Identification of fluid inclusion daughter minerals using Gandolfi X-ray techniques

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Abstract

Unequivocal identifications of individual daughter minerals extracted from fluid inclusions have been obtained using microtechniques in conjunction with the Gandolfi X-ray camera. This development represents a major advance in fluid inclusion research because solid phases from preselected fluid inclusions may now be routinely and unambiguously identified. Application of this technique allows the worker to not only measure the homogenization and freezing temperatures of a fluid inclusion of known origin but also to identify any daughter minerals that might be present in the *same* inclusion, provided that these phases are recognizable both before and after heating/freezing tests, and that the heating/freezing tests have not affected the daughter phases. This procedure yields considerably more information about the physical and chemical conditions attending mineral deposition than is presently available from conventional fluid inclusion analyses.

Introduction

Fluid inclusions are samples of the fluids from which the host crystal grew or samples of fluids that engulfed the crystal at some time after its formation. Because these inclusions are actual samples of the mineralizing fluids, valuable information on the chemical conditions attending mineralization may be obtained if the composition of the inclusions can be determined. This, of course, requires determination not only of the fluid composition but also of the composition of all *solid* phases, *i.e., daughter minerals*, that have precipitated from that solution.

Fluid inclusion daughter minerals are most often identified from their optical and physical properties. Although rapid and nondestructive, this procedure permits only a few daughter minerals to be identified with certainty. Color change following X-ray irradiation has been used to characterize daughter crystals (Vorob'ev and Lozhkin, 1976) but is applicable to only a few minerals (*e.g.*, halite, sylvite, and villaumite) and, even for these species, is not totally diagnostic. In recent years, the SEM and electron microprobe have been used extensively for identification of fluid inclusion daughter phases (*e.g.*, Metzger *et al.*, 1977), but these techniques do not allow for preselection of fluid inclusions to be examined, eliminating the possibility of obtaining both heating/freezing data and daughter mineral identification for the *same* inclusion. Furthermore, elements lighter than sodium cannot generally be determined, and polytypes and polymorphs cannot be distinguished with this method. Raman spectrometric analyses (Rosasco *et al.*, 1975; Rosasco and Roedder, 1979) have provided nondestructive daughter mineral identifications, but these analyses are limited to minerals containing molecular units previously fully characterized by laser-excited Raman spectroscopy and enclosed within materials which do not fluoresce in the laser beam. An additional limitation of this procedure is that ramalogs specially equipped for daughter mineral identification are not generally available. Single-crystal X-ray photographs of materials containing fluid inclusions may show a superimposed powder pattern from included daughter phases provided they are present in sufficient quantity. Roedder and Coombs (1967) used this observation to verify the occurrence of halite daughter crystals within inclusions in feldspar crystals. Coveney and Kelly (1971) used this technique to identify dawsonite enclosed within small chips of quartz. These workers also successfully extracted large polycrystalline aggregates (several hundred microns across?) of this daughter phase from fluid inclusions and verified this identification using standard powder diffraction

techniques. Various other techniques have been suggested for the identification of fluid inclusion daughter crystals and are summarized by Roedder (1972).

At present, X-ray powder diffraction is the single most complete and generally applicable method of mineral identification. In this paper a method for routinely obtaining unequivocal identifications of fluid inclusion daughter minerals extracted from preselected fluid inclusions using microtechniques in conjunction with the Gandolfi X-ray camera (Gandolfi, 1967) is described.

Experimental procedure

Doubly-polished thin-sections and cleavage sections were examined under a microscope and fluid inclusions containing daughter crystals were located. Inclusions lying close to the upper surface were used whenever possible to minimize the amount of host material that had to be removed to reach the inclusion. Preliminary identifications were made, when possible, from an examination of the optical and physical properties of the daughter phases. Heating/freezing tests were also conducted. Occasionally, daughter phases fail to renucleate in inclusions or exhibit different morphologies following heating tests. This behavior limits a worker's ability to continuously monitor a particular phase during experiments. It was not found to be a problem in the present study owing to the types of daughter phases examined. Following successful heating/freezing tests, the sample was mounted onto a glass slide and the inclusion was relocated under the microscope. A small, foot-switch controlled, hand-held drill with a tapered dental diamond burr was used to drill a "moat" around the preselected fluid inclusion, thus isolating the inclusion within a pedestal of host material. The powder produced during this drilling, a combination of drill grit and ground sample, was periodically swept from the working area so that the inclusion could be continuously observed through the polished upper surface of the pedestal. It was desirable that a pedestal of the smallest possible volume remain, but it was also necessary that the inclusion walls not be breached as the contents of the inclusion would then become lost among the drilling debris. When the moat had been extended to a level below that of the inclusion, a finely-sharpened steel probe was used to break the pedestal off at the base. The inclusion, enclosed

within this small fragment of the host crystal, was then transferred to a clean glass slide, using the steel probe, and covered with a second glass slide, producing a simplified version of the crushing stage described by Roedder (1970). While the inclusion was being observed under the microscope, sufficient pressure was applied to the top slide to fracture the host crystal grain through the inclusion, liberating the daughter crystals. A certain amount of restraint was necessary when applying pressure to the sample chip, so that when the grain fractured, the daughter crystals would not be crushed. After separation of the slides, a finely-drawn glass fiber was used to isolate the daughter crystals on one of the slides.

In preparation for mounting the daughter mineral, a Lindemann glass capillary tube was set into a Gandolfi camera sample pin and was drawn to a diameter comparable to that of the crystal to be mounted. This capillary tube thinning was accomplished by touching the free end of the tube to a heated platinum wire and drawing the melted glass to a fine fiber. The crystal was then mounted onto the glass fiber with clear fingernail polish or a solution of collodion in amyl acetate, a procedure developed by Smith and co-workers (Smith and Wein, 1974). The crystal mounting procedure required practice, with results being optimized by the use of the minimum amount of mounting medium and the smallest workable glass fiber diameter. To minimize scattering of the X-ray beam by the glass fiber, it was desirable to mount the crystal onto the end of the fiber. If the mounted crystal was several times larger in at least two dimensions than the fiber diameter at the point of attachment, however, the amount of glass scattering was not found to be significant, and placement of the crystal at the end of the fiber was not essential.

The mounted sample was then mounted in a Gandolfi camera. Careful centering of the sample within the camera was absolutely critical for obtaining a pattern of the maximum sharpness in the least time. Employing CuKα radiation and a 57.3 mm camera cassette with operating conditions of 20 mA and 40 kV, exposure times varied from three to six days, depending upon crystal density and volume. It was necessary to evacuate the camera and use an X-ray film with a low fog level to minimize film darkening due to the scattering of X-rays by air, which would otherwise have rendered the film unreadable after such long exposures.

Applications

During the course of the development of the technique described above, several solid phases were extracted from fluid inclusions and analyzed. In the early part of this study, inclusions containing opaque daughter phases were chosen for examination because, once these crystals were extracted from the inclusions, they could be easily recognized among the host mineral debris. As the handling techniques improved, attempts were made to isolate less distinguishable daughter phases whose identities were not previously known.

Fluid inclusions from porphyry copper deposits commonly contain an opaque phase that is identified as chalcopyrite based upon its triangular cross-section and optical properties (Bodnar and Beane, 1980), and semi-quantitative SEM analyses (Reynolds and Beane, 1979). Figure 1a shows two inclusions in quartz from Copper Creek, Arizona, containing several daughter phases including a triangular opaque mineral. This crystal was removed from the inclusion using the procedure described above, mounted on a glass fiber (Fig. 1b), and a Gandolfi pattern was obtained. Inspection of this diffraction pattern showed that the crystal was indeed chalcopyrite.

Another common solid phase observed in fluid inclusions from porphyry copper deposits is a translucent red, hexagonal crystal identified as hematite (Figs. 1c and d). Extraction and X-ray analysis of several such crystals verified this identification. It has not yet been established that these hematite crystals are in all cases true daughter minerals, but rather may result from auto-oxidation of the inclusion due to hydrogen leakage through the inclusion walls.

Coexisting with the hematite-bearing inclusions observed in quartz from Copper Creek, Arizona, were inclusions having phase relations similar to the hematite-bearing type except that they contained an octahedral opaque mineral instead of a red, translucent mineral (hematite). Even though this mineral did not respond to a magnet (this particular sample was not subjected to heating tests), the crystal was tentatively identified as magnetite. X-ray analysis, however, proved this phase to be hematite (variety martite—a pseudomorph of hematite after magnetite). An SEM examination of this sample would have revealed only the presence of iron and, combined with the observed crystal morphology, this
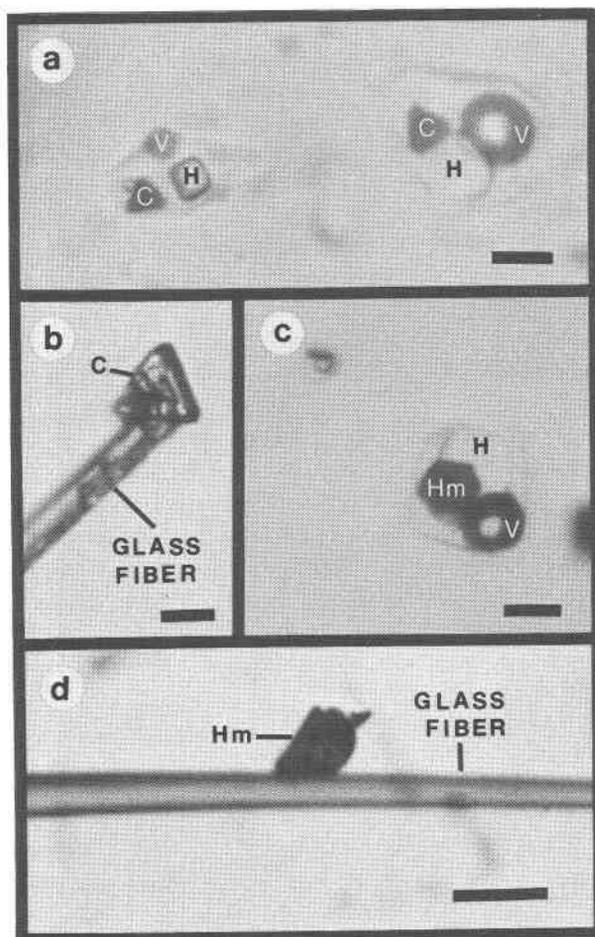
Fig. 1. (a) Multiphase inclusions in quartz from Copper Creek, Arizona, containing halite (H), triangular opaque (chalcopyrite—C), a vapor bubble (V), and several unidentified phases. Photograph taken in transmitted plain light. Scale bar represents 20 μm. (b) Triangular opaque (C) from inclusion shown in Fig. 1a, now mounted onto glass fiber in preparation for X-ray analysis. Photograph taken in reflected plain light. Scale bar represents 10 μm. (c) Multiphase inclusion in quartz from Copper Creek, Arizona, containing halite (H), a translucent, red, hexagonal plate (hematite—Hm), and a vapor bubble (V). Photograph taken in transmitted plain light. Scale bar represents 20 μm. (d) Red hexagonal plate (Hm), from inclusion shown in Fig. 1c, mounted onto glass fiber. Photograph taken in transmitted plain light. Scale bar represents 15 μm.

mineral would probably have been incorrectly identified as magnetite.

The origin of the martite cannot be determined with certainty from the available data. However, the random distribution of red, translucent hematite in some inclusions and opaque martite in others suggests that magnetite daughter minerals formed in some inclusions but failed to nucleate in others.

Hematite became the stable iron oxide phase as the inclusion composition crossed the magnetite-hematite phase boundary, due to cooling and/or diffusive hydrogen loss. This caused alteration of the magnetite to hematite in martite-bearing inclusions and deposition of hematite in some inclusions in which magnetite daughter crystals had originally failed to nucleate. It is possible that auto-oxidation from diffusive hydrogen loss in laboratory heating tests could also cause magnetite to alter to hematite. However, as described above, the sample containing these inclusions was not subjected to heating tests.

Many fluid inclusions from porphyry copper systems contain two clear, cubic daughter crystals and, most often, one of these phases is considerably larger than the other. It is generally assumed that the larger crystal is halite and the smaller one is sylvite. These assignments may be verified by heating tests, due to the significantly different dissolution rates of these two phases with temperature (Roedder, 1971), or freezing tests, because NaCl forms a highly birefringent hydrate, $NaCl \cdot 2H_2O$, at low temperature while sylvite does not (Roedder, 1963). The larger of two such crystals in an inclusion from the Copper Creek porphyry copper system was removed and analyzed. This mineral proved to be sylvite, revealing that the larger of the two clear, cubic daughter phases in porphyry copper inclusions is not *always* halite and that the K/Na ratio of the mineralizing fluids in this case was very high as compared to most porphyry copper deposits (Bodnar and Beane, 1980). If the K/Na ratio of this inclusion had been determined by assuming the larger crystal was halite without verification from heating and then measuring the volumes of the two phases, an incorrect value would have been obtained, although it is unlikely that any workers would use this procedure.

Topaz from Volnya in the U.S.S.R. is particularly well known for the large daughter phase populations of its fluid inclusions (Zakharchenko, 1971). A mass of brownish plates, approximately 20 micrometers in diameter, from one multiphase inclusion in this topaz was extracted and found to be the $2M_1$ polytype of phlogopite. This mineral had not previously been described from this locality. Under 1000× magnification several reddish-brown laths approximately one micrometer in length could be distinguished within the phlogopite. An X-ray pattern could not be obtained from these crystals,

because of the present size limitation of this procedure.

Summary and recommendations

The Gandolfi X-ray procedure described above yields unambiguous identifications of fluid inclusion daughter minerals and is generally applicable to all crystals larger than 2–5 μm in at least two dimensions. This technique also permits different polytypes to be distinguished and pseudomorphism to be recognized. The practical limitation of the method described here is the excessive amount of time required for each daughter mineral characterization as compared to most other identification techniques. From one hour to several tens of hours may be required to extract a daughter crystal and mount it onto a glass fiber, ready for X-ray analysis. The actual length of time depends upon crystal size as well as the physical and optical properties of the daughter mineral relative to that of the host material, *i.e.*, hardness, refractive index, luster, crystal habit, cleavage, *etc.* Furthermore, this method requires considerable manual dexterity and patience on the part of the operator. All of these factors affect the success rate, which can be expected to be initially quite low (approximately 10%) and which will probably never exceed about 50%.

Handling techniques, the limiting factor in this study, could be greatly improved with the use of a better drilling arrangement and the introduction of a micromanipulator. In addition, the extremely long X-ray exposure times required could be at least halved with the use of commonly available high-intensity X-ray generators. Such generators may, in fact, be necessary for the successful identification of minerals containing predominently low scattering elements, *i.e.*, elements lighter in electron density than sodium.

A principal advantage of the present method is the possibility of identifying crystals from individual fluid inclusions that have been previously subjected to heating/freezing tests. However, it must be independently verified that the heating and freezing procedures have not affected the daughter crystals.

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