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FORMATION TEMPERATURES OF SOUTHERN ILLINOIS BEDDED FLUORITE AS DETERMINED FROM FLUID INCLUSIONS[1]

Robert M. Grogan and Raymond S. Shrode

Abstract

Fluid inclusions in fluorite crystals were studied principally to determine the range of temperature of formation of individual crystals. Measurements were made by heating specimens and recording temperatures at which vapor bubbles within the inclusions disappeared. Over-all accuracy, excluding pressure corrections, was of the order of ±2.5° C.

Some of the fluid inclusions are arranged in geometrically regular planes parallel to cube faces. These are apparently of primary origin. Others form bands along former fractures which approximately parallel the cleavage directions and which cut across each other and the primary planes alike. Historically such inclusions have been called "secondary" although "subsequent" is considered a more meaningful designation. Most of the primary inclusions are smoothly rounded and contain petroleum, whereas "subsequent" inclusions range from jagged to smooth in outline and contain principally a clear fluid.

Measurements on primary inclusions indicate that temperatures at which the crystals grew generally ranged from 83° to 115° C., with a mean around 100° C. Commonly the indicated growth temperature increased slightly for some distance outward from the crystal center and then dropped off toward the exterior. Measurements on subsequent inclusions gave results in the range of 112° to 172° C., generally higher than those shown by primary inclusions.

Incomplete bulk analyses of the fluid from inclusions, probably mostly of the subsequent variety, show a preponderance of Ca, Na, and Cl ions, and a total concentration of dissolved material amounting to 45,000 parts per million.

Introduction

Investigations of the temperature of formation of fluorite from deposits in southern Illinois have been carried on in the laboratories of the Illinois State Geological Survey at intervals for a number of years. The method used in all the studies is that in which liquid inclusions within cleavage or sawed plates of the mineral are observed through a microscope equipped with a heating stage, and the temperatures are recorded at which the vapor bubbles within the liquid inclusions disappear. These temperatures are considered to be approximately those at which the fluorite was deposited.

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Initial investigations involving the use of cleavage flakes of fluorite from crystals in different parts of several mines yielded temperature data which, although informative, seemed to lack any pattern or internal consistency. It was decided, therefore, to work out the thermal history of a number of individual crystals in an effort to obtain more useful data. This article describes the major results of this most recent phase of the work and discusses some of its implications.

Fluid inclusions in minerals result from imperfect crystal growth. The fluid in each is assumed to have filled its containing cavity at the above-atmospheric temperature and pressure prevailing when the cavity was closed off. At room temperature the contracted fluid occupies less space than it did at the temperature of entrapment, and a vapor bubble is present in consequence. When the mineral is heated in the laboratory the fluid expands and the vapor bubble shrinks and disappears at a temperature which approximates that prevailing when the cavity was filled and sealed. This temperature is low, however, by an amount proportional to the magnitude of the original pressure, by which the fluid had been somewhat compressed. The true formation temperature is not attained until heating has continued to the point where the pressure exerted by the fluid within the cavity again equals the original pressure. If it is possible to estimate the magnitude of this original pressure, an appropriate correction may be added to the cavity-filling temperature to arrive at a closer approximation of the true temperature of formation.

WORK OF PREVIOUS INVESTIGATORS

Sorby[2] demonstrated, by artificially crystallizing a number of compounds, that crystals formed in free space frequently contain fluid inclusions developed during growth of the crystals, and that the size of the vapor bubbles in the inclusions at room temperature was determined by the temperature and pressure conditions prevailing when the crystal was grown. He concluded that similar fluid inclusions in natural crystals might be used to determine the temperature-pressure relations when those natural crystals were formed.

After a long period in which the nature and importance of Sorby's work was generally overlooked, Newhouse[3] brought to light and applied the method to the study of fluid inclusions in sphalerite crystals from zinc-lead deposits in the Mississippi Valley region. Since that time numerous investigators have employed the principle in studies of formation temperature of various types of crystals and mineral deposits.

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[2] Sorby, H. C., On the microscopical structure of crystals: *Quart. Jour., Geol. Soc. London*, **14,** 453–500 (1858).

[3] Newhouse, W. H., Temperature of formation of Mississippi Valley lead-zinc deposits: *Econ. Geol.*, **28,** 744–750 (1933).

Ingerson[4] discussed theoretical aspects of the method as applied to geologic thermometry and prepared curves showing the relationship between temperature of disappearance of the vapor bubbles and temperature and pressure at the time of formation of the inclusions. Twenhofel[5] investigated a number of inclusions within a slice sawed from a well-formed fluorite crystal and observed decreasing temperature zones from the center to the outside of the crystal. He also noted a change in crystal habit from octahedral in the interior to cubic at the exterior. Bailey[6] applied the method to the quartz of granites, but was handicapped by the small number of inclusions which could be accurately determined as primary. Dreyer, Garrels, and Howland[7] investigated the temperature of formation of halite crystals from undisturbed beds in various salt mines.

Scott,[8] Peach,[9] and Smith[10] employed a decrepitation technique differing from the visual method used by other investigators. They heated mineral fragments in a furnace and recorded the intensity of sound produced by decrepitation of the mineral at various temperatures. From the resulting data, they believe estimates of formation temperature may be made. Kennedy[11] discussed some of the limitations of the decrepitation method and presented new charts, based on recent experimental work, for determining the true temperature of formation from observational data plus estimates of the pressures at the time of crystal growth.

TECHNIQUE

Selection and preparation of specimens. Six crystals were chosen for study on the basis of variety of geographic and stratigraphic location, the

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[4] Ingerson, Earl, Liquid inclusions of geologic thermometry: *Am. Mineral.*, **38,** 375–388 (1947).

[5] Twenhofel, W. S., The temperature of crystallization of a fluorite crystal from Luna County, New Mexico: *Econ. Geol.*, **42,** 78–82 (1947).

[6] Bailey, Sturges W., Liquid inclusions in granite thermometry: *Jour. Geol.*, **57,** 304–307 (1949).

[7] Dreyer, R. M., Garrels, R. M., and Howland, A. L., Liquid inclusions in halite as a guide to geologic thermometry: *Am. Mineral.*, **34,** 26–34 (1949).

[8] Scott, H. S., The decrepitation method applied to minerals with fluid inclusions: *Econ. Geol.*, **43,** 637–645 (1947).

[9] Peach, P. A., A decrepitation geothermometer: *Am. Mineral.*, **34,** 413–442 (1949).

———, Geothermometry of some pegmatite minerals of Hybla, Ontario: *Jour. Geol.*, **59,** 32–38 (1951).

[10] Smith, F. G., and Peach, P. A., Apparatus for the recording of decrepitation in Minerals: *Econ. Geol.*, **44,** 449–451 (1949).

Smith, F. G., Laboratory testing of "pneumatolytic" deposits: *Econ. Geol.*, **44,** 624–625 (1949).

[11] Kennedy, George C., "Pneumatolysis" and the liquid inclusion method of geologic thermometry: *Econ. Geol.*, **45,** 533–548 (1950).

fact that they grew on the walls of vugs and projected freely into open spaces, and the fact that they had at least three well-defined cube faces. Cube faces were the only forms present. All crystals came from bedding replacement deposits of the Cave in Rock district of eastern Hardin County.

From these selected crystals slices about 2.5 mm. thick were cut with a diamond saw. The slices were cut as nearly as possible through the growth centers of the crystals, perpendicular to one crystallographic axis and parallel to the other two.

Measurement of temperatures. The sawed slices were supported horizontally on a piece of 8-mesh copper screen about one-sixteenth of an inch above the bottom of a shallow Pyrex dish about $2\frac{1}{2}$ inches in diameter. Wooden pegs stuck into the screen kept the specimens from moving laterally. Thus the silicone oil, of refractive index close to that of fluorite, which was employed as the heating medium was able to circulate freely around the specimens. The Pyrex dish was placed in a thin transite collar held in the jaws of a mechanical stage. The regular stage on the microscope was replaced by an independent box-like stage of transite, which supports the mechanical stage, a modified Leitz hot stage, and a mirror. When in use, the Pyrex dish was in contact with the surface of the hot stage and could be moved about in a controlled, measurable manner by means of mechanical stage. A thin glass plate placed over the dish cut down loss of heat and spattering of hot oil.

The amount and rate of heat input to the hot stage was controlled by a powerstat. Temperatures were measured with a copper-constantan thermocouple inserted between the specimen and the copper screen and connected through a zero-degree reference junction to a Leeds and Northrup K-2 potentiometer.

During the heating process, the inclusions were observed by transmitted light with a microscope equipped with a long focal length heat-resisting objective. The temperature was allowed to rise slowly to the point of disappearance of the vapor bubble, and the temperature at that instant recorded. The current was then turned off until the temperature had fallen low enough for the bubble to reform, and subsequently raised again to the disappearance point to provide a check on the first reading.

By employing coordinates read from the vernier scales on the mechanical stage, it was possible to prepare accurate diagrams of the sections showing the exact location of inclusions used in temperature measurements.

Accuracy of measurements. Tests involving placing the thermocouple at various points within the bath, both in contact with and away from the copper screen, indicated no measurable temperature gradient within the bath when the heating was slow. When the vapor bubble of an inclusion was clearly visible down to the point of disappearance, duplicate temperature measurements consistently showed a variation of less than 0.5° C. When the visibility of the vapor bubble near the end point was reduced by dark "relief" borders around the inclusion or by small opaque masses within the inclusion, less accuracy was obtainable. By comparing results obtained from partially obscured inclusions with adjacent clear inclusions, it was estimated that the expectable variation due to poor visibility was of the order of ±2° C. or less. Thus the probable variation observed from true end-point temperatures was about ±2.5° C.

RESULTS

The results of the study of one typical crystal slice are shown in Fig. 1. Two well-formed cube faces have been cut and a third is parallel to the plane of the section. Lines representing planes of inclusions connect circles representing individual inclusions used, and the numbers indicate the temperatures of vapor bubble disappearance. There are two kinds of planes of inclusions. One, represented by lines *A–A′* and *B–B′*, is parallel

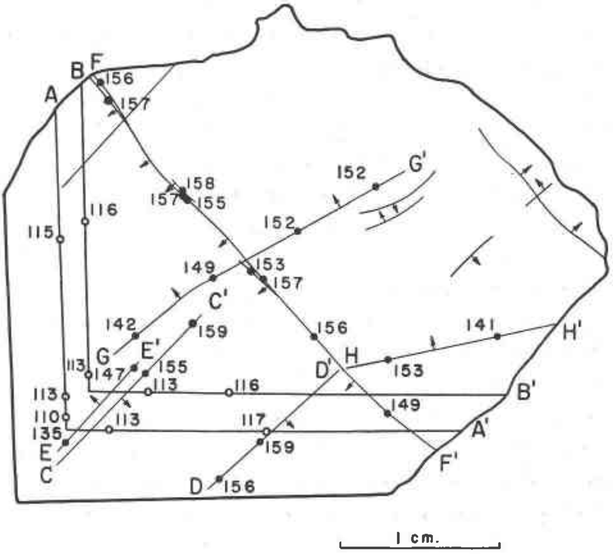

FIG. 1. Slice from a typical fluorite crystal, showing location of planes of fluid inclusions and of inclusions for which temperature determinations were made. Open circles indicate primary inclusions along lines *A–A′* and *B–B′*, parallel to cube faces. Solid circles indicate subsequent inclusions along lines *C–C′* to *H–H′* which follow fairly closely the directions of octahedral cleavage and are inclined to the plane of the slice as shown by the dip arrows. Numbers indicate temperatures in °C. The slice is about one inch square.

to the cube faces and vertical to the plane of the section. The other, represented by lines *C–C′* to *H–H′*, trends at angles to the cube faces and to the plane of the section as shown by the dip arrows. The vertical planes make right angles following the cubic contour of the crystal, but do not cross each other. They parallel bands of coloration which are usually considered zonal growth phenomena. The inclusions along them are ellipsoidal and vary in size from sub-microscopic to megascopic.

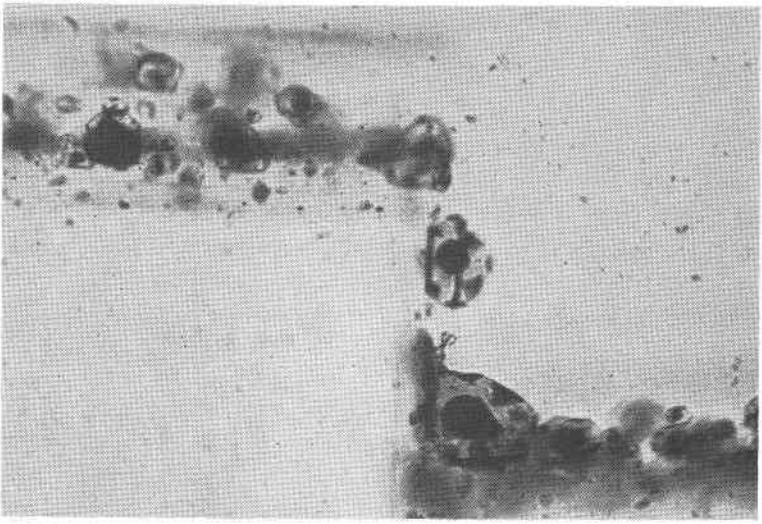

FIG. 2. Primary fluid inclusions along planes vertical to the plane of the slice and parallel to cube faces of the crystal. The offset pattern apparently mirrors an irregularity in a former surface of the crystal. The faint bands paralleling the planes of inclusions are zones of purple coloration common in fluorite crystals. The inclusions contain petroleum, a rounded vapor bubble which photographed black, and small masses of dark opaque material which is probably bitumen.

Many are flattened on the side toward the interior of the crystal, some on two sides where they lie in an interior angle. Figure 2 shows how they look through the microscope. They contain yellow petroleum, small masses of opaque material presumably bitumen, and, at room temperature, a vapor bubble. The petroleum fluoresces under ultra-violet light, contains a low boiling fraction that evaporates quickly when inclusions are opened, and has a carbon-hydrogen ratio of approximately 1:2, as indicated by micro-analysis of a tiny sample.[12] Although all the inclusions in vertical planes examined in this study contained only petroleum, it is possible that inclusions which contain some other liquid might be found.

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[12] Analysis by H. S. Clark, Assoc. Chemist, Illinois State Geological Survey.

The inclusions along planes parallel to the cube faces are considered to be of primary origin and the planes in which they lie to mark successive stages in the growth of the crystals.

The inclined planes of inclusions, Fig. 1, frequently intersect and cross each other, as well as planes parallel to cube faces. Most of them follow more or less closely the octahedral direction of cleavage characteristic of the mineral. Some of these planes are remarkably flat and straight, whereas others undulate or curve somewhat. The appearance under the microscope of crossing inclined planes is shown in Fig. 3 and that of an inclined plane crossing two vertical planes in Fig. 4. Frequently these inclined planes terminate within the crystal along lines paralleling cube faces as shown in Fig. 5. The inclusions on these inclined planes are of various shapes from smoothly oval to irregular and even sharply jagged. Figure 6 shows a group of them which have rather regular shapes. All these inclusions used in the present study contained only a colorless watery liquid and a bubble, but from work on other fluorite crystals from the same district it is known that some contain in addition a drop of yellow petroleum.

It is postulated that these inclusions were formed at various times in

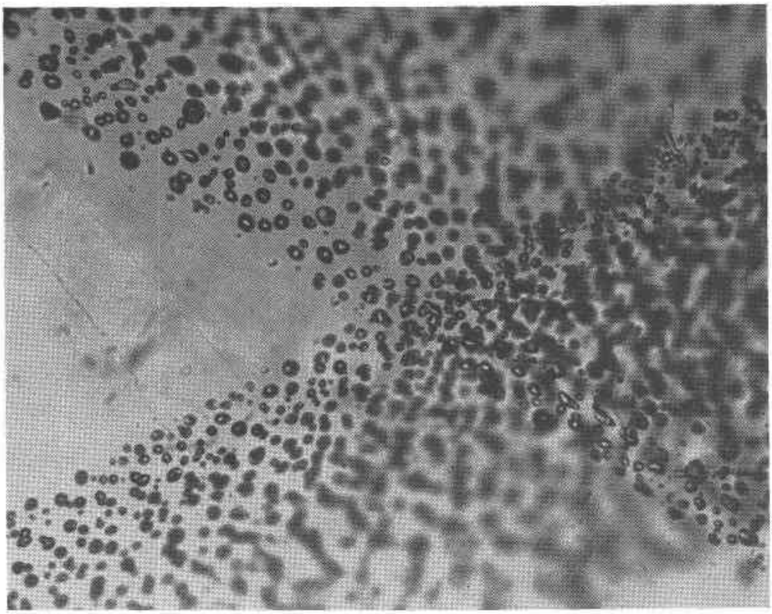

FIG. 3. Appearance of crossing inclined planes of fluid inclusions. Note the continuation without deviation of each plane beyond the line of intersection. Line of sight is normal to one cube face and parallel to two others.

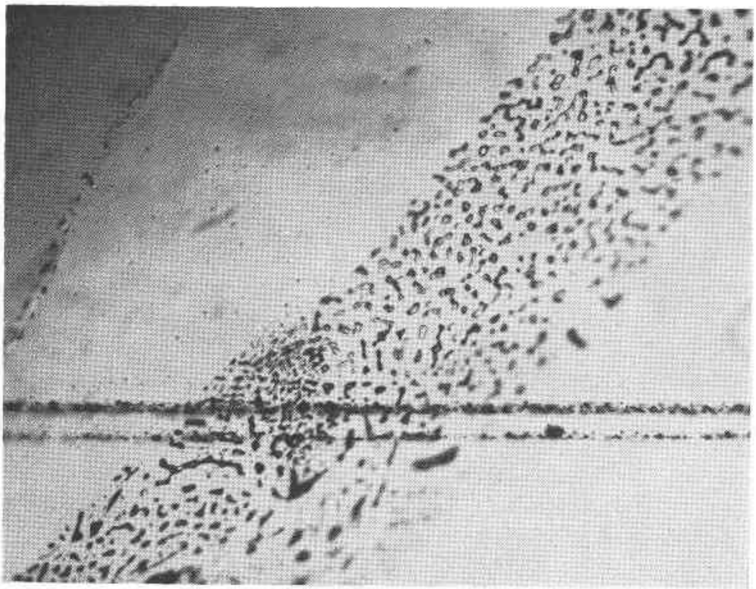

FIG. 4. Inclined plane of fluid inclusions crossing two vertical planes. The vertical planes appear as narrow lines because they lie parallel to the line of sight.

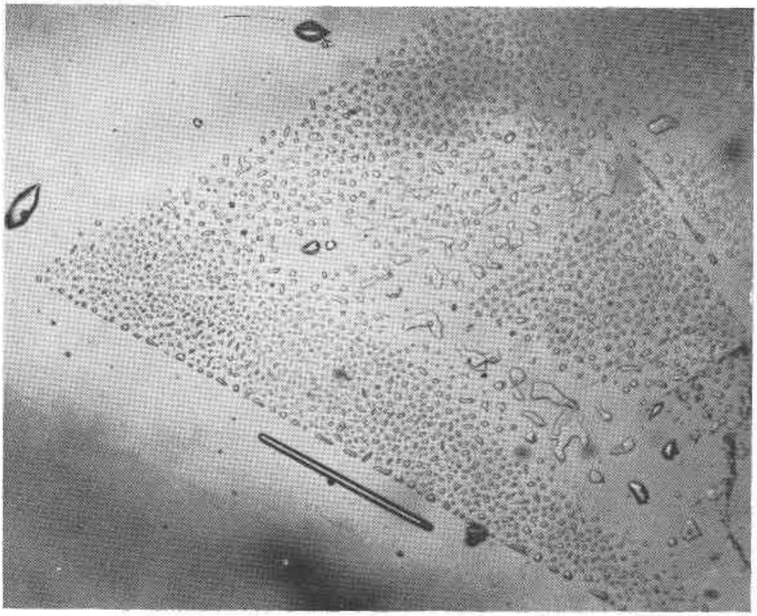

FIG. 5. Inclined plane of fluid inclusions terminating along interior lines parallel to cube faces of a fluorite crystal. As the view is of a cleavage flake instead of a sawed slice, the inclined plane lies normal to the line of sight.

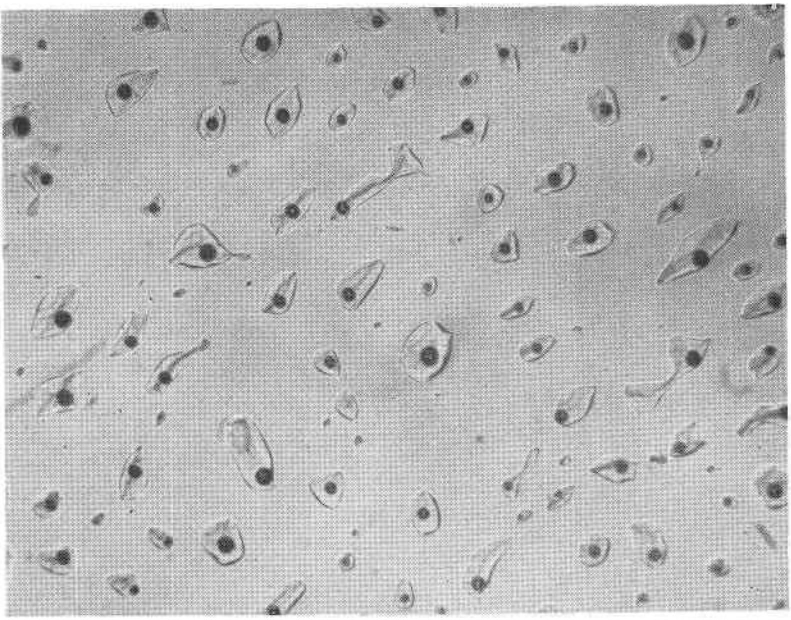

FIG. 6. Group of subsequent inclusions of typical sub-regular outline. The inclusions contain vapor bubbles (the dark round objects) and a colorless watery fluid.

the history of the crystal, along intersecting cleavage and related fracture planes resulting from twisting or warping stresses set up by differential subsidence during formation of the deposit, or to shocks incident to faulting, or sudden temperature changes, even though all the crystals studied were found projecting into open cavities. Liquid inclusions of this type have been called "secondary," but the term "subsequent" inclusions is preferred because they were formed in a different manner from the primary inclusions and subsequent to that part of the crystal in which they are contained. This also avoids possible confusion arising from the many and various geologic meanings already given to the term "secondary."

In the crystal slice diagrammed in Fig. 1, it was found that the average of the temperatures along primary planes *A–A′* and *B–B′* are 113° C. and 115° C. respectively, whereas along the subsequent planes *C–C′* to *H–H′* they ranged from 135° C. to 159° C., some twenty to forty degrees higher. In general, similar features were noted in the other five crystals studied. One, however, contained only subsequent inclusions, some in planes which crossed the boundary between portions of two crystals without break or deviation.

The results of the temperature measurements on the six crystals studied is summarized in graphic form in Fig. 7. The open circles in the columns represent average temperatures along planes of primary inclusions, with the circle nearest the left, in each case, representing the plane nearest the outside of the crystal, that farthest to the right representing the plane closest to the center of the crystal. A rise in temperature from the center outward and then a drop toward the surface is apparent in crystals 2, 3, and 6, the only ones for which data adequate to show that feature are available. The average temperatures along planes of subsequent inclusions are shown by solid circles. In all but one crystal the average subsequent inclusion temperatures are higher than the corresponding average primary inclusion temperatures. Because there are so many planes of subsequent inclusions in crystal 6, only the average of all inclusions from these planes is shown. The range of primary temperatures was from 83° to 115° C. in four crystals, and from 139° to 167° C. in the fifth. No primaries were present in the sixth crystal, crystal 4 of

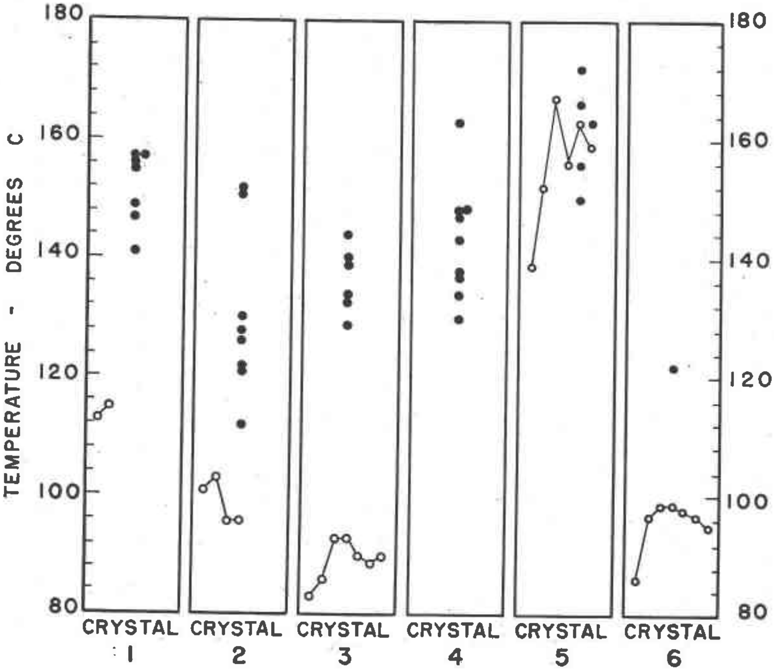

FIG. 7. Graphs of results of temperature measurements on six fluorite crystals. Open circles indicate average temperatures on individual planes of primary inclusions, solid circles the same for planes of subsequent inclusions. In each column the open circle nearest the left represents the primary plane nearest the outside of the crystal, and those to the right represent planes farther toward the interior of the crystal. The relative positions of the subsequent planes cannot be similarly shown.

Fig. 7. The subsequent inclusions gave temperatures in the range of 112° to 172° C.

PRESSURE CORRECTIONS

None of the temperatures listed in the preceding section have been corrected for the compression of the liquid in the inclusions caused by pressure on it at the time the inclusions were formed. As explained by Ingerson and others, the temperatures measured in the laboratory are somewhat lower than the actual temperatures prevailing when the inclusions were formed.

The amount of pressure on a crystal growing at depth, even though the depth were known exactly, is a matter which can only be guessed at in many cases. It could be greater or less than either the weight of the superincumbent rock or the hydrostatic pressure exerted by a column of water extending to the surface. If in the present instance, however, it is assumed that the rock cover on the forming deposit was 3000 feet thick and that the pressure exerted was midway between hydrostatic and that equivalent to the weight of the overlying rock, calculation yields a figure of 2375 pounds per square inch or about 160 bars. Using the correction curves published by Kennedy,[13] we find that this pressure would necessitate adding between 9° and 10° C. to the measured temperature values in order to arrive at the true formation temperature. If the pressure is calculated on the basis of the weight of the overlying rock, the corresponding figures are 3450 pounds per square inch, 235 bars, and 14° C. Either of these temperature corrections is too small to alter in any significant way the geologic implications of the relatively low temperatures recorded by the inclusions.

COMPOSITION OF FLUID IN INCLUSIONS

An attempt has been made to determine the chemical composition of the liquid in the inclusions in a specimen of fluorite from the Cave in Rock district of Illinois. This work was done by B. Brunn at the University of Chicago under the direction of Professor Tom. F. W. Barth. The total amount of liquid in the inclusions was found to be 0.54% of the specimen. The total amount of dissolved salts in the inclusions was found to be 4.5 grams per hundred grams of included liquid, equivalent to 45,000 p.p.m. The analysis was not complete, but showed that the elements in largest amount were Cl, Na, and Ca, with lesser amounts of F, S, Si, Mg, and Fe or Al. Evidently the liquid in the inclusions, excepting the yellow petroleum, is a saline solution containing principally sodium and calcium chlorides.

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[13] Kennedy, George C., *op. cit.*, p. 540.

CONCLUSIONS

Fluorite crystals contain primary inclusions along growth planes parallel to cube faces and subsequent inclusions along octahedral and other fracture planes produced by fracturing during crystal growth. In the six specimens studied, the primary inclusions show uncorrected growth temperatures in the range of 83° to 115° C., whereas subsequent inclusions indicate formation temperatures of 112° to 172° C. These results reemphasize the need for cautious discrimination between primary and secondary inclusions in using any method of geologic thermometry based on liquid inclusions.

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