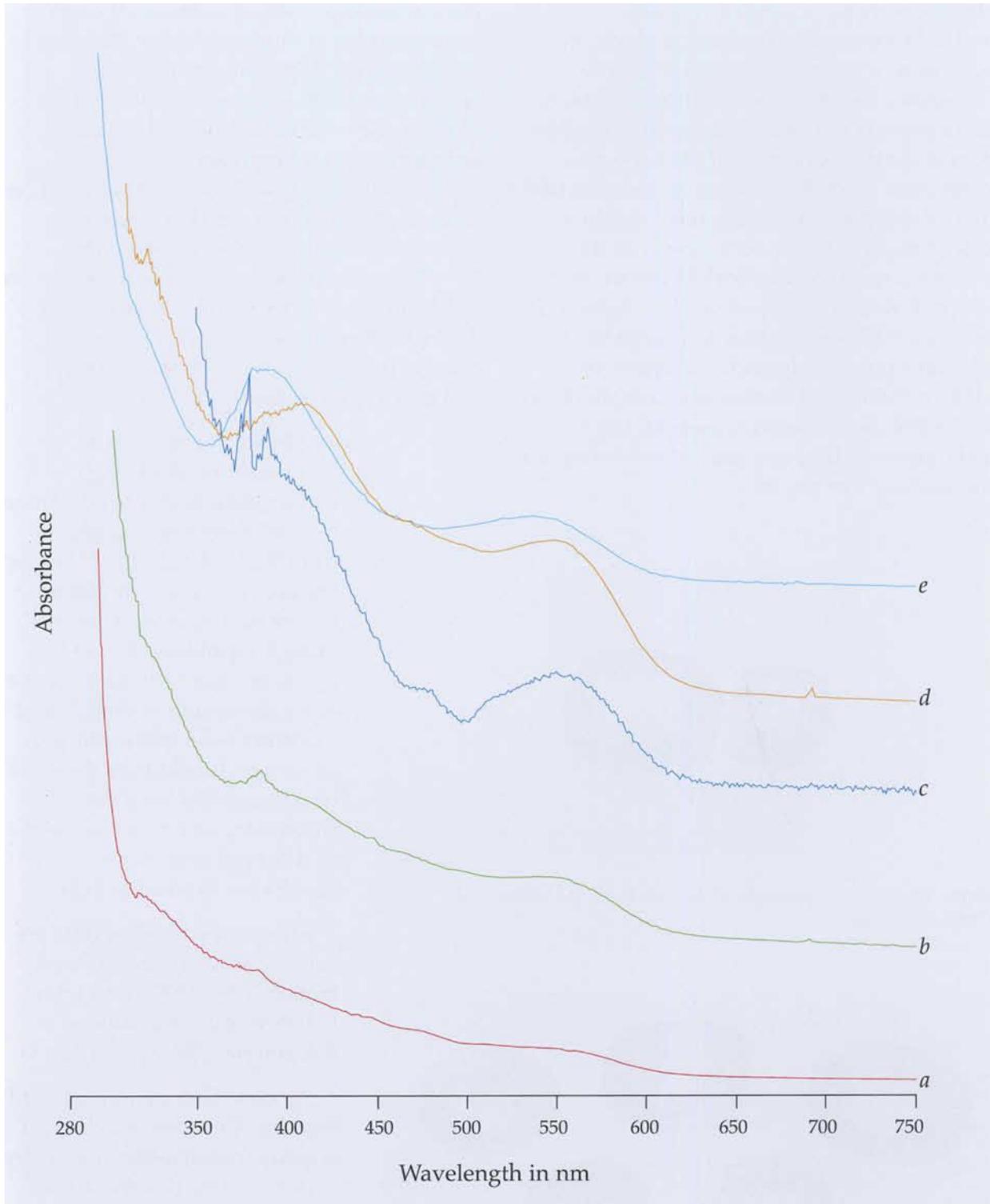
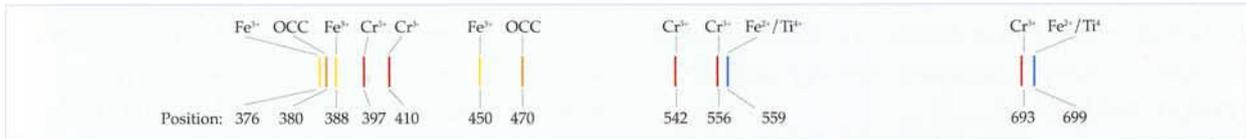


Figure 11: Absorption spectra of untreated yellowish-orange and pinkish-orange padparadscha sapphires from Sri Lanka; the spectra show increasing absorption from red to the violet part of the visible range on which is superimposed the absorption bands of chromium; weak absorption bands of Fe³⁺ are sometimes present, and the presence of a weak band at 470 nm assigned to 'orange' colour centres is also shown. Yellowish-orange samples reveal a strong absorption caused by 'yellow' colour centres and weak chromium bands, and with increasing chromium absorption (a to e), the colour of the samples changes to pinkish-orange or even reddish-orange; spectra b to e are vertically displaced for clarity.

b. Untreated and heat treated yellowish-orange to reddish-orange chromium-bearing sapphires (padparadschas)

Spectroscopic properties of the untreated chromium-bearing samples (Figures 2 a, b, and 12) examined in the present study are consistent with literature data (Figure 11). In yellowish-orange samples, the increasing absorption in the visible range due to yellow colour centres is dominant over the two chromium absorption bands, and in pinkish-orange samples the reverse relationship is observed. Between the two however, there is a continuous transition both in colour and in spectral peak heights and no clear separation between yellowish-orange to orange to pinkish-orange padparadscha 'types' is evident. Additional weak maxima or shoulders in the UV are sometimes present, but the assignment of these spectral features is beyond the scope of this paper.



Figure 12: Untreated padparadschas from Sri Lanka of 1.88 and 3.04 ct. (Photo by M. Glas)



Figure 13: Heat treated padparadschas from Sri Lanka; range of samples from 1.08 to 3.20 ct. (Photo by M. Glas)

It is extremely difficult to decide whether 'orange' colour centres with an absorption at 470 nm together with an additional UV component are present in all untreated padparadschas from Sri Lanka. Although some samples in this study show these peaks they are never dominant. In most such spectra, the weak 470 nm absorption appears in intensities comparable to that found in untreated yellow sapphires (see Figure 8). In some samples a weak $\text{Fe}^{2+}/\text{Ti}^{4+}$ absorption (blue sapphire component) or weak Fe^{3+} absorption bands are also present. The $\text{Fe}^{2+}/\text{Ti}^{4+}$ absorption is seen only in orange to reddish-orange Sri Lankan sapphires with distinct colour zoning, i.e. with yellow, orange, pinkish-orange or reddish-orange and blue colour zones.

Absorption spectra of chromium-bearing, high temperature heat treated orange to reddish-orange sapphires from Sri Lanka (Figure 13) show features which are similar to that of heat treated yellowish-orange sapphires (Figure 14, compare Figure 10); they consist of an absorption in the UV and a distinct band in the 450-470 nm range. In addition, there are two absorption bands of chromium, and many samples of this type also show absorption bands due to Fe^{3+} .

These spectroscopic data are consistent with the results of Notari (1996, 1997), and with the chemical compositions of the samples (Table IV, Figure 5).

As described by Emmett and Douthit (1993), the production of padparadscha-like colours by oxidizing heat treatment of pink Montana sapphires is also

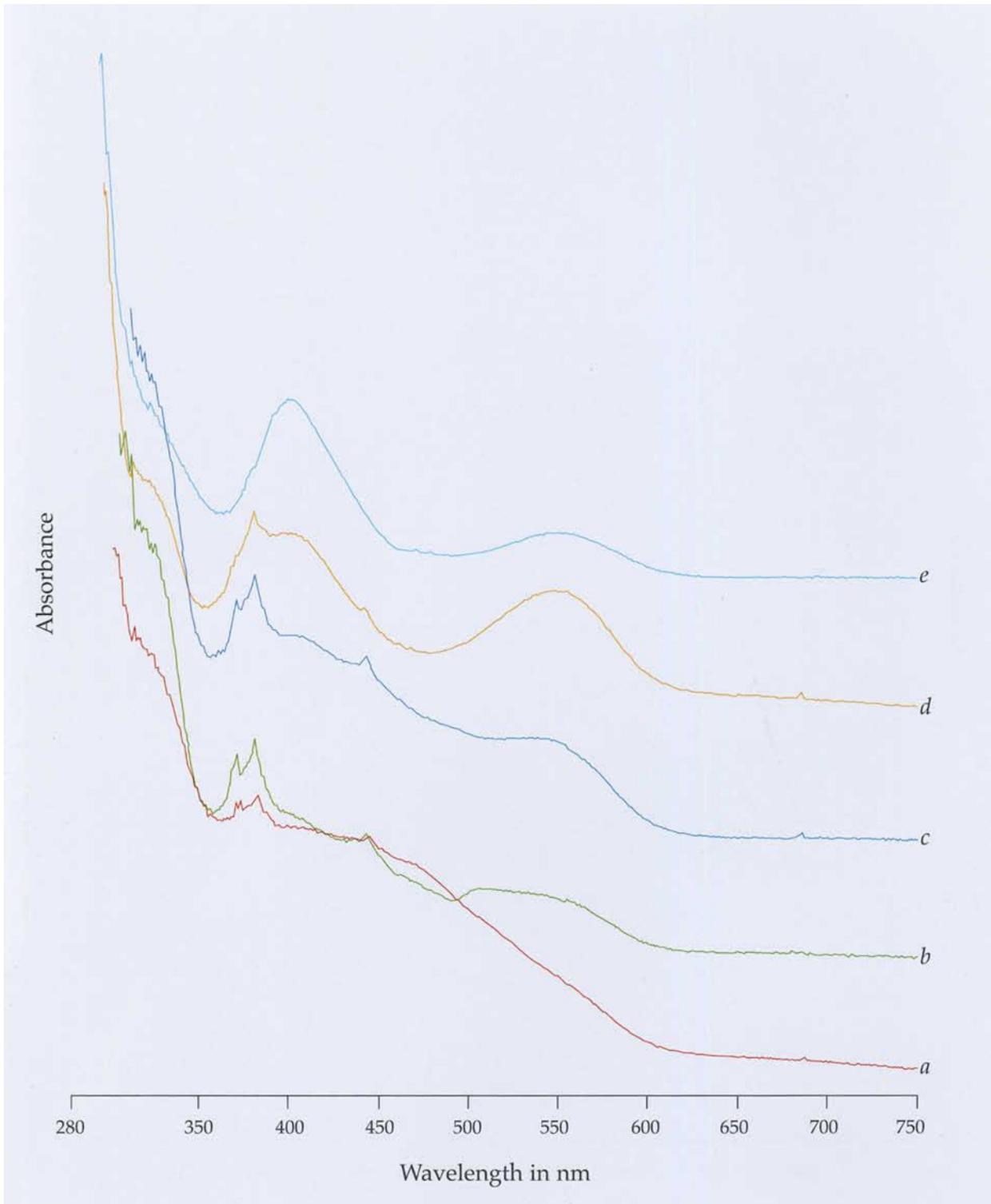
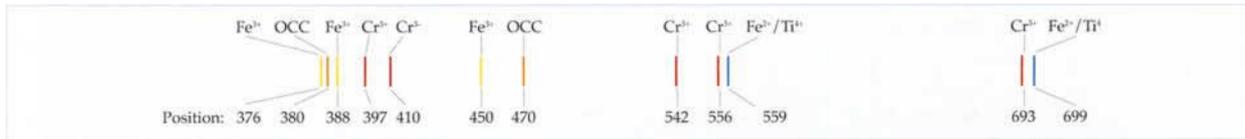


Figure 14: Absorption spectra of heat treated orange to reddish-orange padparadscha from Sri Lanka; the spectra consist of the absorption bands of 'orange' colour centres at 470 nm with an additional UV component and the absorption bands of chromium in corundum; weak absorption bands of Fe³⁺ are sometimes present. Yellowish-orange samples reveal a strong absorption caused by 'orange' colour centres and weak chromium bands; with increasing chromium absorption (a to e), the colour of the samples changes to pinkish-orange or reddish-orange; spectra b to e are vertically displaced for clarity.

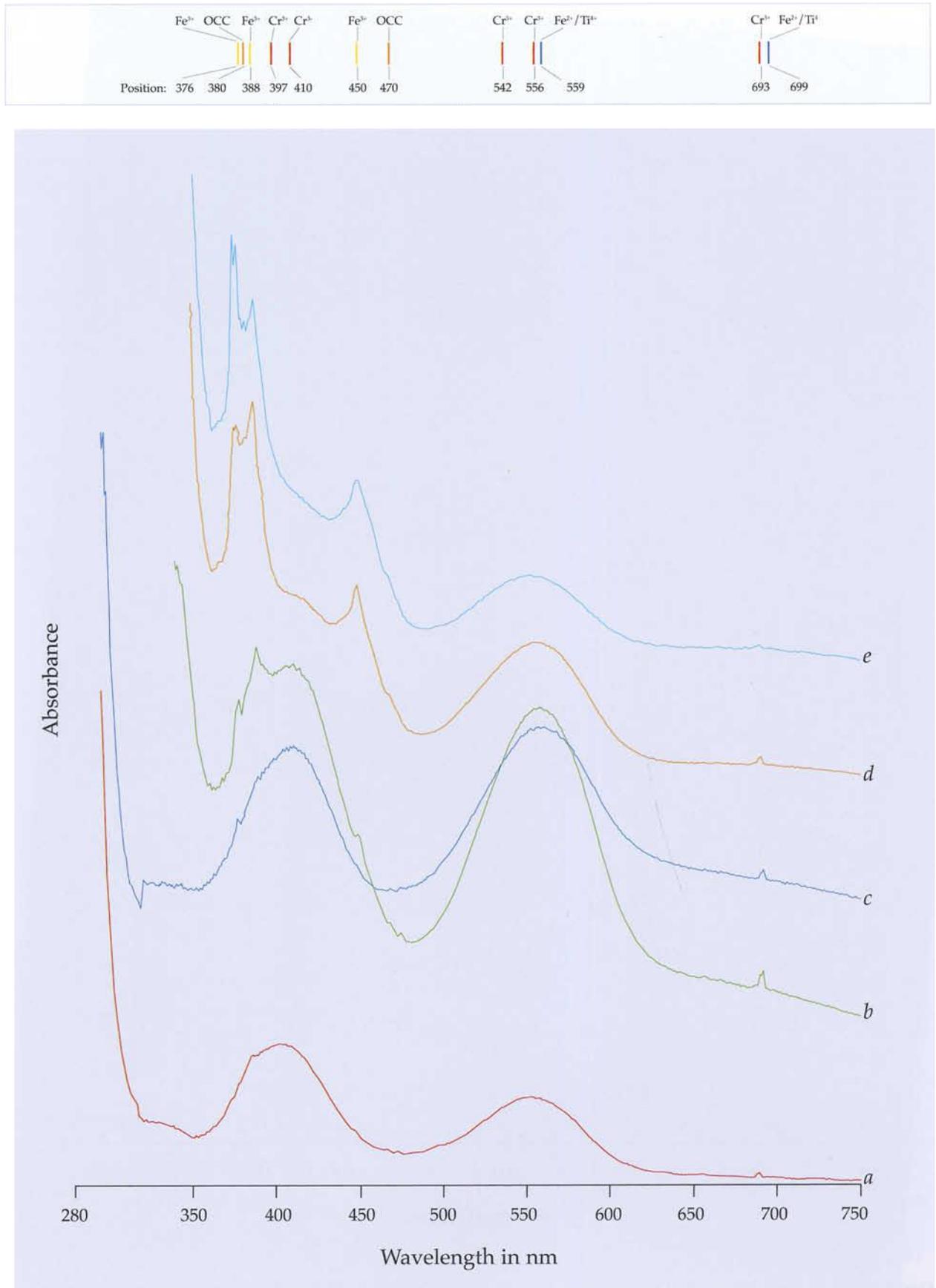


Figure 15: Absorption spectra of untreated sapphires from Ilakaka, Madagascar; pink samples (a) show the absorption spectrum of chromium and, occasionally, weak absorption bands of Fe³⁺; samples with additional Fe²⁺/Ti⁴⁺ absorption (blue sapphire component) are purple or violet (b, c); samples with strong absorption bands of Fe³⁺ are yellowish-orange (d) to brownish-orange or orange-brown (e); spectra b to e are vertically displaced for clarity.

possible. This colour change is caused by the development of 'orange' colour centres in the heat treatment process giving absorption spectra similar to those obtained from Sri Lankan corundums in the present study.

Ilakaka

Ilakaka sapphires show a wide range of colours, dependent on their trace element contents. The wide colour range is comparable to that found in sapphires from Umba, Tanzania and these also show similar spectroscopic and microscopic features (see for example Schmetzer and Bank, 1980, 1981; Gunawardene, 1984; Hänni, 1987; Notari, 1996, 1997, Schmetzer, 1999).

a. Untreated sapphires

According to the chemical (see Table IV, Figure 5) and spectroscopic properties and colour of diffusion treated samples, the untreated samples used for colour improvement by Be-diffusion are related to two colour series, i.e. to samples of the series pink, purplish-pink, purple, purplish-violet, violet (Figure 16a) and to samples of the series pink, yellowish-pink, yellowish-orange, brownish-orange, orange-brown, yellowish-brown (Figure 16b). The brownish-orange colour of some samples with high iron and chromium contents may resemble that of pinkish-orange padparadscha from Sri Lanka

(see Figure 3). Most samples of both colour series reveal a distinct shift of colour when moved from daylight to incandescent light.

The absorption spectra obtained from all untreated Ilakaka sapphires of the first series (Figure 15) show the absorption bands of Cr³⁺ (pink). Also present are weak bands of Fe³⁺ and the strong Fe²⁺/Ti⁴⁺ absorption of blue sapphire. With increasing intensity of the latter absorption band, the colour of chromium bearing samples changes from pink to violet. By simple heat treatment in an oxidizing atmosphere, the band is, at least partly, removed and the samples turn more or less intense pink. A large percentage of the pink Ilakaka sapphires in the trade are heat treated originally purple to violet stones, but there are a few untreated pink sapphires from this source.

Ilakaka sapphires of the second colour series show spectra (Figure 15) with strong overlapping Cr³⁺ (pink) and Fe³⁺ absorption bands (yellow). With increasing intensities of the iron bands, the colour of this type of sapphire changes from pink through yellowish-orange to brownish-orange, orange-brown and yellowish-brown.

b. Beryllium diffusion treated sapphires

Just as there is a wide variety of colour in the untreated material, so the colours of



Figure 16a: Untreated Ilakaka sapphires of the pink to violet colour series; range of samples from 0.51 to 1.38 ct. (Photo by M. Glas)

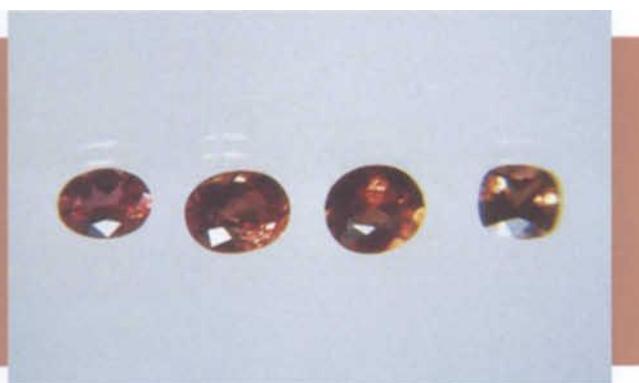


Figure 16b: Untreated Ilakaka sapphires of the pink to orange-brown colour series; range of samples from 0.48 to 1.30 ct. (Photo by M. Glas)

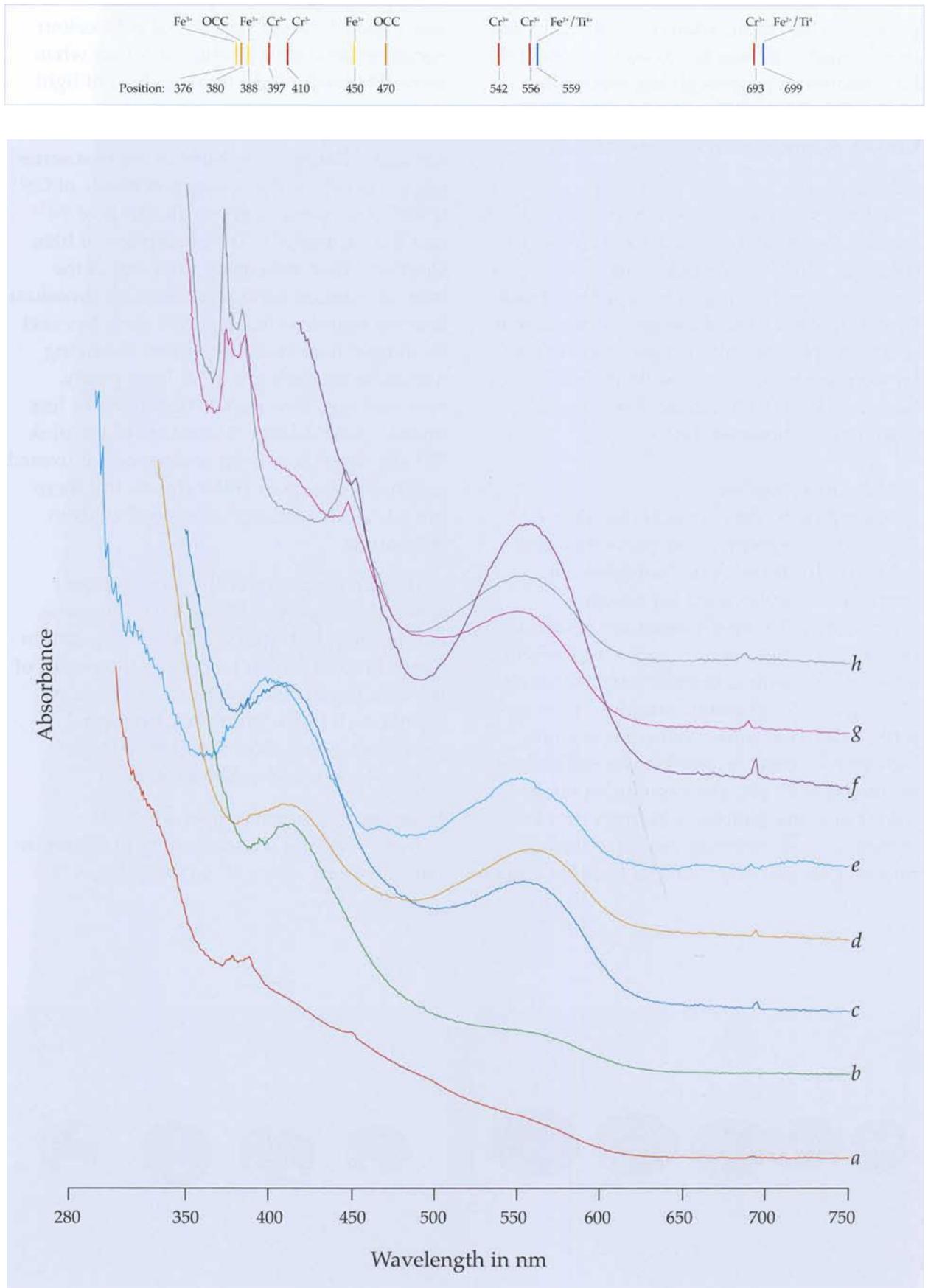


Figure 17: Absorption spectra of Be-diffusion treated sapphires from Ilakaka, Madagascar; differences in the Cr:Fe ratio and the intensity of the 'orange' colour centre cause a wide variety of colours; samples with low chromium and iron contents (a) are yellowish-orange; with increasing chromium contents (b to f), the colour changes to orange, pinkish-orange and orangey-red; samples with higher iron contents (g, h) are reddish-orange or brownish-orange; spectra b to h are vertically displaced for clarity.

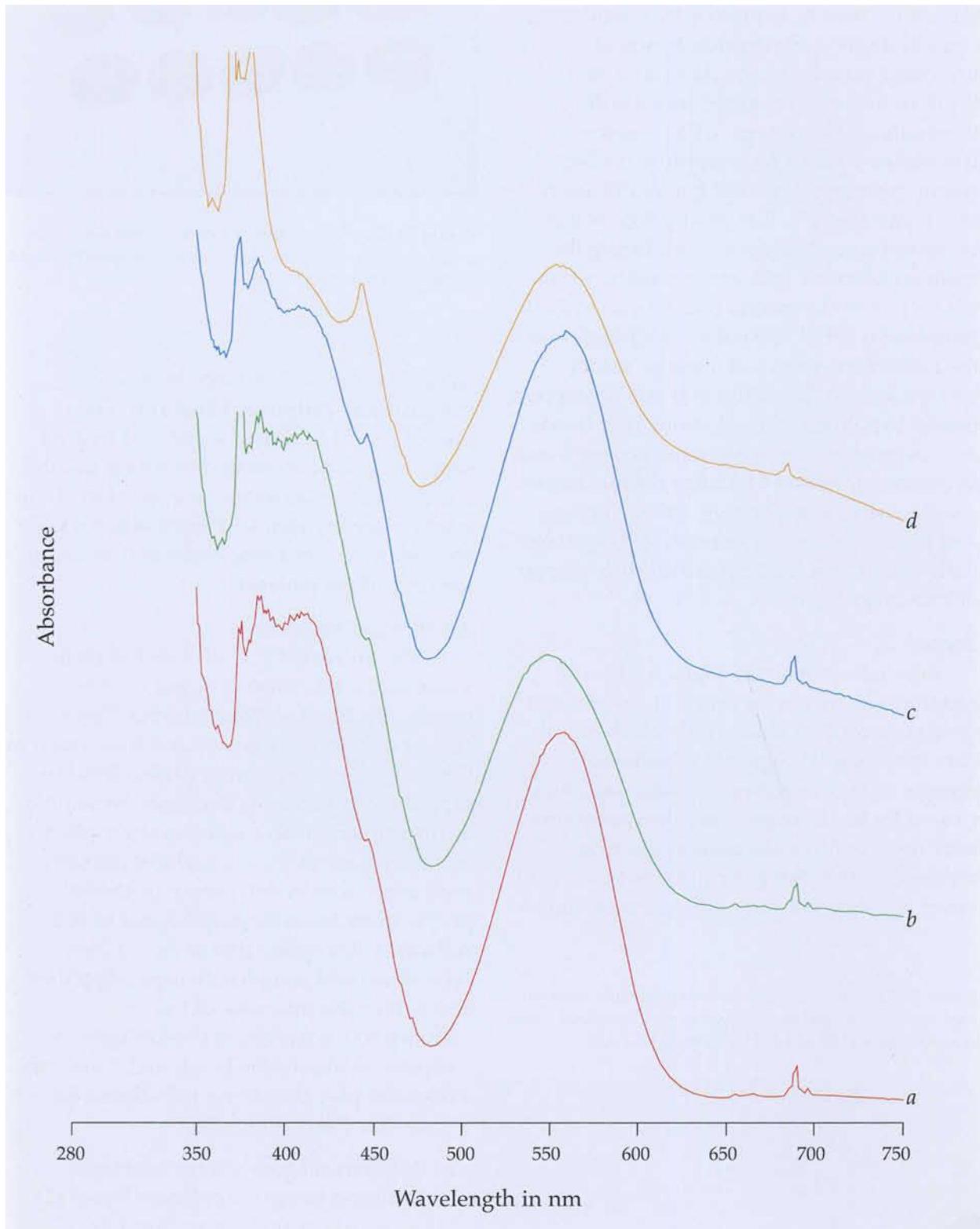


Figure 18: Absorption spectra of untreated rubies and purple to violet sapphires from Songea, Tanzania, consist of a chromium absorption spectrum combined with a more or less intense blue sapphire component; more of the latter causes a colour shift from red towards violet (a to d); spectra b to d are vertically displaced for clarity.

Be-diffusion treated sapphires may be of different shades of pinkish-orange, yellowish-orange, orange and brownish-orange (Figure 19). All absorption spectra (Figure 17) may be explained by considering combinations of absorption bands of untreated samples of the chromium-iron (pink to brownish-orange) series with thermally stable 'orange' colour centres. If there were also a blue sapphire (violet) colour component present before diffusion treatment, the $\text{Fe}^{2+}/\text{Ti}^{4+}$ absorption would be almost completely removed during the treatment process and, consequently, would not be present in spectra of diffusion treated samples. In detail, the colour is a function of the relative intensities of 'orange' colour centres and the chromium and iron absorption bands. Sapphires without strong iron bands are – with increasing chromium contents and decreasing intensity of orange colour centres – yellowish-orange, orange, intense orange and pinkish-orange or orangey-red; samples with higher iron contents are reddish-orange or brownish-orange.

Songea

Although untreated Songea rubies and sapphires show a wide range of colours and spectra, according to spectral and chemical data (see Table IV, Figure 5) of yellowish-orange, orange or reddish-orange sapphires treated by Be-diffusion, only the chromium-bearing sapphires are used as starting materials. Many Songea rubies and purple to violet sapphires reveal a colourless or almost

Figure 20: Untreated Songea sapphires which are commonly used for diffusion treatments are red to purple or violet; range of samples from 0.48 to 3.45 ct. (Photo by M. Glas)



Figure 19: Beryllium diffusion treated Ilakaka sapphires reveal a great variation in colour; range of samples from 0.34 to 0.65 ct. (Photo by M. Glas)

colourless core and a more intense red, purplish-red, purple or violet rim. Thus, the colours of both untreated and treated sapphires are often related to strong colour zoning; i.e. the coloration is a function of the relative sizes of almost colourless cores and the different colour intensities and shades in the rims of the material.

a. Untreated sapphires

In the untreated purplish-red, purple, violet and a few brownish-red sapphires (Figure 20), the absorption spectra (Figure 18) consist of chromium (ruby) and iron-titanium (blue sapphire) absorption peaks. This blue sapphire component is decreased by simple heat treatment in an oxidizing atmosphere and the colour of these sapphires changes somewhat from violet, purple or reddish-purple more towards purplish-red or red. A distinct absorption due to Fe^{3+} is also present in most samples. In these sapphires and rubies the intensity of the Fe^{3+} absorption, however, is weaker than the chromium absorption bands and, thus, iron does not play the strong role discussed above for Ilakaka samples.

b. Beryllium diffusion treated sapphires

Diffusion treated sapphires (Figure 22) show no remaining significant blue sapphire component because this absorption has been almost completely removed by the Be-diffusion treatment.

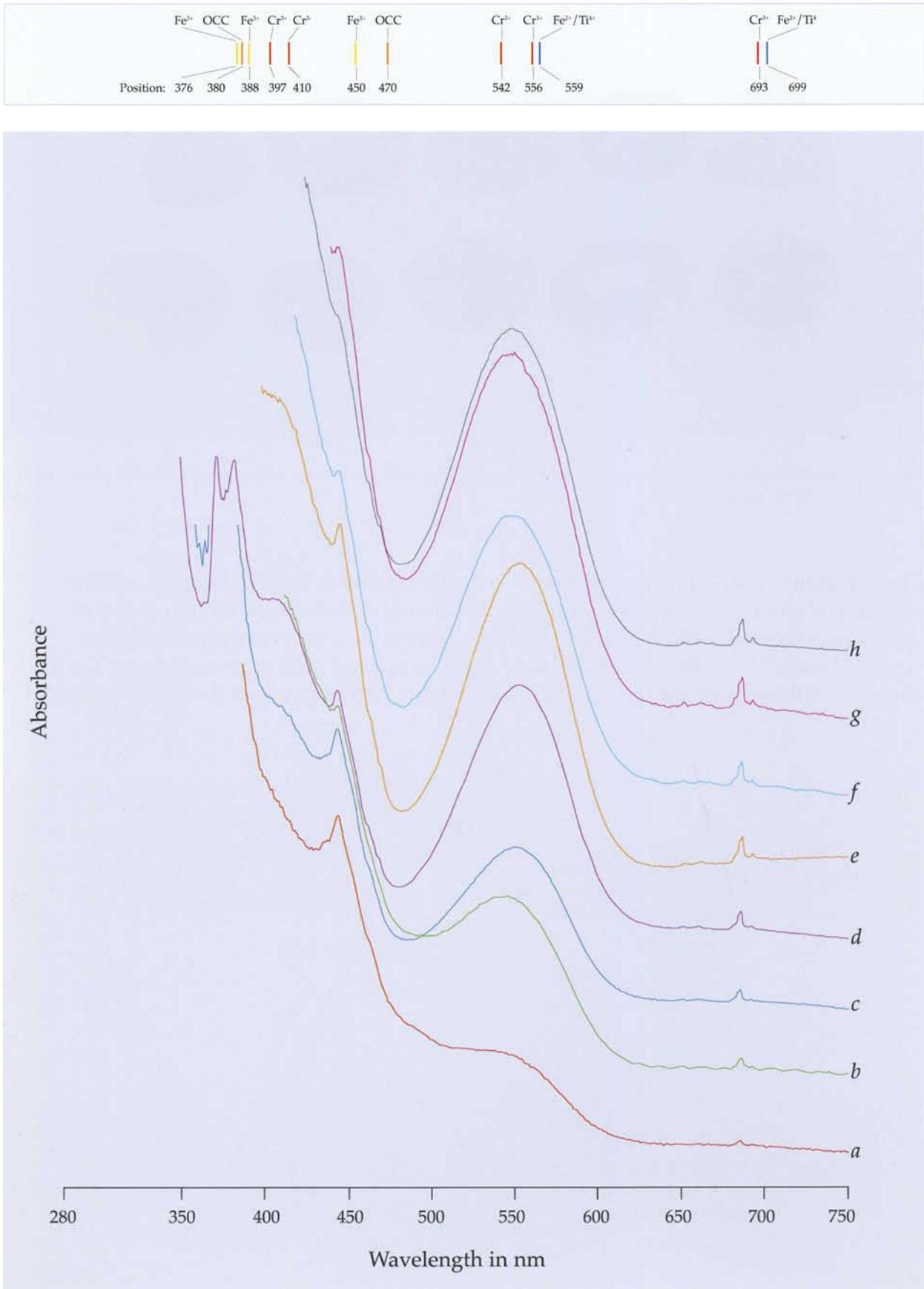


Figure 21: Absorption spectra of Be-diffusion treated sapphires from Songea, Tanzania; according to the chromium content and the intensity of orange colour centres, orangey-yellow, yellowish-orange, orange, pinkish-orange or orangey-red sapphires may be observed (a to h); samples with higher iron contents are reddish-orange; spectra b to h are vertically displaced for clarity.

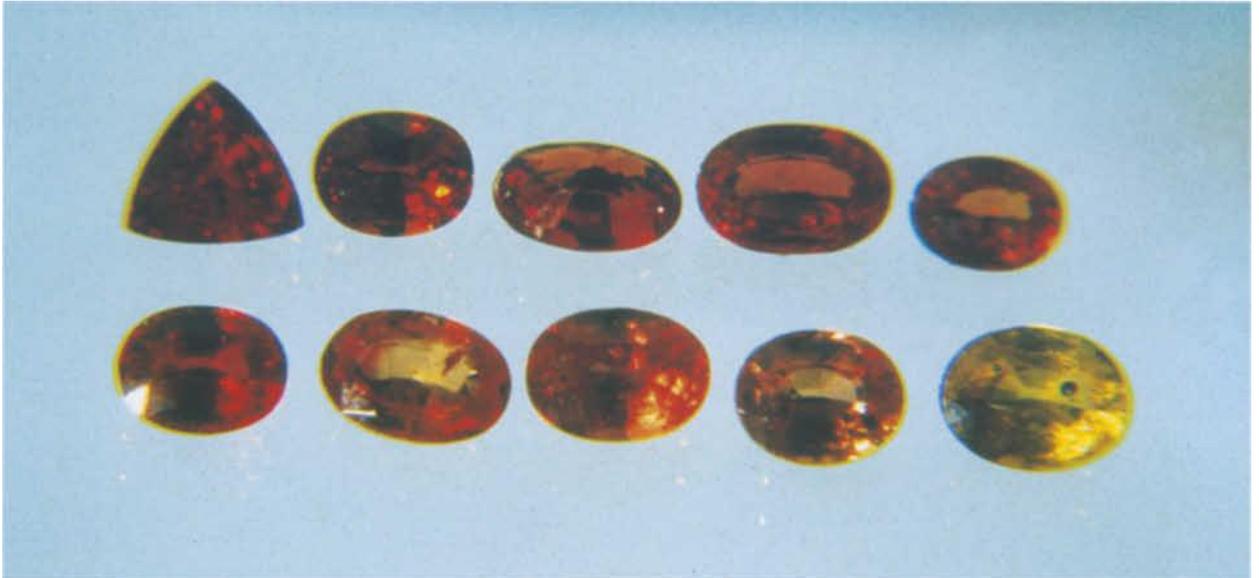


Figure 22: Beryllium diffusion treated sapphires from Songea reveal a great variation in colour; range of samples from 0.30 to 0.64 ct. (Photo by M. Glas)

These samples revealed an absorption spectrum of chromium combined with a spectrum of thermally stable orange colour centres (Figure 21) and the different relative strengths of these cause the range in colours.

Compared to Ilakaka samples, reddish-orange or brownish-orange colours of sapphires with extremely strong iron absorption bands are not observed. On the other hand, orangy-red samples are more

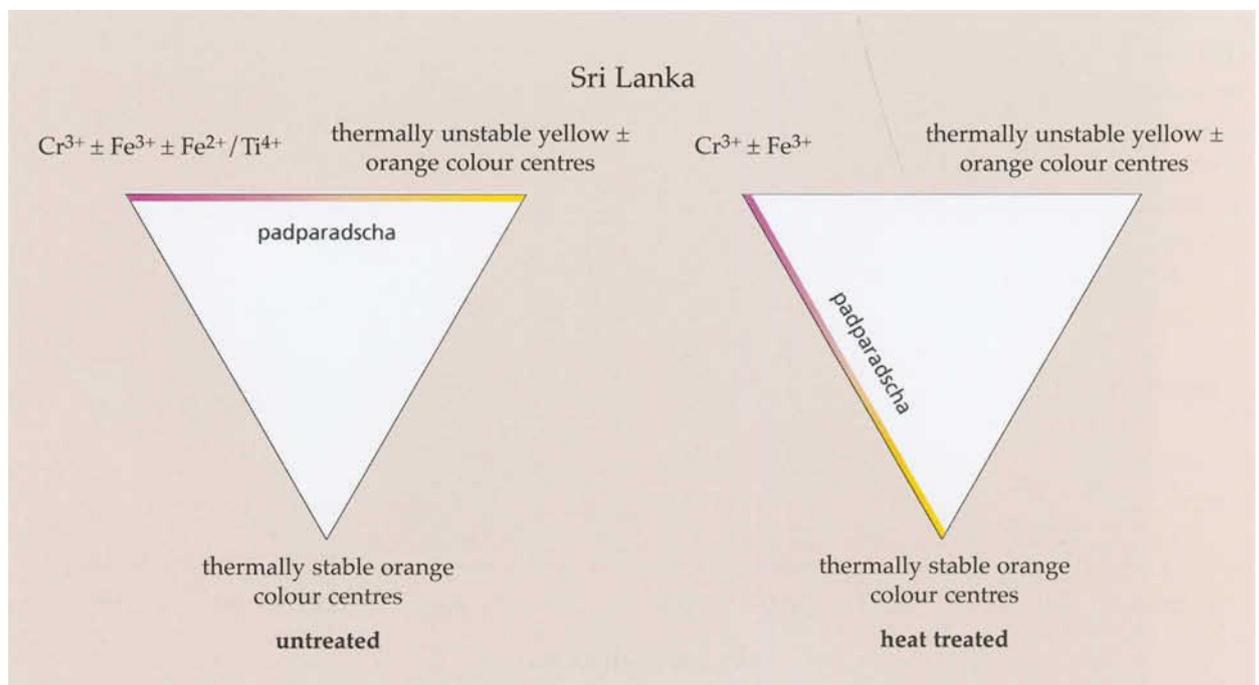


Figure 23a: Schematic representation of causes of colour in untreated and heat treated padparadscha and yellowish-orange sapphire from Sri Lanka; in untreated samples, the dominant causes of colour are thermally unstable 'yellow' colour centres and chromium, with some 'orange' colour centres also being present; in heat treated padparadschas, thermally stable 'orange' colour centres and chromium are present.

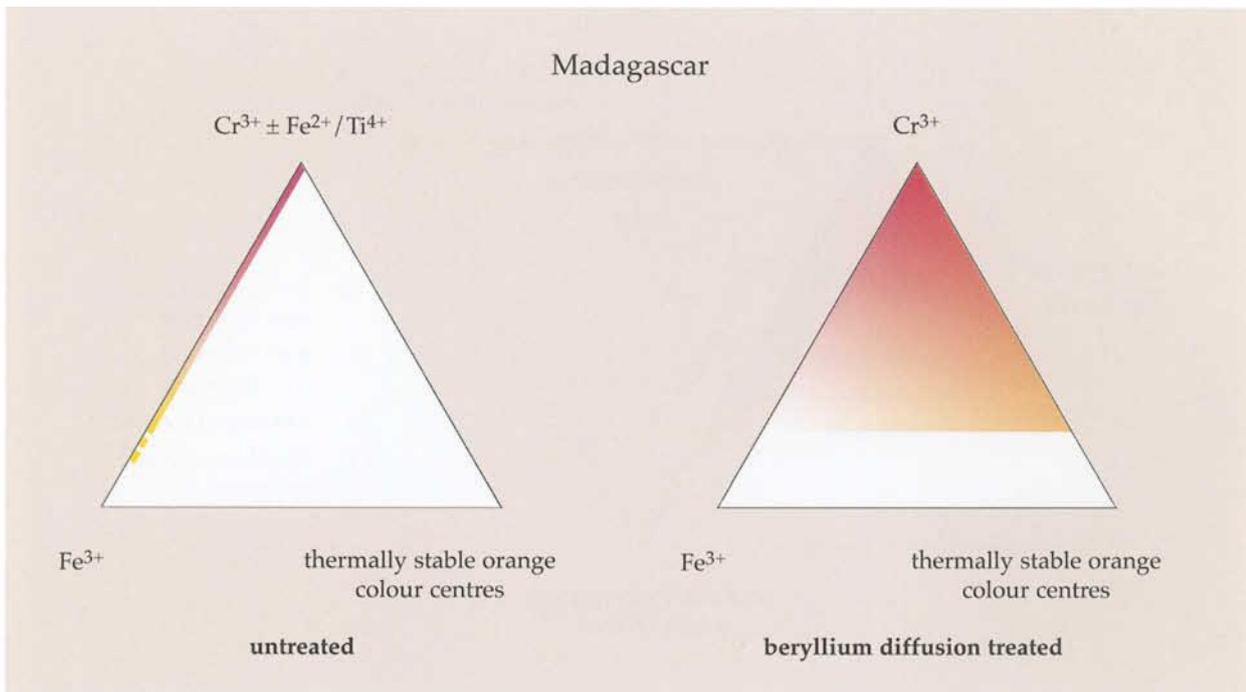


Figure 23c: Schematic representation of causes of colour in untreated and Be-diffusion treated sapphires from Ilakaka, Madagascar; in untreated samples the dominant causes are chromium and iron, with a blue sapphire component also being present in some purple or violet samples; in diffusion treated samples, chromium, iron and thermally stable 'orange' colour centres are present and cause the wide variation of colours observed.

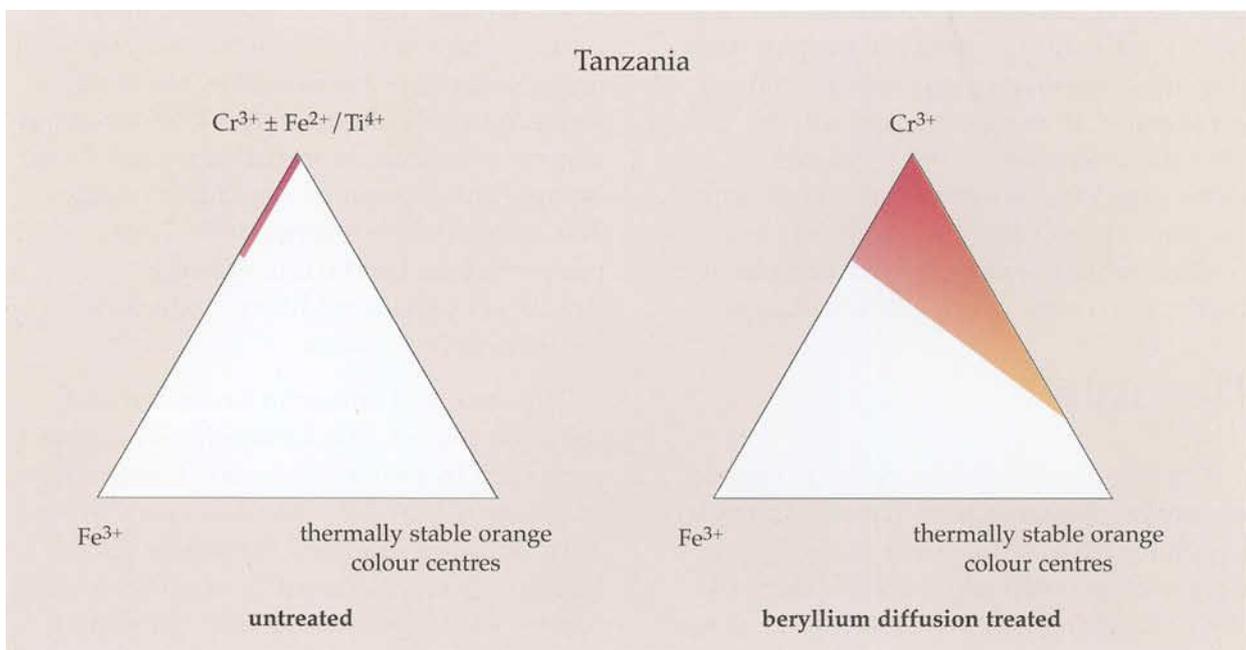


Figure 23b: Schematic representation of causes of colour in untreated and Be-diffusion treated sapphires from Songea, Tanzania; in untreated samples the dominant cause is chromium with a blue sapphire component also being present in some purple or violet samples, absorption bands of Fe^{3+} are subordinate; in diffusion treated samples, chromium and thermally stable 'orange' colour centres are present and cause the wide variation of colours observed.

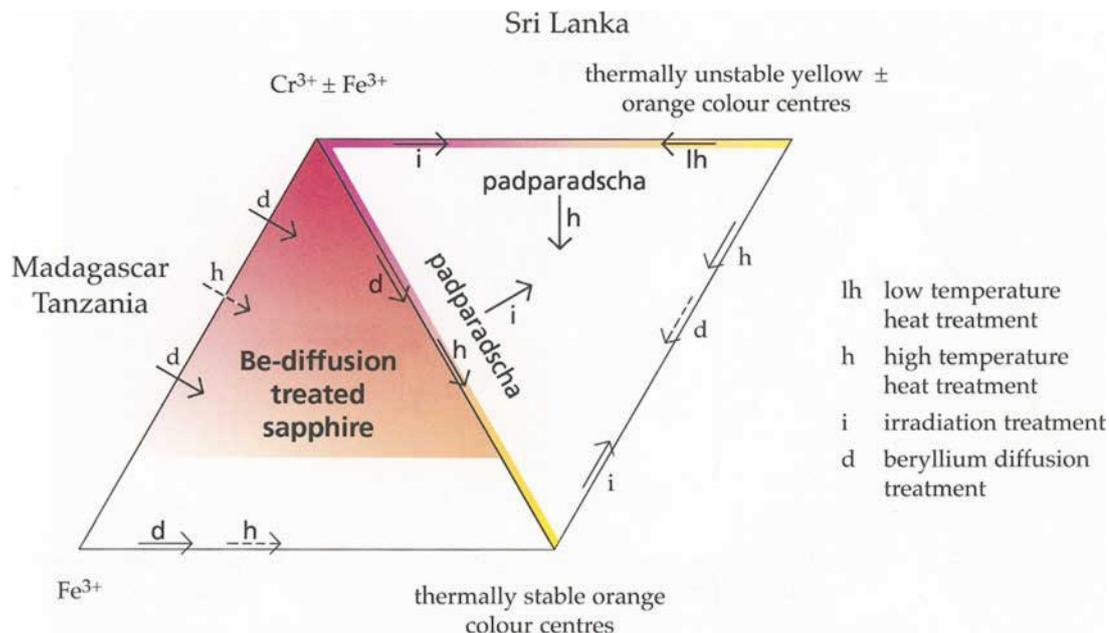


Figure 24: This schematic diagram summarizes the causes of colour in untreated, heat treated and diffusion treated sapphires in the yellow to red colour range; approximate directions of the change of colour by heat treatment, diffusion treatment and irradiation are indicated with arrows. Dashed arrows indicate possible colour changes due to various treatments of specific samples (for example heat or diffusion treatment of originally yellow, chromium-free sapphires), which were not explicitly described in the text.

Thermally unstable 'yellow' and/or 'orange' colour centres are present in untreated padparadscha and yellow sapphires from Sri Lanka. Thermally stable 'orange' colour centres are developed by simple heat treatment or by diffusion treatment of samples from different localities. These thermally stable 'orange' colour centres add to the main causes of colour present before treatment, i.e. iron and chromium.

often found, and this is consistent with the higher chromium contents of samples from this area. Again, a colour series can be arranged with increasing intensity of chromium absorption bands versus decreasing intensity of orange colour centres, i.e. from yellowish-orange to orange and pinkish-orange or orangey-red, samples with higher iron contents are reddish-orange.

Discussion

Considering the results presented above, we might present untreated and heat treated sapphires from Sri Lanka in triangular diagrams to better illustrate the causes of their colour (Figure 23a). Even if some visual colour impressions might be very similar, there is a clear separation between unheated and heat treated materials. The colours of unheated sapphires are due to thermally unstable 'yellow' colour centres and chromium and may show also an additional

weak 470 absorption of 'orange' colour centres. The colours of heat treated yellowish-orange sapphires are caused by thermally stable 'orange' colour centres. If chromium is also present, these heat treated sapphires are orange, pinkish-orange or reddish-orange. The colours of both types of Sri Lanka padparadscha can be intensified by irradiation causing additional extremely unstable colour centres.

The causes of colour in untreated and diffusion treated Ilakaka sapphires are also presented in similar schematic triangular diagrams (Figure 23b). The dominant causes are chromium, iron and thermally stable colour centres; no thermally unstable colour centres are found in sapphires from this locality. It is evident that orange colour centres are added to the iron- and chromium-related coloration of untreated sapphires by the diffusion process. The Fe:Cr ratio varies widely in natural and treated material causing the great variety of colours observed.

Triangular diagrams (*Figure 23c*) show the causes of colour in untreated and diffusion treated samples from Songea, Madagascar. As for the Ilakaka sapphires, the basic causes are iron, chromium and thermally stable colour centres, but the Fe:Cr variation is smaller. More intense colours are due to generally higher chromium contents. Colour changes on treatment are due to the formation of orange colour centres and the decrease in any blue sapphire component. None of the diffusion treated orange samples examined contained more iron than chromium.

A schematic diagram (*Figure 24*) summarizes colours, their causes and the reaction to various treatments of untreated, heat treated and beryllium diffusion treated sapphires from all three localities. Thermally unstable 'yellow' and/or 'orange' colour centres are removed by low temperature heat treatment. High temperature heat treatment causes the development of thermally stable 'orange' colour centres. By beryllium diffusion treatment, similar or identical 'orange' colour centres are developed. By irradiation, unstable colour centres are added to the pre-existing coloration. This type of radiation induced coloration is extremely unstable and can be removed by low temperature heat treatment or upon simple exposure to daylight.

Further research

What could be the next steps in research? According to the fact that some samples, which became yellow or orange-yellow by diffusion treatment, had trace element ratios with $(\text{Mg} + \text{Be}) > \text{Ti}$, but also with $\text{Mg} > \text{Ti}$ (see, for example, the analyses presented by Pisutha-Arnond *et al.*, 2004), the difference in colour change between normal heat treatment and diffusion treatment in such samples is questionable. In other words: the real necessity of beryllium diffusion for samples with $\text{Mg} > \text{Ti}$ is not clear because such samples do not need the addition of beryllium to create a trace element distribution with $(\text{Mg} + \text{Be}) > \text{Ti}$. Thus, such sapphires should transform to yellow or orange-yellow also

without the addition of beryllium (according to the models of Häger and Emmett).

To evaluate the colour change of such samples and to confirm the model described above, slices or pieces of colourless samples should be subjected to both heat and diffusion treatment in order to compare the intensity of colour change of treated samples originating from the same crystal after both types of treatments. It would be of considerable interest if the model were to be confirmed by determination of the trace element chemistry of sapphires which do not become yellow or orange-yellow by normal heat treatment but do so by Be-diffusion treatment. The trace element chemistry should confirm that the Ti-Mg-Be ratio is really $\text{Mg} < \text{Ti}$ for samples which do not turn yellow or orange-yellow by simple heat treatment, but $(\text{Mg} + \text{Be}) > \text{Ti}$ for the same samples, which become yellow or orange-yellow by diffusion treatment. At present, such analytical data are available for one originally blue diffusion treated sapphire (Pisutha-Arnond *et al.*, 2004), and data from more samples should confirm the model. Furthermore, it would be interesting to search for originally colourless samples which do not become yellow following heat or Be-diffusion treatment. Is the chemistry of such samples after diffusion treatment really $\text{Ti} > (\text{Mg} + \text{Be})$?

To clarify the role of iron and chromium and the charge compensating mechanism between Be, Mg, Ti, Cr and Fe, the reaction of samples with different magnesium, titanium, iron and/or chromium contents to both, heat and diffusion treatment, should also be examined. For this research the treatment of colour zoned samples, e.g. the diffusion treatment of zoned Songea rubies and sapphires and the comparison of trace element contents and colour change in identical growth zones within untreated and treated parts of the same sample should provide interesting information. Up to now, traverses across treated samples have mostly been done without detailed knowledge of any zoning within the untreated material and without information about the crystallographic growth sectors that were analysed and their orientation within the sapphire crystals studied.

Additional research is also necessary to understand:

- The structure of 'yellow', 'orange', 'brownish' and 'brownish-violet' colour centres in detail (related to various absorption maxima such as 500, 470, 420 and 380 nm);
- The nature of the defect or defects causing thermally unstable 'yellow' and/or 'orange' colour centres in untreated Sri Lankan sapphires, which is as yet unknown;
- For synthetic and natural Be- and/or Mg-bearing untreated or diffusion treated sapphires, the detailed structures of defect centres which are related to various possible (Be-Mg-Fe-Cr) clusters and how they cause colour; and details of their formation and reaction upon heat treatment.

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Book Reviews

Crystal growth and development interpreted from a mineral's present form

B.Z. KANTOR, 2003: *The Mineralogical Almanac*, Moscow. pp 128, illus. in colour, soft-cover. ISBN 5 900395 46 4. Price €39.00. *The Mineralogical Almanac* 6/2003.

As almost every opening (double-page spread) of this quite attractively illustrated book shows at least two photographs of fair size the text is in fact quite short. The author's thesis is that the present appearance of a mineral can give you clues to at least some of the vicissitudes which it has undergone through (I suppose, recent) geological time. The chapters cover, among other subjects, twinning, crystal families, order and disorder and the development of stalactites. There is a bibliography but it is too short to be really useful: the quality of the photographs is fair. It is not carping to say that the author's style and perhaps some uncertainty in the translation from the original Russian to English do not make for easy reading. It is not quite clear what points, rather than descriptions, the author is trying to make. None the less the various roads taken by the author can be followed by the reader even if he reaches a destination different to the one imagined at the opening of the text. M.O'D.

Geology of gems

E. YA KIEVLENKO, 2003. English edn. Ocean Pictures Ltd., 4871 S. Dudley St, Littleton CO 80123-1942, U.S.A. pp 432, xxxii, illus. in colour, hardcover. ISBN 5 900395 25 1. Price [from Germany] €99.

This very large text on appropriate and attractive heavy paper and translated from the Russian, is a praiseworthy attempt to review and describe the geological occurrence of inorganic ornamental materials (other than diamond but including amber) and is the only survey of this kind to appear in

English for many years. I am discounting Van Landingham's rather misleadingly titled *Geology of world gem deposits* (1985), as this was a compilation and reproduction of papers by various authors.

The present text covers the major gem minerals in general order of importance. Each chapter follows a similar scheme in which a general description of the material is followed by notes on geological genetic types of deposits. Taking beryl as an example, the author lists pegmatites, greisens (ultramafic and carbonate black shale) hydrothermal and placer deposits. For tourmaline we are given pegmatites, contact metasomatic deposits, metamorphic and placer deposits.

Careful attention to the contents is necessary as there is no index, a very serious omission to say the least. There is no heading for quartz though both amethyst and chalcedony have individual entries. While allowing for the inevitable difficulties in translation it is hard to escape a first suspicion that the treatment of the main subject may be eccentric – this is always a possibility with a large single-author work. Further reading dispels this impression to a large extent.

Though the book is large there are no black and white photographs; however most openings show at least one diagram. Coloured illustrations are placed together in a separate section at the end of the text. The type-face is clear and the lines double-spaced, considerately for the determined reader.

To examine the text more closely I chose the chapter on tourmaline, expecting to find at least a mention of the work on California pegmatites by Jahns and Wright (1951) – it is there and includes two reproduced diagrams. This was a relief! The major tourmaline deposits are well presented. In general in this and other chapters Russian deposits are covered first. The garnet group is equally well handled and includes some descriptions of kimberlite pipes, making up for the absence of a diamond chapter!

More than 900 references are given in a separate section at the end of the main text. The abbreviations of titles of the major journals in Russian are expanded before the reference section

begins. The colour plates at the end of the book show spectacular examples of gem minerals and are, in general, well reproduced (though it is hard to distinguish between azurite and malachite in the picture of St. Isaac's Cathedral at St Petersburg – this is hardly a serious fault. Sizes and provenance are given.

Though it is not cheap, I am happy to be able to recommend this book not only on the grounds of the scarcity of similar monographic treatments of the subject in English but also because so much information is so well presented. There are some inconsistencies – nomenclature includes some names not now encouraged – but faults are few. M.O'D.

The petrographic microscope

D.E. KILE, 2003. *The Mineralogical Record*, Tucson, AZ, U.S.A. pp 96, illus. in colour. Softcover. Special publication no.1.

This account of the history, aim, design and workings of the petrographic microscope forms the first of a new and welcome series from *The Mineralogical Record*. Microscopes of this kind are collected as much as used and no doubt dealers in scientific instruments will welcome this issue. The sub-title is 'Evolution of a mineralogical research instrument' and the first chapter explains the author's use of the adjective petrographic rather than the more familiar petrological through the terms refer to the same instrument – it is only the usage which varies. Succeeding chapters deal with plane-polarized light with the evolution and development of the microscope through the early 1900s. Accessory equipment could be quite considerable and is described. The use of the universal stage made the microscope a formidable tool and other devices, including the Michel-Levy comparator and the numerous accessories used with reflective light microscopy are not forgotten.

The bibliography extends to 10 pages and the photographs are clear and informative. M.O'D.

Gem-A Conference 2004

To be held on Sunday 31 October at Kempton Park Racecourse,
Sunbury on Thames, Middlesex

In conjunction with the late autumn Rock 'n' Gem Show

Keynote lecture

Tom Chatham: Created diamonds ... a stone who's time has come ... are you ready?

Dr Ronald L. Bonewitz: Placer sapphire mining in Montana, USA

Elisabeth Strack: Cultured pearls

Ross N. Chapman: Australian opal

Adrian Levy: The Amber Room – the fate of the world's greatest lost treasure

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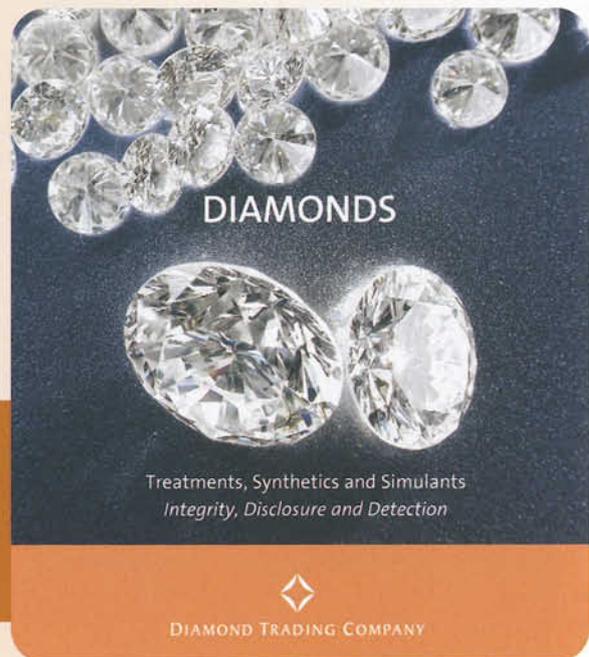
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Proceedings of the Gemmological Association and Gem Testing Laboratory of Great Britain and Notices

Photo Competition

The 2004 Photographic Competition on the theme 'Imaginative Images' drew a record number of entries of very high quality, illustrating creative gem cuts and mineral carvings, fanciful inclusions and gems, as the inspiration of jewellery design.

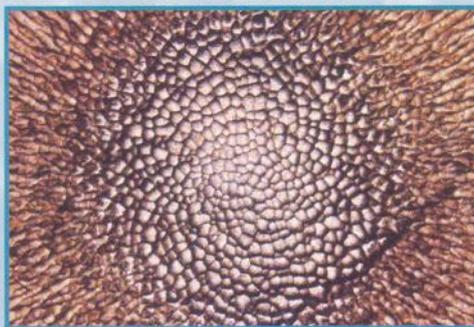
First Prize

Alan Hodgkinson FGA DGA,
Portencross by West Kilbride, Scotland
– *Limonite framework in topaz*



Second Prize

Zeng Chunguang FGA,
Singapore – *Macle diamond*



Third Prize

Susan Stocklmayer FGA, Perth,
Western Australia – *Pearl centre*

We are pleased to announce that the prizes were sponsored by Harley UK, and the Association is most grateful to them for their generosity. The winning entries will be exhibited at the Annual General Meeting to be held on 14 September and at the Gem-A Annual Conference on 31 October.

Donations

The Council of Management are most grateful to the following for responding to the appeal for donations. Donation levels were Circle of Benefactors (£5000 and above), Diamond (£1000 to £4999), Ruby (£500 to £999), Emerald (£250 to £499), Sapphire (£100 to £249) and Pearl (£25 to £99).

The following join those donors listed in previous issues of *The Journal*.

Gem-A Circle of Benefactors

David M. Robinson Ltd, Liverpool

Diamond Donation

Anonymous donor

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Robert B.R. Gau FGA, Taipei, Taiwan,
R.O. China

Robert L. Rosenblatt FGA, Salt Lake City,
Utah, U.S.A.

Christopher D. Tarratt FGA, Stoneygate,
Leicestershire

Gifts

The Association is most grateful to the following for their gifts for research and teaching purposes:

Maggie Campbell Pedersen FGA, London, for a plastic statuette of a horse purchased on E-bay for £7.00 but described as '17th century rare cherry amber'!

The **Diamond Trading Company** for literature on diamonds and mining.

Makhmout Dومان, Arzawa Mineralogical Inc, for natural and synthetic yellow diamond grit, and a faceted demantoid from Russia; crystals and faceted samples of diaspore and kammererite, a blue chalcedony cabochon and a faceted honey-coloured opal from Turkey; demantoid garnet crystals from Iran; tourmaline rough from East Africa; Mali garnet rough; spinel crystals from Vietnam; and a faceted 5.17 ct aquamarine from Pakistan.

Jean-Marie Duroc-Danner FGA, Geneva, Switzerland, for a half boule and a brilliant-cut sample of cobalt-doped green synthetic Verneuil sapphire imitating emerald, produced by Djeva, Monthey, Switzerland.

John R. Führbach FGA, Amarillo, Texas, U.S.A., for the following rough: agate, alabaster, obsidian, moldavite var. bediasite, opalized chert (UV fluorescent), Whitetail

deer teeth, petrified palm tree root and petrified wood from Texas; shells from Texas/Gulf of Mexico; augite, labradorite (not bytownite), peridot (including specimens from Kilbourne Hole) and smithsonite from New Mexico; amethyst and baboon teeth from Zambia; orthoclase feldspar from Nevada; amethyst from Brazil/Zambia; beryl and emerald from Brazil; serpentine sawn rough with demantoid crystals attached from Canada; volcanic rock from Tien Shan Mts, Kyrzygstan; flint, quartz and pink crystals (not identified).

Vanessa Paterson, Arnold, Nottingham, for crystals including peridot from Pakistan, garnet, feldspar, spinel octahedra in matrix and black onyx; faceted danburite and black onyx; and synthetic specimens including cubic zirconia, colourless and bi-coloured flame fusion corundum boules, hydrothermal and flame fusion ruby, flux spinel, flux melt emerald, Kyocera Polar opal, opal doublet, faceted alexandrite, faceted colourless and yellow YAG, and synthetic zincite.

Alexandros Sergoulopoulos FGA DGA, Athens, Greece, for a 0.32 ct laser drilled diamond.

Members' Meetings

Midlands Branch

On 30 April at the Earth Sciences Building, University of Birmingham, Edgbaston, Terry Davidson gave an illustrated talk entitled *Bond Street Jewellers of the 19th and 20th centuries*. The meeting also included the Branch AGM when David Larcher, Gwyn Green, Elizabeth Gosling and Stephen Alabaster were re-elected President, Chairman, Secretary and Treasurer respectively.

On 26 June at Barnt Green the annual Summer Supper Party was held.

North East Branch

On 19 May at the offices of Evans of Leeds Ltd, Millshaw, Leeds, Maggie Campbell Pedersen gave a presentation entitled 'Organics – gems from life'.

North West Branch

On 19 May at Church House, Hanover Street, Liverpool 1, Mark Barrows gave a talk on gem diamonds as a commercial commodity and an overview of the diamond industry in general.

On 16 June at Church House Peter Buckie gave a presentation entitled 'Valuations – are they worth it?'

Scottish Branch

The Annual Scottish Branch Conference was held in Perth from 30 April to 3 May. The keynote speaker was John Koivula of the GIA Research Laboratory. A report was published in the June issue of *Gem & Jewellery News*, 13(2), pp 44-45.

On 14 June at the British Geological Survey, Murchison House, West Mains Road, Edinburgh, Fred Woodward, an expert in the study of molluscs and their conservation, gave a talk entitled 'Scottish pearls'.

South East Branch

The Annual South East Branch Conference was held from 28 to 31 May in Idar-Oberstein, Germany. A report will be published in the September issue of *Gem & Jewellery News*.

Membership

Between 1 April and 30 June 2004 the Council of Management approved the election to membership of the following:

Honorary Life Members

It was unanimously agreed that Professor Dr Edward J Gübelin of Lucerne, Switzerland, and John I. Koivula of Carlsbad, California, U.S.A., be awarded Honorary Life Memberships in recognition of their work on gemstone inclusions.

Fellowship (FGA)

Andronikou, Stamatina, Didsbury, Lancashire, 2004
Kwok Nai Chiu, Hong Kong, 2004
Lalitha, R., Chennai, India, 2004
Latumena, Warli, Jakarta, Indonesia, 2004
Leung Kit Ling, Junk Bay, Hong Kong, 2004
Lowe, Mimi, San Francisco, California, U.S.A., 2002
Panjikar, Jayshree, Mumbai, India, 1997
Sequeira, Sylvia, Mumbai, India, 1996
Tseng Chien Min, Changhua City, Taiwan, 2004
Yeung Ho Man, Hong Kong, 2004

Diamond Membership (DGA)

Chan Kin Yuen, Hong Kong, 2004
Cheng, Suk Man, Hong Kong, 2004
Heywood, Natalie L., Enfield, Middlesex, 2004
Ho Siu Ming, Hong Kong, 2004
Johnson, Adam Jules, Edgbaston, West Midlands, 2004
Kau Yuk Ming, Eddie, Hong Kong, 2004
Paterson, Deborah Louise, Northampton, 2004
Wat Wing Suet, Hong Kong, 2004

Associate Membership

Bayoumi, Nevin, London
Di Dio, Alfredo, Avellino, Italy
Harris, Nigel, Cockermouth, Cumbria
Hewa Gamage, Srinath Prasanna, Nugegoda, Sri Lanka
Jensen, Karen, L, Houston, Texas, U.S.A.
McQuaid, Rory, Otley, West Yorkshire
Makohon, Galina, Harrow, Middlesex
Meechan, Margaret, London
Michalcova, Silvia, London
Music, Laurence, Northwood, Middlesex
Olumuyiwa, Remi, Brentford, London
Plain, Lyndsey, Pogmoor, Barnsley, South Yorkshire
Price, Carol, Calgary, Alberta, Canada
Pugh, Madeleine, Canterbury, Kent

Pye, Collette, Liverpool, Merseyside
 Quinlan, Doe, London
 Quint, Camilla M., London
 Rentsch, Jean-Marc, Zurich, Switzerland
 Steller, Helen Rachael, Whitefield, Greater
 Manchester
 Sumanaweera, Hiran K, Dar es Salaam, Tanzania
 Sutton, Bruce David, Windsor, Berkshire
 Tosinthiti, Chom, Chiang Mai, Thailand
 Wilkinson, June, Peterborough, Cambridgeshire
 Williams, Yvona, Newmarket, Suffolk
 Yartey, Eric, Southall, Middlesex

Laboratory Membership

Gabi S. Tolkowsky & Sons BVBA, Antwerp,
 Belgium

Transfers

Diamond Membership to Fellowship and Diamond membership (FGA DGA)

Borahan, Fatma O., Istanbul, Turkey
 Deligiannis, Marios, Athens, Greece
 Ngan Hin Wah, Michael, Hong Kong

Fellowship to Fellowship and Diamond membership (FGA DGA)

Barnett, Catherine E., Balham, London
 Jackson, Antoinette, London
 Lee Young Ji, Kyunggido, Korea
 McMillan, Emma L., Solihull, West Midlands

Associate membership to Fellowship and Diamond membership (FGA DGA)

Filadelfeos, Eleni-Anna, Athens, Greece

Associate Membership to Fellowship (FGA)

Holman, Meryan, London
 Singh, Gurmit, New Delhi, India
 Underwood, Thom, San Diego, California,
 U.S.A.

Associate Membership to Diamond Membership (DGA)

Berthault, Alexandra, London
 Hislop, Donna, London
 Kaffo, Moulero Bassiti., Hounslow, Middlesex
 Lesetedi, Madichaba-Nzapheza, Billesley,
 Birmingham, West Midlands
 Prince, Ronald F., Richmond, Surrey

Obituary

Anthony French FGA

A tribute by Michael O'Donoghue

Tony French, one of the best-known dealers in rare gemstones and pioneer of the gemstones for students scheme by which items from his stock were lent to examination candidates and others, died suddenly and unexpectedly near his Somerset home on Tuesday 27 April 2004.

Tony was born in Peckham, south London, but was evacuated in the early years of the Second World War to Horsham, Sussex. Sadly, during this time his mother and an aunt were killed in an air raid. Tony began to study for and succeed in many of the examinations of the textile trade in which he spent a number of years.

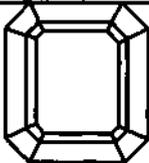
The London gemmology world will remember Tony's partnership with the late Alan Fleming and Christopher Cavey, both FGA's, in Roughgems, a near-unique venture which became well-known first for charoite and then for Russian specimens of diamonds in matrix. When Alan retired to New Zealand and Christopher started his own business, Tony carried on Roughgems until moving to Brockenhurst in the New Forest to take on a jewellery shop with his wife Nola. Tony then ran his gemstone business from their home in Evercreech, Somerset, and commuting, for Nola, became a fixed feature of their life until recently when she retired.

Both ends of the two enterprises were supervised by a succession of 'French' dogs – the late André and Pierre, and Raoul who is still happily with Nola and helping her in many ways.

Tony had an enviable stock of fine and rare gemstones, most from Sri Lanka but including unusual synthetic stones too. His manual skills enabled him to produce beautiful furniture and ornaments in wood, many of which he sold.

Tony was a big man in every way and could have been nothing but English; he was able to keep critical thoughts and opinions to himself rather than voice them - this was a notable victory. He was very kind. His epic battles with computers and printers remained unresolved at the end with honours about even. Though he had ceased smoking his pipes which ought to be in a smokers' museum as a lesson to rookie smokers, I shall always think of him when I encounter pipe smoke. I already miss him.

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Forthcoming Events

- 22 August **South East Branch:** Can provenance be valued? *David Lancaster*
- 12 September **South West Branch:** An afternoon with organics. *Maggie Campbell Pederson*
- 14 September **London:** Annual General Meeting.
- 15 September **North West Branch:** Emeralds. *Alan Hodgkinson*
- 24 September **Midlands Branch:** Colour in natural and artificial diamonds.
Professor Alan Collins
- 29 September Private Viewing of the Crown Jewels with David Thomas,
the Crown Jeweller
- 6 October **Scottish Branch:** The coloured stone business from a global perspective.
Guy Clutterbuck
- 19 October **Scottish Branch:** Inclusions in amber. *Neil Clark*
- 20 October **North West Branch:** The trade industry today. *Marcus McCallum*
- 29 October **Midlands Branch:** Gems of the seven continents. *E. Alan Jobbins*

Gem-A Conference 2004

To be held on Sunday 31 October
at Kempton Park Racecourse,
Sunbury on Thames, Middlesex

In conjunction with the Rock 'n' Gem Show

Keynote speaker: Tom Chatham

Further details are given on p.184

- 1 November **Presentation of Awards:** Goldsmiths' Hall, London EC2
- 16 November **Scottish Branch:** Gemstones of Mozambique. *Roger Key*
- 17 November **North West Branch:** Branch AGM and social evening
- 26 November **Midlands Branch:** Bring and Buy Sale and Quiz
- 4 December **Midlands Branch:** 52nd Anniversary Dinner

contact details

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e-mail gema.northeast@gemro.com
- North West Branch: Deanna Brady 0151 648 4266
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e-mail scotgem@blueyonder.co.uk
- South East Branch: Colin Winter on 01372 360290; e-mail info@ga-seb.org
- South West Branch: Richard Slater on 01635 553572;
e-mail rslater@dnfa.com

Gem-A Website

For up-to-the-minute information on Gem-A events visit our website on www.gem-a.info

Guide to the preparation of typescripts for publication in *The Journal of Gemmology*

The Editor is glad to consider original articles shedding new light on subjects of gemmological interest for publication in *The Journal*. Articles are not normally accepted which have already been published elsewhere in English, and an article is accepted only on the understanding that (1) full information as to any previous publication (whether in English or another language) has been given, (2) it is not under consideration for publication elsewhere and (3) it will not be published elsewhere without the consent of the Editor.

Typescripts Two copies of all papers should be submitted on A4 paper (or USA equivalent) to the Editor. Typescripts should be double spaced with margins of at least 25 mm. They should be set out in the manner of recent issues of *The Journal* and in conformity with the information set out below. Papers may be of any length, but long papers of more than 10 000 words (unless capable of division into parts or of exceptional importance) are unlikely to be acceptable, whereas a short paper of 400-500 words may achieve early publication.

The abstract, references, notes, captions and tables should be typed double spaced on separate sheets.

Title page The title should be as brief as is consistent with clear indication of the content of the paper. It should be followed by the names (with initials) of the authors and by their addresses.

Abstract A short abstract of 50-100 words is required.

Key Words Up to six key words indicating the subject matter of the article should be supplied.

Headings In all headings only the first letter and proper names are capitalized.

A **This is a first level heading**

B *This is a second level heading*

First and second level headings are in bold and are ranged left on a separate line.

Third level headings are in italics and are indented within the first line of text.

Illustrations High resolution digital files, for both colour and black-and-white images, at 300 dpi TIFF or JPEG, and at an optimum size, can be submitted on CD or by email. Vector files (EPS) should, if possible, include fonts. Match proofs are essential when submitting digital files as they represent the colour balance approved by the author(s).

Transparencies, photographs and high quality printouts can also be submitted. It is recommended that authors retain copies of all illustrations because of the risk of loss or damage either during the printing process or in transit.

Diagrams must be of a professional quality and prepared in dense black ink on a good quality surface. Original illustrations will not be returned unless specifically requested.

All illustrations (maps, diagrams and pictures) are numbered consecutively with Arabic numerals and labelled Figure 1, Figure 2, etc. All illustrations are referred to as 'Figures'.

Tables Must be typed double spaced, using few horizontal rules and no vertical rules. They are numbered consecutively with Roman numerals (Table IV, etc.). Titles should be concise, but as independently informative as possible. The approximate position of the Table in the text should be marked in the margin of the typescript.

Notes and References Authors may choose one of two systems:

(1) The Harvard system in which authors' names (no initials) and dates (and specific pages, only in the case of quotations) are given in the main body of the text, (e.g. Collins, 2001, 341). References are listed alphabetically at the end of the paper under the heading References.

(2) The system in which superscript numbers are inserted in the text (e.g. ... to which Collins refers.³) and referred to in numerical order at the end of the paper under the heading Notes. Informational notes must be restricted to the minimum; usually the material can be incorporated in the text. If absolutely necessary both systems may be used.

References in both systems should be set out as follows, with *double spacing* for all lines.

Papers Collins, A.T., 2001. The colour of diamond and how it may be changed. *J.Gemm.*, 27(6), 341-59

Books Balfour, I., 2000. *Famous diamonds*. 4th edn. Christie's, London. p. 200

Abbreviations for titles of periodicals are those sanctioned by the *World List of scientific periodicals* 4th edn. The place of publication should always be given when books are referred to.



Contents

Gem corundum deposits in Vietnam	129
Pham Van Long, Hoàng Quang Vinh, Virginie Garnier, Gaston Giuliani, Daniel Ohnenstetter, Thérèse Lhomme, Dietmar Schwarz, Anthony Fallick, Jean Dubessy and Phan Trong Trinh	
The causes of colour in untreated, heat treated and diffusion treated orange and pinkish-orange sapphires – a review	149
Karl Schmetzer and Dietmar Schwarz	
Book Reviews	183
Proceedings of the Gemmological Association and Gem Testing Laboratory of Great Britain and Notices	185

*Cover Picture: Limonite framework in topaz.
Photography by Alan Hodgkinson, FGA DGA, Portencross by West Kilbride, Scotland.*

First Prize in the 2004 Photographic Competition (see p.185).

The Gemmological Association and Gem Testing Laboratory of Great Britain

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