Kennedy, G. C. (1950) Pressure—volume—temperature relations in water at elevated temperatures and pressures. *Amer. J. Sci.* **248,** 540–564.

Kleber, W. (1940) Kristallographische Untersuchungen am Aragonit unter besonderer Berucksichtigung des Vorkommens am Erzburg, Steirmark. *Neues Jahrb. Mineral, Abt. A*, **Beil.-Bd. 75,** 465.

MacDonald, G. J. F. (1956) Experimental determination of calcite—aragonite equilibrium relations at elevated temperatures and pressures: *Amer. Mineral.* **41,** 744–756.

Wray, J. L., and Daniels, F. (1957) Precipitation of calcite and aragonite: *J. Amer. Chem. Soc.* **79,** 2031.

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ON THE CAUSE OF ASTERISM IN STAR CORUNDUM

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Introduction

It has been generally accepted that asterism in corundum (star rubies and sapphires) is caused by needles or rutile (TiO_2) aligned along crystallographic planes of the corundum (*e.g.* Webster, 1962). The evidence given ty Tait (1955) was: (1) the presence of titanium, (2) the needle-like habit, and (3) the square cross-section of the needles. Based on the analogy with rutilated quartz, and by eliminating octahedrite and brookite by the morphology, rutile was accordingly identified. This type of evidence, however, is explained equally well by either TiO_2 or the compound aluminum titanate Al_2TiO_5.

Corundum Growth Considerations

The technique for the laboratory growth of star rubies and sapphire has been revealed in patents by the Linde Division of the Union Carbide Corp. (Burdick *et al.*, 1949, 1954). Corundum is grown by the Verneuil technique with the addition of, preferably, 0.1 to 0.3 percent titanium oxide in the feed powder. The corundum as grown is clear, but develops asterism upon heat treatment at 1100 to 1500°C (Webster, 1962; Burdick *et al.*, 1949, 1954) due to precipitation of the excess titanium, the solubility of which is exceeded at this temperature.

The phase diagram of the Al_2O_3:TiO_2 system has been studied by Bunting (1933) and by Lang, Fillmore and Maxwell (1952). The relevant parts of these studies are included in Figure 1. There is a slight uncertainty as to whether Al_2TiO_5 melts congruently or incongruently near 1860°C in the shaded region, but this does not affect the present discussion. Similarly, there may be other forms of Al_2TiO_5 besides the α form which is stable above 1820°C, and the β form stable below 1820°C. Ac-

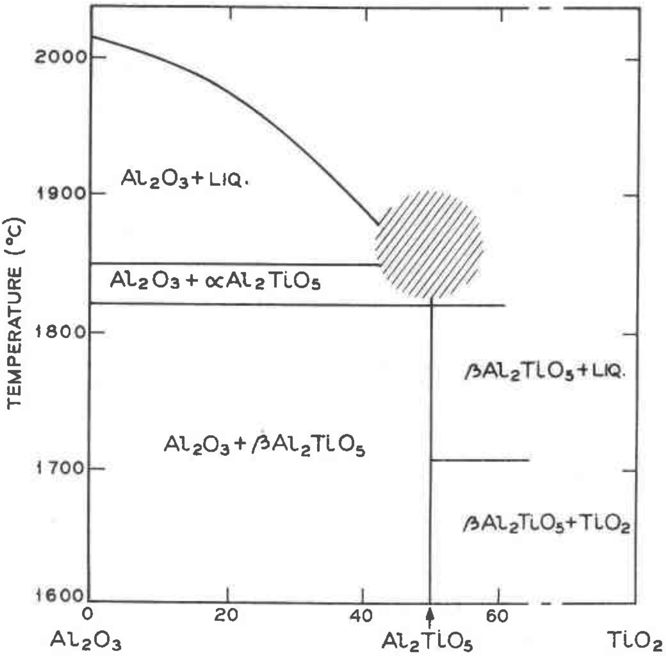

FIG. 1. Phase relations in the Al rich side of the Al_2O_3:TiO_2 system after Lang, Fillmore and Maxwell (1952); uncertainties exist in the shaded region.

cording to this phase diagram, Al_2TiO_5 is the phase that should separate out from the corundum when the solubility is exceeded at temperatures near the melting point of corundum.

Confusion, however, enters in the temperature region below 1600°C. According to Lang, Fillmore and Maxwell (1952), β-Al_2TiO_5 becomes unstable, dissociating into $Al_2O_3+TiO_2$ again at lower temperatures. They reported 90 to 98 percent Al_2TiO_5 at 1600°C, and only 2 to 10 percent Al_2TiO_5 at 1200–1350°C. Hamelin (1951) similarly states that in the presence of 5 percent boric acid at 1250°C no Al_2TiO_5 is formed after 1 hour, but complete conversion was obtained at 1450°C in 10 minutes. Based on these results the asterism in synthetic corundum would be expected to originate from TiO_2. In a study on the solubility of TiO_2 in Al_2O_3, Winkler, Sarver and Cutler (1966) however prepared Al_2TiO_5 by firing at 1400°C for 2 hours and obtained Al_2TiO_5 with no unreacted Al_2O_3 or TiO_2. Yamaguchi (1944) also obtained Al_2TiO_5[1] at 1400°C. A quick check, heating an intimate mixture of Al_2O_3 and TiO_2 at 1300°C for 3 hours, produced essentially no Al_2TiO_5, consistent with Lang *et al.*,

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[1] Yamaguchi gave the name tieilite to β-Al_2TiO_5, but did not observe it in nature.

(1952). It may well be that small amounts of impurities can affect the stability of Al_2TiO_5, and accordingly the precipitate in synthetic star corundum cannot be predicted on the basis of these studies.

Phase diagrams applying to the Al_2O_3- and TiO_2-containing systems during the formation of natural star rubies and sapphires are not available. Nor is it possible to extrapolate the already uncertain melt and sinter conditions discussed above to the magmatic, metamorphic, or hydrothermal conditions during the growth of naturally occurring corundum at much lower temperatures. Accordingly, either TiO_2 or Al_2TiO_5 could be expected in natural asteriated corundum.

The compound Al_2TiO_5 has an orthorhombic structure (8,9) (*Bbmm*, V_h^{17}) isomorphous with pseudo-brookite Fe_2TiO_5 (Yamaguchi, 1944; Austin and Schwartz, 1953). Lattice parameters given by Austin and Schwartz (1953) are $a = 9.436$, $b = 9.648$, $c = 3.557$, so that rectangular or near-square morphology is possible; needles have been observed (Lang *et al.*, 1952). Accordingly needle morphology considerations are inadequate for distinguishing between TiO_2 and Al_2TiO_5 in asteriated corundum.

EXPERIMENTAL

Pale blue star sapphires from Ceylon, obtained from the International Gem Corp., New York, and synthetic star ruby from the Linde Company, were examined by optical microscopy, electron microscopy, and by electron probe microanalysis.

Optical examination showed the typical arrangement of three sets of needle-like inclusions in the basal plane as illustrated by Tait (1955). The needles were square to rectangular in cross-section; in some cases they appeared to be empty (hollow). A number of irregularly shaped and placed inclusions were also observed in the natural material, but were not further investigated. Needle diameters ranged from a few tens of microns in diameter down. In the synthetic material the needles were much smaller and could not be used for further examination.

Attempts were made to take plastic replicas from polished and fractured surfaces for electron microscopy in the hope of pulling out a needle and obtaining electron diffraction patterns. A number of attempts did not yield any usable replicas.

Electron probe microanalysis was performed on a Cambridge Microscan instrument. The sapphire samples were polished on diamond powder on polystyrene, ending up with $\frac{1}{4}$-μ diamond, vapor coated with carbon in vacuum, and analyzed for the $AlK\alpha_1$ line by use of a gypsum crystal and for the $TiK\alpha_1$ line by using a lithium fluoride crystal. A check was also run across the whole spectral range of the instrument but no other

TABLE 1. ELECTRON BEAM MICROANALYSIS CONCENTRATIONS AS INTENSITY RATIOS COMPARED TO THE PURE METAL

Titanium Content:	
Calculated for Al_2TiO_5	0.257
Found in inclusion	0.329
Calculated for TiO_2	0.607
Aluminum Content:	
Calculated for Al_2O_3	0.332
Found in bulk of corundum	0.254
Calculated for Al_2TiO_5	0.134
Found in inclusion	0.052
Calculated for TiO_2	0.0

elements were detected, either in the inclusions or in the bulk of the sapphires.

Examined in titanium radiation inclusions showed up as intense emission regions when they were on the surface, but more weakly when they were below the surface as established by optical microscopy. Accurate measurements were performed on an inclusion which was approximately 30 microns by 20 microns in size, the largest found. Reference standards of pure aluminum and titanium were used to give the concentration value of Table 1 in terms of intensity ratios. The calculated intensity ratios were obtained correcting only for X-ray absorption (Birks, 1963). Fluorescence and atomic number corrections are expected to be of minor importance.

DISCUSSION

In the electron probe microanalysis of small, thin specimens there is the danger of spurious readings from picking up radiation from the matrix above, to the sides, or from below the specimen. Optical examination showed that there was no corundum overlaying the inclusion. The approximately flat regions obtained in Figure 2 confirm that the surrounding corundum was not contributing. The slight slope, however, indicated that the inclusion was probably quite thin and varying in thickness, so that the titanium reading obtained would be on the low side. Accordingly the values of Table 1 clearly rule out the possibility of Al_2TiO_5 and confirm TiO_2. The Al reading from the inclusion is expected to be on the low side due to the strong absorption of the Al radiation by the TiO_2. Since the inclusion is thin, some Al radiation is expected to be observed even from TiO_2.

The inclusions in the synthetic ruby available were found to be too

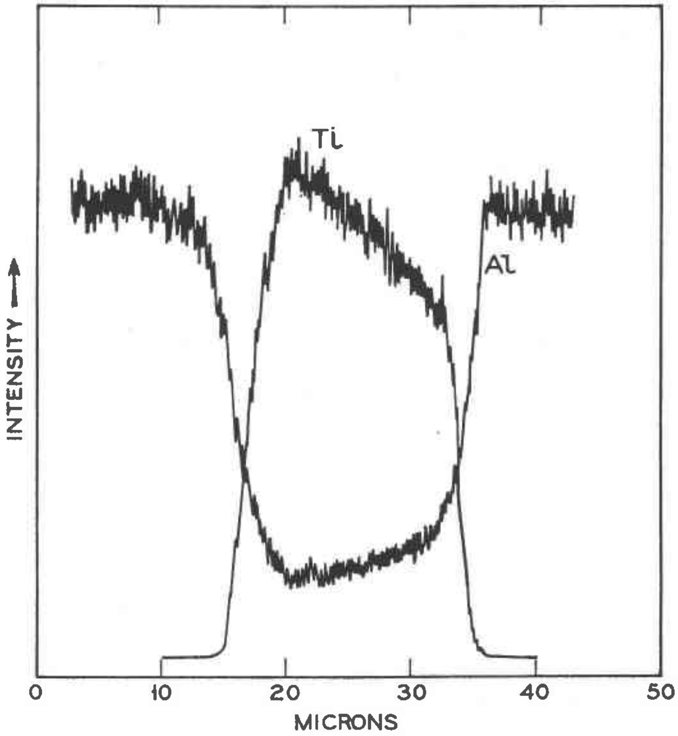

FIG. 2. Electron probe microanalysis curves across inclusion in Ceylon star sapphire taken with Al and Ti radiation.

small for analysis, but on the basis of the phase diagram considerations discussed could be either TiO_2 or Al_2TiO_5. The possibility remains that natural star corundum which grew under different conditions from the sample here examined could contain Al_2TiO_5 needles.

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REFERENCES

AUSTIN, A. E. AND C. M. SCHWARTZ (1953) *Acta Crystallogr.* **6**, 812–13.

BIRKS, L. S. (1963) *Electron Probe Microanalysis.* Interscience Publishers, New York, p. 125 ff.

BUNTING, E. N. (1933) *J. Res. U. S. Nat. Bur. Stand.* **11**, 719–725.

BURDICK, J. N. AND J. W. GLENN (1949) *U. S. Pat. 2,488,507* Nov. 15, 1949.

——— AND R. A. JONES (1954) *U. S. Pat. 2,690,062,* Sept. 28, 1954.

HAMELIN, M. (1951) *Bull. Ceram. Soc. (France)* **11**, 14–16.

LANG, S. M., C. L. FILMORE AND L. H. MAXWELL (1952) *J. Res. U. S. Nat. Bur. Stand.* **48,** 298–312.
TAIT, A. S. (1955) *J. Gemology* **5,** 65–72.
WEBSTER, R. (1962) *Gems,* Vol. 1, Butterworths, Washington, D. C., p. 307.
WINKLER, E. R., J. F. SARVER AND I. B. CUTLER *J. Amer. Ceram. Soc.* **49,** 634–637.
YAMAGUCHI, G. (1944) *J. Japan Ceram. Assn.* **52,** 6–7.

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THE INFRARED SPECTRUM OF DAWSONITE

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INTRODUCTION

As part of a broad program on minerals research by the U.S. Bureau of Mines, infrared spectroscopy is being used at its Morgantown, W. Va., laboratories for the study of various minerals of current interest to both Government and industry. One of these is the mineral dawsonite, a basic carbonate of sodium and aluminum, $NaAl(CO_3)(OH)_2$. A recent report (Smith and Milton, 1966) describes relatively abundant deposits of this mineral as a rock-forming constituent of oil shale in the Piceance Creek Basin of northwestern Colorado. This occurrence has created interest in dawsonite as a potential ore of aluminum. In addition, alkalized alumina (synthetic dawsonite) prepared by the reaction of aluminum sulfate and sodium carbonate, is being tested by the Bureau of Mines as an absorbent for sulfur dioxide in flue gas. This note presents the infrared spectrum of pure natural dawsonite, compares it qualitatively with synthetic dawsonite, and demonstrates that infrared spectroscopy to 200 cm^{-1} is a reliable method for the identification and possible quantitative analysis of this mineral.

EXPERIMENTAL

Dawsonite is a colorless to white transparent mineral and occurs as rosettes of bladed to acicular crystals (0.05–0.5 mm) (Stevenson and Stevenson, 1965), as thin incrustations, or as sedimentary nodular accretions. A few milligrams of pure dawsonite were isolated microscopically (40–100×) from each of the three sources shown in Table 1. The relative hardness of 3 for dawsonite greatly facilitated its isolation from the matrix minerals. About 0.5 mg of the isolated sample was weighed on a microbalance, ground for 5 minutes with 500 mg of cesium iodide in an agate