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Fluid inclusions in sedimentary and diagenetic systems

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Abstract

Some of the major problems in sedimentary geology can be solved by using fluid inclusions in sedimentary and diagenetic minerals. Important fluids in the sedimentary realm include atmospheric gases, fresh water of meteoric origin, lake water, seawater, mixed water, evaporated water, formation waters deep in basins, oil, and natural gas. Preserving a record of the distribution and composition of these fluids from the past should contribute significantly to studies of paleoclimate and global-change research, is essential for improving understanding of diagenetic systems, and provides useful information in petroleum geology. Applications of fluid inclusions to sedimentary systems are not without their complexities. Some fluid inclusions exposed to natural conditions of increasing temperature may be altered by thermal reequilibration, which results in stretching, or leakage and refilling, of some fluid inclusions. Similarly, overheating in the laboratory can also cause reequilibration of fluid inclusions, so fluid inclusions from the sedimentary realm must be handled carefully and protected from overheating. Natural overheating of fluid inclusions must be evaluated through analysis of the most finely discriminated events of fluid inclusion entrapment, fluid inclusion assemblages (FIA). Consistency in homogenization temperatures within a fluid inclusion assemblage, consisting of variably sized and shaped inclusions, is the hallmark of a data set that has not been altered through thermal reequilibration. In contrast, fluid inclusion assemblages yielding variable data may have been altered through thermal reequilibration. If a fluid inclusion assemblage has not been altered by thermal reequilibration, its fluid inclusions may be useful as geothermometers for low- and high-temperature systems, or useful as geobarometers applicable throughout the sedimentary realm. If a fluid inclusion assemblage has been altered partially by thermal reequilibration, techniques for distinguishing between altered and unaltered fluid inclusions may be applied.

In studies of global change, fluid inclusions can be used as sensitive indicators of paleotemperature of surface environments. Fluid inclusions also preserve microsamples of ancient seawater and atmosphere, the analysis of which could figure prominently into discussions of past changes in chemistry of the atmosphere and oceans. In petroleum geology, fluid inclusions have proven to be useful indicators of migration pathways of hydrocarbons; they can delineate the evolution of the chemistry of hydrocarbons; and they remain important in understanding the thermal history of basins and relating fluid migration events to evolution of reservoir systems. In studies of diagenesis, fluid inclusions can be the most definitive record. Most diagenetic systems are closely linked to temperature and salinity of the fluid. Thus, fluid inclusions are sensitive indicators of diagenetic environments.

Keywords: Fluid inclusions; Global change; Diagenesis; Paleoclimate; Petroleum geology

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1. Introduction

In keeping with the focus of this volume, this paper will concentrate on major recent advances in fluid inclusions from sedimentary systems, and will lay the groundwork for some future research directions. It is not designed to be a complete literature review nor is it designed to summarize the systematics of working with fluid inclusions in detail. To get more complete and practical coverage of the subject, see the book by Goldstein and Reynolds (1994) and summaries by Roedder (1984) and Touret (1994). In this paper, I do intend to focus on the problems that can be solved with fluid inclusions from sedimentary systems, what particular focus we must have to deal with fluid inclusions in these systems, what some of the newest advances are, and what particular benefits such studies may produce.

The subject of fluid inclusions in sedimentary systems must include all of those systems forming at Earth's surface and those that extend more deeply below the surface until conditions leave the diagenetic realm and enter the metamorphic realm, let us say temperatures below about 200°C. This would include evaporites formed from evaporation of saline surface and ground water, physical and chemical reactions in the subaerial realm, and physical and chemical reactions in the subsurface, where a multitude of fluids exist including oil, gas, and aqueous fluids of various origin. Although normally one might consider that glacial ice would be included in this realm, the abundant studies of fluid inclusions of air trapped in glacial ice will not be discussed here.

2. Fluids of the sedimentary realm

In dealing with fluid inclusions in sedimentary systems, one should consider various fluids (Fig. 1a). At the surface of course is the mixture of gases in the atmosphere, a fluid with a poor geologic record (Berner, 1990) the past composition of which is incredibly important in developing a model for climate change into the future.

Freshwater of meteoric origin is another important fluid associated with the sedimentary realm, and includes freshwater precipitating on sediment and soil surfaces as rain water, fresh lake and groundwater, and groundwater and lake water, ultimately of meteoric derivation, compositionally modified through rock–water interaction and evaporation. Clearly, identifying fluids that have been derived from meteoric precipitation is important in reconstructing paleoclimate; alteration through rock–water interaction and evaporation also figures prominently in understanding paleoclimate. For oil and gas exploration and stratigraphy, stratigraphic surfaces of meteoric influx typically are depositional sequence boundaries. Meteoric waters also are diagenetically reactive and are important in the distribution and heterogeneity of carbonate reservoir rocks. Finally, meteoric waters altered through surface reactions such as evaporation and weathering, and subsurface processes such as rock–water interaction are those that make up most lake waters. Determining the composition of such ancient lake waters figures prominently in reconstruction of paleoclimate history through reconstructing water budgets of the past and determining the paleo-drainage basin configuration.

Seawater is another fluid that is common near the surface of the Earth. Today, this fluid is relatively uniform in composition and maintains a salinity near 35 ppt, but in the past, the total salinity may have varied, isotopic compositions varied, and ratios of major, minor and trace ions may have been different than what they are today. The chemistry of seawater may have changed so significantly through time, that even the major carbonate mineral precipitating from it has changed through time (Sandberg, 1983) giving rise to ancient seas dominated by aragonite/high-Mg calcite precipitation and seas dominated by calcite precipitation. This variation in seawater chemistry is further supported by secular variation in the composition of evaporite minerals, with seawater of one age giving rise to Mg-rich bitterns and seawater of another age giving rise to K-rich bitterns (Hardie, 1996). Understanding secular variations in the composition of seawater is important as a paleoclimate indicator, for understanding the evolution of organisms (Stanley and Hardie, 1998), and is also important for understanding the paleoecology of ancient environments, tectonic controls on global cycling of chemical constituents in nature, and the diagenetic effect of seawater composition on carbonate sediments.

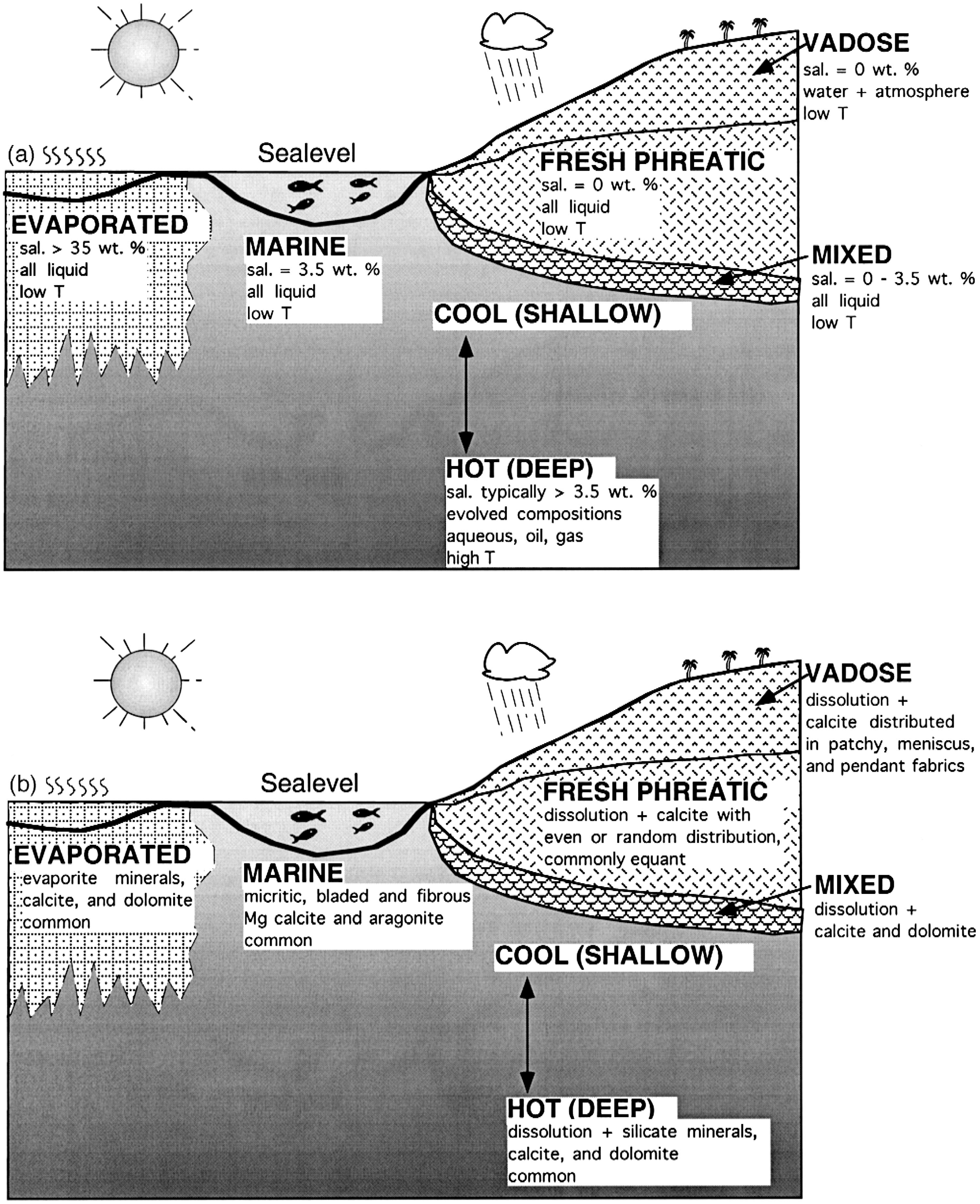


Fig. 1. Schematic representation of environments in sedimentary systems with characteristics of fluids applicable to fluid inclusion work (a) and diagenetic processes important for each environment (b).

Seawater that has been modified through evaporation or meteoric dilution of seawater falls in to another class of fluids important in sedimentary systems. Brackish waters, created by dilution of seawater with meteoric water, are important diagenetic fluids, which may be responsible for dissolution of carbonate minerals and precipitation of calcite and dolomitization (Land, 1973; Goldstein and Reynolds, 1994). Seawater that has been modified through evaporation is a diagenetically reactive fluid that may be important in precipitating calcite, dolomite and evaporite minerals (Goldstein et al., 1998).

As one moves more deeply into the sedimentary section, a wide variety of subsurface fluids may be encountered, along with the temperature and pressure increase normally encountered along any thermobaric gradient. Aqueous fluids ultimately may have been derived from meteoric and marine fluids, but typically, these have been altered so extensively through processes of evaporation at the surface, evaporite dissolution or other types of rock–water interaction that they have achieved compositions significantly different from their parent fluids. These basinal fluids typically are very salty, may achieve concentrations well above those of marine fluids, and contain ion ratios that reflect their evolution. Many of these fluids are quite important for precipitation of diagenetic minerals such as feldspars, quartz, anhydrite, calcite, and dolomite. In addition to aqueous systems, the subsurface may contain petroleum and various compositions of natural gas derived from organic matter.

3. Diagenetic importance

In addition to this simple list of fluids in nature there is an incredibly significant economic incentive for understanding fluid history and diagenesis. Diagenetic reactions are some of the most important in controlling porosity and permeability in aquifers and in oil and gas reservoirs (Fig. 1b). The diagenesis of sedimentary rocks, and carbonates in particular, can be closely linked to origin of the fluid responsible for diagenetic alteration.

Diagenesis can even be linked to surface environment. Most sediments are deposited from marine fluids at Earth-surface temperatures. In the tropics, seawater is supersaturated with respect to aragonite and calcite down to water depths on the order of 500–1000 m in the Pacific and 2000 m in the Atlantic. At higher latitudes, seawater is less likely to be supersaturated with respect to carbonate minerals. Common diagenetic phases known to precipitate from seawater include fine-grained (micritic) cements of Mg-calcite or aragonite compositions and coarser Mg-calcite and aragonite cements with a variety of morphologies (James and Choquette, 1990a). Low-Mg calcite and dolomite are also known from these systems (Major and Wilbur, 1991; Vahrenkamp and Swart, 1994). When seawater is mixed with freshwater of meteoric origin, there is some evidence for dissolution of carbonate minerals as well as evidence for precipitation of low-Mg calcite in some settings and replacement of carbonate minerals with dolomite (Land, 1973; Goldstein and Reynolds, 1994; Frank and Lohmann, 1995). Where seawater evaporates, a variety of evaporite minerals may precipitate, as well as dolomite, low-Mg calcite, and possible unstable carbonates like Mg calcite and aragonite (Goldstein et al., 1998). In areas where the carbonate sediments are exposed subaerially, meteoric waters may percolate downward through the sediment in the area above the water table, encouraging dissolution of unstable carbonate minerals and precipitation of calcite (James and Choquette, 1990b). At and below the water table, meteoric fluids may mix with other meteoric fluids of differing CO_2 content, encouraging dissolution of carbonate minerals. Dissolution of unstable carbonate minerals and outgassing of CO_2 encourages precipitation of calcite in this setting. In all of the above settings minor silicate diagenesis is also possible and is greatly dependent on the composition of the pore fluids and their modification by chemical components provided through interaction with the sediment. With deeper burial in basins and with increasing age of carbonate sediments, the originally metastable minerals of original carbonate sediments give way to more stable mineralogies. As one goes deeper into the sedimentary section into a burial setting, or as warm fluids from deeper in a basin are injected toward the surface, many diagenetic reactions are driven by change in temperature. Among these are dissolution of minerals as well as precipitation of feldspars, quartz and carbonates. So, given a sequence of diagenetic phases in any ancient rock, determining the diagenetic environment of its precipitation boils down to being able to determine two or three basic characteristics of the fluid that precipitated it: the salinity, the temperature, and the pressure. These three parameters are those most easily determined from fluid inclusions, so, given preservation of the right suite of fluid inclusions, the analysis of fluid inclusions in diagenetic minerals is probably the most unambiguous method for determining diagenetic histories.

4. How representative are fluid inclusions?

4.1. Mechanisms for alteration of fluid inclusions

One of the many processes that could alter fluid inclusions from their originally entrapped character is diffusion of inclusion components through the host mineral. In the diagenetic realm, it is probable that solutes and water do not diffuse to a significant degree. Although H_2 is uncommon in most sedimentary systems, hydrogen is the component that is most likely to diffuse through minerals (Hall et al., 1989; Morgan et al., 1993). It is not well known the degree to which this is a problem in sedimentary systems; it would be prudent to assume that hydrogen can diffuse, potentially altering deuterium isotopic compositions and other compositions of fluid inclusions. Otherwise, it appears that diffusion is not a major concern in the sedimentary realm.

Inclusion fluids could alter if they react irreversibly with their mineral host after their initial entrapment. Such compositional changes most likely are significant only if fluid inclusions form in a metastable diagenetic mineral, such as high-Mg calcite. However, the degree to which trace element systems reequilibrate compositionally with their mineral hosts is currently unknown. This is an area of investigation that will require intensive research in the future as technologies advance to allow for routine analysis of composition of inclusion fluids.

One might also wonder if there were irreversible chemical changes in inclusion fluids. In the sedimentary realm, the most important concern would be in organic fluids, which are inherently metastable. It is well known that many petroleum fluid inclusions contain brownish solids that do not dissolve upon heating. Some of these solids may have been trapped as solids in the inclusions, but undoubtedly some have precipitated from the original fluid after its entrapment, providing strong evidence for changes in the chemical makeup of those inclusion fluids after entrapment. At this time, it us unknown to what degree oil fluid inclusions are altered by post entrapment chemical alteration. In addition, aqueous fluids in sedimentary basins typically have some amount of dissolved organic compound (Collins, 1975; Carothers and Kharaka, 1978; Hanor, 1980). These organics may break down after entrapment, causing an irreversible chemical change to an aqueous system. The degree to which this is a problem is as yet unknown, however, consistent observations of fluid inclusion homogenization temperatures yielding values less than entrapment temperature, and the low organic content of many diagenetic fluids argue against this as a ubiquitous problem.

It stands to reason that intense deformation would breach fluid inclusions and cause them to be refilled with a new fluid (Goldstein, 1986). In samples in which such deformation has occurred, it is best to avoid working with the fluid inclusions unless the inclusionist is interested in conditions of deformation. Deformed samples typically are easily identified through petrographic means, with carbonates typically showing abundant deformation twins and other minerals showing undulose extinction, through-going healed fractures, or other evidence of deformation.

It is now well known that many minerals may recrystallize in the diagenetic realm. Most carbonate minerals have shown both petrographic and diagenetic evidence of recrystallization or neomorphism, and recrystallization of feldspars is well known in diagenetic systems. Any apparently primary fluid inclusions in such systems contain fluids present during recrystallization of the mineral phase, and do not contain the fluids of initial precipitation (Goldstein, 1986). Undoubtedly, the most powerful tool in recognizing recrystallization in diagenetic minerals is careful petrographic study in which compositional variation is observed to cut across concentric or sector growth zoning observed in cathodoluminescence, etching, UV-epifluorescence. back-scattered electron imaging, or compositional staining. Such simple textural relationships are the foundation on which most diagenetic studies are built.

4.2. Heterogeneous entrapment

It is well known that for the density and composition of a fluid inclusion to be representative of conditions of entrapment, the inclusion must have been trapped as a single homogeneous fluid. For many diagenetic and sedimentary systems, this is the case; there is only a single homogeneous fluid in the system and that is all that is trapped in fluid inclusions. Contrary to popular belief, it is not true that all sedimentary fluids are saturated with respect to methane; commonly, aqueous fluids are undersaturated with respect to methane and there is only a single homogeneous aqueous phase.

However, in nature there are many settings where immiscibility is possible, leading to entrapment of multiple phases during an event of fluid inclusion entrapment, heterogeneous entrapment. In the vadose zone, the near-surface setting above the water table, both water and air exist in pores (Goldstein, 1986). Below the water table, there are settings in which immiscible bubbles of methane and other gases may exist. Deeper in the sedimentary pile, a separate gas phase or liquid petroleum phase may exist in the presence of an aqueous liquid phase. Finally, it is possible to entrap solid mineral particles, organic matter or even bacteria along with an aqueous phase during fluid inclusion entrapment.

For each of these settings, it is clear that heterogeneous entrapment of more than one phase is possible. In systems of heterogeneous entrapment, the bulk density of fluid inclusions is different from that of the original system so homogenization temperatures typically are meaningless. Systems of heterogeneous entrapment (or necking down after a phase change, e.g. Fig. 3) may be recognized by variability of phase ratios among all of the inclusions genetically related to a single event of fluid inclusion entrapment. If phase ratios are consistent among all of the inclusions genetically related to a single event of fluid inclusion entrapment, then it is likely that only a single homogeneous fluid was entrapped, and that those fluid inclusions have the potential to preserve the density and composition of the original fluid present during entrapment. Further, a typical aqueous fluid inclusion that was trapped as a single homogeneous aqueous liquid in the high-temperature diagenetic environment, is typically only able to nucleate a vapor bubble occupying no more than 15% of the volume of a fluid inclusion (Goldstein, 1993). If a single aqueous inclusion contains more than 15 vol.% bubble and if, among all of the inclusions genetically related to a single event of fluid inclusion entrapment, there is more than 15 vol.% vapor, heterogeneous entrapment of a gas and liquid phase is likely. So, the careful fluid inclusionist working in sedimentary systems must constantly be aware of the possibility of heterogeneous entrapment. Finding evidence for it provides important constraints on the fluid system and avoids the possibility of misinterpreting fluid inclusion data by incorrectly assuming that fluid inclusions were entrapped as a single homogeneous phase.

4.3. Necking down after a phase change

It is now well known that fluid inclusions may change their shape over time through the process known as necking down. Typically, change in shape involves a tendency for inclusions to evolve from irregular shapes to more globular or negative crystal shapes to attain the state of lowest surface free energy (Roedder, 1984). In any mineral, the change in shape of an inclusion may even cause an originally larger inclusion to pinch off into multiple smaller inclusions. Given necking down of a two-phase fluid inclusion, a necked inclusion that happened to trap a bubble would have a density much lower than the original inclusion fluid, and a necked inclusion that only trapped liquid would have a density much higher than the original inclusion fluid. This process, can severely alter fluid inclusion densities to the point of making homogenization temperature data meaningless.

In sedimentary systems, one might wonder the degree to which necking down of inclusions, in the presence of more than one fluid phase, might be important. It can be incredibly important! The process of necking down is known to take place most rapidly at higher temperatures (Bodnar et al., 1985; Brantley, 1992). To evaluate the importance of necking down for sedimentary systems, let us first examine a natural aqueous fluid inclusion system, trapped at low temperature or at high temperature, and then subsequently heated. In this system, the fluid inclusions remain in the one phase field during heating (Fig. 2), and any necking down during that heating, preserves the original density in all inclusions. The fluid inclusions may remain representative of fluid density of the original diagenetic system. However, during cooling of fluid inclusions trapped at high temperatures, only a minute temperature drop is necessary before a fluid inclusion's isochoric path intersects the vapor–liquid line (Fig. 3). This means that during much of the cooling history of a high-temperature fluid inclusion, a bubble may be present.

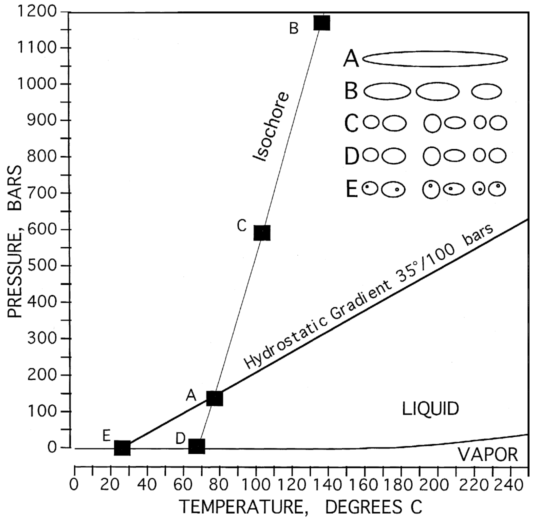


Fig. 2. $P-T$ phase diagram for pure water with an isochore for pure water and the liquid–vapor field boundary. If a fluid inclusion were trapped at 75°C (A) and were then heated during burial to 130°C (point B), the inclusion would remain in the liquid field. If it were to neck down at point B and then were to neck down again during cooling to 100°C (point C), new inclusions would be formed that were of the same density as the original single inclusion. With further cooling to 68°C (point D) a vapor bubble can nucleate but generally does not nucleate unless there is further cooling. Once the inclusions have reached room temperature (point E) all have nucleated bubbles. Each inclusion now has the same ratio of vapor–liquid and homogenizes at point D. This is the temperature of homogenization that the single original fluid inclusion would have produced. Necking down has had no effect on homogenization temperature (after Goldstein and Reynolds, 1994).

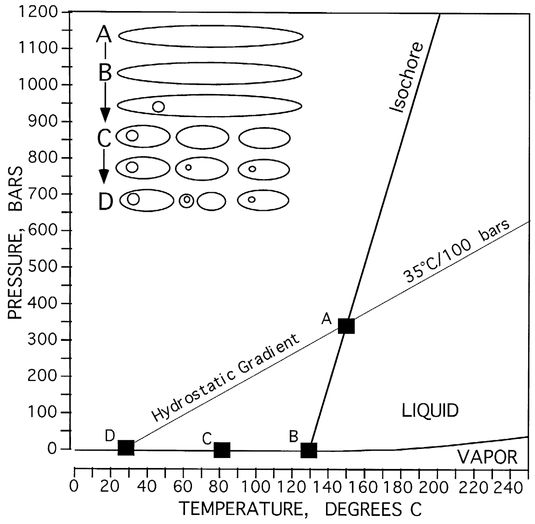


Fig. 3. $P-T$ phase diagram for pure water with an isochore for pure water and the liquid–vapor field boundary shown. If a fluid inclusion were entrapped at point A, and were then cooled during uplift to point B, a vapor bubble would be stable at this temperature but would not nucleate until further cooling toward point C. After the bubble has nucleated and the inclusion has cooled to point C, the inclusion may neck down to form several fluid inclusions, only one of which contains the vapor bubble. With further cooling toward point D, bubbles may nucleate in the remaining all-liquid inclusions. As the inclusions are cooled to surface temperature (point D), more necking down may occur and the bubble may be split between two inclusions. At, point D, none of the necked down inclusions have the same density as the original inclusion trapped at A. Also, none of these inclusions will homogenize at point B, they will either homogenize at lower or higher temperatures because they necked down after a phase change occurred in the fluid inclusion (after Goldstein and Reynolds, 1994).

As a fluid inclusion necks down to form multiple inclusions, the bubble will preferentially separate into one new inclusion or another, creating fluid inclusions of highly variable density that differ from the density of the original fluid inclusions.

Inclusionists must learn to recognize evidence for necking down after a phase change to be able to evaluate the validity of density data gathered from homogenizing fluid inclusions. Many fluid inclusionists mistakenly observe two fluid inclusions that appear to be almost connected, two inclusions with a neck joining them, and use this as the only evidence that would be indicative of necking down. Whereas it is true that many of these fabrics have been generated through necking down, these are probably the oddballs, the ones that were caught in the act of necking down without progressing to its logical negative crystal or globular conclusion. Observe almost any planar array of secondary inclusions, with negative crystal shape, to see that necking down commonly completes its journey toward regular shapes. With this in mind, it would be a good idea to use something other than shape to identify evidence for necking down after a phase change. Remember that a typical aqueous fluid inclusion that was trapped as a single homogeneous aqueous liquid in the high temperature diagenetic environment, is typically only able to nucleate a vapor bubble occupying no more than 15% of the volume of a fluid inclusion. If a single aqueous inclusion contains a bubble occupying more than 15% of the volume of the inclusion, then necking down after a phase change or heterogeneous entrapment are both possibilities. If, among all of the inclusions, genetically related to a single event of fluid inclusion entrapment, there is more than 15 vol.% vapor, then heterogeneous entrapment of a gas and liquid phase is likely. Furthermore, after necking down of a high-temperature fluid inclusion after a phase change, gas-rich and liquid-rich inclusions are commonly paired petrographically. Look for this pairing as an indication of necking down after a phase change. If you find evidence for necking down after a phase change, do not trust homogenization temperatures or observations of phase ratios. The density of the original fluid inclusion has been altered!

4.4. Nucleation metastability

It is well known that some fluid inclusions at room temperature do not contain the equilibrium assemblage of phases because of problems with nucleation. This includes the nucleation of solid phases (daughter minerals) but more importantly, involves problems with nucleation of a bubble in a liquid-filled fluid inclusion. In sedimentary systems, it is common to find fluid inclusions that exist at room temperature as a single liquid aqueous phase. Some of these were trapped at or below room temperature and therefore should not have a bubble, but others were trapped at higher temperature and would have a bubble stable at room temperature if one could nucleate. In natural systems that have not been heated artificially, it appears that there are many controls on whether bubbles nucleate in high-temperature fluid inclusions. Size appears to be important. The smallest inclusions are less likely to nucleate a bubble. Temperature of entrapment is also important; the lower the density (higher the temperature of entrapment) then the more likely it is that a fluid inclusion will nucleate a bubble. Composition appears to be important as well, but this control appears to be quite complex. It is now well known that it is possible to nucleate bubbles (through super cooling) in fluid inclusions trapped close to room temperature (Roberts and Spencer, 1995; Newell and Goldstein, 1999; Benison and Goldstein, 1999), and many have observed that for tiny fluid inclusions, even fluid inclusions with densities that should yield homogenization temperatures as high as 100°C, bubbles have not nucleated. However, in large numbers of fluid inclusion studies, especially ones with mixed densities, there appears to be a common lower cutoff of homogenization temperatures from about 40°C to 60°C. This suggests that a common nucleation boundary for bubbles forming in fluid inclusions is at densities that would yield homogenization temperatures of around 50°C. Thus, in the absence of necking down after a phase change, the presence of all liquid fluid inclusions, that are in the same size range as two-phase inclusions, suggests that the all-liquid fluid inclusions were trapped at a temperature below about 50°C.

4.5. Thermal reequilibration

Perhaps the greatest concern for fluid inclusion preservation in diagenetic minerals is their reequilibration from internal overpressure, induced by natural heating or heating during sample preparation. If a fluid inclusion was trapped as a single liquid phase, and then was buried through a lithostatic or hydrostatic thermobaric gradient (Fig. 4), it is clear that the fluid inclusion would be internally overpressured relative to ambient conditions. It is now well known that many fluid inclusions respond to this internal overpressure through decrepitation or stretching to

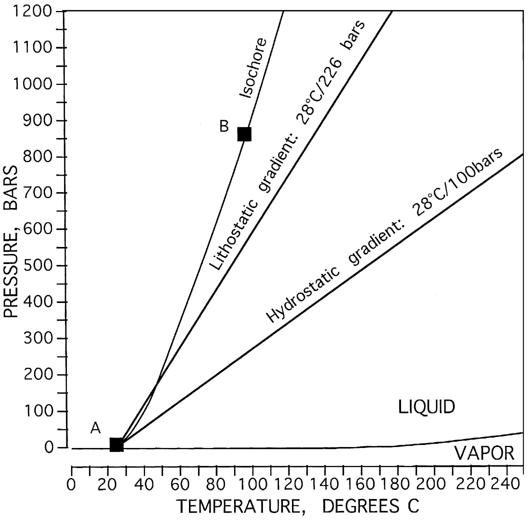


Fig. 4. $P-T$ aqueous phase diagram for pure H_2O with hydrostatic thermobaric gradient of 28°C/100 bars and lithostatic thermobaric gradient of 28°C/226 bars superimposed. If a fluid inclusion were trapped at surface conditions (point A) and were then subjected to further heating during burial to point B, the fluid inclusion's internal pressure would rise significantly above the surrounding hydrostatic pressure and lithostatic pressure at that temperature (after Goldstein and Reynolds, 1994).

relieve the high internal pressures (Bodnar and Bethke, 1984; Goldstein, 1986; Comings and Cerconne, 1986; Burruss, 1987a; Mclimans, 1987; Prezbindowski and Tapp, 1991). If a fluid inclusion responds through permanent plastic deformation, its volume is increased to decrease the internal overpressure, producing a lower density that would yield a new, higher homogenization temperature (Fig. 5). Although the fluid density changes as a result of stretching, the composition remains identical to its original composition.

Alternatively, if a fluid inclusion were to decrepitate to relieve its high internal pressure, the inclusion could open itself to ambient pore fluid. If this were to occur, the contents of the fluid inclusion would leak and equilibrate with the fluid in the pore space (Fig. 6). Eventually, the inclusion's conduit to the surface could heal and the original fluid inclusion cavity would be present in its original position, but the fluid inclusion would now yield a higher homogenization temperature and contain a fluid different from what it originally contained (Goldstein, 1986). This mechanism, of leakage and refilling, together with the mechanism of stretching, is known as thermal reequilibration.

Because many fluid inclusions in the sedimentary realm experience conditions of increasing temperature after initial entrapment, it is important to evaluate the degree to which fluid inclusions are altered by thermal reequilibration. It is now well known that some minerals are better containers for confining internal overpressure than others. One of the controls on thermal reequilibration is tensile strength of the mineral, which is, in part, related to its hardness (Turgarinov and Vernadsky, 1970), and affected by cleavage. If one were to ask if there is any mineral medium that can be trusted as strong enough to resist any thermal reequilibration of fluid inclusions, one would have to say that none exist (Goldstein and

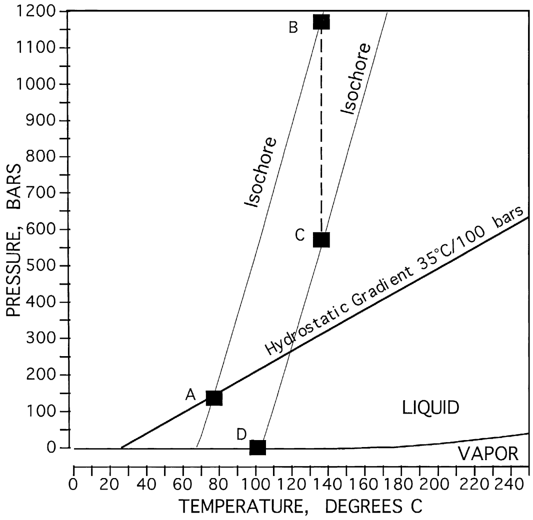


Fig. 5. $P-T$ phase diagram for water illustrating stretching of an all-liquid fluid inclusion during heating beyond temperature of entrapment. If the fluid inclusion were trapped at point A (75°C) and were then heated further during burial, the inclusion's internal pressure would follow an isochore toward point B, and its internal pressure would increase greatly compared to the surrounding hydrostatic pressure. If the inclusion were to stretch from this internal overpressure, its volume would increase and density and pressure would decrease. This event is represented by a drop to point C, and places the inclusion on the new isochore. Cooling of the inclusion would result in $P-T$ conditions within the inclusion intersecting the vapor–liquid curve at about 100°C; the inclusion now has the density that would produce T_h measurements of 100°C. If the inclusion had never stretched, it would have yielded a T_h at 65°C (after Goldstein and Reynolds, 1994).

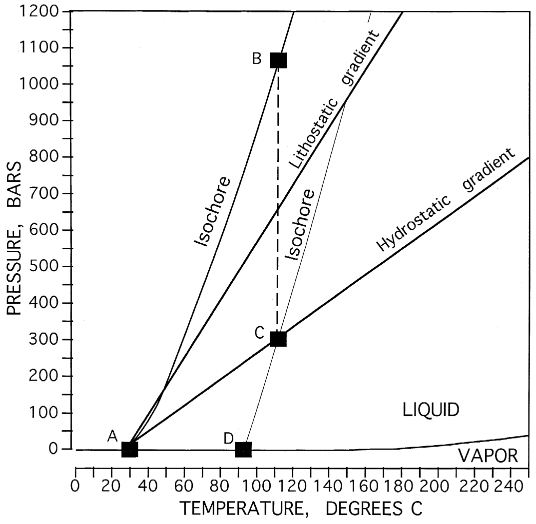


Fig. 6. $P-T$ phase diagram for pure H_2O with hydrostatic thermobaric gradient of 28°C/100 bars and lithostatic thermobaric gradient of 28°C/226 bars superimposed. If a fluid inclusion were trapped as liquid at the surface (A) and were then heated during burial, the fluid inclusion's internal pressure would rise along an isochore toward point B. At point B, the inclusion is internally overpressured relative to the surrounding hydrostatic thermobaric gradient. If the inclusion were to decrepitate from internal overpressure, it would immediately equilibrate with the conditions in the surrounding pore fluid and jump down to point C on the hydrostatic thermobaric gradient (if the example were for lithostatic, this would be possible too). Because the inclusion has decrepitated it can refill with whatever pore fluids happen to be present at the time of opening of the inclusion. Rehealing of the inclusion followed by cooling would result in inclusion $P-T$ conditions following a new isochore (different density and possibly different composition) that intersects the vapor–liquid curve at a higher temperature (point D). This thermal reequilibration causes an increase in homogenization temperature of fluid inclusions and may result in their refilling with new fluids (after Goldstein and Reynolds, 1994).

Reynolds, 1994). Because the internal overpressures developed in an overheated fluid inclusion is so great, it is best to assume that at least some thermal reequilibration is possible, even in relatively hard minerals like quartz. Likewise, if one were to ask if there is a particular mineral in which any degree of overheating will allow for total thermal reequilibration of fluid inclusions, one would also have to say no such mineral has yet been demonstrated. Much discussion of the relative weakness of the mineral halite has found its way into the literature (Roedder and Belkin, 1979), but it appears that there still exists a good possibility for fluid inclusions in halite to remain unaltered even though they have been heated to some degree (Lowenstein and Spencer, 1990; Casas et al., 1992; Benison and Goldstein, 1999). Moreover, cleavable minerals like calcite and fluorite have received the same bad press, but there is still strong evidence that reequilibration is not total in these mineral matrices and that it is quite possible for them to produce good data. So, no matter what the mineral, we as fluid inclusionists should consider that fluid inclusions in any mineral could have been altered by thermal reequilibration, but that thermal reequilibration has not necessarily affected every fluid inclusion in the mineral. The most important thing we can do as fluid inclusionists in the sedimentary realm is to evaluate the degree to which fluid inclusions have been altered by thermal reequilibration, and to develop methods for separating altered fluid inclusion data from unaltered fluid inclusion data.

It is clear that there are several controls on whether a particular fluid inclusion will reequilibrate or not. Of course, the strength of the mineral is one control, but also the density and occurrence of dislocations, and the orientation of cleavage directions in the crystal relative to the position of the inclusion. The point is that each fluid inclusion in a particular mineral will behave differently during overheating. It appears that size is quite important (Lacazette, 1990; Fig. 7) the larger the inclusion, the more likely it is to thermally reequilibrate due to internal overpressure. Some tiny inclusions appear to be quite resistant to thermal reequilibration, even in a relatively weak mineral like calcite, but size is not the only significant variable. Over a given size range in the same mineral, with the same degree of internal overpressure, some fluid inclusions appear resistant to thermal reequilibration and others do not (Fig. 7). In theory, the effect of shape and orientation of shape in the crystal should dominate this variation. It is well known that spherical shapes are highly resistant to deformation from internal overpressure and that more irregular shapes with sharp angles have stress raisers that encourage deformation, especially if the stress raiser is oriented along a zone of weakness in the crystal. For this reason, given the variable sizes, shapes, and orientations of fluid inclusions trapped in the same conditions, the weakest fluid inclusions will

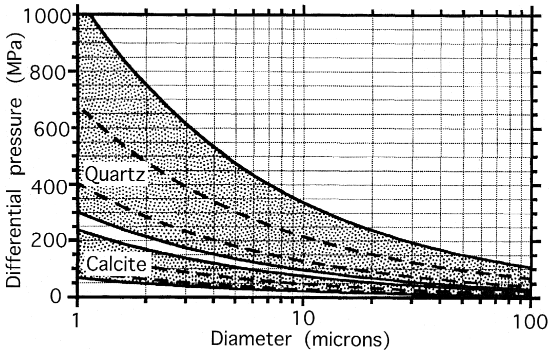


Fig. 7. Differential pressure (internal inclusion pressure — external pressure) in MPa (bars/10) required for decrepitation of fluid inclusions of various shapes and sizes in calcite and quartz. Base of each shaded area is the differential pressure at which the weakest shape modeled should decrepitate. Top of each shaded area is the differential pressure at which the strongest modeled shape should decrepitate. Dashed lines within each shaded area define the differential pressure at which decrepitation should occur for shapes of intermediate strength. No inclusions should decrepitate at conditions below each shaded area. All inclusions should decrepitate above each shaded field. Curves are defined using shape factors in Lacazette (1990) and illustrate the relationship between size and differential pressure of decrepitation for inclusions of a given shape within each mineral. Notice the important controls of both size and shape on whether a fluid inclusion decrepitates. See Lacazette (1990) for more details. After Lacazette (1990).

reequilibrate with the lowest internal overpressures and the strongest fluid inclusions may never reequilibrate. Because of that variable response to internal overpressure, thermal reequilibration alters assemblages of fluid inclusions that were originally consistent in composition and density; they become fluid inclusions that are more variable in density and perhaps variable in composition. The altered assemblage of inclusions may contain resistant inclusions that essentially remain unaltered, preserving the original density and composition of the original inclusions, and may contain fluid inclusions that have been reequilibrated at many points on the pressure–temperature–composition path experienced during heating of the fluid inclusions.

5. The fluid inclusion assemblage approach

Consider a group of fluid inclusions of various sizes and shapes, each trapped as a single homogeneous phase at the same time, under the exact same conditions. One would expect that these fluid inclusions would each yield the same homogenization temperatures and that they would each yield the same compositional data. However, if these variably sized and shaped fluid inclusions were then subject to natural overheating, one would expect that some of the fluid inclusions would thermally reequilibrate with a tiny amount of overheating, and that others might not reequilibrate at all. During overheating, some inclusions might even reequilibrate multiple times and each fluid inclusion would likely reequilibrate from a different amount of internal overpressure, essentially at a different temperature. Given this type of behavior, one would expect that after thermal reequilibration, an originally consistent group of inclusions would now yield highly inconsistent homogenization temperatures and may even yield inconsistent compositional data. Such variability in homogenization temperature and composition, in a group of fluid inclusions all originally trapped under the same conditions, is our best indication of thermal reequilibration.

The only way to evaluate problems with thermal reequilibration is to identify those inclusions trapped at the same time and evaluate if they provide variable or consistent data. For that reason and because it provides the most detailed information about fluid history, the “fluid inclusion assemblage” approach is the preferred method to be applied to sedimentary rocks and other rocks containing fluid inclusions. A fluid inclusion assemblage (FIA) is “the most finely discriminated, petrographically associated, group of inclusions” (Goldstein and Reynolds, 1994). For example, an FIA could be composed of all of the inclusions trapped along a single healed fracture, or all of the inclusions trapped in the most finely discriminated growth zone in a single crystal. In other words, the FIA approach is one in which the inclusionist is forced to identify a single event of fluid inclusion entrapment, resolved to as close to an instant of geologic time as will the petrographic relationships allow. If the fluid inclusions in a single FIA yield variable microthermometric data, which does not result from necking down after a phase change or heterogeneous entrapment, then either the fluid inclusions were trapped over an originally wide range of conditions, unresolvable as a single event of entrapment by the petrography, or the inclusions were originally entrapped under the same conditions and were later partially altered by thermal reequilibration. Given such variable data, the safest interpretation to make is that the inclusionist does not know the degree to which the data are good or are bad. Such variable FIAs normally cannot be used to make interpretations about original conditions of entrapment of fluid inclusions. Based on empirical observations of many systems, a good cutoff to define as consistent data in an FIA is if more than 90% of the fluid inclusions in the FIA are within 10–15°C. If in this consistent FIA, inclusions are of variable sizes and shapes, every measurement may be meaningful. If on the other hand, the data from an FIA were more widespread, it would appear that fluid inclusions might have been altered by thermal reequilibration. One of the great weaknesses in many fluid inclusion studies is that the FIA approach is not followed, and because of that, detailed information is lost, and it is impossible to evaluate the validity of the data.

6. Fluid inclusion petrography

The most important part of most fluid inclusion studies in sedimentary rocks is the petrographic analysis of samples. The first step is typically at large scale (core or outcrop), gathering samples for finer work to achieve the crosscutting and stratigraphic relationships. Then samples must be prepared to prevent alteration of the fluid inclusions.

6.1. Sample handling

Because of problems with thermal reequilibration and metastability of fluid inclusions that have been heated in the laboratory, all fluid inclusion studies must avoid samples that have been heated in ways other than normal geologic heating. This means that old thin sections and their rock chips, which have been heated for mounting, are not appropriate for a fluid inclusion study. Outcrop samples that have been heated by fires are also inappropriate. Well cuttings that have been gathered from the drilling of oil and gas wells also should be avoided for the most part, because the history of heating during their drying is unknown. Core and plugs that have been subjected to porosity and permeability analysis typically have been heated as well and must be avoided. When sampling core, it is especially important to show that they have not been subjected to whole-core analysis for porosity and permeability, because such heating is not always immediately obvious from casual observation of a core sample.

During preparation, it is important to get the best optics possible so samples typically are doubly polished. However, all mounting must be done with room-temperature techniques to avoid any heating of the samples. Furthermore, cutoff of samples must be done so as to avoid fracturing and heating, so most labs use low-speed cutoff saws that avoid damage to the sample. Finally, all preparation must be done so as to avoid damage; that means that one must be quite gentle in preparing the samples, never exerting too much pressure and never allowing samples to heat due to friction.

Once doubly polished thick sections have been prepared, they must be protected from damage. Any staining of minerals, which typically involves etching of minerals with an acid, must be avoided, as the etching typically destroys all of the fluid inclusions in the sample. Heating under an electron beam in a SEM or in a cathodoluminescence stage must also be avoided, because of the heating that is generated. Also, during microthermometric work, every effort must be made to preserve the fluid inclusions. For example, that means that heating of aqueous inclusions, to measure homogenization temperature, must be done before freezing, because freezing of low-temperature fluid inclusions typically results in disappearance of the bubble. These inclusions commonly leak or stretch from the freezing process and are no longer useful for measurement of homogenization temperature. When samples are heated, it is important that they not be heated beyond their homogenization temperature before their homogenization temperatures are first measured. If inclusions have been overheated in the lab, then it is possible that they have been thermally reequilibrated to a higher homogenization temperature.

6.2. Origin of fluid inclusions

The most important part of a typical fluid inclusion study in sedimentary rocks is petrographic analysis of samples to determine if the fluid inclusions present will answer the scientific question posed. Some samples may be dominated by primary fluid inclusions, whereas secondary, pseudosecondary, or fluid inclusions of indeterminate origin may dominate others. In many samples, the fluid inclusions of indeterminate origin dominate. The careful fluid inclusionist in sedimentary systems must always be able to admit that the origin of certain fluid inclusions is unknown.

6.3. Primary fluid inclusions

One of the areas in which fluid inclusionists in sedimentary rocks seem to run into trouble is the identification of primary fluid inclusions. Primary fluid inclusions are identified by petrographic criteria. Essentially, there is only one valid criterion for identification of primary fluid inclusions, and that is the identification of a petrographic relationship to growth of the crystal. For example, in calcite, it is common to identify primary fluid inclusions by their occurrence in alternating inclusion-rich and inclusion-poor bands (Fig. 8A). Another criterion that applies to calcite is the preferential orientation or shape of fluid inclusions in growth direction (Fig. 8A). For dolomite, similar criteria apply; fluid inclusion occurrence might define growth zonation (Fig. 8B) or inclusions might be oriented in growth direction. For anhydrite, which is a common coarse precipitate in diagenetic systems, similar growth banding may be defined by fluid inclusions (Fig. 8C) or elongate fluid inclusions may be confined to internal, growth-defined cores of the crystals. Diagenetic quartz commonly may occur as coarse crystals (megaquartz) in which primary fluid inclusions typically are defined by alternating inclusion rich and inclusion poor growth bands, cloudy, inclusion-rich cores defined by growth boundaries, fluid inclusions oriented in the direction of growth, or fluid inclusions trapped along twins. In sandstones, diagenetic quartz is found most commonly as syntaxial overgrowths on detrital grains. In these overgrowths, primary fluid inclusions are found distributed most commonly along the contact between the detrital grain and the overgrowth (Fig. 8D). It is well known that such contacts are zones of weakness where the overgrowth could be fractured away from the detrital grain, leading to reequilibration of fluid inclusions. Primary fluid inclusions can also be recognized in overgrowths from their orientation relative to growth direction and confinement to growth zones (Fig. 8D). Diagenetic overgrowths on detrital feldspars are also well known. Primary fluid inclusions in such overgrowths are most commonly recognized by their orientation relative to growth direction (Fig. 8F). Halite is a very common mineral of the sedimentary realm. Halite that has grown into open water typically has abundant primary fluid inclusions that define cloudy and less cloudy growth zones (Fig. 8G). Coarse gypsum crystals also commonly contain primary fluid inclusions that are recognized by their distribution along growth zones and their orientation in growth direction (Fig. 8F).

6.4. Fluid inclusions primary to recrystallization

One of the most important discoveries of recent years has been the observation that fluid inclusions can be trapped during recrystallization of diagenetic minerals. Recrystallization, in the sense we are using it here, commonly involves a compositional change from a somewhat unstable to a more stable mineral phase through a process of dissolution and reprecipitation, mediated by a fluid phase. Commonly, one compositional growth zone in a crystal is unstable relative to other compositional growth zones. Because of this, recrystallization commonly attacks individual growth zones within other stable growth zones, trapping fluid inclusions that appear as if they were trapped during initial growth of the crystal. Such internal recrystallization is well known in diagenetic dolomite and calcite (Folk, 1965; Wojcik et al., 1994; Luczaj and Goldstein, 2000). In dolomite, finding rhombohedra with cloudy, inclusion-rich cores is quite common (Fig. 9A). For most of these, it is almost impossible to use standard transmitted light microscopy to determine if inclusions were trapped during initial growth or during recrystallization. In baroque (saddle) dolomite especially, a radiating (fir-tree-like) pattern is defined by the distribution of fluid inclusions (Fig. 9B). Such a pattern may result from the recrystallization of an internal growth zone, which caused entrapment of fluid inclusions.

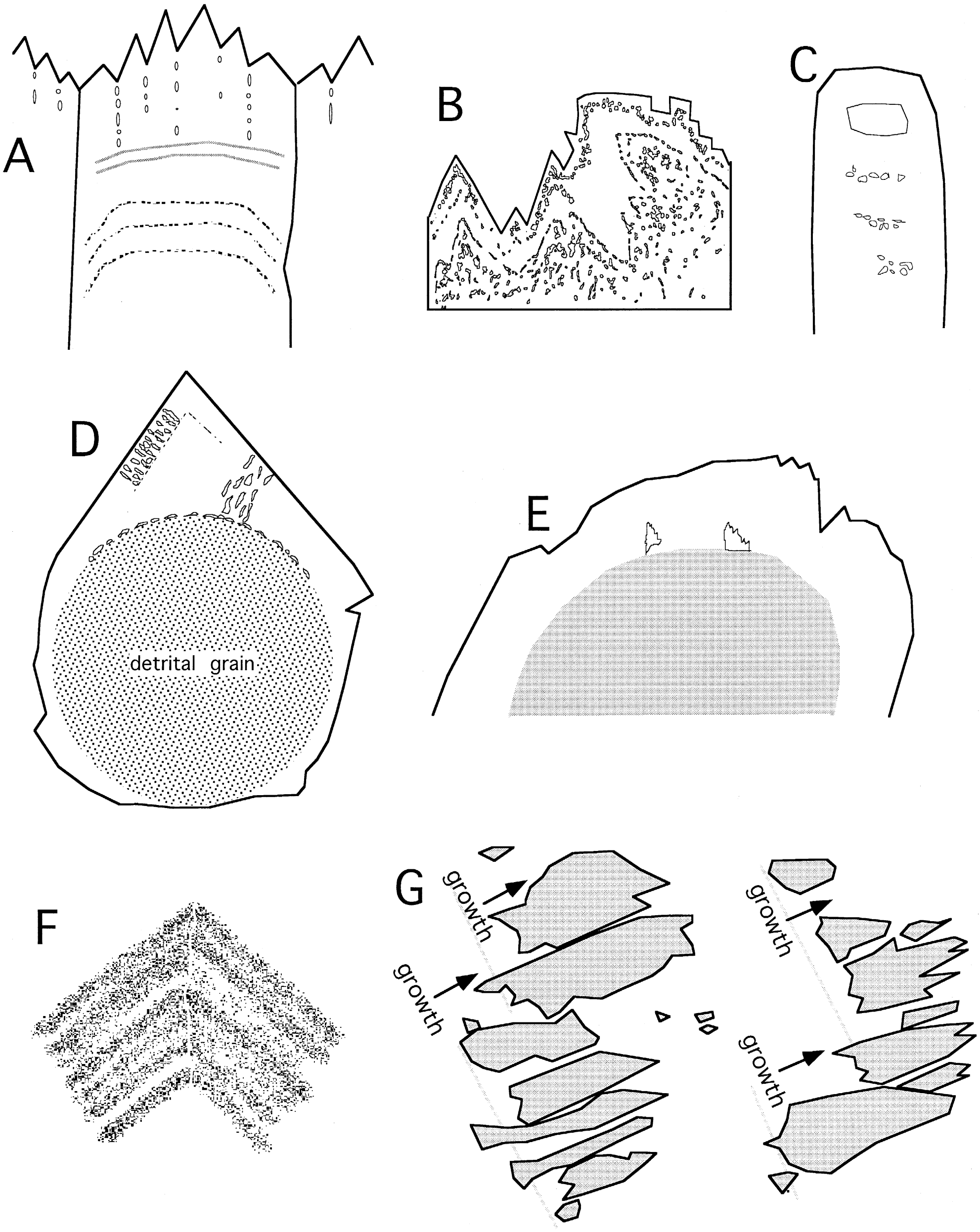


Fig. 8. Sketches of distribution of primary fluid inclusions in various minerals of the sedimentary realm (modified from Goldstein and Reynolds, 1994). (A) Calcite; (B) Dolomite; (C) Anhydrite; (D) Quartz overgrowth; (E) Feldspar overgrowth; (F) Chevron halite; (G) Gypsum (modified from Lowenstein, written communication).

In calcite, it is common for one growth zone to be inclusion rich (Fig. 9C and D). This growth zone may be single or one of many growth bands, or may form the core of the crystal. For most of these occurrences of calcite, it may be difficult to use standard transmitted light microscopy to determine if

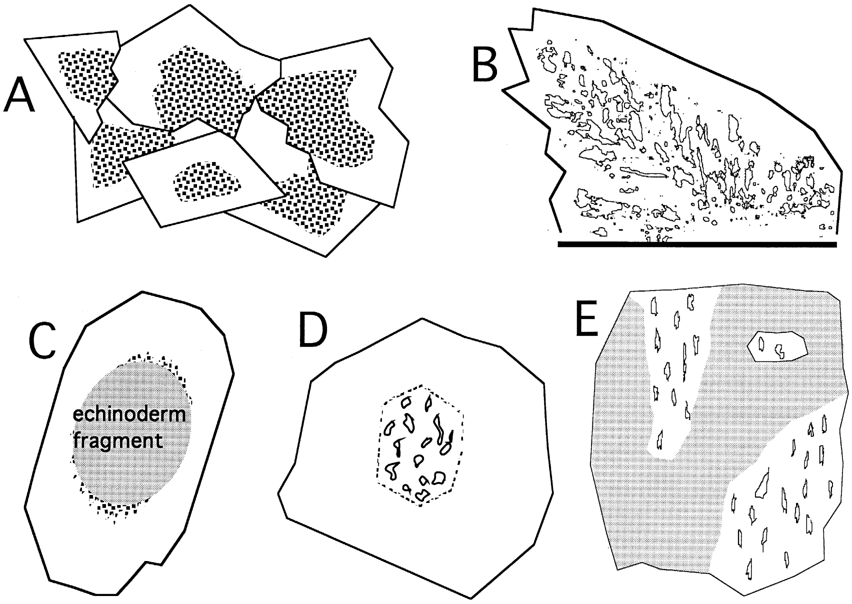


Fig. 9. Sketches of distribution of primary fluid inclusions, some of which might result from recrystallization of internal parts of crystals (modified from Goldstein and Reynolds, 1994). (A) Dolomite with cloudy cores; (B) Baroque dolomite with internal "fir-tree" arrangement of fluid inclusions; (C) Early calcite growth zone in syntaxial overgrowth on echinoderm fragment; (D) Cloudy core in calcite crystal; (E) Partially recrystallized detrital feldspar containing fluid inclusions in recrystallized parts of grain.

inclusions were trapped during initial growth or during recrystallization. Finally, it is common for detrital feldspars to recrystallize during diagenesis. Such recrystallization may result in inclusion-rich patches that are primary to the recrystallization of the grain (Fig. 9E).

Fluid inclusionists who work in the sedimentary realm must use petrographic methods to determine if fluid inclusions were trapped during initial growth of cement or during some later stage of recrystallization. Not doing so defeats the purpose of putting fluid inclusion entrapment into the context of a careful paragenetic framework. The most helpful approach for identifying fluid inclusion entrapment during recrystallization is careful study of petrographic relationships that are visible only by looking at compositional variation in the mineral chemistry. The compositional variation in a mineral that has not recrystallized will be reflected in either concentric or sector growth zoning (Fig. 10A). For minerals that have recrystallized, the primary compositional zoning will be cross cut by compositional areas reprecipitated during recrystallization (Fig. 10B and C). Therefore, fluid inclusionists concerned with most diagenetic minerals must evaluate the possibility of entrapment of primary fluid inclusions during recrystallization by evaluating the distribution of compositional domains in the crystal of interest. Methods useful in petrographically identifying compositional variation in cements include cathodoluminescence microscopy (Barker and Kopp, 1991; Van den Kerkhoff and Hein, 2001; Munz, 2001), back scattered electron imaging (Wojcik et al., 1994), UV epifluorescence (Burruss, 1991), staining (Dickson, 1965) and mild etching of polished specimens (Folk, 1980).

6.5. Petrographic model for diagenetic systems

Once fluid inclusion assemblages have been isolated, petrographic work alone can lead to significant interpretations about the environment of entrapment and the post-entrapment history of fluid inclusions (Goldstein, 1993). The first part of this approach requires isolation of FIAs, for it only can apply to

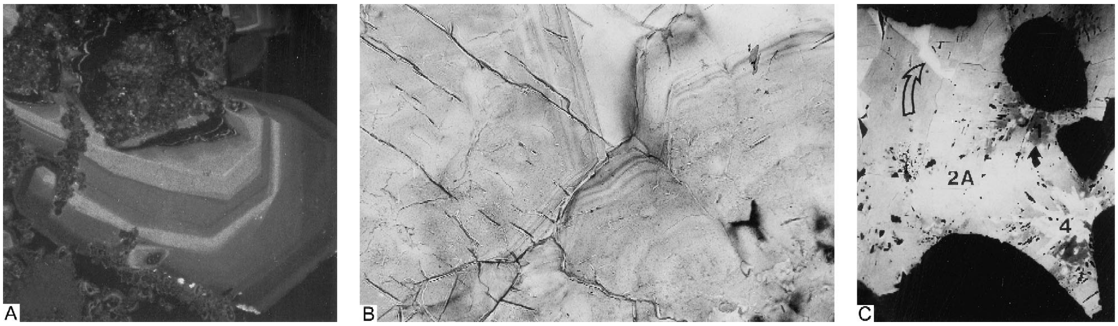


Fig. 10. Photomicrographs illustrating various types of distribution of compositional areas in carbonate minerals. (A) Cathodoluminescence photomicrograph illustrating concentric growth zoning in calcite (width is 300 μm); (B) Transmitted light photomicrograph of calcite stained with alizarin red S and Potassium ferricyanide, illustrating alternating concentric growth zones in outer parts of crystals and recrystallized patches in crystal interiors (see interior of crystal on left. Width is 0.88 mm; (B) Back scattered electron image of baroque dolomite/ankerite with radiating areas of recrystallization and fluid inclusion entrapment. Dark irregular core (filled arrow) is corroded and partially replaced by late bright phase (4) in radiating pattern. Intermediate brightness ankerite (2A) dominates. Numbers are as those in Wojcik et al. (1997). Width is 260 μm. Modified from Wojcik et al. (1997).

fluid inclusions that were initially entrapped under the same set of conditions. Furthermore, the reaction to reequilibration is most easily evaluated if fluid inclusions are of variable size and shape, so the inclusions of the FIA must be of variable size and shape for interpretations to be made.

Once an FIA has been isolated, it must be shown that the liquid phase of inclusions is aqueous and not hydrocarbon in composition. This is accomplished by studying samples using UV epifluorescence microscopy. If inclusions fluoresce, then they are composed of oil and this petrographic model does not apply, but if they lack fluorescence, then they are most likely to be aqueous in composition.

The next step is to examine the variability of liquid-to-vapor ratios among fluid inclusions of the FIA. If all-liquid fluid inclusions are observed, then the petrographic means discussed earlier must be used to rule out their origin from necking down after a phase change. If they have not formed from necking down after a phase change, then it must be shown that they are not significantly metastable, by showing that they are in the same size range as two-phase inclusions (not just the small inclusions), and by showing that bubbles cannot be nucleated by cooling in a kitchen freezer for high salinity inclusions, or in a refrigerator for low-salinity inclusions. If this can be shown, the liquid-filled fluid inclusions represent entrapment at low temperature, less than about 50°C.

After necking down after a phase change has been ruled out, the petrographer must then evaluate the consistency of the liquid-to-vapor ratios for two-phase fluid inclusions in the FIA. If vapor-to-liquid ratios are highly variable, then entrapment in a heterogeneous system is indicated. If vapor-to-liquid ratios are somewhat consistent, then entrapment at high temperature or near complete thermal reequilibration is indicated. If vapor-to-liquid ratios are so consistent that each fluid inclusion would yield the same homogenization temperature, then fluid inclusions were trapped at high temperature and have not been altered by thermal reequilibration.

The pressure can be determined in the gas phase of fluid inclusions through crushing the sample in an immersion medium (Roedder, 1970). If bubbles collapse upon crushing, then the fluid inclusion was either originally entrapped or reequilibrated at high temperature. If the bubble expands significantly, then inclusions were trapped or reequilibrated significantly below the surface. If the bubble remains the same size, the inclusions were trapped near the surface at one-atmosphere pressure.

The combination of these various tests are useful in identifying diagenetic environments of fluid inclusion entrapment and post-entrapment alteration. This model (Fig. 11) is not inclusive of all diagenetic systems but is useful in identifying formation in the low-temperature phreatic zone, the low temperature vadose zone, and the high-temperature, burial envi-

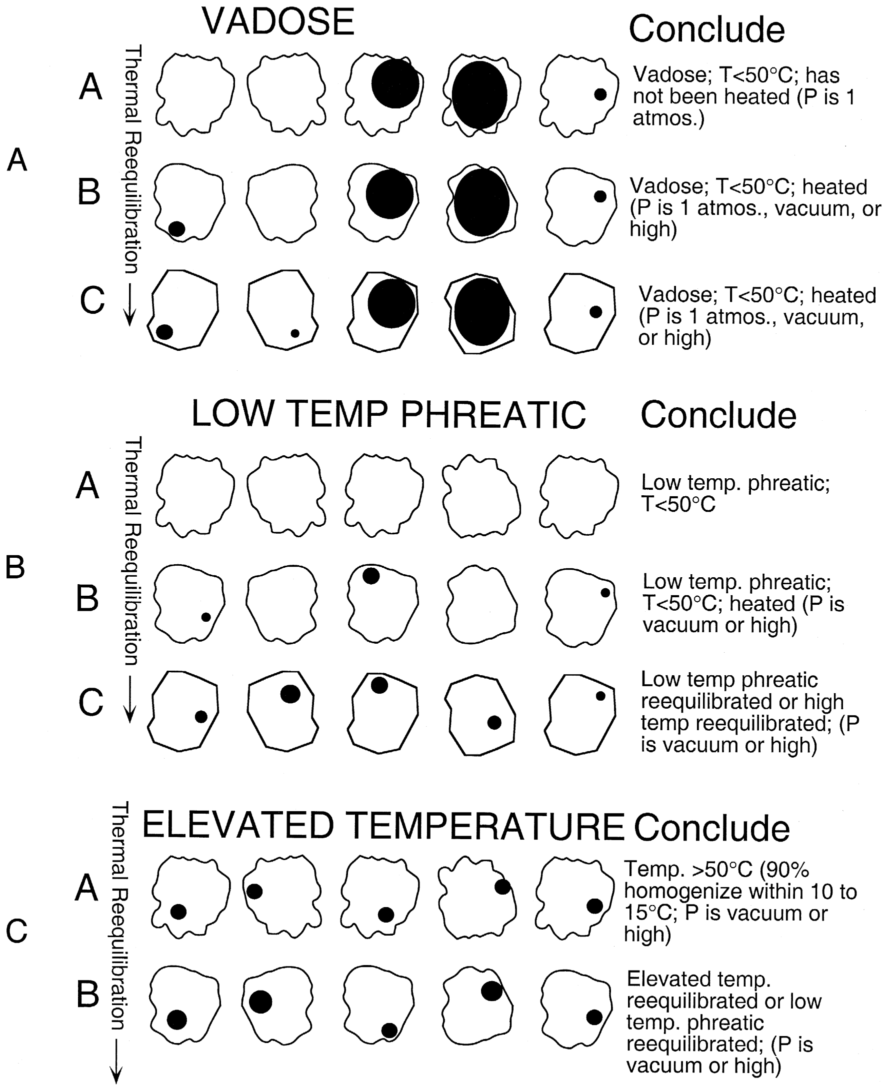


Fig. 11. (A) Schematic illustration of room-temperature distribution of vapor-to-liquid ratios within a fluid inclusion assemblage of vadose-zone origin. Conclusions refer to interpretations that can be made about diagenetic environment given the additional observations associated with each conclusion presented. Sample sizes and shapes are only diagrammatic. Assume that fluid inclusions within each assemblage are of various sizes and shapes. A – Assemblage before any thermal reequilibration. B – Assemblage after moderate thermal reequilibration. C – Assemblage after significant thermal reequilibration. (after Goldstein and Reynolds, 1994). (B) Schematic illustration of room-temperature distribution of vapor-to-liquid ratios within a fluid inclusion assemblage of low-temperature phreatic origin. Conclusions refer to interpretations that can be made about diagenetic environment given the additional observations associated with each conclusion presented. Sample sizes and shapes are only diagrammatic. Assume that fluid inclusions within each assemblage are of various sizes and shapes. A – Assemblage before any thermal reequilibration. B – Assemblage after moderate thermal reequilibration. C – Assemblage after significant thermal reequilibration. (after Goldstein and Reynolds, 1994). (C) Schematic illustration of room-temperature distribution of vapor-to-liquid ratios within a fluid inclusion assemblage of high-temperature origin. Conclusions refer to interpretations that can be made about diagenetic environment given the additional observations associated with each conclusion presented. Sample sizes and shapes are only diagrammatic. Assume that fluid inclusions within each assemblage are of various sizes and shapes. A – Assemblage before any thermal reequilibration. B – Assemblage after thermal reequilibration. (after Goldstein and Reynolds, 1994).

ronment. Furthermore, it can be use to identify later alteration through thermal reequilibration.

7. Types of fluids in inclusions

Most fluids in the diagenetic realm are incredibly complex in composition. One of the best examples of this is seawater, a highly concentrated fluid (about 3.5 wt.%) that has major amounts of, Na^+, Mg^{2+}, Ca^{2+}, K^+, Sr^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, Br^-, F^-, and B and minor amounts of many other elements. In addition, composition of organic and inorganic gases and hydrocarbon liquids are also quite complex. Working with phase equilibria and microthermometry requires that the fluid inclusionist either carefully characterize the composition of the fluid or make some assumptions as to what a good model might be for the composition of the fluid. Some of the most common model (simple) compositions and examples of the phase equilibria that would apply to their interpretation are summarized in the following section. Although it is well known that there is much more complexity than what is represented by these simple models, these models should at least provide a starting point for interpreting fluid inclusion phase behavior.

7.1. Freshwater

Relatively pure H_2O is common in sedimentary systems, especially near the surface and in shallow parts of basins. In sedimentary systems that have not been subject to hydrothermal activity, freshwater exists in the one-phase field, at a pressure above the vapor–liquid field boundary or boiling curve (Fig. 12). It is not until these fluids are trapped or reequilibrated in fluid inclusions at high temperature, and then cooled, that they reach the two-phase field boundary. The fresh-water system is best identified by its behavior during microthermometric cooling of fluid inclusions. The melting temperature of ice for these fluid inclusions is 0°C. At room temperature, fluid inclusions with this composition will have an aqueous liquid phase and may or may not have a bubble or a gas phase.

7.2. Methane

Relatively pure methane is common near the surface where it results from biogenic degradation of organic matter (fermentation or CO_2 reduction), and deeper in the subsurface where it results from thermogenic cracking of kerogen. In sedimentary systems, a single methane phase exists, above the -82.1°C critical point (Fig. 13). At room temperature, methane fluid inclusions commonly are identified by their dark and single-phase appearance. Upon cooling, these inclusions are easy to identify because they commonly separate into distinct gas and liquid phases below the critical point and melt at the triple point for methane at -182.5°C. At room temperature, crushing studies show that these inclusions exist at high pressures.

7.3. H_2O–NaCl

Aqueous solutions dominated by NaCl are common in many natural systems of the sedimentary realm. In fact, this system is so common and such a good approximation for even more complex salt solutions, that when the composition is not well known, inclusionists commonly interpret their fluid inclusion salinities as if they were from the H_2O–NaCl system, calculating salinities in wt.% NaCl equivalent. With corrections for salinity, these fluids behave similarly to the pure water system in that natural, non-hydrothermal pore fluids exist at a pressure well above the boiling curve (Fig. 12). Nucleation of a bubble only occurs after inclusion fluids have been trapped or reequilibrated at higher temperature and then cooled. Fluid inclusions from this model system are typically easily identified. The presence at room temperature of halite daughter minerals is the most obvious indication. Low-temperature microthermometric phase behavior is even more useful. Look for eutectic melting behavior between the metastable eutectic at -28°C and the stable eutectic at -21.2°C. During warming of frozen fluid inclusions, the identity of the last phase to melt and the temperature of its melting (in the presence of a bubble) are useful for evaluating the salinity of the solution (Fig. 14). Inclusionists should determine if the last phase to melt is ice, hydrohalite, or halite,

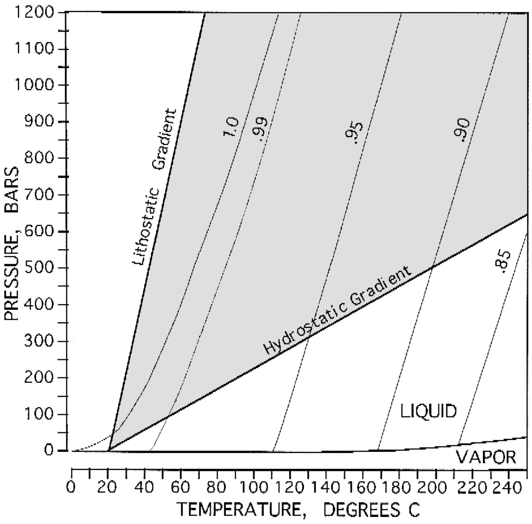


Fig. 12. P–T projection of the H_2O system for diagenetic P–T conditions. Labeled contours are lines of constant density in g/cm^3. The shaded area shows P–T conditions that can be found in the diagenetic realm (modified from Goldstein and Reynolds, 1994).

and evaluate the temperature of that melting to determine salinity.

7.4. H_2O–NaCl–$CaCl_2$

Aqueous solutions dominated by NaCl and $CaCl_2$ are well known deep in sedimentary basins where brines have undergone significant rock–water interaction. Although brine composition deep in basins can be quite complex and may have many more components, this class of brines serves as a good model for the composition of many sedimentary brines. With corrections for salinity and salt composition, these fluids behave similarly to the pure-water system in that natural, non-hydrothermal pore fluids exist at a pressure well above a boiling curve (Fig. 12). Nucleation of a bubble only occurs after inclusion fluids have been trapped or reequilibrated at higher temperature and then cooled. The applicability of this system, to your inclusions is best identified by microthermometric cooling of fluid inclusions. After such inclusions have been frozen, they typically yield eutectic melting temperatures near 50°C. Eutectic melting temperatures below about 40°C are consistent with the presence of abundant divalent cations (Davis et al., 1990). The equilibrium eutectic for this system is at −52°C, so definite eutectic melting at this temperature would be a positive indication that this system applies. Determining ion ratio and salinity using microthermometric observations requires observation of the eutectic, an intermediate melting event and a final melting event. In practice, making these observations with confidence is difficult.

7.5. Seawater

Seawater is one of the most important fluids in the sedimentary realm. There are many diagenetic systems that can clearly be tied to the marine sediment–water interface. Such ties are cross-cutting and stratigraphic relationships that either exclude the possibility of fluids other than those derived from seawater, or that directly link diagenesis to a marine process such as deposition of marine internal sediment or submarine erosion. Typically, such prior geologic knowledge, that the seawater system is the one to apply, is the only evidence used to apply the seawater model to fluid inclusions. With corrections for salinity and salt composition, seawater-derived fluids behave similarly to the pure-water system in that natural, non-hydrothermal pore fluids exist at a pressure well above the boiling curve (Fig. 12). Nucleation of a bubble only occurs after inclusion fluids have been trapped or reequilibrated at higher temperature and then cooled. Typically, the salinity of seawater must be determined by the temperature of final melting of ice (Fig. 15).

7.6. H_2O–NaCl–CH_4

Saltwater solutions containing dissolved methane are important particularly in the subsurface of sedimentary basins. In general, solubility of methane into brine is relatively low, so it is common for methane to reach saturation with respect to aqueous solutions. With increasing depth in a basin (higher temperature and pressure) methane's solubility increases (Fig. 16). Increase in salinity decreases the solubility of methane, so understanding this system requires careful characterization of the composition of fluid inclusions (Fig. 16). Solubility curves plotted in P–T

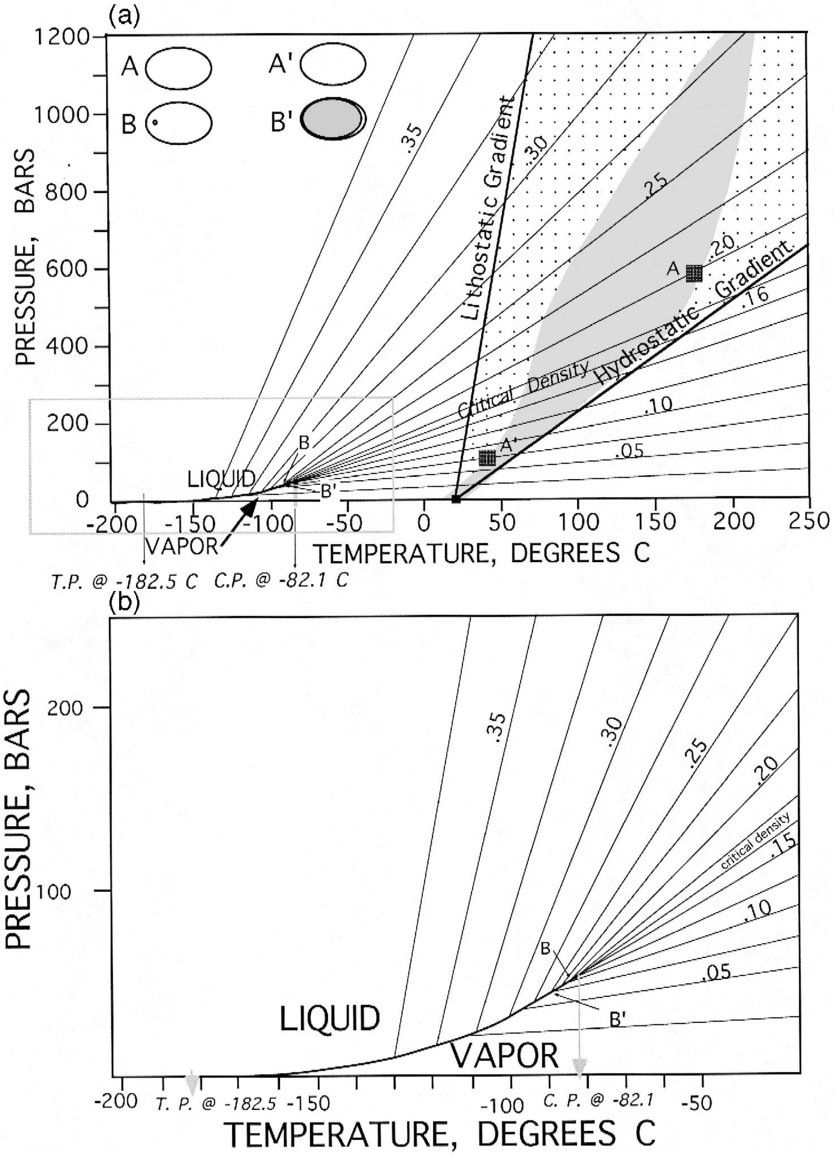


Fig. 13. (a) P–T plot of the CH_4 system. Labeled contours are lines of constant density in g/cm^3. The light shaded area shows the P–T conditions found in the diagenetic realm; for comparison, the darker shaded area shows the P–T regime present in nearshore Gulf basin sediments (from Hanor, 1980). The area outlined by the rectangle is enlarged in (b). Critical point is at −82.1°C, 46.3 bars; triple point is at −182.5°C (modified from Mullis, 1979).

space are essentially the same as bubble-point curves, the curves defining immiscibility in the range of geologic interest. Entrapment of fluid inclusions from an immiscible system of methane and saltwater is likely to lead to entrapment of an end-member methane-rich fluid (appears as one phase and dark at room temperature), an end-member water-rich fluid (appears as liquid with a small bubble), and as mixtures of the two. Phase equilibria of the methane-rich end member would approximate that of pure methane (Fig. 13). If the aqueous-rich end member of an immiscible system were entrapped, or

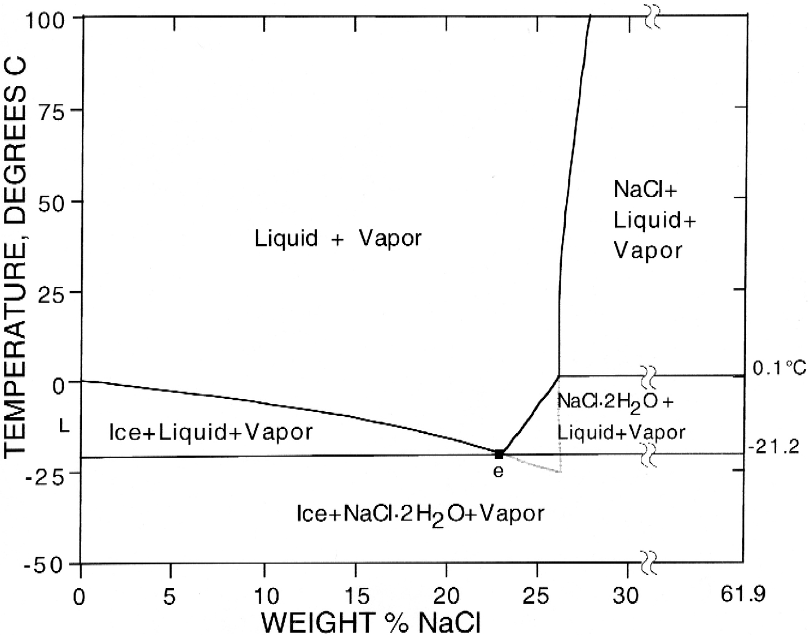


Fig. 14. (A) *T–X* plot for the lower temperature, lower salinity portions of the system H_2O–NaCl. Each point on this diagram is at equilibrium vapor pressure. Produced from Crawford (1981), Roedder (1984) and Hall et al. (1988).

an aqueous fluid inclusion from a system undersaturated with respect to methane were entrapped, the phase equilibria of a fluid inclusion would follow a predictable path (Fig. 17). Evidence that is useful in identifying the presence of the H_2O–NaCl components are similar to the criteria discussed above for the H_2O–NaCl system. Identifying the presence of methane uses criteria similar to those developed for the methane system above. In addition, some inclusions may form clathrates upon cooling, and upon crushing water-rich inclusions at room temperature, bubbles in water-rich inclusions would be found to be under pressure. Application of the specific phase equilibria for each fluid inclusion requires relatively thorough characterization of methane content and salinity.

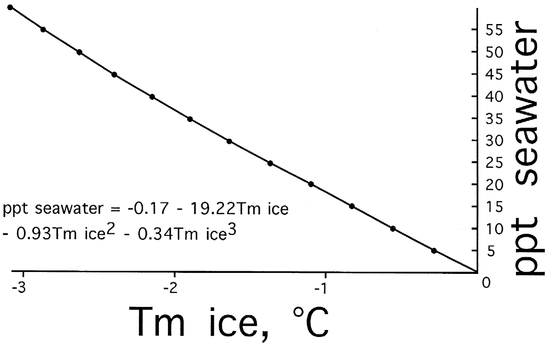


Fig. 15. Seawater freezing point depression constructed from data of Lyman and Fleming (1940). Note that data do not extend above a salinity of 55 ppt. (after Goldstein and Reynolds, 1994).

7.7. Petroleum

Petroleum in fluid inclusions is best identified by its tendency to fluoresce when excited with ultraviolet light. Some petroleum fluid inclusions do not fluoresce brightly enough to be detected with standard microscopic methods; these include some condensates (gas-rich inclusions with a thin rim of oil) and some oil inclusions that have lost their volatiles. Although most oil inclusions are colorless in transmitted light, some may be identified by yellowish or brownish color. Other fluid inclusions with oil can be identified by particularly odd low-temperature microthermometric behavior that is inconsistent with

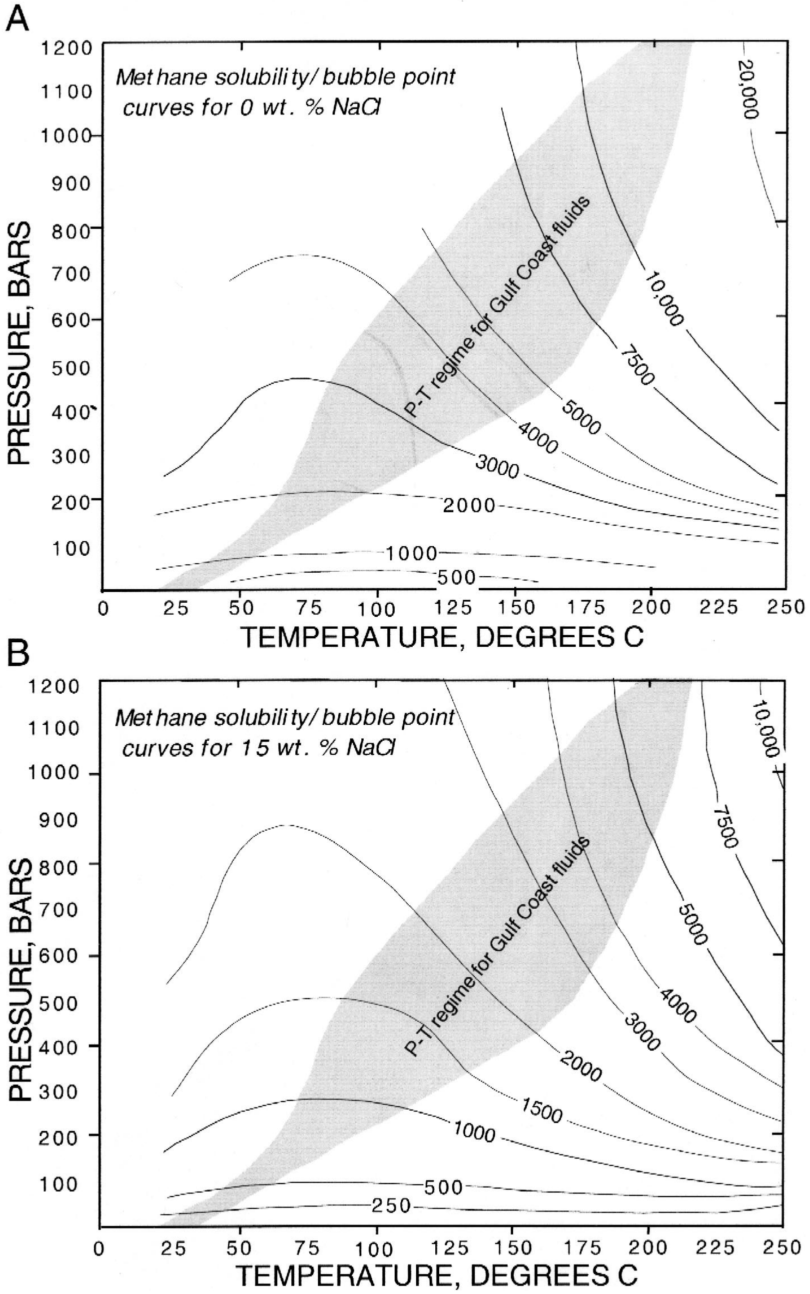


Fig. 16. Intersections of isoplethic planes for H_2O-rich fluid with various amounts (ppm) of CH_4 with the H_2O–CH_4 immiscibility surface projected onto a single P–T diagram. (a) H_2O–CH_4 fluids containing no NaCl. (b) H_2O–CH_4 fluids containing 15 wt.% NaCl. Modified from Hanor (1980).

other fluids. Phase behavior of oil fluid inclusions can be quite difficult to model because petroleum compositions are so complex (Munz, 2001). Given petroleum fluid inclusions with quite different compositions, one would expect markedly differing phase behavior (Fig. 18). This means that careful character-

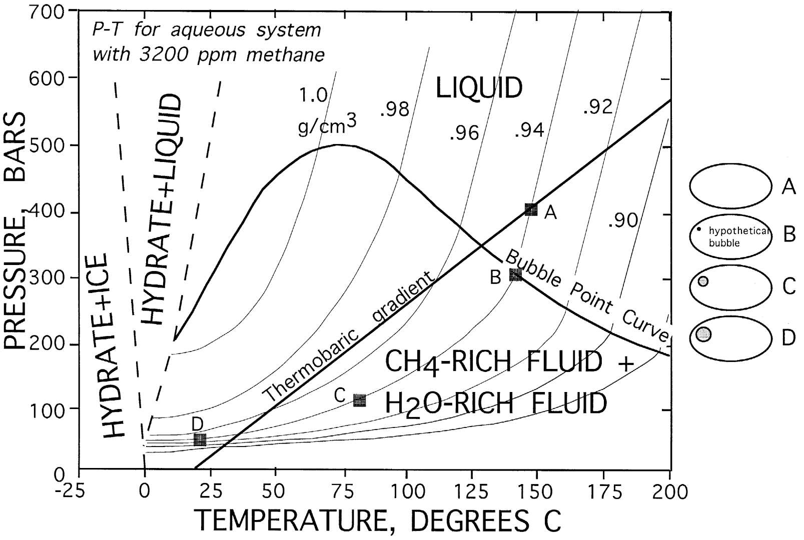
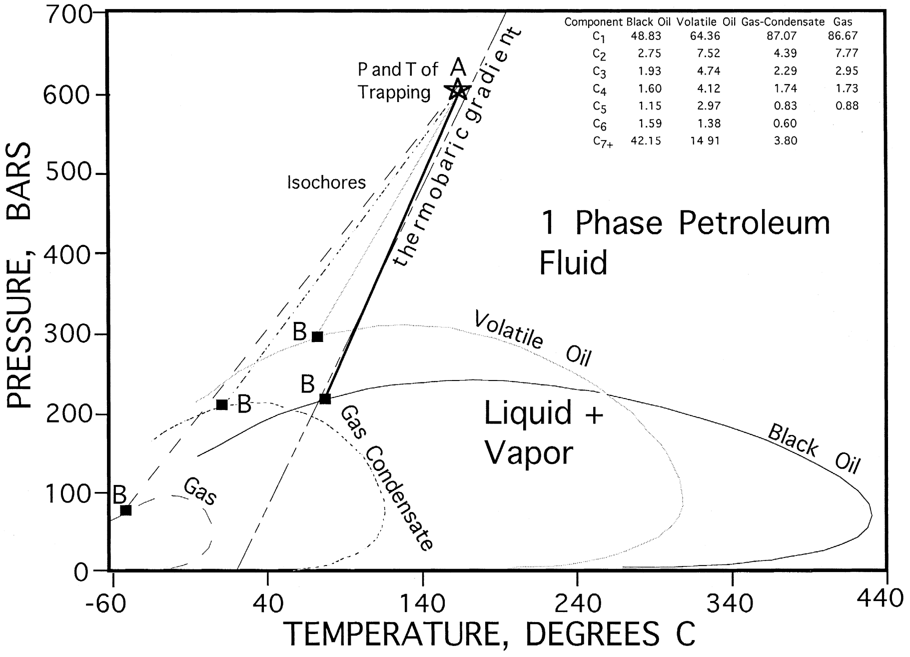


Fig. 17. *P–T* phase diagram for H_2O–CH_4 system with 3200 ppm CH_4. Sketches of inclusions to right of plot schematically show proportions of the phases in an inclusion at several *P–T* conditions (A, B, C, D). Thermobaric gradient is 32°C/100 bars. Modified from Hanor (1980).



Component	Black Oil	Volatile Oil	Gas-Condensate	Gas
C_1	48.83	64.36	87.07	86.67
C_2	2.75	7.52	4.39	7.77
C_3	1.93	4.74	2.29	2.95
C_4	1.60	4.12	1.74	1.73
C_5	1.15	2.97	0.83	0.88
C_6	1.59	1.38	0.60	
C_{7+}	42.15	14 91	3.80	

Fig. 18. *P–T* phase diagram showing immiscibility curves and isochores of four "generic" petroleum fluids without H_2O, derived from commercially available software (EQUI-PHASE: D.B. Robinson Research, Edmonton, Alberta, Canada) modified from Burruss (1992). Mol% of components modeled are presented in the upper right. Within the envelopes two petroleum fluids would coexist; outside the curves only a single petroleum fluid would exist. The thermobaric gradient shown is 25°C/100 bars. As pointed out by Burruss (1992), with decreasing mol% CH_4 and with increasing mol% of the high molecular weight components (C7 and higher), the curves shift to higher positions, and the slopes of the isochores increase (the fluid becomes less compressible).

ization of compositions should be needed to accurately characterize the phase equilibria of fluid inclusions in this system.

8. Geothermometry from fluid inclusions

Procedures for interpreting the degree to which aqueous fluid inclusion assemblages preserve original homogenization temperatures can be complex. Flow charts of procedures and logic are helpful in evaluating the observations from each FIA (Figs. 19–23).

8.1. FIA with consistent homogenization temperatures

The FIAs that are best for interpreting temperature of entrapment consist of variably sized and shaped aqueous inclusions in which 90% of the homogenization temperatures are within 10–15°C (Fig. 20). These simple observations rule out problems with thermal reequilibration, and thus, each homogenization temperature measured, in such an FIA, is a record of the minimum entrapment temperature of the fluid inclusion. The degree to which these homogenization temperatures underestimate true entrapment temperature depends on the amount of gas dissolved in aqueous inclusions, the compositional control on the isochoric slope, and the pressure of entrapment. Ultimately these factors control the "pressure correction" that corrects homogenization temperature to true entrapment temperature.

To correct homogenization temperature to entrapment temperature, the composition of fluid inclusions must be constrained so that the position of the bubble point or vapor–liquid phase boundary is known, and so that the isochoric path is known. Never apply a pressure correction unless the composition of the fluid inclusion is known well enough to determine the fluid inclusion's path in P–T space. For gas-poor aqueous inclusions, the correction is typically large and is applied by making an assumption about the pressure of entrapment or thermobaric gradient along which the fluid inclusion was entrapped (Fig. 24). For gas-rich aqueous inclusions, a large pressure correction is typically not needed because homogenization takes place at high pressure, close to the conditions of entrapment (Fig. 25).

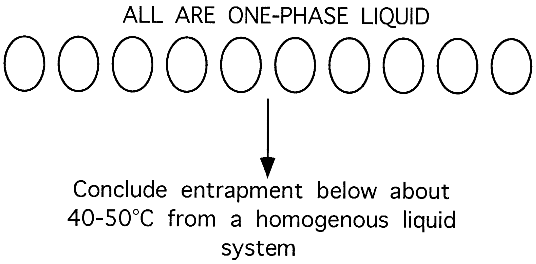


Fig. 19. Flow chart illustrating procedures for interpreting a fluid inclusion assemblage consisting of all-liquid fluid inclusions (after Goldstein and Reynolds, 1994).

8.2. FIA with highly variable homogenization temperatures

If within an FIA, phase ratios among fluid inclusions (and homogenization temperatures) are highly variable, most homogenization temperatures are meaningless because the variability likely resulted from necking down after a phase change or heterogeneous entrapment from an immiscible system (Figs. 22 and 23). If necking down after a phase change can be ruled out, the explanation remaining is immiscibility. With immiscible entrapment of aqueous liquid and gas inclusions at high temperature, the liquid-rich aqueous end members could give consistent homogenization temperatures (if they have not been reequilibrated). Those homogenization temperatures are equal to the entrapment temperatures and do not need to be corrected for pressure. In the case of evidence for oil/water immiscibility, if the end member oil-rich fluid inclusions and the end-member aqueous-rich fluid inclusions yield the same homogenization temperatures, then the system was gas saturated and the homogenization temperatures are equal to entrapment temperature. Finally, if in an FIA, all-liquid inclusions are present and do not result from significant metastability or necking down after a phase change, then entrapment temperature was less than about 50°C (Fig. 22).

8.3. FIA with slightly variable homogenization temperatures

On the other hand, many FIAs produce only slightly variable homogenization temperatures (Figs.

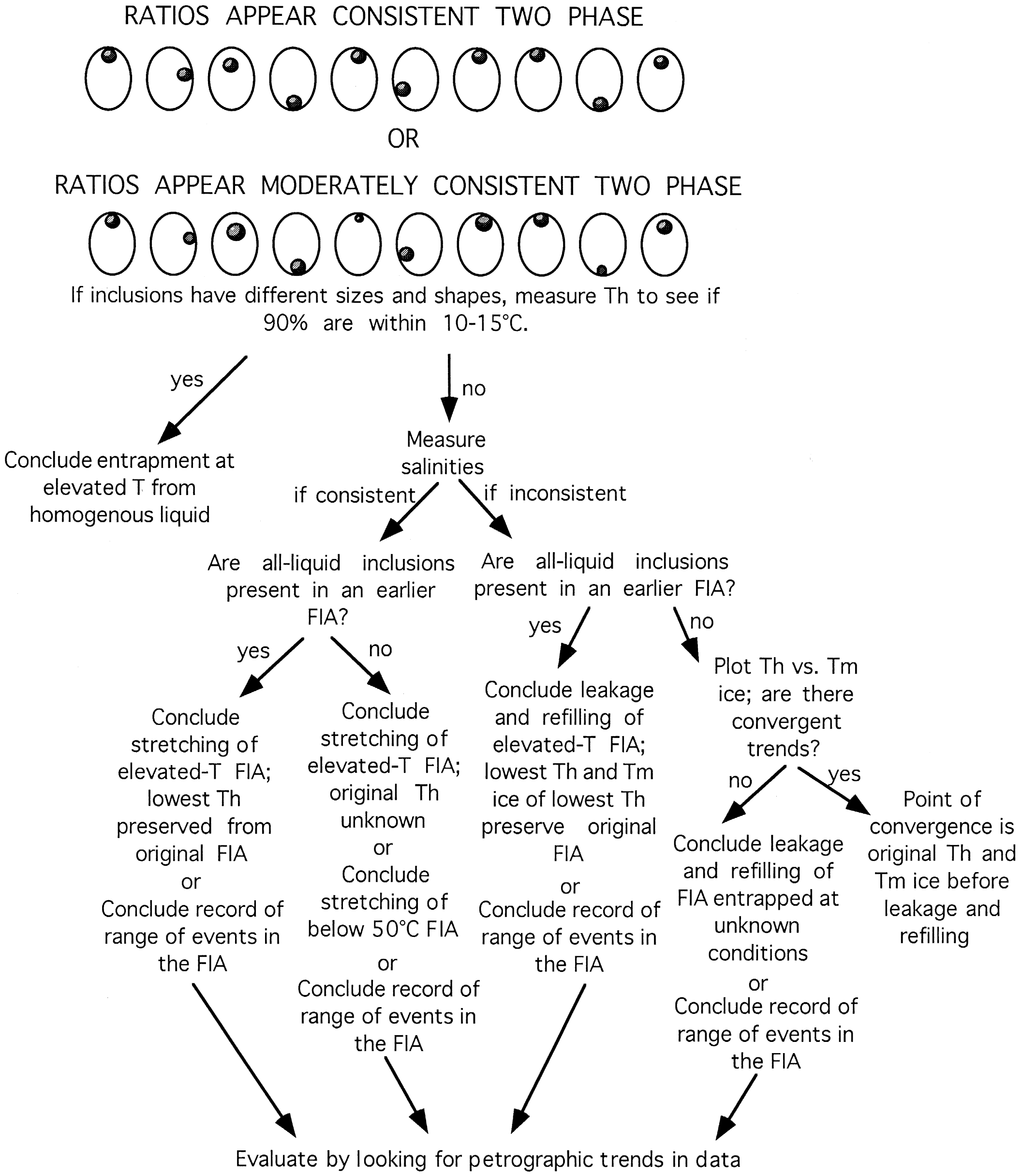


Fig. 20. Flow chart illustrating the procedure for interpreting a fluid inclusion assemblage with apparently consistent or moderately consistent phase ratios. Inclusions are of various shapes and sizes (after Goldstein and Reynolds, 1994).

20 and 21). Again, if all-liquid inclusions are present and do not result from significant metastability or necking down after a phase change, then the entrapment temperature was less than about 50°C (Fig. 21). In systems lacking all-liquid inclusions, other methods must be applied to evaluate the degree to which the original fluid inclusions are preserved or have reequilibrated.

It is well known now that two mechanisms of thermal reequilibration are important, stretching, and

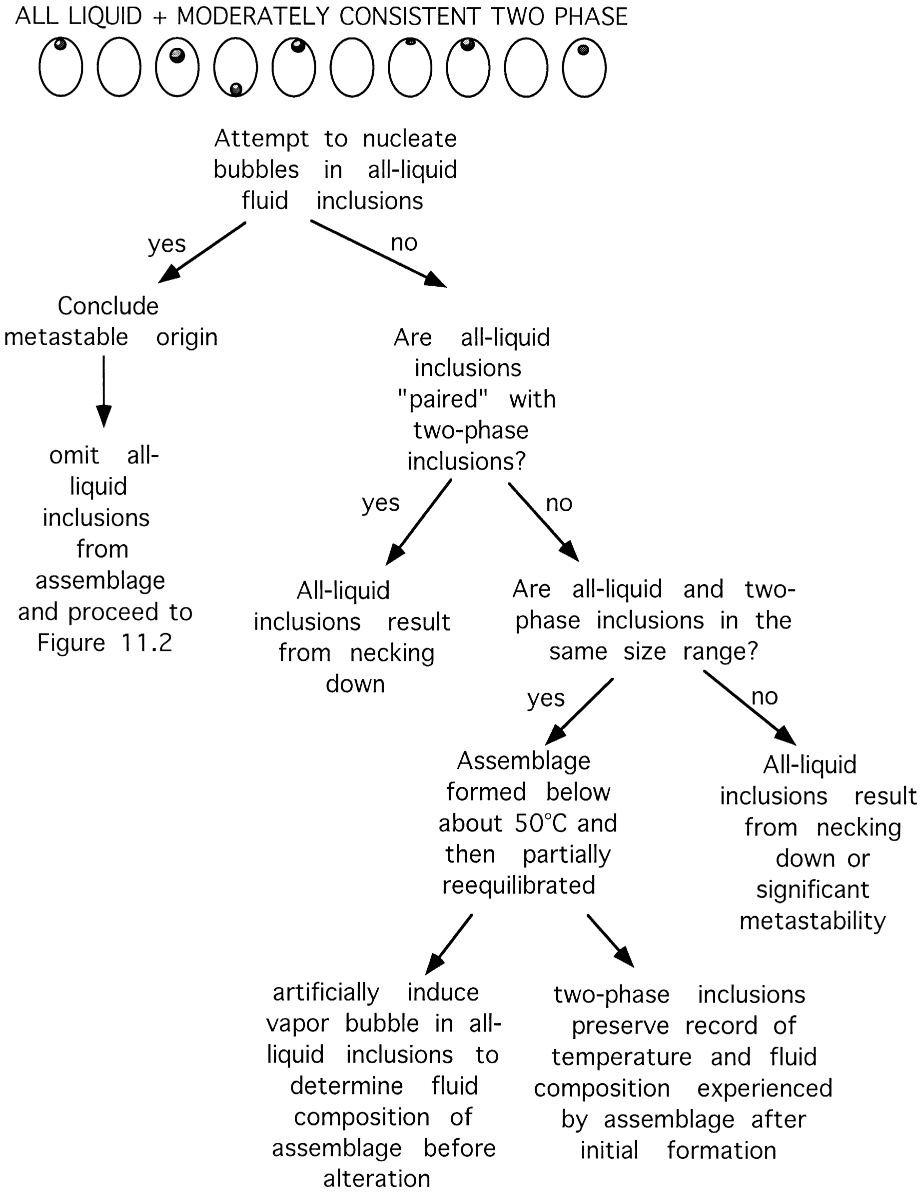


Fig. 21. Flow chart illustrating procedure for interpreting fluid inclusion assemblage with moderately consistent phase ratios together with all-liquid fluid inclusions. Inclusions are of various shapes and sizes (after Goldstein and Reynolds, 1994).

leakage and refilling. It is also well known that in many sedimentary basins, there is a positive correlation between depth (temperature) and salinity of pore fluids (Hanor, 1984). Given a history of thermal reequilibration of fluid inclusions, one would predict that some fluid inclusions would stretch and that others would leak and refill, producing FIAs with inclusions that lie along convergent trends. The point of convergence would indicate the homogenization temperature and salinity prior to reequilibration of the fluid inclusions (Fig. 26). The point of convergence is a minimum entrapment temperature for the

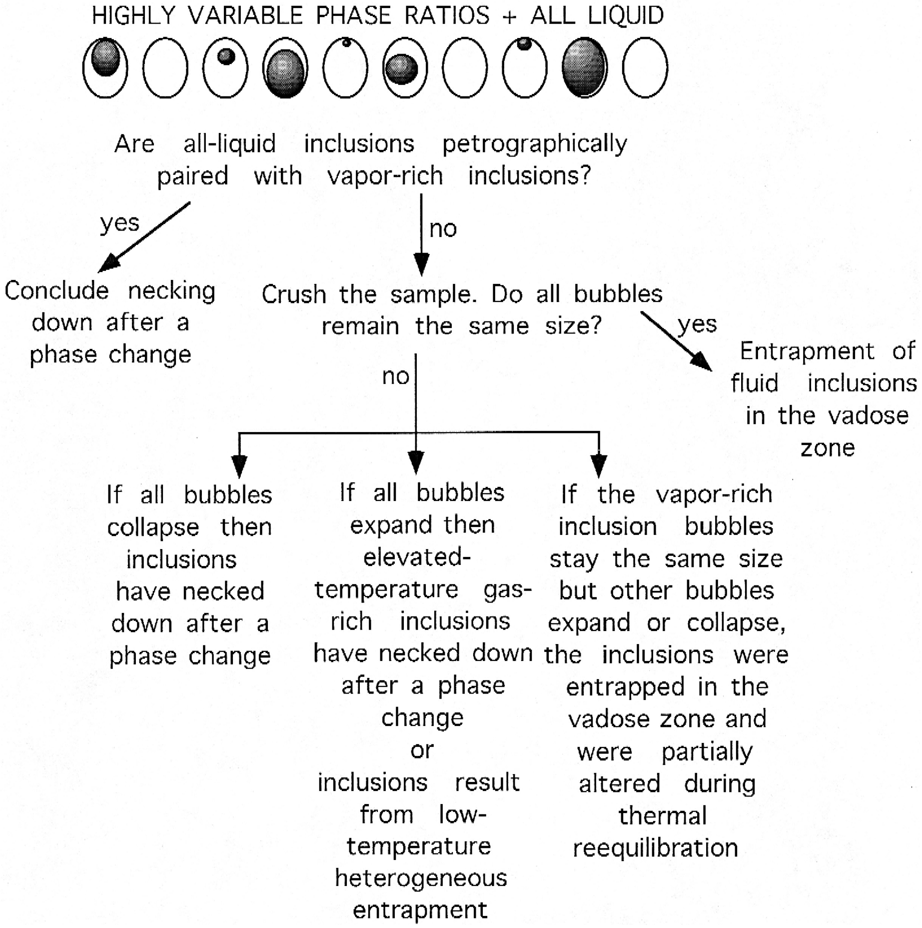


Fig. 22. Flow chart illustrating procedure for interpreting a fluid inclusion assemblage consisting of all-liquid fluid inclusions together with inclusions of highly variable phase ratio. Inclusions are of various shapes and sizes (after Goldstein and Reynolds, 1994).

FIA before reequilibration and can be used for application of a pressure correction to interpret temperature of entrapment.

For some FIAs, temporal resolution is too low to sample an instant in time. For these, further analysis of the petrographic distribution of homogenization temperatures within the FIA are helpful in evaluating data. Given a thick growth zone containing primary fluid inclusions, one might compare the homogenization temperatures from the inner part of the zone to those of the outer part of the zone. Consistent increases in homogenization temperatures outward indicate an increase in temperature through time. A consistent decrease in homogenization temperature outward indicates a decrease in temperature through time (Fig. 27).

Finally, the tendency for fluid inclusions to reequilibrate from overheating, yields a statistical probability for partial reequilibration of fluid inclusions in weak minerals at peak temperature. If one were to measure homogenization temperatures of all inclusions in a sample of calcite, it is likely that its uppermost mode, or its highest FIA, would closely approach, but not quite reach the maximum temperature experienced (Barker and Goldstein, 1990). Thus, in a soft mineral like calcite, the highest-temperature FIA, or highest mode in all the homogenization temperature data would have a statistical probability

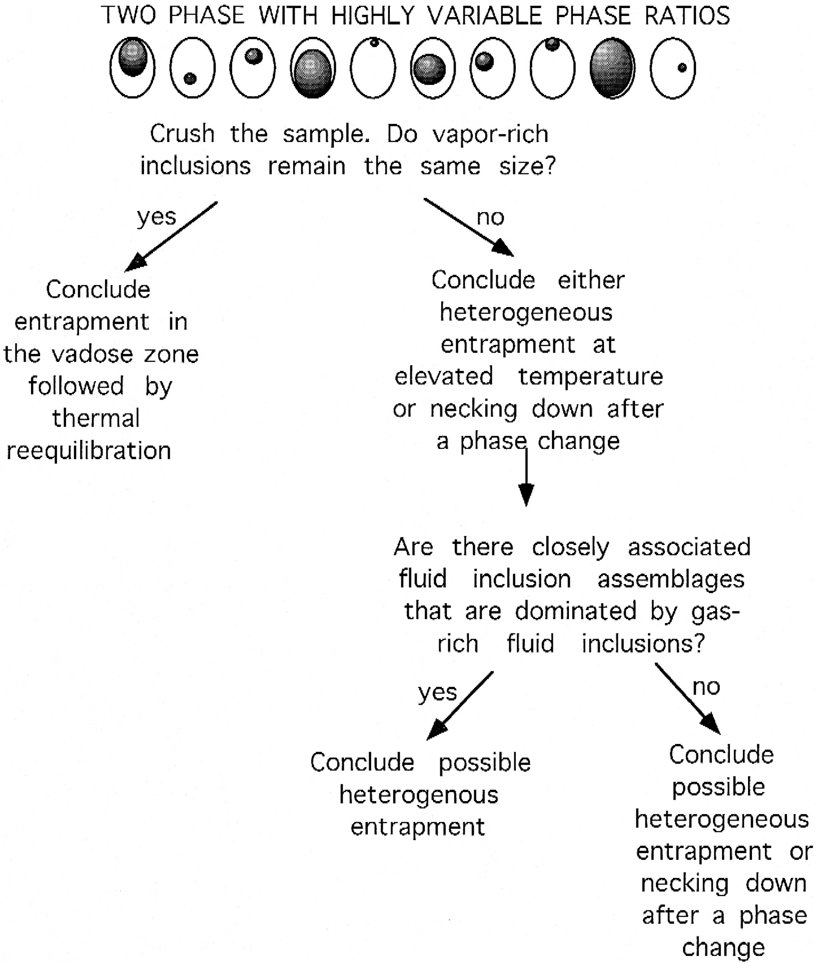


Fig. 23. Flow chart illustrating procedure for interpreting a fluid inclusion assemblage with highly variable phase ratios and without all-liquid fluid inclusions. Inclusions are of various shapes and sizes (after Goldstein and Reynolds, 1994).

of yielding a close approach to the maximum temperature the rock has experienced (Fig. 28). This value could have nothing to do with the original conditions of entrapment of the fluid inclusions, but yield data on thermal history important in reconstruction of thermal, tectonic and stratigraphic history.

9. Geobarometry from fluid inclusions

Fluid inclusions are one of the only geobarometers available for the sedimentary realm. Because pressure can be translated to burial depth or water depth, there is a variety of environmental information and burial history information that can be gleaned from fluid inclusions.

9.1. Minimum pressure of entrapment

Minimum pressure of fluid inclusion entrapment can be attained simply through crushing of samples with fluid inclusions, under an immersion medium, and using Boyle’s Law to calculate pressure before crushing. This pressure, at room temperature, greatly underestimates the true entrapment pressure.

Alternatively, if the composition of the fluid inclusion and its homogenization temperature has been determined, the pressure at the point of homogeniza-

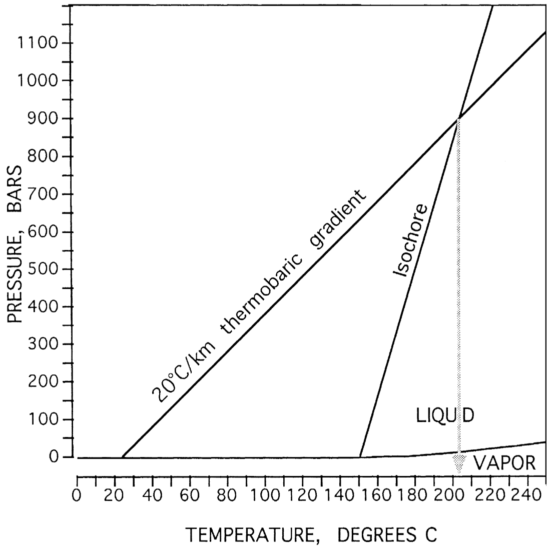


Fig. 24. Phase diagram for pure water with one of the isochores for pure water and the liquid–vapor field boundary. If a fluid inclusion were to homogenize at 150°C, and were composed of pure water, the inclusion must have been entrapped along the isochore drawn. If one were to apply a pressure correction based on a present day thermobaric gradient of 20°C/100 bars, one would interpret entrapment temperature to be 203°C.

tion can be determined This pressure will greatly underestimate the pressure of entrapment in gas-poor aqueous inclusions, but may approach the pressure of entrapment in aqueous inclusions trapped with significant dissolved gas.

9.2. Entrapment pressure with consistent homogenization temperatures

Given FIAs consisting of fluid inclusions with variable sizes and shapes, and yielding consistent homogenization temperatures, the pressure of entrapment can be determined. To determine pressure of entrapment, one must first determine the composition and homogenization temperature of the fluid inclusions. This defines an isochoric path along which the fluid inclusions had been entrapped. Similar to what was done above to determine temperature of entrapment (Figs. 24 and 25), an assumption must be made about the thermobaric gradient at the time of entrapment, or the temperature at the time of entrapment. The points at which these assumptions intersect the isochore defines the pressure of entrapment.

9.3. Entrapment pressure with evidence for immiscibility

In many of the low-temperature systems preserving all-liquid fluid inclusions, gas-rich fluid inclusions are also preserved. These gas-rich inclusions contain immiscible gases that were trapped as separate phases. Because temperature of entrapment is similar to lab temperature, crushing the samples to determine the pressure in gas-rich inclusions is a direct measure of the pressure of entrapment. Such analyses have been applied successfully to identify the vadose zone (Goldstein, 1990), depth and timing of near-surface diagenesis (Newell and Goldstein, 1999) and should be useful in reconstructing water depth in basins with evaporites, and with other subaqueous precipitates (Goldstein and Reynolds, 1994)

For some systems that existed at high temperature, there is abundant evidence for immiscibility in which a gas phase had separated from an aqueous phase. For these systems, petrographic evidence must be used to support the occurrence of immiscibility. Then, the gas-rich fluid inclusion end member must be found, its composition determined, and its homogenization temperature measured. These data define an isochore along which the inclusions were

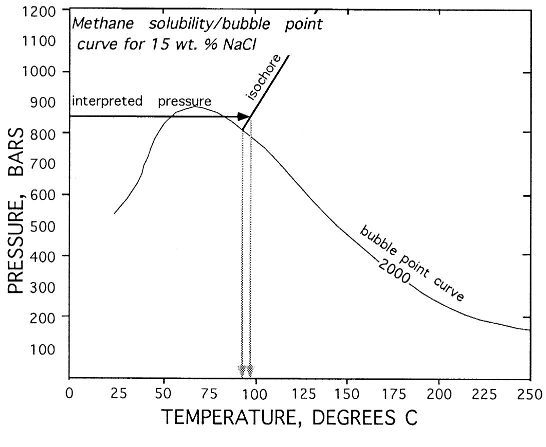


Fig. 25. Phase diagram illustrating bubble point curve for 2000 ppm methane in 15 wt.% NaCl solution. Isochore drawn is for homogenization temperature at about 92°C. The isochore that projects from the 2000 ppm bubble point curve is for an interpretation of 2000 ppm methane present in the inclusion. Prior knowledge of pressure of entrapment of 850 bars is used to interpret the temperature of entrapment of 96°C.

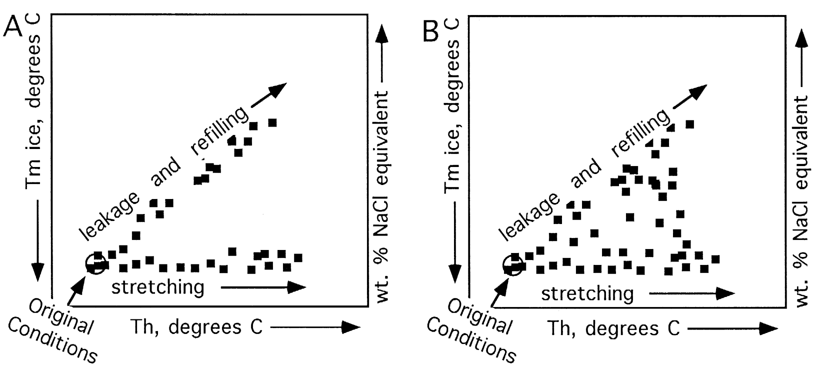


Fig. 26. Bivariate plots of T_h and T_m ice from moderately variable FIAs may yield convergent trends that converge on the conditions of initial FIA entrapment, and define leakage and refilling trends that reflect the conditions experienced during thermal reequilibration of inclusions during progressive burial heating. (A) Mechanism of reequilibration for each inclusion does not change. (B) Mechanism of reequilibration for each inclusion varies (after Goldstein and Reynolds, 1994).

entrapped. Then, the aqueous-rich end member must be found. Since it was entrapped from an immiscible system, its homogenization temperature is equal to the entrapment temperature. The point of intersection of the entrapment temperature and the isochore for the gas-rich end member inclusion defines the pressure of entrapment (Fig. 29). Alternatively, if the composition of the aqueous-rich end member can be determined, then a bubble point curve can be con-

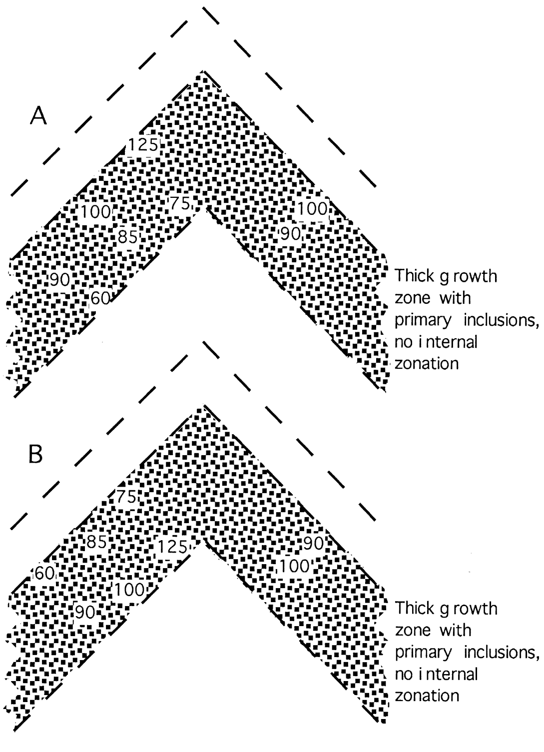


Fig. 27. Schematic illustration of fluid inclusion Th data distributed throughout a single thick growth zone. (A) Increase in T_h outward indicates increase in temperature through time. (B) Decrease in T_h outward indicates trend of decreasing temperature through time (after Goldstein and Reynolds, 1994).

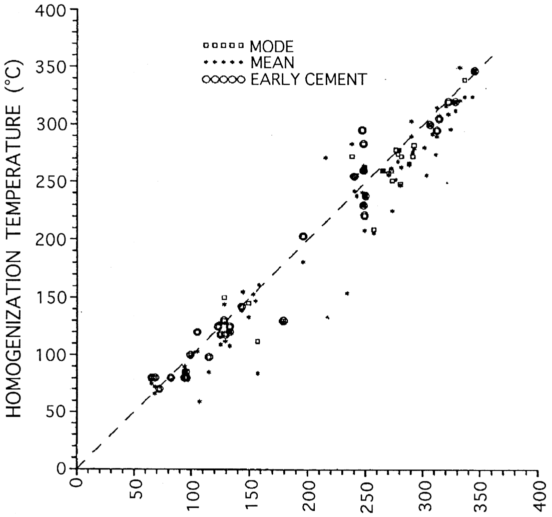


Fig. 28. Scatter plot of aqueous T_h data from calcite (means or upper mode) versus the present peak temperature. Dashed line of 1:1 correlation is for reference. The early cements are noted for comparison with later cements and cements of unclear origin. Notice how T_h data closely approach present peak temperature (after Barker and Goldstein, 1990).

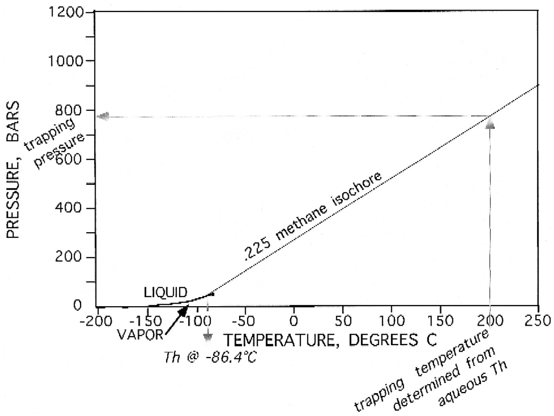


Fig. 29. Given methane–water immiscibility, the unique pressure and temperature of fluid inclusion entrapment can be determined. If the aqueous end member homogenizes at 200°C, then the temperature of trapping is 200°C. If the methane phase of the methane-rich end member homogenizes to liquid at −86.4°C (ignoring the invisible water), then the inclusions were entrapped along the .225 methane isochore. The pressure at which this isochore intersects the entrapment temperature is the trapping pressure for the fluid inclusions (after Goldstein and Reynolds, 1994).

structed for the system. The pressure on that bubble point curve at the temperature of homogenization is the pressure of entrapment.

Finally, given immiscibility of two phases, such as an oil phase and an aqueous phase at high temperature, careful characterization of the composition of each fluid might allow for characterization of the *PVT* properties of each. If true homogenization temperature were measured for each, then it might be possible to construct *P–T* paths along which each was entrapped (isochores). The point of intersection of these could indicate the temperature and pressure of entrapment. It is important to remember that application of this approach would be quite difficult, requiring thorough characterization of the composition of the fluid inclusions.

10. Fluid inclusions and global change

One of the most important areas of inquiry facing us all is future change in Earth's surface environment. One of the only ways of predicting the future is in understanding the past, and fluid inclusions will figure prominently into this type of research. One of the important questions about the past deals with change in atmosphere–ocean chemistry through time. Fluid inclusions of seawater in marine carbonate minerals are unique samples that may provide us with a record of past change in composition of the seawater–atmosphere system (Johnson and Goldstein, 1993). Fluid inclusions in marine evaporites provide a similar, though less directly preserved, record of past change in the composition of the seawater–atmosphere system (Tim Lowenstein, personal communication).

Further, it is possible that the composition of earth's atmosphere can be analyzed directly by extracting fluid inclusions. One example is the preservation of air bubbles in amber (Berner and Landis, 1988), but there are problems with preservation of original compositions in this matrix. A better possibility exists in cumulate halite crystals, which formed as floating rafts at the water–air interface. These crystals are well known to contain fluid inclusions of trapped air providing an opportunity for analysis of ancient atmosphere chemistry (Lowenstein et al., 1994). Speleothems are also well known to contain inclusions of trapped air (Goldstein, 1986), but typically the air in caves deviates from that of the open atmosphere, so any quantitative work on the composition of ancient air in speleothems will have to reconstruct open atmosphere composition from cave atmosphere composition.

Fluid inclusions from non-marine settings also provide direct and indirect records of paleoclimate. In lake systems, it is well known that fluid composition is related to relative aridity, essentially the water budget. Fluid inclusions in lacustrine evaporites provide exceptional records of overall salinity and composition, useful in reconstructing the relative aridity of climate (Lowenstein et al., 1994, Wenbo et al., 1995). Benison et al. (1998) used laser Raman spectroscopy to evaluate pH of fluid inclusions in lacustrine halites, which also has implications for residence time of fluids in ancient lakes. Other work on fluid inclusions in speleothems has produced isotopic data on meteoric fluids, useful in reconstructing paleoclimate signals (Harmon et al., 1979). Further, fluid inclusions in evaporites and lake tufas could also provide useful data on depth of lake waters which could be useful in understanding relative aridity of the climate during entrapment.

Finally, fluid inclusion data from near-surface systems are very useful in providing paleo-atmosphere temperature. A good example of this is in halite from shallow lake systems. Fluid inclusions are supercooled to generate bubbles, and bubbles are heated to homogenization (Roberts and Spencer, 1995). In shallow water systems, no pressure corrections are needed so homogenization temperatures are the same as entrapment temperatures. Fluid inclusions of this sort provide useful climate data for the Holocene and Pleistocene (Lowenstein and Brown, 1998) as well as for very ancient systems (Benison and Goldstein, 1999). It is possible that similar homogenization temperature data could be gained from speleothem calcite and other coarse mineral phases that precipitate near Earth's surface.

11. Oil exploration and development

In recent years, fluid inclusion work has become a very important tool in oil exploration and development. Not only have fluid inclusions figured prominently in understanding the diagenetic controls on porosity evolution and thermal history, but fluid inclusion work has been important in evaluating the history and pathways of hydrocarbon migration. Petroleum fluoresces with UV epi-illumination, and its color of fluorescence is tied to maturity and API gravity (Lumb, 1978; McLimans, 1987; Tsui, 1990) providing an important record of composition of petroleum fluid inclusions. Furthermore, careful petrographic analysis of fluid inclusions within the context of diagenetic history has also proven useful. Individual events of petroleum migration commonly can be recognized by cement superpositional or crosscutting relationships. Detailed study of these relationships, together with homogenization temperature measurements, is quite useful in understanding reservoir systematics (Pottorf et al., 1997; Brennan and Goldstein, 1998). Furthermore, the extraction and analysis of hydrocarbon fluid inclusions provides useful information for determining hydrocarbon migration history and for evaluating the composition of hydrocarbons (Burruss, 1987b, Karlsen et al., 1993; Hall, 1996; Smith, 1997). In recent years, attempts have been made to interpret the *PVT* relationships of oil in fluid inclusions to better evaluate temperature and pressure of entrapment. This work determines the volume of gas and liquid in fluid inclusions to supplement modeling of the *PVT* relationships (MacLeod et al., 1996). Although this appears to be useful information that may help in the interpretation of oil-filled fluid inclusions, an analysis of the errors involved in the volume determinations and assumptions about composition would be a useful addition. All in all, fluid inclusion technologies figure prominently in the petroleum industry and will continue to do so as analytical technologies develop further.

12. Fluid inclusions and diagenetic systems

Most diagenetic studies rely on a combination of petrography and on isotopic and trace element analysis of diagenetic minerals. Of these techniques, the petrography typically provides the most unequivocal constraints on diagenetic history. Stable isotopic and trace element techniques, however, typically provide ambiguous results because of the many unconstrained variables that affect the composition of mineral phases. Most diagenetic systems are defined by the temperature, pressure and salinity of the fluids active in them. For that reason, fluid inclusions are one of the best techniques for constraining the diagenetic history of sedimentary rocks. Fluid inclusions have been successfully (and unambiguously) applied to all diagenetic systems (Goldstein and Reynolds, 1994). Such systems include low-temperature and high-temperature ones that have never been heated and buried, but also include many low temperature and high temperature systems that have been buried and heated beyond their conditions of entrapment. Where present, fluid inclusions, coupled with petrography, are probably the best techniques for tackling problems in diagenesis.

13. Conclusions

The future looks bright for fluid inclusion studies in sedimentary rocks. The last fifteen years has seen a revolution in the way fluid inclusion studies have been done in sedimentary rocks, a revolution brought about by the discovery that some of the fluid inclusions in sedimentary rocks reequilibrate from natural overheating. This discovery led to the development of a new approach, the fluid inclusion assemblage approach. With this, the future looks encouraging. There are many applications in sedimentary rocks tailor-made for studies of fluid inclusions. Among those are diagenetic studies, studies of petroleum systems, temperature and pressure studies to focus on tectonic, stratigraphic, and economic systems, and applications to paleoclimate and chemistry of the ancient oceans and atmosphere. With the large number of applications available, it is likely that new uses for fluid inclusions in sedimentary rocks will continue to evolve. That is not to say that there will be no new problems discovered. We, as fluid inclusionists, need to remain forever vigilant in evaluating the quality of our data and our interpretations, continuing to question our findings so that fluid inclusion studies in sedimentary systems advance.

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