FILLING TEMPERATURES OF H_2O—CO_2 FLUID INCLUSIONS AND THEIR SIGNIFICANCE IN GEOTHERMOMETRY

F. G. SMITH AND W. M. LITTLE

University of Toronto, Toronto, Canada

ABSTRACT

The theoretical significance of the filling temperature of fluid inclusions containing significant amounts of both water and CO_2 is discussed in terms of H_2O—CO_2 mutual solubility. It is shown that the filling temperature can be lower, higher, or equal to the temperature of formation. The method of geothermometry, suggested by Smith in 1953, which is based on the recognition of the cases where the filling temperature is equal to the temperature of formation, is discussed in detail. Six examples are given of its tentative application to minerals from tin deposits, for which temperatures of formation in the 300–400°C range were obtained.

INTRODUCTION

The theoretical significance of temperature of filling of fluid inclusions (containing essentially water and a bubble of water vapour), was discussed in one of the earliest papers on the subject of fluid inclusions (Sorby, 1858), and in more recent reviews by Ingerson (1947, 1955) and Smith (1953). The main point brought out is that the filling temperature can only be considered as a minimum temperature of formation, which can be as much as 200–300°C lower than the actual temperature of formation, depending on the pressure during mineral formation. This pressure correction, for which only a rough approximation can usually be made, is the main difficulty involved in using inclusions of this type as geothermometers.

The corresponding significance of the filling temperature of inclusions containing substantial amounts of both water and CO_2 has not been as thoroughly discussed in the literature. This would seem desirable, because with this type of inclusion the relation between the filling temperature and the temperature of formation may in some cases be quite different from that of the normal water—water vapour type, and under certain circumstances, filling temperature measurements may give the temperature of formation directly with no pressure correction (Smith, 1953).

IDENTIFICATION AND CLASSIFICATION OF H_2O—CO_2 INCLUSIONS

The presence of both water and CO_2 in a fluid inclusion is generally recognized by the appearance of a third fluid phase when a two-phase
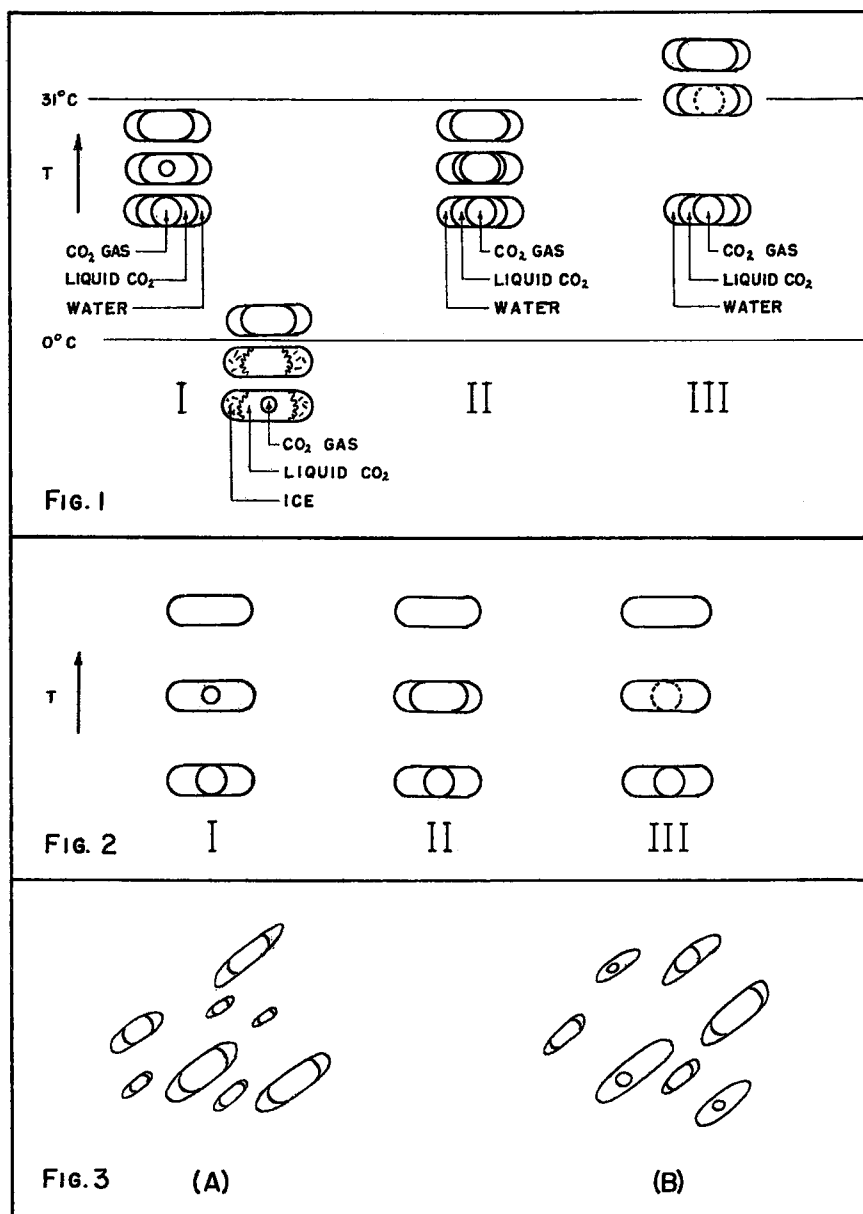
FIG. 1. Schematic phase transformations (three-phase to two-phase on heating, and two-phase to three-phase on cooling) shown by H_2O—CO_2 fluid inclusions at low temperatures.

FIG. 2. Schematic phase transformations (two-phase to one-phase on heating) shown by H_2O—CO_2 fluid inclusions.

FIG. 3. Schematic representation of two classes of H_2O—CO_2 fluid inclusions: (A) uniform H_2O/CO_2 ratio, and (B) variable H_2O/CO_2 ratio.

fluid inclusion is cooled to some temperature below 31°C (the critical temperature of CO_2). The three phases are considered to be essentially water, liquid CO_2, and CO_2 gas (see Fig. 1). In a few cases the phases have been definitely identified, by index of refraction measurements on the water and liquid CO_2 (Brewster, 1826), observations on the freezing of the water (Little, 1955), and measurements of the temperature at which the CO_2 phases exhibit critical phenomena (Sorby, 1869; Hartley, 1876; Erhard & Stelzner, 1878; Johnsen, 1920; Little, 1955). In almost all other cases, the temperatures at which the three-phase condition changes to a two-phase one, and the two-phase to a one-phase, are similar enough to allow this identification to be assumed.

H_2O—CO_2 inclusions can be classified by the manner in which the three-phase to two-phase, and the two-phase to one-phase transformation occurs. As is shown in Fig. 1, the three-phase to two-phase transformation can result from either the contraction of the gas bubble until it disappears, the expansion of the gas bubble until no liquid CO_2 is left, or the fading out of the CO_2 liquid—gas interface. The transformation from the two-phase to one-phase condition (Fig. 2), may also occur in three ways, either by the contraction of the CO_2 bubble until it disappears, the expansion of the bubble until it fills the cavity, or the fading out of the interface. The manner in which the three-phase to two-phase transformation occurs has no bearing on the type of two-phase to one-phase transformation that occurs at higher temperature.

A further binary classification can be made on the basis of whether the H_2O/CO_2 ratio in the inclusions of a specimen or suite of specimens is consistent or inconsistent (see Fig. 3). This has an important genetic significance, which will be discussed below.

THEORETICAL SIGNIFICANCE OF FILLING TEMPERATURE

The significance of the filling temperature of H_2O—CO_2 inclusions is a matter of mutual solubility in the system H_2O—CO_2, and because of this it is fundamentally different from that of water—water vapour inclusions, where the question is one of simple liquid—vapour relationships.

Although there are very little quantitative data on H_2O—CO_2 mutual solubility in the pertinent temperature—pressure range (temperatures up to 400°C and pressures up to 4,000 bars), from trends shown by other two-component systems, and observations made on H_2O—CO_2 inclusions in minerals, it is possible to construct a schematic phase diagram which is sufficient for the present purposes.

Such a diagram is shown in Figure 4, in which, for simplicity, only temperatures above the critical temperature of CO_2 are considered. Volume is a constant (as would be the case in a fluid inclusion if the
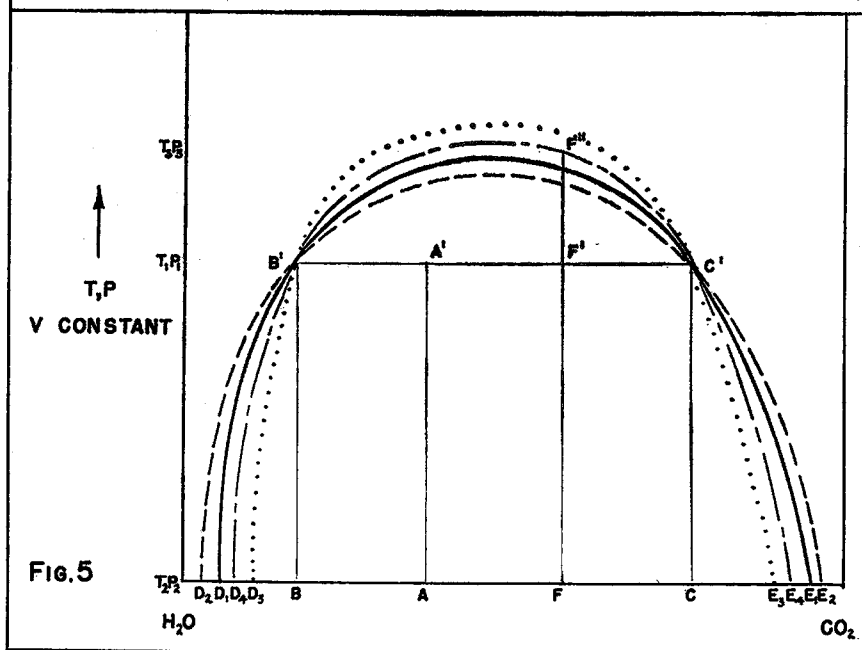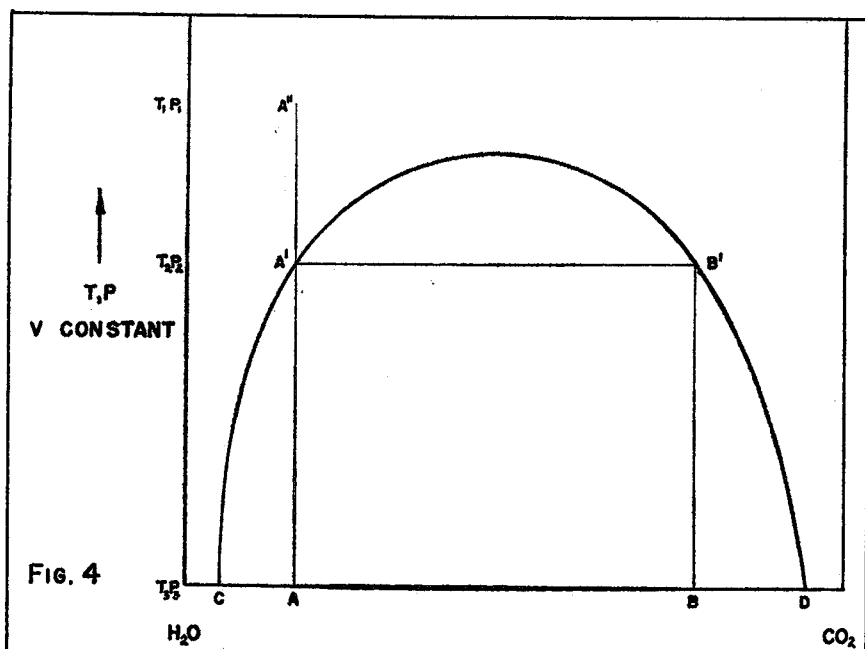
FIGS. 4 and 5. Schematic H_2O—CO_2 mutual solubility relations, as discussed in the text.

relatively minor effects due to the compressibility and thermal expansion of the host mineral are neglected), and as a result pressure increases with temperature. The solubility curve is of the normal type, and its general shape is confirmed by observations on the two-phase to one-phase transformation of H_2O—CO_2 fluid inclusions. The one-phase condition has been obtained in all inclusions that have been tested, either by the disappearance of the CO_2-rich phase (indicating that the solubility of CO_2 in water increases with temperature), the disappearance of the water-rich phase (indicating increasing solubility of water in CO_2), or by the disappearance of the interface (showing that in at least some cases the solubility curve has a critical solution point).

In discussing the significance of the filling temperature, two situations must be considered: (1) the aqueous phase was undersaturated with CO_2 at the time it was included in a growing mineral, and (2) it was saturated with CO_2 and a CO_2-rich phase also was present.

The one-phase case is shown in Figure 4. If an inclusion forms at T_1P_1 from an H_2O—CO_2 solution of composition A, and the solubility curve $C\ A'\ B'\ D$ is applicable, the following changes would occur as the temperature decreases. Between T_1 and T_2 only one phase, of composition A, would be present. At T_2, however, a CO_2-rich phase of composition B would start to form, and with further cooling the amount of the CO_2-rich phase would increase, and the composition of the two phases would change following the solubility curve, until at T_3 phases of composition C and D are present in the ratio $A–D:C–A$. The filling temperature of such an inclusion is T_2, which, it will be noted, is *below the temperature of formation*.

Formation of inclusions in a two-phase H_2O—CO_2 system is treated in Figure 5. If the system has an overall composition of A, and the solubility curve $D_1B'C'E_1$ applies, at T_1P_1 an H_2O-rich phase of composition B and a CO_2-rich phase of composition C will be present. Inclusions forming under these conditions might trap either of these phases or mixtures of the two.

If only the water-rich phase (of composition B) is entrapped, the solubility curve for this new system can be shown by $D_2B'C'E_2$. Because of the difference in overall composition, the curve will be quantitatively different from that of the original system, but will still have the same general form and pass through the end points B' and C'. On cooling such an inclusion, a CO_2-rich phase of composition C would appear immediately below T_1, and with further cooling, the amount of the CO_2-rich phase would increase and the composition of the two phases would change following the solubility curve. The filling temperature obtained on reheating such an inclusion is T_1, *the temperature of formation*.

A similar result is obtained in the case where only the CO_2-rich phase (composition C) is trapped in an inclusion. The solubility curve will have

the form $D_3B'C'E_3$, passing through the end points B' and C' and having the same general shape as the previous ones. On cooling, a water-rich phase of composition B will appear immediately below T_1, and as the cooling continues the amount of the water-rich phase will increase and the composition of the two phases will change following the solubility curve. As in the previous case, the filling temperature of such an inclusion will be T_1, *the temperature of formation.*

If the H_2O- and CO_2-rich phases are trapped together as a mechanical mixture in an inclusion, the results would be different. If the overall composition of the inclusion is F, and the solubility curve $D_4B'C'E_4$ applies, as the temperature is lowered, the relative amount and composition of the phases will vary, until at T_2 phases D_4 and E_4 are present in the ratio $F-E_4:D_4-F$. On heating such an inclusion, however, the filling temperature will not be reached until T_3, which is *above the temperature of formation.*

The relation between filling temperatures and temperatures of formation can be summarized as follows. If only one H_2O—CO_2 phase is present under the conditions at which an inclusion formed, the filling temperature will generally be below the temperature of formation. The only exceptions will be the unlikely situation of the solution being at its exact saturation point, or supersaturated. If both an H_2O- and a CO_2-rich phase are present at the time of formation, inclusions of either of these phases will have filling temperatures equal to the temperature of formation, but those which trap some mixture of the two will have filling temperatures greater than the temperature of formation.

USE OF H₂O—CO₂ INCLUSIONS IN GEOTHERMOMETRY

In assessing filling temperature data on H_2O—CO_2 inclusions, it is obviously very important to know whether one or two H_2O—CO_2 phases were present at the time of formation. It should usually be possible to determine this however. If the volume of bubble : volume of cavity ratio in the inclusions in a specimen is relatively constant, the one-phase condition is indicated; if the ratio is highly variable in inclusions which appear to have formed at the same time, the two-phase condition probably existed. Justification for this interpretation is given by observations on fluid inclusions in artificial minerals grown in water solutions. Crystals grown under conditions of constant temperature and a constant pressure above the vapour pressure have inclusions with constant bubble : cavity ratios, while those grown under conditions of boiling contain inclusions with highly variable ratios (Sorby, 1858; Buckley, 1951).

In cases where a mineral grew in a one-phase H_2O—CO_2 system, the filling temperature provides a minimum temperature of formation, which, as is the case of water—water vapour inclusions, is subject to correction

for pressure. The calculation of this pressure correction, however, not only requires a knowledge of the pressure at the time of formation (which at best can only be roughly approximated), but also accurate thermodynamic data on the system H_2O—CO_2 (which at present are not available in the temperature pressure range desired).

In cases where it can be demonstrated that the mineral grew under the two-phase condition however, as was pointed out by Smith (1953), it should be possible to determine the temperature of formation directly from filling temperature measurements. Although individual inclusions would likely show fairly wide variations in their filling temperatures, the values for both H_2O-rich and CO_2-rich inclusions should approach a minimum, which would be close to the temperature of formation. The H_2O-rich inclusions could be expected to show lower filling temperatures, since it would be more likely for an inclusion to trap only the continuous water-rich phase than only a bubble of the CO_2-rich phase.

This method of inclusion geothermometry has several decided advantages. It gives the temperature of formation directly, without the necessity of a correction for pressure. Not only are precise thermodynamic data not required, but the contents of the inclusions need not even be identified. Although the argument was presented for the H_2O—CO_2 system in particular, the same rationale applies to any two-fluid phase multi-component system in which the mutual solubility of the major components increases with temperature. The requirements of the method are that it can be demonstrated that the minerals grew in a two-fluid phase multi-component system, some of the inclusions trap only one of these two phases, the mineral grew under fairly constant temperature—pressure conditions, a distinction can be made between primary and secondary inclusions, and that no leakage of fluid occurs after an inclusion is formed. None of these requirements would appear to present serious problems. The method has one inherent error, in that the filling temperature measurements duplicate the effects of the temperature of formation on the host mineral but not the pressure of formation, but calculations by Ingerson (1957) show that this effect is negligible. The main restriction on the applicability of the method is likely to result from the restriction of H_2O—CO_2 inclusions to certain types of mineral deposits. From present information their most common occurrence is in minerals from the late stages of pegmatite formation, and in high temperature veins.

No systematic search has been made for specimens which meet the requirements of this method, but in a recent study of the inclusions in cassiterite and associated minerals (Little, 1955), a number of cases were found in which it can be applied. These are not ideal examples for demonstrating the method since there is no direct proof that some of the requirements are met, but since it is probable that the specimens do meet

the requirements, the results are thought to be worth recording at this time. Filling temperature measurements on inclusions in these specimens are listed in Table 1.

TABLE 1

Spec. No.	Mineral and type of deposit	Locality	Filling temp. of inclusions (H₂O-RICH) ($t°C$)	(No.)	(CO₂-RICH) ($t°C$)	(No.)
1.	Cassiterite (pegmatite)	Malaya	361	3	366	3
2.	Apatite (quartz vein)	Ehrenfried-ersdorf	378–428	8	398	5
3.	Cassiterite (quartz vein)	Belgian Congo	358–374	13	378	1
4.	Cassiterite (quartz vein)	Belgian Congo	320–386	12	344–350	3
5.	Topaz (quartz vein)	Belgian Congo	313–323	14	342–376	5
6.	Cassiterite (quartz vein)	Tasmania	280–290	2	334	2

The filling temperature measurements were made using an air-heated heating stage, with a probable accuracy within ±5°C. Calibration with a Thomas "Micromelt" set, and by observing the melting points of thin shavings of Sn, Pb, and Zn, indicated a reproducibility of ±3°C. The magnification used, 450X, only allowed a few relatively large inclusions to be tested, but measurements of the bubble : cavity ratio (using higher magnification), showed that in all of the specimens, the tested inclusions were representative of a very large number.

In all the specimens, the CO₂-rich inclusions showed a third fluid phase when cooled to some temperature below 31°C. In the two-phase condition, just above room temperature, their bubbles are relatively large (occupying over 60% of the cavity), and on heating the bubbles *expand* until they fill the cavity. The bubbles in the H₂O-rich inclusions are relatively small (less than 40% of the cavity), and on heating *contract* until they disappear. With inclusions having such different characteristics, the only likely explanation for the very close correspondence of the filling temperatures of the two types in specimens 1–4, is that they represent the approximate end points of an equilibrium system which was present at the time the inclusions formed. For specimens 5 and 6, the correspondence is still fairly close, and the higher filling temperatures of the CO₂-rich inclusions could easily result from some of the H₂O-rich phase being trapped with the CO₂-rich phase

With these specimens it was not possible to show that the H₂O-rich inclusions contained some CO₂, which would have to be the case if they represented a phase of an H₂O—CO₂ system. No additional phase was

produced by cooling the specimens by means of liquid air to temperatures well below the freezing point of the water solution in the inclusions. However, there is no necessity that the solubility of CO_2 in water in the temperature—pressure range at which the inclusions likely formed, is sufficient to allow such a cooling test to show observable amounts of an additional phase. On the whole, the negative evidence of the cooling tests would not appear to override the positive evidence for formation from a two-phase H_2O—CO_2 system given by the similarity of the filling temperatures of the two types of inclusions. It was also not possible to demonstrate that the inclusions in these specimens are primary ones, although this would appear to be the case. The other requirements do appear to be met however: the similarity of the filling temperatures of the two types of inclusions (which at temperatures other than the temperature of formation would have different internal pressures) is strong evidence against leakage, and the similarity of the filling temperatures of all of the inclusions in an individual specimen indicates relatively stable conditions of temperature and pressure during their formation.

On the whole, it would appear that these specimens probably meet the requirements of the method, and that their temperatures of formation were in 300–400°C range given by the filling temperature measurements.

REFERENCES

BREWSTER, D. (1826): On the refractive power of the two new fluids in minerals, with additional observations on the nature and properties of these substances. *Trans. Royal Soc. Einburgh*, **10**, 1–14.

BUCKLEY, H. E. (1951): *Crystal growth.* New York, John Wiley and Sons Inc.

ERHARD, T., & STELZNER, A., (1878): Ein Beitrag zur Kenntniss der Flüssigkeitsein-schlüsse in Topas. *Min. und Pet. Mitt.*, **1**, 450–458.

HARTLEY, W. N. (1876): The identification of liquid carbon dioxide in mineral cavities. *Monthly Microscopical Jour.*, **15**, 170–175.

INGERSON, E. (1947): Liquid inclusions in geologic thermometry. *Am. Mineral.*, **32**, 375–388.

JOHNSEN, A. (1920): The paragenesis of alpha quartz and carbon dioxide. *Sitz. Bayer Akad. Wiss., Math.—Phys. Klasse*, 321–328.

LITTLE, W. M. (1955): A study of inclusions in cassiterite and associated minerals. *Unpublished Ph.D. Thesis, University of Toronto.*

SMITH, F. G. (1953): *Historical development of inclusion thermometry.* University of Toronto Press, Toronto.

SORBY, H. C. (1858): On the microscopic structure of crystals, indicating the origin of minerals and rocks. *Jour. Geol. Soc. London*, **14**, 453–500.

———— (1869): On the microscopical structures of some precious stones. *Monthly Microscopical Jour.*, **1**, 41–45.