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HEAT TREATING SAPPHIRES FROM THE ANAKIE DISTRICT, AUSTRALIA

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ABSTRACT

Systematic heat treatment of sapphires from the Anakie District, Queensland, Australia, was used to study the effects of heat on color and clarity and to determine heat treatment parameters for maximising enhancement potentiality. About four kilos of rough, mixed-quality sapphires from the Anakie District were cleaned, classified, and heat-treated using different parameters under controlled atmospheric conditions. Heat treatment experiments showed that, regardless of the atmosphere used, 'silk' may be partially dissolved by 1400 °C, and fully dissolved from 1650 °C upwards. Clearing the 'silk' increases the transparency of these sapphires, thus increasing their value. Heat-treating green to yellow sapphires did not produce sapphires with significant market value. Blue to green stones produced better results. Selected, nearly colorless, silky, and brownish-spotted sapphires produced the best results. Careful control of heating and cooling rates can prevent cracking. The specimens were heated, by type and by batch, with sapphires heated by type yielding slightly better results than the sapphires heated by batch.

BACKGROUND SUMMARY

Stutchbury first reported[1] that sapphires were found in Australia as a result of gold prospecting operations in N.S.W. during 1851. The discovery of sapphires "in a number of localities near the small railway station of Anakie in central Queensland" was first recorded by Dr R.L. Jack in 1892[2]. Today, large commercial mechanized operations and smaller concerns are involved in mining Central Queensland sapphires from alluvial deposits widely distributed in Rubyvale, Sapphire, Willows-Glenalva, Tomahawk Creek, and other areas in the Anakie District.

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The well established practice of heating Australian sapphires to enhance their clarity and colour is said to have originated in Germany several decades ago[1]. In Thailand, since the 1970s, home-made coke furnaces have been used exclusively for the heat treatment of the Australian sapphires[3-6]. Today most heat treatment of sapphires is performed in Thailand using various combinations of heat treatment equipment and methods. Other heat treatment facilities are located in the USA[7], Sri Lanka, Japan, Australia, Germany and elsewhere.

DESCRIPTION OF THE SAPPHIRES

About 20,000 carats of commercial mine-run rough sapphires from the Anakie District were used in this study. The weight of each specimen rough ranged from 0.15 to 15+ carats. The batch consisted of yellow, yellow-green, green-blue, blue, blue-green, and intermediate colored sapphires of light, medium, and dark tone. Some stones were characterised by brownish spots that contrasted against a greenish-blue or bluish body colour. Others were parti-coloured yellow-green and blue, blue and colourless, etc. Most of the sapphires displayed prominent colour zoning with an alternating pattern primarily parallel to basal pinacoid and hexagonal prism faces. Many sapphires appeared brownish in reflected light, while others appeared milky-bluish. Some, showed yellow-orange stains on the surface and in surface-reaching cracks. Most were translucent to transparent, strongly dichroic, and had a silky appearance.

PREPARATION FOR HEAT TREATMENT

Prior to heat treatment, all sapphires were prepared by the author in the following manner:

Cleaning

A tumbling drum-type apparatus was used for cleaning the rough sapphires. The sapphires were placed inside the rubber drum of the tumbler and soaked overnight for a few hours in hydrofluoric acid mixed with water. Periodically the tumbler was turned on to accelerate the chemical reaction. Some stones (non-corundums) turned opaque chalky-white and were removed from the load. Yellow-orange iron oxide stains and spots, located on the surface or entrapped in cracks, were completely removed

by this cleaning. Finally, all stones were rinsed with distilled water.

Identification

Orange to red-brown orangy zircons were easily identified and removed from the batch. Caution was exercised not to remove the brown-spotted sapphires that may be confused with other minerals, as the brown spots are chromophoric impurities required for the development of a heat-induced blue colour. Transparent colourless substances such as feldspars, pleonaste (spinel), and other minerals visually identified as non-corundums, were removed from each cleaned load.

HEAT TREATMENT METHODS AND PROCEDURES

Heat Treatment Equipment

The Anakie sapphires were heat-treated in a special vertical muffle top-bottom loaded furnace that had an actual maximum operating temperature for continuous use to 1800 °C. This furnace was engineered and fabricated by the author.

The furnace (Fig.6) consisted of three modules (a power supply and controls, the furnace, and water-cooling) mounted on wheels and integrated to each other. Additional auxiliary-monitoring equipments were also employed. Selected gases were mixed in a atmosphere control apparatus specially designed by the author. This apparatus was equipped with flowmeters, pressure gauges, and other components necessary to produce a gas mixture with a precisely controlled oxygen fugacity of 10^{0} to 10^{-15} range. The final gas mixture was purged into the open-loop muffle system during heating. All processes were performed utilizing different heating parameters, and under fully controllable atmospheric conditions, as indicated in the flow diagram (Fig.3), and the x-y plot (Fig.5).

Heating by type

This method requires proper classification of the sapphires into types based on common characteristics observed in identical lighting conditions. Heating the sapphires, based on type classification, provides a direct comparison of the results obtained - thus determining the best heating process for each type. Proper classification of sapphires, by type, is more important than setting heating parameters since a wrong classification would result in setting wrong heating parameters, thus producing different results.

The Anakie District sapphires, used in this study, were classified on a sorting table equipped with transmitted fluorescent light. As all varieties of sapphire are unlikely to be encountered either in a specific mining area, or in a given lot of sapphires, the classification used in this article does not necessarily represent all possible types found in the Anakie District.

For convenience, the Anakie sapphires were grouped into types of similar appearance. Based on the author's experience, an error factor of about 12 per cent is to be expected with this classification. Figures 1&2 provide tabulated results and corresponding yields of each type following each specific heat-treatment.

TYPE RUN	TYPE 1 Blue-greyish	TYPE 2 Dark blue-greyish	TYPE 3 Brown spot or steak	TYPE 4 Green Blue	TYPE 5 Blue-green	TYPE 6 Parti-colour	TYPE 7 Dark blue-green	TYPE 8 Milky	TYPE 9 Yellow, Yellow-green, green
R#1	85% bluish 15%+ blue-greenish	85%+lighter blue 15% no change		20%* green-blue 80% blue-green	100% light blue		15% lighter blue-green 85% no change	70% blue 30% bluish transparent	82% no change 14%* bluish 4% bicoloured
R#2	100% blue 30% dark 60% medium 10% light	100% lighter blue		25% green-blue 75% blue	100% lighter blue	100% more transparent No change in colour			75% no change 25% bluish
R#3	90%+ blue 10%* greyish	85% lighter blue 15% blue-green	100% blue	47% blue 53%+ blue-green	80% lighter blue 20% lighter green-blue	50% blue 4% parti-colour 30%+ green			86% no change 14%+ bluish
R#4	75% + blue 27% greyish	Similar to R#3		90% blue 10% +parti-colour	90% lighter blue 10%+lighter blue-green	100% lighter, more transparent	50% lighter blue-green 50% no change		
R#5	100%+ blue (Similar to R#2)	Similar to R#3	50% blue 50% blue-green	63%+ light blue 37% blue-green	100% lighter blue	100% intense parti-colour, transparent	60% lighter blue-green 40% no change	75% blue 25% bluish Transparent	
R#6	84%+ bluish 16%* greenish	Similar to R#3		45%+ green-blue 55% blue	100% lighter blue	100% intense parti-colour, more transparent	80% lighter blue-green 20% no change	100% blue Transparent	
R#7		Darker blue		80%+ muddy green 20%+ bluish greenish	95% muddy green 5% blue-green			100%* very dark blue (Black)	
R#8	Silk removed			Silk removed	Silk removed				
BEST PRO-CESS	R#2	R#2	R#3	R#4	R#6	R#3	R#6	R#6	None

Fig.1. Tabulation of heating process performed on Anakie District sapphires that had been classified bt type
Note: #Not suitable for cutting +Suitable for cabs

TYPE	Best Process	Before Heating	After Heating
Type 1	R #2	blue/greyish	60% medium blue
Type 2	R# 2	dark blue-grey	100% lighter blue
Type 3	R# 3	brown spot	100% blue (dark, med., light)
Type 4	R# 4	green-blue	90% bluish (dark, med., light)
Type 5	R# 6	blue-green	100% lighter blue
Type 6	R# 3	parti-color	56% blue (dark, med.,light)
Type 7	R# 6	dark blue-green	80% lighter blue/green
Type 8	R# 6	milky	100% blue (dark, med., light)
Type 9	none	yellow-green	no improvement in colour

Fig. 2. Optimal yield of heat-treated Anakie District sapphires, based on best heat-treatment process for type (classisication) of sapphire

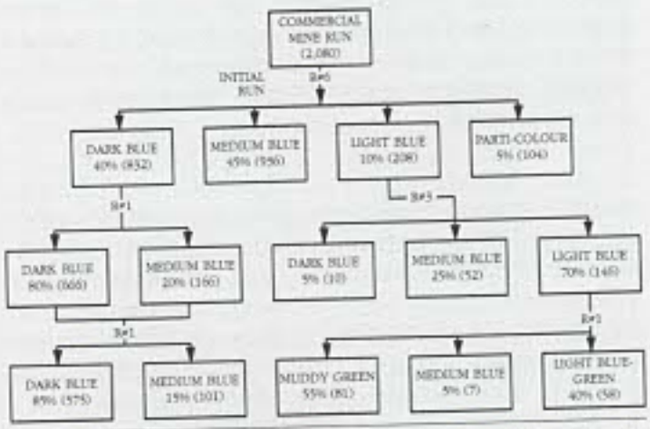

Fig. 3 Batch heating processes for Anakie District sapphires

Type 1: Medium blue-greyish with or without greenish tinge

These sapphires were characterized by blue parallel to the c-axis (∥c) and grayish perpendicular to the c-axis (⊥c) colouration, often with a greenish tinge, silky, transparent to translucent.

In all heat-treatments the 'silk' was dissolved, thus increasing transparency. The dark, medium, and light blue stones that were produced after heating were often characterized by colour zoning. Run #2 produced both the best yield and the best quality sapphires. All heat-treated sapphires were suitable for cutting.

Type 2: Dark blue-greyish

These sapphires were dark blue (∥c) and greyish (⊥c), similar to type 1, and translucent to opaque.

After heat-treatment, and regardless of the atmosphere used, 'silk' was cleared, their dark blue colour lightened, and the sapphires appeared more transparent. At the same time, a light greenish tinge was observed in some specimens following heat-treatment (Fig. 7). Best results were obtained from run #2, in which nearly all specimens turned a lighter blue and were all suitable for cutting. Some of these sapphires were reminiscent of their Sri Lankan counterparts. In all other heat-treatments (except run #7) about 85 per cent turned a lighter blue colour that was mostly suitable for cutting cabochons.

Type 3: Brownish spot/s on bluish or greenish 'body color'

These sapphires had a bluish or greenish 'body color' and were additionally characterised by the presence of silk and brownish spots and/or streaks in various configurations.

Best results were obtained from run #3, when almost all sapphires turned blue (Fig. 8). After heat-treatment of some sapphires, the brown spot turned into an intense blue spot, while the remaining sapphire turned a medium to light blue color. Subsequent heat treatment experiments (not described in this study) could not remove or diffuse this intense blue coloured spot.

Type 4: Green-blue

These sapphires appeared more green than blue and were often characterised by prominent color zoning and/or silk.

Best results were obtained from run # 6.

Type 5: Blue-green

These sapphires were more blue than green.

After heat-treatment (runs #3, #4, #5, #6), they were more transparent, but most lost some of their original blue-green colour and appeared lighter blue-green. Other blue-green sapphires partially turned blue (Fig. 9). Run #2 produced both the best yield and quality sapphires. All were suitable for cutting.

Type 6: Parti-colors

These sapphires were characterised by parti-colouration, that is yellow and blue, etc. in various configurations.

After heat-treatment their colours were intensified (Fig.10) and became more transparent. Run #3 produced the best results overall.

Fig. 6. Crucible and associated parts being loaded into a vertical muffle furnace by the author. ©T.Themelis.

Type 7: Dark blue-green to dark green-blue

These sapphires were characterised by the presence of dense amounts of 'silk' that made them appear very dark blue to green, almost black.

Run #6 produced the best results, with over 80 per cent of the sapphires turning a lighter blue with increased transparency. All were suitable for cutting.

Type 8: Milky

These sapphires were translucent to opaque as varying amounts of 'silk' caused them to appear milky in reflected light.

After heat-treatment all the stones turned blue regardless of the heating parameters used. Best results were obtained from run #6. This run produced nearly uniform blue colours (dark, medium, and light tones) of increased transparency. Some of these stones were quite attractive and reminiscent of their Sri Lankan counterparts.

Type 9: Yellow, yellow-green and greenish

This type included all shades of yellow, greenish or yellowish to greenish with little or no trace of secondary colors. They were usually characterised by strong dichroism in yellow and green.

No heat-treatment produced marketable colours of economic significance. These sapphires were characterised by very little or no 'silk'.

Attempts to develop blue colour in hydrogen atmospheric conditions were not successful. Therefore, further heat-treatment experiments for this type were abandoned.

Heating by batch

For this method, sapphires were heat-treated in a batch (without type classification), as received from the supplier, and using predetermined heating parameters.

Fig. 7. Natural type 2 dark blue sapphire (right) turned lighter blue (left) after heat-treatment under R #2 conditions. ©T.Themelis.

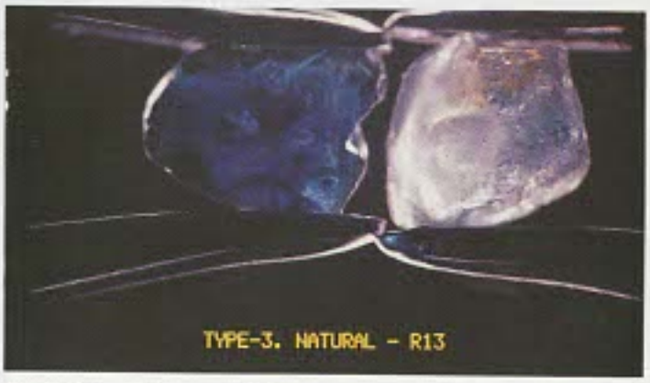

Fig. 8. Natural type 3 light blue sapphire with brown spot (right) turned medium dark blue (left) after heat-treatment under R #3 conditions. ©T.Themelis

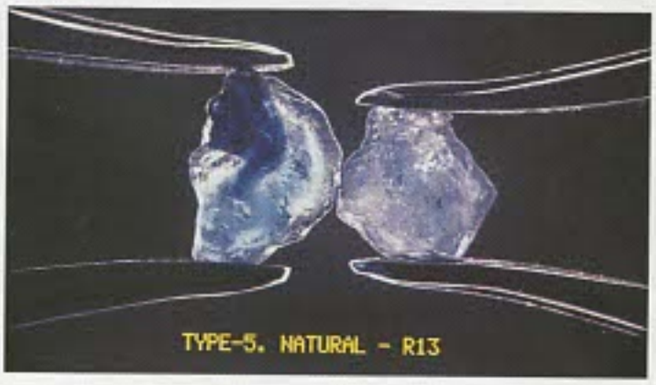

Fig. 9. Natural type 5 blue-green sapphire (right) turned partially blue (left) after heat-treatment under R #6 conditions. ©T.Themelis

Fig. 10. Natural type 6 parti-colour sapphire (right) turned blue, but with an inhomogeneous color (left), after heat-treatment under R #3 conditions. ©T.Themelis

After initial heating (run #6), medium blue and parti-coloured sapphires deemed to be suitable for cutting were removed from the batch. The remaining dark blue and light blue sapphires were reheat-treated (run #1 and run #3), using different heat-treatment parameters. After this heating medium blue sapphires deemed suitable for cutting were removed. Remaining sapphires were yet again heat-treated (run #1 and run #7) till the entire batch was exhausted. Figure 3 details the general flowchart of the batch heat-treatment processes performed, and their corresponding yields as indicated in figure 4.

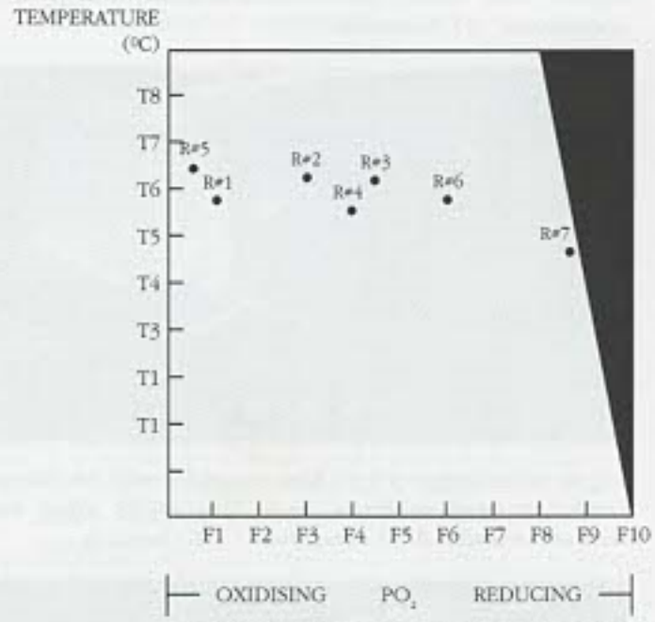

Fig. 5. The author's x-y plot where the x-axis represents the processing temperature (T8 being the melting point of corundum and T1 proportionally lower). The y-axis represents the oxygen fugacity (pO_2) with F1 a "strong oxidizing atmosphere" and F10 a "strong reducing atmosphere". R #1-7 represents process run numbers. Note: Specific values are not provided due to proprietary nature of the author's heat-treatment processes.

Overall appearance	No. sapphires	Per cent yield after heat-treatment
Dark blue	575	27.6
Medium blue	1,262	60.7
Light blue	58	2.8
Parti-color	104	5.0
Muddy- green	81	3.9
TOTAL	2,080 pcs.	100.0

Fig. 4. Summary of yields obtained from batch heat-treatment processing of 2,080 commercial mine-run sapphires from the Anakie District, Queensland.

Summary and Conclusions

1. Carefully controlled rates of heating and cooling, from room temperature to about 900°C, prevented the cracking of sapphires and the ceramics associated with the heat-treatment furnace. Very few fractures were noted in the heat-treated stones.

2. Careful control of the rate of cooling, that is 20°C/minute, from the operating temperature of 1800°C to about 1200°C prevented the recrystallization of rutile, regardless of heating parameters used. All the specimens appeared to attain increased transparency.

3. Type 8 (milky-silky) sapphires, when heated over 1400°C, turned blue regardless of the atmospheric conditions.

4. Heat-treatment performed under strong reducing atmosphere, using hydrogen-based gas mixtures, produced undesirable results as demonstrated by run # 7. Almost all types of sapphire turned a muddy green or black colour that was not suitable for cutting. In fact, if the reducing atmosphere had been increased, the sapphires would have gradually lost their oxygen content and turned blackish. This undesirable change has been observed by the author in other similar heat-treatment projects.

5. Run # 8 was performed on selected type 1, 4 and 5 silky sapphires. Depending on the sapphires, the diameter of their silk 'needles' ranged from 0.02 mm ('thin needle') to 0.08 mm ('thick needle'). After heat-treatment, most 'thin silk' was dissolved with the stones becomming increasingly transparent. The 'thick silk' was only partially dissolved and appeared as 'dotted' or 'interrupted' lines. In summary: during successful heat-treatment 'thick silk' takes longer to dissolve than 'thin silk'.

In special heating processes (not indicated in the plotting diagram), needles of 'silk' were partially dissolved when heated to 1400°C. The sapphires appeared blue and more transparent, regardless of the heating parameters used.

6. After heating, even at a temperature of 1800°C, sapphires were easily removed from the crucible without adhering together, or to the crucible itself. This fact demonstrates the importance of cleaning the sapphires prior to heating. It was also observed that, in all processes, the final color of the sapphires was established 1-2 days after heat-treatment.

7. Sapphires heat-treated by type yielded slightly better results than sapphires heated by batch. It is the author's opinion that high quality sapphires should be heat-treated by type. Commercial and lower quality sapphires should be heat-treated by batch, provided a proper methodology has been established by the heat-treater. Figures 2 and 4 compare recovery yields.

Disclaimer

The mixture of gases used in the heat-treatments described in this paper are poisonous, and/or highly explosive, especially when used in conjunction with high temperatures used during heat-treatment of sapphires. The author discourages the use of these gases and practices, unless the heating processes and procedures are performed by qualified technical personnel under suitable laboratory conditions.

Acknowledgment

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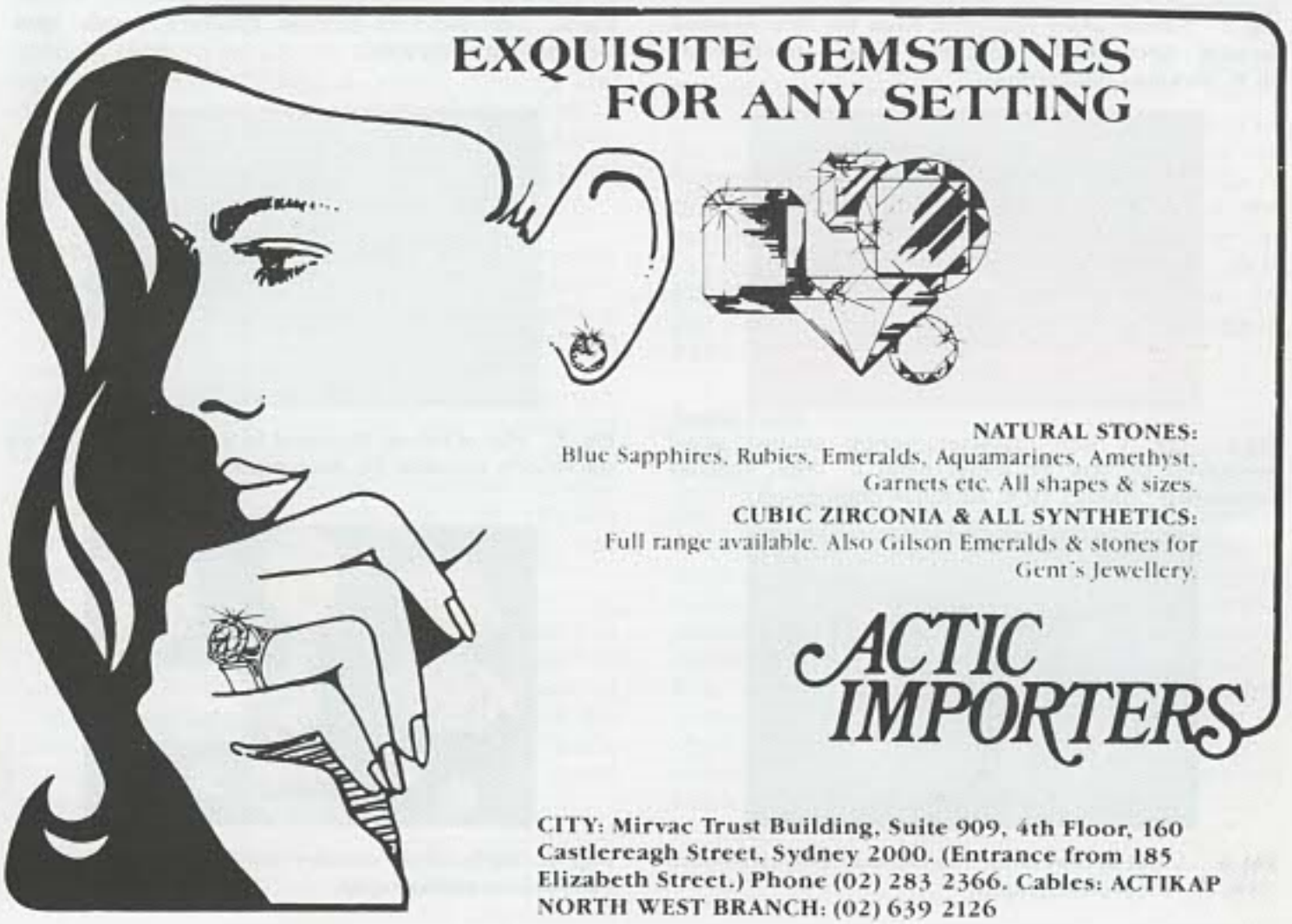
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