Diagenetic palaeotemperatures from aqueous fluid inclusions: re-equilibration of inclusions in carbonate cements by burial heating

R. C. Burruss

US Geological Survey, Box 25046, MS 921, Denver, Colorado 80225, USA

Abstract

Diagenetic palaeotemperatures determined from aqueous fluid inclusions can be affected by re-equilibration during burial heating. Calculations based on the observed behaviour of inclusions in fluorite under external confining pressure allows prediction of the temperatures and depths of burial necessary to initiate re-equilibration of aqueous inclusions in the common size range 40 to 4 μm. Heating of 20° to 60 °C over the initial trapping temperature may cause errors of 10° to 20 °C in the homogenization temperature. This suggests re-equilibration may cause aqueous inclusions in carbonates to yield a poor record of their low-temperature history, but a useful record of the maximum temperature experienced by the host rock. Previous work suggests inclusions containing petroleum fluids will be less susceptible to re-equilibration.

KEYWORDS: palaeotemperatures, fluid inclusions, carbonates, fluorite.

Introduction

THE theoretical basis for interpreting palaeotemperature from homogenization temperature is well known (Roedder, 1984; Shepherd et al., 1985; Burruss, 1987). The process of re-equilibration (resetting) of homogenization temperatures to values different from the original temperature of formation is described by a number of researchers (Leroy, 1979; Burruss and Hollister, 1979; Bodnar and Bethke, 1984; Wilkins, 1986). The purpose of this paper is to examine whether resetting is a significant problem for determining diagenetic palaeotemperatures from fluid inclusions that have been continuously heated by burial subsidence. This question is important because diagenetically altered sediments commonly contain several generations of cement, each of which could contain fluid inclusions. These cements could record the pressure–temperature history of the rock if later, higher temperatures do not re-equilibrate earlier inclusions formed at lower temperatures. Re-equilibration of inclusions in early cements has been suggested by Moore and Druckman (1981) as the cause of high temperatures in otherwise early cements. Recently Goldstein (1986) has discussed the evidence for re-equilibration of aqueous inclusions in low temperature vadose and phreatic carbonate cements.

The basic problem is illustrated in Fig. 1, modified from Burruss (1987). As a rock subsides, the temperature and pressure of the pore fluid increase along a geothermal-pressure gradient (line G), while the internal pressure and temperature in the inclusion increase along line I, an isochore, or line of constant volume. For an inclusion trapped at 100 °C and 2.7 km depth (point A) an additional 1.5 km of subsidence to point B will cause the internal pressure in the inclusion to increase until it is 400 bars greater than the external pore fluid pressure on the enclosing grain. This internal pressure can cause the crystal to plastically deform, 'stretch' (Bodnar and Bethke, 1984) or to brittly deform, 'decrepitate', in which fractures may extend from the inclusion to the grain boundary causing leakage (Roedder, 1984).

Although mechanically different, the most important distinction between these two processes is that decrepitation can cause fractures that reach the grain boundary of the host mineral whereas stretching does not. Decrepitated inclusions can exchange fluid with the environment and will reset not only temperature and pressure but also chemical composition.

Calculations

There are few quantitative studies of the conditions that cause inclusions to deform and reset
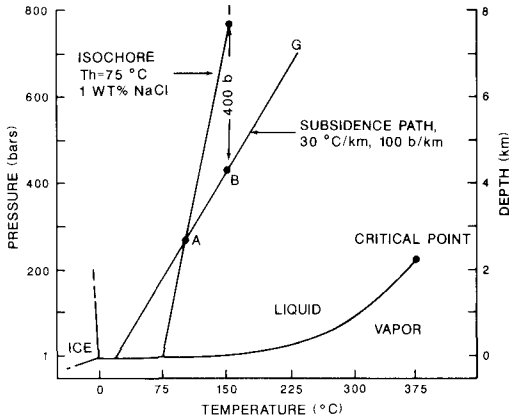
FIG. 1. Pressure–temperature diagram for low salinity (1 wt.% NaCl) aqueous inclusions homogenizing to liquid at 75 °C. This illustrates the forces driving re-equilibration of inclusions during burial heating. An inclusion trapped at A will have an internal pressure 400 bars greater than the surrounding pore pressure on the host mineral when the rock has subsided to an additional 1.5 km to point B. The increase in pressure with depth is assumed to be hydrostatic.
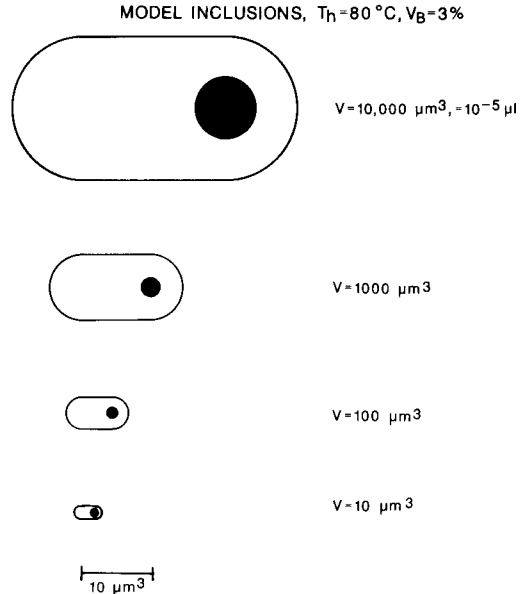

FIG. 2. The size range of model fluid inclusions illustrating the range of dimensions that include the volume range of 10 to 10000 μ^3. This volume range is typical in sedimentary rocks and is used in the text for calculating the effect of size on re-equilibration of inclusions. Temperature of homogenization, $T_h = 80$ °C; volume of vapour bubble (V_b) = 3% total inclusion volume.

by stretching or decrepitation. The most extensively studied minerals are quartz (Leroy, 1979; Pecher, 1981) and fluorite (Bodnar and Bethke, 1984; Rowan et al., 1985). Of these, the work of Rowan et al. (1985) is most directly applicable to the evolution of sediments. In that work, fluorite was heated in a hydrothermal apparatus to examine the amount of overheating necessary to reset aqueous inclusions under an external confining pressure. The authors then combined the results of these experiments with the previous work of Bodnar and Bethke (1984) on fluorite at 1 atmosphere pressure, to develop an equation that describes the stretching behaviour. The equation is:

$$P_S = -178 \log V + 0.7 P_{ex} + 1019 \text{ bars} \quad (1)$$

where P_S is the internal pressure (bars) necessary to initiate stretching, P_{ex} is the external pressure (bars), and V is the volume of the inclusions in cubic micrometers.

The experimental results clearly show that the size of the inclusion is important. Large inclusions ($10^4 \mu m^3$) stretch at lower pressure differentials than small ($10^1 \mu m^3$) inclusions. Fig. 2 illustrates inclusions that are modelled as cylinders with hemispherical ends. The range of volume, 10^4 to $10^1 \mu m^3$, and largest dimension, 40 μm to 4 μm,

span the inclusion sizes typically observed in cements, although small inclusions are the most abundant.

Assuming that calcite or dolomite have mechanical properties similar to fluorite, equation (1) can be used to define the burial conditions necessary to initiate stretching of inclusions in common diagenetic cements. Fig. 3 illustrates these conditions for inclusions trapped at two different temperatures during burial. For pure water, trapped as inclusions at 40 °C at point A (1.5 km burial at 20 °C/km, 10 °C surface temperature), the homogenization temperature (T_h) should be about 20 °C. As Roedder (1984) pointed out, the surface tension effects in water cause such an inclusion to be one phase at room temperature so that T_h can not be measured. Goldstein (1986) reports one phase aqueous inclusions from a number of low-temperature, phreatic cements.

If the rock containing such inclusions is continuously heated during subsidence, the external pressure and temperature increase along the geothermal-pressure gradient labelled G (20 °C/km and 100 bars/km, hydrostatic pressure gradient). The internal pressure in the inclusions
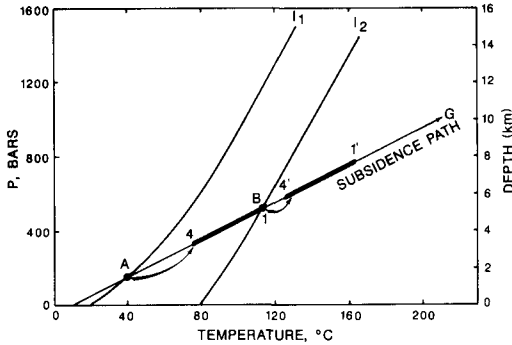
FIG. 3. Pressure–temperature diagram similar to Fig. 1 showing the range of P–T conditions during subsidence in which inclusions trapped at points A and B would begin to stretch. Isochores I_1 and I_2 define the change in internal pressure with changing temperature in inclusions A and B respectively. The heavy line segments labelled 4–1 and 4'–1' are the ranges of conditions during subsidence where inclusions trapped at A and B, respectively, will begin to re-equilibrate. The numbers correspond to the logarithm of the volume of inclusions shown in Fig. 2 (i.e. $10\,000\ \mu^3$, log $V = 4$). This illustrates the fact that small inclusions ($10\ \mu^3$, log $V = 1$) require higher temperatures to initiate resetting than large inclusions.

FIG. 4. Pressure–temperature diagram modified from Fig. 3 to show the P–T conditions necessary to cause at least a $+10\,°C$ error in the homogenization temperature measurement. The P–T paths shown only apply to large (log $V = 4$) inclusions. Similar analysis of small inclusions shows that about $20°$ to $60\,°C$ of additional burial heating will cause at least $+10\,°C$ error for inclusions in size range of $10\,000$ to $10\ \mu^3$.

increases rapidly along isochore I_1. By substituting a range of volumes of inclusions from Fig. 2 and the external pressures along G, into equation (1), the pressure necessary to initiate stretching can be calculated. The heavy line labelled 4 to 1 is the locus of pressure–temperature conditions where stretching could begin for inclusions with volumes ranging from $10\,000\ \mu m^3$ to $10\ \mu m^3$ (the 4 and 1 correspond to the log of the volume of inclusions with this maximum and minimum volume range). Similarly, for inclusions formed at B, interval pressure increases along isochore I_2 and stretching could begin in the range of burial depths and temperatures labelled 4' to 1'.

These calculations indicate that additional heating during subsidence is capable of initiating stretching. What is more important however is estimating the amount of heating necessary to cause a significant error in the interpretation of trapping temperatures. To model this aspect of the problem, consider an error of $+10\,°C$, and hypothetical inclusion B in Fig. 3. This inclusion, if undisturbed, would homogenize at $80\,°C$ and would have a trapping temperature of $113\,°C$ along a $20\,°C/km$, hydrostatic pressure gradient ($100\ bars/km$). If, after trapping inclusions at this temperature, the rock continued to subside, the internal pressures in the inclusions would increase along I_3 as shown in Fig. 4. At point a, the internal
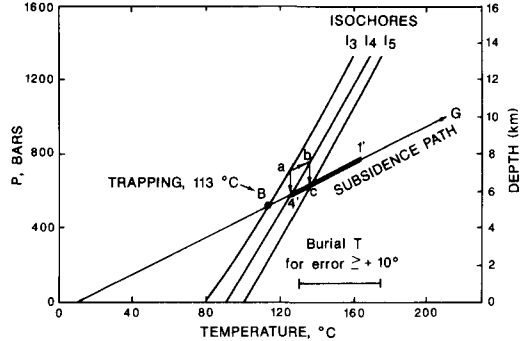
pressure is high enough that equation (1) predicts large inclusions (log $V = 4$) would begin to stretch. If this pressure causes decrepitation, the large inclusions could reset to the external P and T at point 4' on subsidence path G. These re-equilibrated inclusions would contain fluids with the density of isochore I_4 and would homogenize at $90\,°C$, a $+10\,°C$ error.

The work of Rowan et al. (1985) and Bodnar and Bethke (1984) suggests that the probability of decrepitation at the minimum pressures to cause stretching is very low and higher internal pressures are needed. In the above example, once the pressure in large inclusions (log $V = 4$) reaches point a, additional heating (subsidence) would cause measurable stretching so that the internal pressure in the inclusion would change along a path from a to b. If the temperature at b ($135\,°C$) is the maximum burial temperature, stretching may stop. The density of the fluid in the inclusion would have changed to that at point b, again on isochore I_4. This change in density is sufficient to cause $+10\,°C$ error in the homogenization temperature. If after stretching to point b the inclusion decrepitated, the inclusion fluid would have a density at point c along the subsidence path. This fluid density is isochore I_5 which has a homogenization temperature of $100°$, a $+20\,°C$ error. For these hypothetical, large inclusions of pure water, additional heating of $22\,°C$ by about $1\,km$ of subsidence (original trapping at $113\,°C$, subsidence to $135\,°C$) causes errors of $+10°$ to $20\,°C$. As pointed out in the discussion of equation (1)

and Fig. 3, stretching behaviour is a strong function of the size of the inclusion. Thus, although the large inclusions in the above examples are reset to various temperatures, the small ones (10^2 to 10^1 μm^3) may be unaffected. Applying equation (1) to the smallest inclusions (10^1 μm^3) trapped at the original conditions (113 °C) suggests they must be heated to at least 175 °C to cause a +10 °C error in the trapping temperature. Thus, to reset all the inclusions in the size range 10^4 to 10^1 μm^3 trapped at 113 °C would require about 60 °C of additional heating by continued subsidence. In this example, 60 °C of additional heating corresponds to about 3 km of subsidence (20 °C/km geothermal gradient). This amount of subsidence will vary with changes in the geothermal gradient.

Discussion

Equation (1) allows construction of a number of scenarios for re-equilibration of fluid inclusions during subsidence. The strong dependence of stretching behaviour on inclusion size suggests that simple tests of stretching can be made by plotting the size of a single generation of inclusions versus homogenization temperature. Large inclusions should re-equilibrate the most and have higher homogenization temperatures than the small inclusions.

Estimated volume of inclusion versus homogenization temperature is shown in Fig. 5 for the observations of Smith (1984). These measurements were made on inclusions in cathodoluminescently zoned carbonate cements. Based on petrography, stable isotopes, and trace elements, the earliest dolomite cements appear to have precipitated from marine pore waters at depths of burial of less than 1 km, yet the homogenization temperatures are much higher than expected. If the early inclusions in dolomite cements have been reset, the predicted trend is not obvious in the observations. There may be several reasons for the failure of this test, and any generalizations may be premature, but one possible explanation is as follows: As large inclusions stretch and ultimately decrepitate, small inclusions are created through fracture healing and necking down as illustrated by Roedder (1984, Figs. 2–15 and 3–9, respectively). Therefore, even if early diagenetic, small inclusions survived later heating, they may be difficult to distinguish from the population of small inclusions formed from large, decrepitated inclusions. Small inclusions adjacent to larger, decrepitated inclusions in quartz from a high-grade metamorphic terrain have been described and named 'decrepitation clusters' by Swanenburg (1980).
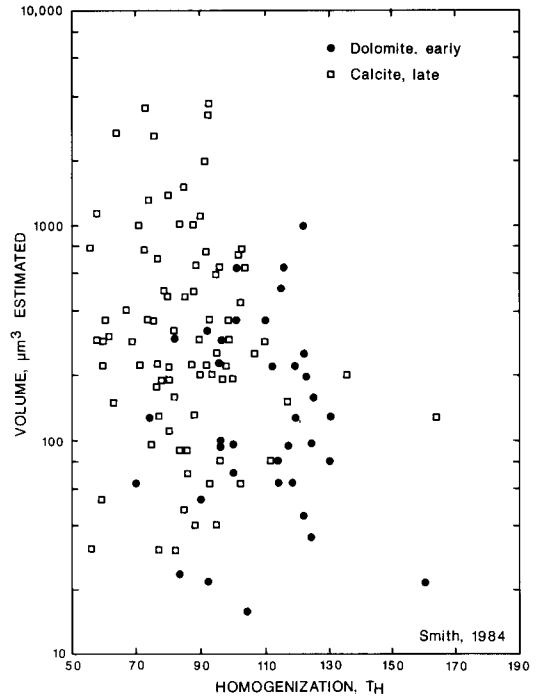

FIG. 5. Size versus homogenization temperature for inclusions studied by Smith (1984). There is complete overlap in the two parameters for inclusions in both early and late cements. Inclusion volume was calculated from Smith's area estimates by using the smallest of the stated dimensions as the third dimension. See text for discussion.

There is an obvious need for other tests to discriminate reset inclusions from unaffected inclusions. Goldstein (1986) has pointed out that stretched, but not decrepitated inclusions retain their chemical composition. Low salinity meteoric or marine salinity inclusions with high homogenization temperatures in an otherwise early, low-temperature cement may be chemically representative of the original aqueous fluid trapped in the inclusion. Burruss (1987) pointed out that stretching should be less common in petroleum inclusions because of the higher compressibility of these fluids compared to water. Careful comparison of the behaviour of aqueous and petroleum inclusions in the same sample may yield clues about whether any of the aqueous inclusions have re-equilibrated.

Studies of dislocations associated with inclusions may provide additional information. Reeder and Ward (1985) used transmission electron microscopy (TEM) observations of artificially stretched inclusions in dolomite to show that there

is a greater density of dislocations around stretched inclusions than around unaffected inclusions. R. J. Bodnar (pers. comm., 1986) has proposed using such TEM studies to attempt to quantify the amount of stretching an inclusion has experienced. Recent work on fluorite by Wilkins (1986) demonstrates that the density of dislocations around artificially stretched inclusions can be measured by SEM observations on etched surfaces. This approach may be valuable because the instrumentation is more readily accessible to fluid inclusion researchers than TEM techniques.

Finally, it must be pointed out that the model calculations are limited in their generalization. The amount of temperature rise discussed, 20° to 60 °C, applies strictly to fluorite containing pure water inclusions. Aqueous fluids with salinities up to halite saturation are more compressible than pure water in the temperature range of diagenesis (Potter and Brown, 1977). Therefore the temperature rise necessary to re-equilibrate inclusions with natural, saline fluids will be somewhat greater than that modelled in this paper. Fluid inclusion researchers can apply the methodology presented here to examine whether re-equilibration is a serious problem in their samples. Even if resetting has occurred in early cements, it tends to cause inclusions to behave as 'maximum recording thermometers'. Therefore, at the very least, the measurements on inclusions in sedimentary rocks will place limits on the highest temperature reached during diagenesis.

Conclusions

Re-equilibration is an important factor to be considered when using fluid inclusions directly to determine diagenetic palaeotemperatures. Model calculations based on the observed behaviour of fluorite under confining pressure suggests that large inclusions with volumes of 10^4 μm^3 (~40 μm largest dimension) will begin to re-equilibrate after only a 20 °C temperature rise above the trapping temperature. Smaller inclusions (down to 4 μm largest dimension) may withstand larger amounts of overheating, but temperature rises of 60 °C may reset all inclusions in the size range of 40 to 4 μm largest dimension. The amount of subsidence necessary to cause these temperature rises is dependent on the geothermal gradient. This strictly applies only to minerals with the mechanical properties of fluorite containing pure water inclusions, but is certainly a guideline for considering the problem in carbonate minerals. Methods for discriminating between re-equilibrated and unaffected inclusions need to be developed and tested.

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