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— NEWS AND VIEWS —

Geochemistry

Uses for synthetic fluid inclusions in quartz crystals

from Edwin Roedder

FLUID inclusions are small droplets of the fluids from which crystals grew and are found in many minerals, both natural and synthetic. In natural gem minerals, fluid inclusions diminish their clarity, and hence their value; in synthetic crystals they detract from the useful mechanical, electrical or optical properties for which the crystals are grown. Why then should anyone want purposely to form microscopic inclusions of fluid in otherwise optically clear quartz crystals? Yet S.M. Sterner and R.J. Bodnar¹ have recently developed a procedure to do just that, and have shown that the resulting inclusions are valuable in a surprisingly wide range of geochemical and mineralogical studies that may help us to understand better the natural processes that may have taken place millions of years ago.

Sterner and Bodnar start with solid cylinders of clear quartz, cut from a fluid-inclusion-free natural crystal. These are heated and then cracked by quenching in water. The cracked but still intact cylinders are dried and sealed into thin-walled noble-metal capsules with the starting materials appropriate to generate the desired fluid composition under the experimental conditions. The collapsible capsules are then subjected to external pressures of 0.5–7 kbar, while being heated to 200–850°C, for periods of between 3 hours and 87 days, before being quenched.

During the time at elevated temperature and pressure, the fractures in the quartz crystal are healed by dissolution and recrystallization of the crack surfaces, thereby decreasing the total surface energy

(see Fig. 1). In so doing, small portions of the capsule fluid are trapped within the new growth — samples of the fluid, sealed in single crystal quartz 'bottles'. Thus, these new synthetic inclusions are analogous to the 'secondary' inclusions found in most natural quartz crystals (Fig. 2). (Secondary inclusions are those that are formed by the healing of fractures in a pre-existing crystal; the fractures are generally caused by external stress.) Possible applications include the study of inclusion-trapping mechanisms and rates, post-trapping changes and even the determination of phase equilibria and pressure, volume and temperature data on otherwise experimentally very difficult high-temperature, high-pressure hydrothermal systems.

The full range of uses for these synthetic fluid inclusions has yet to be explored but applications already discussed by Sterner and Bodnar¹ have some fascinating ramifications. Fluid inclusions, both natural and synthetic, undergo various phase changes on cooling after becoming enclosed in their crystal host. Henry Clifton Sorby (the 'father of fluid inclusions') showed in a study 127 years ago² that these phase changes could be observed and reversed in the laboratory while heating the host crystal under the microscope. The most common phase change observed occurs because liquids shrink at a much higher rate than crystals. Thus, if a hot liquid is sealed into a relatively rigid, fixed-volume crystal 'bottle' and then cooled, differential shrinkage of the liquid relative to the crystal will cause the formation of a vapour bubble in the liquid. Sorby observed the point when this bubble disappeared in a crystal on a microscope heating stage and used it as a measure of the temperature at which the cavity had originally been sealed, perhaps millions or

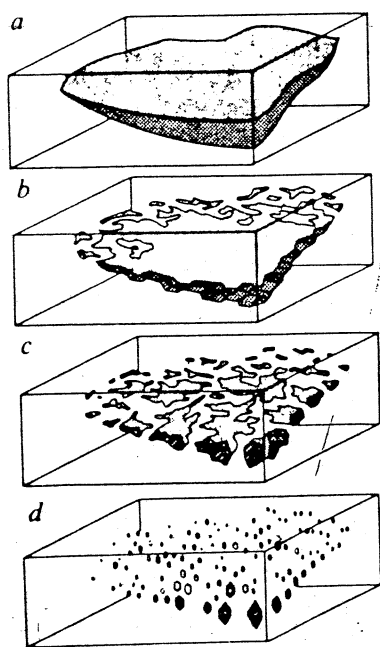


Fig. 1. Stages in the healing or 'necking down' of a crack in a quartz crystal resulting in secondary negative crystal inclusions (from ref. 3).

billions of years earlier. Each tiny inclusion (and ordinary white quartz may contain 10^9 inclusions per cm^3) is, in effect, a built-in thermometer, recording the temperature of a past event.

Sorby's proposal to use fluid inclusions in this manner — only one of his many brilliant ideas — was, and still is, the subject of considerable discussion. In part this debate arose because the geothermometric data from fluid inclusions contradicted some of the preconceived notions of the day, and in part because of the difficulty in assuring that the geological conditions under which an inclusion formed actually fulfilled the several relatively simple but necessary assumptions behind the method. Previous studies of fluid inclusions accidentally trapped in synthetic industrial quartz crystals, grown under approximately known conditions, have verified the general validity of the concept of inclusion geothermometry. Several minor problems have, however, interfered with the widespread use of the method, not the least of these being, surprisingly, that of accurately calibrating the microscope heating stages³. The most common application of synthetic inclusions made with the new method may be as a device for calibrating instruments.

In the years since Sorby's work, fluid inclusions have provided much geological information in addition to temperature. Measurements of phase changes visible under the microscope at temperatures ranging from roughly -190°C upwards, and with appropriate conditions and caveats, can provide data on the density, pressure and the major solute and solvent compositions of the fluids at the time of trapping. Most of these data simply cannot be obtained from any other source. In the search for metallic ore deposits, it would obviously be desirable to understand the chemical processes that resulted in transport of the ore metal to the site of the ore body, and its precipitation there. This requires an understanding of the chemistry of the ore-forming fluid; with a few rare exceptions, the only samples we have of these fluids are in microscopic fluid inclusions.

The past few decades have seen a tremendous increase in studies of the composition of such inclusions. Many of these have involved the use of new methods of ultra-microchemical analysis, such as laser-activated micro-Raman spectroscopy and laser-ionized mass spectrometry. Such methods have attempted to overcome the difficult problems of extraction and chemical (or isotope) analysis of major and trace constituents of these inclusions, without serious loss or contamination. In addition to the exceedingly small total sample size (frequently less than 10^{-9}g) usually available, the problem of finding suitable analytical standards has been particularly limiting. The new synthetic inclusion technique developed by Sterner and Bodnar permits the preparation of optimum standards for both microscopy and chemical analysis — inclusions of the same

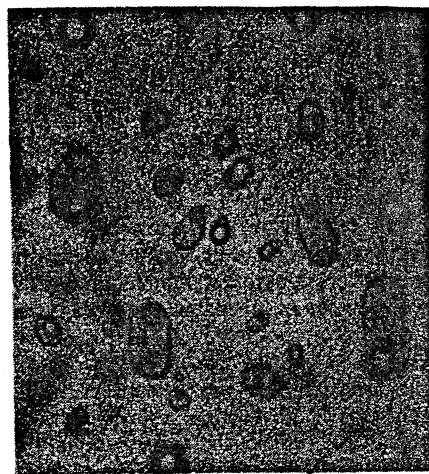


Fig. 2. Synthetic fluid inclusions in quartz. Those with small bubbles (of CH_4) initially trapped liquid and are now dominated by a carbonate; those with large bubbles trapped vapour and are largely CO_2 ; $\times 156$ (photomicrograph courtesy of S.M. Sterner and R.J. Bodnar).

size range, enclosed in the same host mineral and containing fluids of known density and composition.

Still another application, with a particularly exciting potential, is the use of these synthetic inclusions in studies of the physical chemistry of otherwise difficult chemical systems. N.P. Ermakov⁴ pointed out 35 years ago that fluid inclusions in transparent minerals are unique miniature 'visual autoclaves', permitting visual observations of high-temperature and high-pressure phase assemblages and critical phenomena. Bodnar and Sterner⁵, have explored the use of synthetic inclusions in pressure-volume-temperature studies of hydrothermal systems and Bodnar *et al.*⁶ have gone on to show how valuable these synthetic inclusions can be in the determination of the phase-equilibrium properties of the system $\text{H}_2\text{O}-\text{NaCl}$ to $1,000^\circ\text{C}$ and 1,500 bar. Such data are necessary for an understanding of several important groups of ore deposits that have formed from hot, extremely saline fluids and are also useful in understanding the mechanism and energetics of volcanic eruptions such as that at Mount St Helens in May 1980. Conventional experimentation is very difficult because these fluids are exceedingly corrosive. The use of even a few trial runs with synthetic inclusions to locate the critical fluid parameters could reduce the effort involved in larger-scale experiments, or the inclusion technique itself could even be used for the entire phase-equilibrium study. □

1. Sterner, S.M. & Bodnar, R.J. *Geochim. cosmochim. Acta* 48, 2659 (1984).
2. Sorby, H.C. *Geol. Soc. London quart. J.* 14, 453 (1858).
3. Roedder, E. *Fluid Inclusions, (Rev. Mineralogy) Vol. 12* (Mineral Soc. Am., Washington, D.C. 1984).
4. Ermakov, N.P. *Research on Mineral-Forming Solutions* (Kharkov, Univ. 1950) (in Russian, translated in Yermakov, N.P. *et al. Int. Ser. Monog. Earth Sci.*, 22 (1985)).
5. Bodnar, R.J. & Sterner, S.M. *Geochim. cosmochim. Acta*, (in the press).
6. Bodnar, R.J., Burham, C.W. & Sterner, S.M. *Geochim. cosmochim. Acta* (in the press).

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