EXAMINATION OF THREE-PHASE INCLUSIONS IN COLORLESS, YELLOW, AND BLUE SAPPHIRES FROM SRI LANKA

By Karl Schmetzer and Olaf Medenbach

Three-phase inclusions in untreated natural colorless, yellow, and blue sapphires from Sri Lanka were found to consist of liquid and gaseous carbon dioxide as well as needle-like to tabular crystals of diaspore. The identification of diaspore was accomplished through the use of a microscope-mounted drill system and an improved version of the Gandolfi X-ray camera. Technical details for both methods are given. The conditions under which diaspore forms as a daughter mineral in corundum are briefly discussed.

Three-phase (solid, liquid, and gas) inclusions are commonly found in emeralds from certain localities, such as Muzo and Chivor in Colombia. Occasionally, similar three-phase inclusions are seen in other gem materials such as rubies and sapphires. For example, the *Photoatlas of Inclusions in Gemstones* (Gübelin and Koivula, 1986) provides two photographs of three-phase inclusions in blue sapphires from Sri Lanka. In both cases, the liquid and gaseous phases are described as CO2, but while the black solid phase in one example is identified as graphite (Gübelin and Koivula, 1986, p. 352), the transparent, needle-like mineral inclusions in the second (pp. 78–79) are not specified. Three-phase inclusions in natural pink and violet sapphires from Nepal were recently described by Kiefert and Schmetzer (1986, 1987). In samples from this new occurrence of gem-quality corundum, tabular flakes of doubly refracting mineral inclusions were determined to be the Ca-bearing mica, margarite, by X-ray powder diffraction and electron microprobe analysis. In one sample of yellow sapphire from Sri Lanka, small three-phase inclusions consisting of a transparent, doubly refracting tabular crystal, a liquid, and a gaseous substance were observed as well, but no exact determination of these phases could be performed at that time (Schmetzer, 1987).

To establish the identity of the transparent solid phase in some of the three-phase inclusions in sapphire from Sri Lanka, the authors examined more than 300 samples of colorless, yellow, and blue sapphires from this area. In the past, a number of different techniques have been applied to the identification of individual daughter minerals in multiphase inclusions, for example, laser-excited Raman spectroscopy, scanning electron microscopy, and electron microprobe investigations, as well as Gandolfi X-ray techniques (e.g., Rosasco et al., 1975; Metzger et al., 1977; Rosasco and Roedder, 1979; Zolensky and Bodnar, 1982). If the inclusions are not exposed at the surface of the host crystal, laser-excited Raman spectroscopy is the only one of these techniques that is non-destructive, but the equipment required is not widely available.

The most comprehensive chemical and crystallographic information on daughter minerals in multiphase inclusions is obtained by a combination of SEM-EDS (Stockton and Manson, 1981) or an electron microscope, with X-ray diffraction microtechniques. A key problem with any of these methods is the time-consuming procedure for selecting and preparing the small particles to be identified, and the possible loss of the minute daughter minerals when the sample is crushed. This problem can be avoided, however, by the use of a special microscope-mounted drill technique to open the cavities. In combination with X-ray diffraction using a modified Gandolfi camera, we successfully applied this technique to identify the transparent solid component of three-phase inclusions in colorless, blue, and yellow sapphires from Sri Lanka.

About the Authors

Dr. Schmetzer is research associate at the Mineralogisch-Petrographisches Institut der Universität Heidelberg, D-6900 Heidelberg, Federal Republic of Germany; Dr. Medenbach is research associate at the Institut für Mineralogie der Ruhr-Universität, D-4630 Bochum, Federal Republic of Germany.

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DESCRIPTION OF THE THREE-PHASE INCLUSIONS

We observed two- and three-phase inclusions in approximately 20% of the more than 300 untreated colorless, light yellow, bluish, or blue sapphires from Sri Lanka that we examined. All of these inclusions were in the form of thin tabular negative crystals with the tabular face of the negative crystal parallel to the basal pinacoid (0001) of the corundum host. The tabular negative crystals were filled with liquid and generally contained one gaseous bubble, which was able to move around without any restriction within the negative crystals. In about 30% of the negative crystals, needle-like to tabular transparent mineral inclusions were observed (figure 1); examination with crossed polarizers showed that they were doubly refractive (figure 2). These mineral inclusions were attached to the walls of the negative crystals. In some cases, they lay diagonally across the entire cavity; in others, they projected into the cavity and terminated inside the negative crystals (again, see figures 1 and 2).

Identification of the Liquid and Gas Phases. Two-phase inclusions in natural corundum from Sri Lanka have been described as consisting of liquid and gaseous CO₂ (Gübelin and Koivula, 1986; Koivula, 1986). We confirmed that the liquid and gaseous phases of the inclusions we examined were also CO₂ by measuring the homogenization and freezing temperatures of several inclusions.

First, the temperature of several crystals was slowly increased by gentle heating of the immersion liquid. During this process, a continuous decrease in the volume of the gas bubble was observed (again, see figure 1) and the temperature of the immersion liquid was measured exactly at the point of homogenization (figure 1, bottom). Within the limits of experimental error, the homogenization temperatures measured for the liquid and gaseous components of three-phase inclu-
sions in several crystals were found to be in the range of 28°-31°C, that is, below the critical temperature of CO₂ (31.2°C).

However, contrary to the assertion by Koivula (1986), we feel that homogenization temperatures of the liquid and gaseous components of two-phase inclusions are not sufficient to make a precise determination of the chemical nature of the material trapped in corundum host crystals, since homogenization temperatures generally vary with the density and/or composition of the inclusions (cf. Roedder, 1972). Thus, determination of the temperatures at which the inclusions freeze is also necessary to characterize them accurately. For the material trapped in corundum from Sri Lanka, we recorded a freezing temperature of ~56°C, which is close to the freezing temperature of carbon dioxide (~56.7°C). This confirms that the liquid and gaseous components of three-phase inclusions in corundum from Sri Lanka are almost pure carbon dioxide.

Identification of the Solid Phase. We identified the transparent needle-like to tabular solid components of the three-phase inclusions by X-ray diffraction using an improved Gandolfi camera. For this part of the study, we selected three samples that contained numerous typical needle-like daughter crystal inclusions. Each sapphire was then sawed to position a cavity with three-phase inclusions just below the surface. After polishing the face, we carefully opened one cavity in each sapphire using a special microscope-mounted drill system.

The drill system used here is based on a suggestion by Verschure (1978) and was originally developed to isolate small single crystals from thin sections. A similar procedure using a dental micro-drill to open cavities with daughter minerals has also been described by Graziani (1983). The instrument we used adapts a diamond micro-drill to the objective of a polarizing microscope (figure 3).

Progressive manual adjustment of the stage height produces a cylindrical sample no more than 50 μm in diameter, with a height corresponding to the thickness of the section drilled through, that can be picked out with a needle. The drilling process can be supervised optically through a planar glass cover, and the H₂O coolant for the drill also provides a satisfactory immersion medium. Samples obtained in this manner (either attached to the core or picked out of the cavity) are ideally suited for optical study (e.g., on a spindle stage) or single-crystal X-ray investigations. This system may also be used to isolate homogeneous parts of larger, chemically zoned crystals for further study after electron microprobe analysis of the same section (see Medenbach, 1986; Graziani, 1983).

In the present study, after the microdrill was used to open inclusion cavities near the surface of each sapphire, several of the small daughter crystals were carefully selected and mounted onto a glass fiber for X-ray powder diffraction analysis by means of a Gandolfi camera. The Gandolfi camera is generally applied to X-ray microparticle phase analysis if the materials to be identified are not to be powdered (Gandolfi, 1964, 1967). In the present case, as in most of these cases, only very small amounts of the single crystals or polycrystalline aggregates were available.

To obtain good powder-type diffraction patterns, the operator must place the sample to be X-rayed at the precise intersection of two independent rotation axes, that is, the conventional Debye-Scherrer axis and the Gandolfi axis, which is inclined 45° to the former. While sample adjustment was difficult and time-consuming with the original Gandolfi camera, modified Gandolfi cameras as well as additional centering devices have been developed (Nuffield, 1975; Geißmüller et al., 2023).
Another solution to the adjustment problem is presented by Süssleiz-Fornefeld and Schmetzer (1987). The basic principle is the introduction into a modified camera of a complete goniometer head as sample holder instead of a simple glass fiber. The adjustment is accomplished by use of an inner thread for crystal translation parallel to the Gandolfi axis in addition to the two perpendicular sets of arcs and slides of the conventional goniometer head. The camera adjustment system enables three perpendicular translations and two perpendicular rotations, and thus the precise adjustment of the crystal at the intersection point of the two rotation axes. As a result, good-quality powder diffraction patterns of the daughter crystals in the three-phase inclusions were obtained and subsequently matched to JCPDS file number 5-355—diaspore, \( \alpha\)-Al\(\text{OOH} \). Because the pattern was definitive, a planned follow-up chemical analysis by electron microprobe was deemed unnecessary.

**DISCUSSION: THE FORMATION OF DIASPORE IN CORUNDUM FROM SRI LANKA**

Although most gem-quality corundum and other gem minerals from Sri Lanka originate from secondary deposits, research has been undertaken to characterize the primary sources of these gem minerals (e.g., Katz, 1971, 1972; Dahanayake, 1980; Dahanayake et al., 1980; Munasinghe and Dissanayake, 1981, 1985; Katz, 1986). Corundum is found in sillimanite-bearing high-grade metamorphic rocks, which were formed under pressure/temperature (PT) conditions characteristic of pyroxene granulite facies. During the formation of corundum under these PT conditions—that is, at high pressure with decreasing temperatures in the system \( \text{Al}_2\text{O}_3\cdot\text{H}_2\text{O} \) (see Deer et al., 1962)—diaspore becomes the stable mineral phase instead of corundum. At lower pressures, böhmite, \( \alpha\)-Al\(\text{OOH} \), becomes stable instead of corundum. The formation of böhmite within cavities or negative crystals in one sample of corundum from Sri Lanka is described by Sahama et al. (1973). In the experience of the present authors, however, the \( \text{Al}_2\text{O}_3\cdot\text{H}_2\text{O} \) polymorph diaspore is more abundant in three-phase inclusions in corundum from this locality. Similar-appearing daughter minerals have been described in three-phase inclusions in corundum from Malawi (Grubessi and Marcon, 1986), but were reported as probably being rutile. Further examination should be done to confirm their identity before diaspore can be considered an identifying characteristic of the Sri Lankan origin of sapphire.

The presence of this particular type of three-
REFERENCES


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