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Ti-Fe MINERAL INCLUSIONS IN STAR SAPPHIRES FROM THAILAND

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ABSTRACT

Star sapphires from Bang Kacha, Chanthaburi province, Thailand were investigated for their iron and titanium contents with regard to exsolved needles and mineral inclusions. The instrument used was the EPMA-WDS (Electron Probe Microanalysis - Wavelength Dispersive Spectrometer), with the techniques of element mapping and spot analyses. The results suggest that the exsolved 'needles' are not rutile or hematite as stated in literature. The 'needles' are probably a mineral of the ilmenite-hematite series, ilmenite, or a spinel; while other opaque inclusions are magnetite-hercynite.

Keywords: Electron microprobe, Ti-Fe mapping, exsolved 'needle', corundum, point analysis, ilmenite-hematite, spinel.

INTRODUCTION

Star corundums from Thailand are composed chiefly of black star and golden star sapphires (Hughes, 1997). These are found in association with other varieties (e.g. blue-green, yellow sapphires) in the alluvium derived from alkali basalts at, for example, Bang Kacha, Bo Phloi, Den Chai and Nam Yun. Bang Kacha is the locality where star sapphires are found more abundantly and in larger average size than elsewhere in Thailand. Moon & Phillips (1984, 1985, 1986) proved by electron diffraction methods that the 'silk' in black Australian sapphire consisted of solid solutions of minerals of the ilmenite and hematite series.

Moon & Phillips (1985) also referred to asterism in black star sapphire from Bang Kacha, Thailand, the subject of the present study. The hercynite inclusions associated with aligned ferrian ilmenite 'needles' were illustrated in Moon & Phillips (1986). These resemble the mineral inclusion association illustrated in this paper. Also. Pearson (1990) described Australian star sapphire that contained both rutile and possible ferrian ilmenite exsolutions, but in different orientations relative to the prism faces. Hughes (1997) stated that sapphires from Australia and Thailand were similar in their occurrence and suites of inclusions; but he claimed that only rutile 'silk' and/or hematite 'silk' and 'plates' produce the star effect in Thai sapphires. Weibel & Wessicken (1981) also stated that the stars in black-star sapphires from Thailand were caused by hematite lamellae.

THE PROBLEM

The yellow-brown 'needles', in star sapphires from several localities in Thailand, precipitate on the {0001} plane in three directions with the angles of 60° between each trend. The length of these 'needles' is perpendicular to the 1st order hexagonal prism faces {10$\bar{1}$0} of the sapphires. The 'needles' are the exsolved phase that cause the chatoyancy and asterism (star) which are seen if these sapphires are cut and polished *en cabochon*. They accumulate along the growth zoning of the sapphire host as illustrated on figure 1. In certain samples, the 'needles' occur in association with inclusions of black spinel of mainly magnetite-hercynite composition as shown in figure 2.

Note: The representative composition of magnetite-hercynite (BKCEP4-SP2) in wt% was: TiO_2 = 1.84, Al_2O_3 = 30.53, Fe_2O_3 = 31.21, FeO = 33.58, MnO = 1.48, MgO = 0.45, Na_2O = 0.52. Percentages of end members were: spinel = 2.3, hercynite = 50.6, galaxite = 4.2, magnetite =38.4, ulvöspinel = 4.5. Using the solvus diagram (Fig. 5) of Turnock & Eugster (1962) gave a minimum temperature of crystallization for this spinel of 860 °C.

These analyses were performed by the SEM-EDS (Electron Microscope equipped for Energy Dispersive Spectrometry).

In polished sections of these samples of star sapphires, 'needles' exposed on the cut surface showed strong dispersion under the reflected light

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Element	Crystal	Spectrometer No.	Standard used	Line of electron transition between atomic shells
Fe	LIF (lithium fluorite)	2	Fe_2O_3	Ka
Ti	LPET (Large pentaerythritol)	3	Rutile (TiO_2)	Ka

Table 1. Summary of the EPMA-WDS conditions for analysis of the star sapphire (sample BKCEP9).

microscope. These 'needles' were analysed by the SEM-EDS. However, the results were not accurate due to the fact that the widths of 'needles' were too small (~1 μm) for analysis by the electron beam. The analytical result (in wt% oxide) for the 'needles' (TiO2 = 3.04, Al2O3 = 87.92, FeO = 9.22, Na2O = 0.27, Total = 100.45) was probably contaminated by alumina from the host corundum However, high Ti and Fe contents imply that these 'needles' are neither pure rutile nor hematite. They may be the ilmenite or an ilmenite-hematite solid solution mineral, according to Moon & Phillips (1984), or possibly a spinel. To clarify this problem, a 6-ray star sapphire from Bang Kacha, Chanthaburi Province, was chosen for investigation of its iron (Fe) and titanium (Ti) content by the electron microprobe, using the techniques of trace element mapping and spot analysis.

Methods

Sample BKCEP9 was embedded in the epoxy resin and attached to the glass slide. It was then cut and polished into a section about 100 μm thick that is illustrated in figure 1. The section was coated with carbon, by an evaporation technique, to provide a path for the probe current and prevent charging before analysis (Reed 1996, 1997). The CAMECA-SX100 EPMA-WDS, at the University of Manchester, was employed for this purpose. SXRAY computer software was set to automatically run the machine. Conditions for analysis were 30 kV of the accelerating voltage, and 60 nA of the beam current. Mapping for Fe and Ti was accomplished by rastering the beam over the sample grain, with 8 μm between each pixel to cover an area of (4000 μm x 4000 μm. The total number of pixels was 262,144 (512 along x-axis and 512 along y-axis). Details of the technique are given by Schmetzer *et al.* (1998).

The four spots analysed across the areas of 'needle' accumulation (Again see figure 1), and the analytical conditions, are summarized in Table 1. Running time for each analysis (together with 9 other trace elements) was 12 minutes.

Point number	1	2	3	4
Fe_2O_3*	1.844	1.830	1.808	3.334
TiO_2	0.013	0.026	0.009	0.375

*Fe_2O_3 has been recalculated from the total FeO.

Table 2. Weight per cent (wt%) oxide obtained from the analysis of the star sapphire (sample BKCEP9) by the EPMA.

Results & Discussion

The results of elemental mapping (Fig. 3) indicated that the 'needles' contained both titanium and iron. This suggests that the exsolved phase is likely to be either a solid solution mineral of ilmenite-hematite series, ilmenite, or a spinel. Spot analyses (Table 2) were made to confirm the result of the element mapping, and are plotted on the graph (Fig. 4) to show the variation in the content of these two elements from rim to core in the one sample.

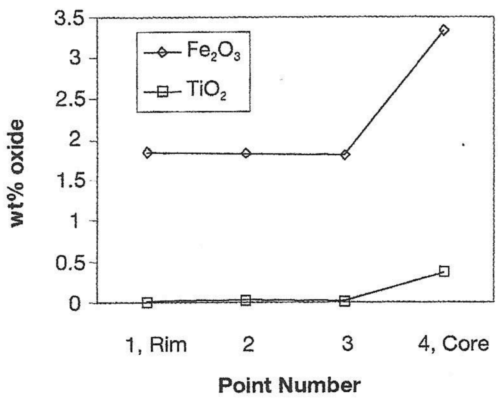

Fig. 4. TiO_2 and Fe_2O_3 contents in the star sapphire sample (BKCEP9) from Bang Kacha. Analysis points 1, 2 and 3 contain similar amounts of the two oxides, but point 4 (in the area of high density of 'needles') has higher contents of both elements. The higher Fe and Ti in point 4 is due to a greater density of 'needles' at this point. The other points have greater contamination from the corundum matrix due to lower densities of needles in these locations.

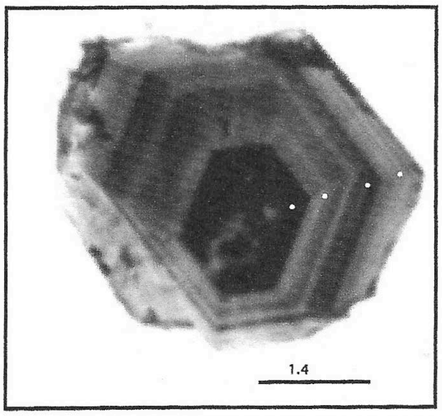

Fig. 1. Polished section of a star sapphire (sample BKCEP9) from Bang Kacha, Chanthaburi, Thailand, which was prepared for analysis by the EPMA. The section shows growth zoning with accumulation of exsolved 'needles' of brown to black colours. 'Needles' also were abundant in the core of the sapphire. The location of analyses, which are indicated by the numerals 1-4, correspond to the point numbers in Table II and Figure 4. [Transmitted light with PPL].

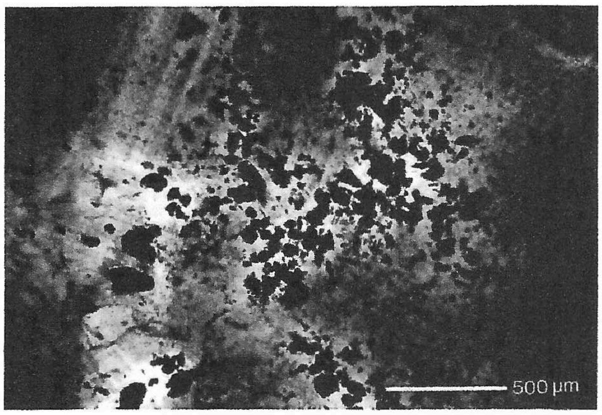

Fig. 2. Black platelets of magnetite-hercynite associated with yellow-brown 'needles' in star sapphire (BKCEP4) from Bang Kacha. The 'needles' have accumulated along the hexagonal growth zoning of the sapphire, with orientations perpendicular to the 1st order hexagonal prism faces {10-10} of the sapphire. [Viewed parallel to the basal pinacoid (0001) in transmitted light with PPL].

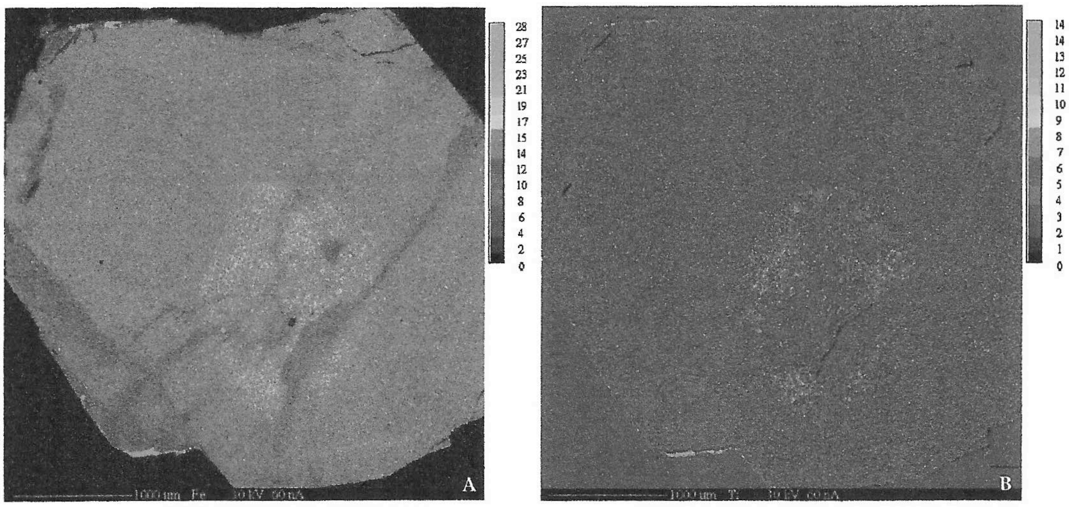

Fig. 3. Images of iron and titanium mapping on the surface of sample BKCEP9 as illustrated in figure 1.

A. Indicating the count rates for Fe (quantified by low to high colour codes black (blue→green→yellow→orange→red) and collected by the spectrometer for corresponding the Fe content in the area of the grain. Iron disperses throughout the corundum matrix, and is abundantly accumulated in the 'needles'.

B. The pattern of titanium count rates indicates that Ti content is abundant in and mainly confined to the zonal areas where 'needles' accumulate. Ti content it is more pronounced than Fe content.

According to Sutherland *et al.* (1998), these magnetite-hercynite inclusions are typical of those found in growth-banded sapphires associated with basalt The estimated temperature of crystallization of the magnetite-hercynite inclusion in this study is close to the estimated 900 °C temperature of formation of sapphire-magnetite from a nearby Thailand locality (Khao Wua) that was studied by Coenraads *et al.* (1995). This suggests that sapphires from both localities might have been crystallized in the same geological environment. Extensive discussion of equilibrium temperature for sapphires from basaltic terrain can be found in Sutherland *et al.* (1998).

Conclusion

This study suggests that the exsolved 'needles' associated with magnetite-hercynite in Thai star sapphire are not pure rutile or hematite as stated by Hughes (1977), or by Weibel & Wessicken (1981). It is more likely a mineral of the ilmenite-hematite solid solution series, ilmenite, or a spinel, which produces the asterism and/or chatoyancy in these Thai sapphires. The sample of Bang Kacha star sapphire contained high Fe dispersed throughout the grain; whereas titanium mainly concentrates in the area of the exsolved 'needles'.

This study did not prove conclusively the identity of the mineral/s responsible for the 'needles' in Bang Kacha sapphire. These, obviously, will need to be identified by other techniques.

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