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CHAPTER 1. INTRODUCTION TO FLUID INCLUSIONS

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INTRODUCTION

When a crystal grows in the presence of a fluid phase, some of the fluid may be trapped as imperfections in the growing crystal to form fluid inclusions. The trapped fluid may be liquid, vapor, or supercritical fluid, and the composition of the trapped fluid may include essentially pure water, brines of various salinity, gas or gas-bearing liquids, and silicate, sulfide or carbonate melts, among others. As noted by Roedder (1984), some workers use the term *fluid inclusion* to describe only those inclusions that have trapped a fluid and have remained in the fluid state during cooling to ambient temperatures. With that narrow definition, however, inclusions that originally trapped silicate melt and now contain glass \pm crystals (*cf.* Thomas *et al.* 2002), or solid carbon dioxide inclusions in diamond that were originally trapped as high density liquid carbon dioxide (Schrauder & Navon 1993), or unusual aqueous inclusions that trapped a calcium chloride-rich brine and now contain crystalline antarcticite without any liquid (Schiffries 1990), would not be considered fluid inclusions. The broader and more modern approach that will be followed here is to use the term "fluid inclusion" to refer to any inclusion that trapped a phase that was a fluid at the temperature and pressure of formation, regardless of the phase state of the inclusion as observed at laboratory conditions. For clarity, terms such as "silicate melt inclusion", "crystallized melt inclusion", "solid carbon dioxide inclusion" and others may be used as necessary to describe inclusions that now contain phases other than liquid or vapor at room temperature, with the understanding that all of these are in fact fluid inclusions.

Fluid inclusions are a common feature of minerals. In fact, it is much more common to find crystals with optically-resolvable fluid inclusions ($\approx 1 \mu\text{m}$) than it is to find crystals with no visible fluid inclusions. Even gemstones, which are sought because of their beauty and apparent perfection, often contain large inclusions that are,

in some cases, characteristic of the area or mine where they were found (Roedder 1986).

Fluid inclusions sufficiently large to study with the heating and freezing stage include those with sizes greater than about 12 micrometers. There is no upper limit to the size of natural fluid inclusions, but those with dimensions greater than a few millimeters are uncommon. As noted by Roedder (1984), the number of inclusions in a given sample generally increases with decreasing inclusion size, and some milky quartz and calcite may contain as many as 10^9 fluid inclusions per cm^3 . Although it is not possible with present technology to conduct microthermometric analysis of inclusions less than about 1 micrometer in diameter, there is likely a continuum in inclusion size from those that are resolvable with the petrographic microscope (~ 1 micrometer) down to those that are sub-micrometer size (Fig. 1-1A, B), including those composed of only a few water molecules and have dimensions measured in Angstroms. Using transmission electron microscopy (TEM), Green & Radcliffe (1975) observed 1 nanometer diameter carbon dioxide inclusions in olivine, with a continuum in size from these submicroscopic inclusions to those about 5 micrometers in diameter and easily resolvable with a petrographic microscope. The physical and chemical properties of these nano-inclusions could be significantly different than properties of larger microscopic fluid inclusions. Nevertheless, these sub-microscopic inclusions represent an important reservoir for volatiles in the deeper portions of the earth (Bell & Rossman 1992), and exsolution of volatiles originally dissolved in nominally anhydrous minerals during cooling and uplift might lead to the formation of later fluid inclusions (Spear & Selverstone 1983).

The physical and chemical conditions that might lead to the formation of fluid inclusions are many, and some are limited to certain minerals or even specific crystal faces in individual minerals

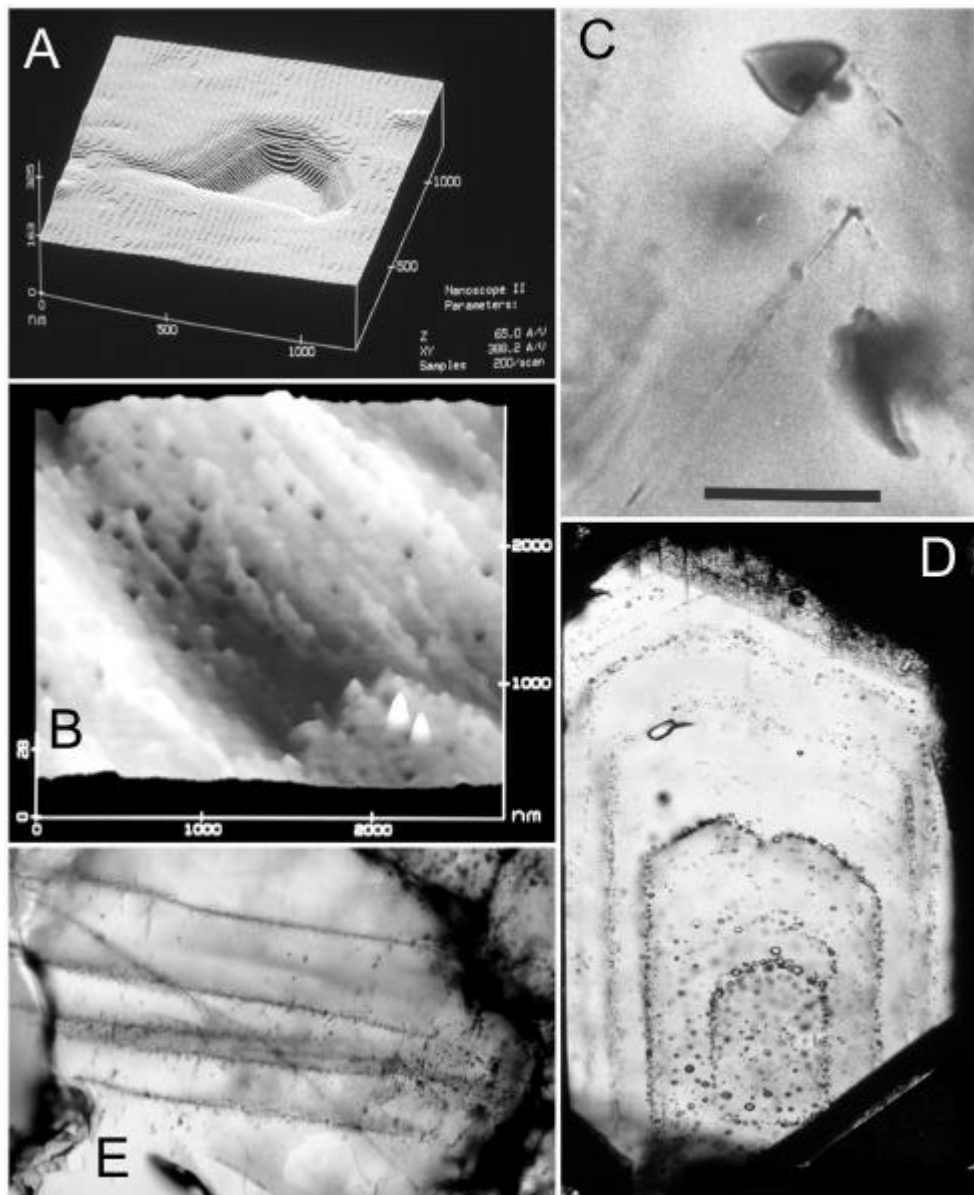


FIG. 1-1. (A). Atomic-Force Microscopy image of an 80 nm deep pit with an area $\sim 500 \text{ nm} \times \sim 300 \text{ nm}$ on an albite cleavage surface. The pit is thought to represent a sub-microscopic fluid inclusion in the albite crystal. (from Hochella *et al.* 1990). (B). Atomic-Force Microscopy image of a dissolving calcite rhombohedral surface showing numerous small (several tens of nm) pits in the crystal surface. During subsequent crystal growth, each of these pits is likely to become a sub-microscopic fluid inclusion (unpub. image, courtesy of M.F. Hochella, Jr.). (C) Calcite crystal from a vein in the Monterey Formation, California, showing a large, primary petroleum inclusion along a growth surface. The scale bar represents $25 \mu\text{m}$ (from Bodnar 1990). (D) Orthopyroxene phenocryst in basaltic andesite from White Island, New Zealand, showing numerous growth zones outlined by primary silicate melt inclusions and trapped solid inclusions. The crystal is approximately 2 mm long. (from Rapien 1998). (E) Quartz crystal from the Morro Velho gold mine, Brazil, showing several trails of secondary fluid inclusions cutting the crystal. Width of field of view is approximately 3 mm.

(cf. Watanabe 1987). For a more detailed discussion of these processes, the reader is referred to Goldstein & Reynolds (1994, Chapter 2) and Roedder (1984, Chapter 2). For an interesting historical perspective of ideas concerning the formation and study of fluid inclusions, the reader is referred to Yermakov (1965; sometimes also spelled Ermakov in western translations). Below, I summarize the basics of fluid inclusion origin, classification and selection, and provide one example of the selection criteria one might apply to choose fluid inclusions for study.

TEMPORAL CLASSIFICATION OF FLUID INCLUSIONS

There are many ways to classify fluid inclusions (Roedder, 1984; Goldstein, 2003), but one of the most useful classification schemes relates the timing of formation of the inclusion relative to that of the host mineral (Fig 1-2). Accordingly, *primary fluid inclusions* are formed during, and as a direct result of, growth of the surrounding host crystal. If a crystal fractures after it has been formed, some fluid may enter the fracture and become trapped as *secondary fluid inclusions* as the fracture heals. Thus, secondary inclusions are trapped after crystal growth is complete. If fracturing occurs during growth of the crystal, *pseudosecondary fluid inclusions* may be trapped during continued crystal growth. Such inclusions are sometimes referred to as *primary-*

secondary inclusions in the older Soviet literature. Petrographically, the occurrence of pseudo-secondary inclusions is similar to secondary inclusions, but the latter are followed by additional crystal growth. Sometimes the origin of the inclusions relative to formation of the crystal cannot be determined with confidence and the inclusion origin is said to be *indeterminable* (Goldstein, 2003).

Primary inclusions form when fluid is trapped on the active growing surface of a crystal. In mineralogy class, the face of a growing crystal is often portrayed as a perfect surface, with atoms being added to the surface in a very regular fashion. While this is true in the broadest sense, at the atomic scale the growing surface shows considerable topography (Zhang & Nancollas 1990). Recent advances in analytical techniques, such as TEM and atomic-force microscopy (AFM), now permit these surfaces to be viewed at the atomic scale, revealing the many irregularities that occur (Hochella *et al.* 1990). Growth spirals may develop if the growing crystal contains screw dislocations. In addition, etch pits and etch hillocks may develop on the crystal surface in response to changing degrees of saturation of the fluid - these features provide ideal sites for entrapment of fluid. Other processes, such as precipitation of solids on a growing crystal face, or nucleation of an immiscible fluid phase that adheres to the crystal face (imagine the CO₂ bubbles that nucleate on the inside surface of

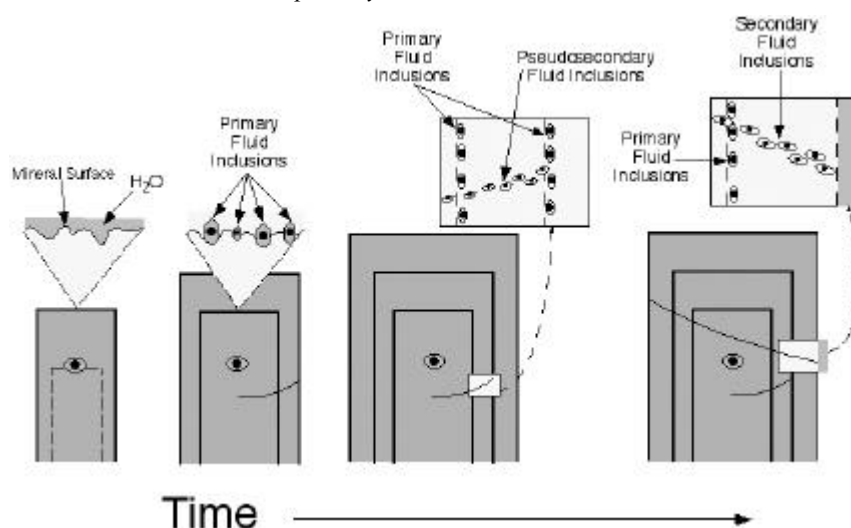


FIG. 1-2. Schematic representation showing the formation of primary, secondary and pseudosecondary inclusions during crystal growth.

a beer bottle when it is opened) may "poison" the surface and lead to formation of inclusions as the crystal continues to grow.

Determining the temporal classification of any given fluid inclusion is critical to interpreting the origin and evolution of the host mineral, yet this determination is often difficult. Roedder (1984; Table 2-1) lists the various morphological and petrographic criteria that have been used to determine the origin of fluid inclusions. Among the most diagnostic criteria for a primary origin are inclusions trapped along growth surfaces in crystals (Fig. 1C, D; Fig. 2). Episodic increases in crystal growth rates, resulting from rapid temperature (or pressure) or fluid composition changes, or from deposition of foreign particles on the growing surface (*cf.* Voigt & Brantley 1991), may lead to trapping of primary inclusions on the growth surface. Watanabe (1987) noted that inclusions were abundant on the fastest growing faces of corundum crystals, but were rare to absent on faces that grew more slowly. Roedder (1984) has also noted that one or a few fluid inclusions distributed randomly within the cores of crystals is good evidence for a primary origin, especially if the inclusions are large relative to the enclosing crystal (*cf.* Thomas *et al.* 2002). Note, however, that inclusions that appear to be randomly distributed in three dimensions within a crystal can result from overlapping planes of secondary inclusions (Goldstein, 2003). One property that has been used in the past to indicate a primary origin is the shape of the inclusions. Thus, negative-crystal-shaped inclusions have been interpreted to be primary, regardless of their location and/or distribution within the crystal. Today, based mainly on results of crystal growth and synthetic fluid inclusion studies, it is well known that secondary inclusions with a negative-crystal-shape are common (*cf.* Sterner & Bodnar 1984), and that inclusion shape alone cannot be used to determine the timing of inclusion formation (relative to the host crystal). Moreover, Bodnar *et al.* (1985) describe the process of "fluid inclusion maturation", whereby originally large, irregularly shaped inclusions evolve with time to become smaller and more regularly shaped. Note that inclusion shape can be used in some cases to indicate a primary origin, as in the case of fluid inclusions in calcite that taper in the direction of crystal growth (Goldstein, 2003) (Fig. 1.1C).

Secondary fluid inclusions are easily identified if they occur along a fracture that crosscuts the entire crystal (Fig. 1E). While it is unlikely that truly secondary inclusions on fractures that crosscut the entire crystal would be mis-interpreted as primary fluid inclusions, it is likely that some primary (or pseudosecondary) inclusions have been interpreted to be secondary. Sisson *et al.* (1993) observed the formation of fluid inclusions under the microscope during crystallization of KH_2PO_4 crystals. The inclusions were formed by sealing etch pits and other surface irregularities to form planar arrays that would be interpreted to be secondary based on petrographic characteristics. Johnson (1990) similarly observed primary fluid inclusions in planar arrays in experimentally grown forsterite crystals. These inclusions would likely be interpreted to be secondary because many of the planes are perpendicular to growth faces. In an experimental study of crack-healing in quartz, Brantley (1992) noted the formation of dislocations with hollow cores that trap fluid as inclusions. As the crystals continue to grow, the dislocations propagate along with the growing crystal to produce trails of fluid inclusions that extend to the outer surface of the crystal. Observation of such fluid inclusions along trails that extend from the outer surface of a crystal into the interior would likely be interpreted as secondary (or perhaps pseudosecondary if the trail did not extend completely to the edge of the crystal).

To some, the term "secondary inclusion" offers a negative connotation, with the implication that secondary inclusions should be avoided during microthermometric analysis. While this may be true in some instances, whether or not one *should* study secondary fluid inclusions depends on the geologic problem that is being studied. For example, the quartz grain shown in Figure 1E is from a mineralized vein in the Morro Velho gold deposit, Brazil. In this deposit, gold was introduced into the veins relatively late. If one examines polished sections of these veins under reflected light, bright gold flakes are observed along linear trails in the quartz - these are the same trails that host the secondary inclusions. In this case, the gold was introduced into the veins by the fluids that are now trapped as secondary fluid inclusions in the quartz. Thus, if one is interested in understanding the P-T conditions and fluid composition associated with

gold transport and deposition, it is the secondary inclusions that should be studied, not the primary inclusions in these veins.

FLUID INCLUSION ASSEMBLAGE

As noted above, determining the temporal classification of inclusions may be difficult, resulting in a fluid history that is equivocal. To minimize the emphasis on the primary, secondary and pseudosecondary classification of inclusions, Goldstein & Reynolds (1994) introduced the concept of the Fluid Inclusion Assemblage (FIA) to describe *a group of fluid inclusions that were all trapped at the same time*. An FIA thus defines the most finely discriminated fluid inclusion trapping event that can be identified based on petrography (Goldstein, 2003). This requirement further implies that the inclusions in the FIA were all trapped at approximately the same temperature and pressure, and all trapped a fluid of approximately the same composition. Therefore, the FIA represents a “fluid event” in the history of the system, and the fluid in the inclusions making up the FIA represents the fluid that was present during that event. Note that Goldstein & Reynolds (1994; especially their Fig. 7.1B) describe examples in which the homogenization temperature (and, presumably, the trapping temperature) is not constant within an FIA but, rather, shows systematic increases parallel to the growth direction. In this case, petrographic observations confirm the presence of a relatively thick growth zone that formed during an increasing temperature fluid event.

The requirement that the inclusions within an FIA were all trapped “at the same time” is relative and the absolute amount of time of the event will vary according to the environment of formation. In a shallow terrestrial or submarine geothermal system, where temperature and fluid composition might vary significantly over a time scale of days or weeks, fluid inclusions in an FIA might have been trapped over a period of days or less. In a deeper metamorphic environment where pressure-temperature-composition (PTX) conditions may remain reasonably constant for years or tens to hundreds of years, “at the same time” could apply to inclusions trapped over a period of several years to tens or hundreds of years. Brantley *et al.* (1990) conducted experimental studies of crack healing in quartz at hydrothermal conditions to investigate the time scales involved in inclusion

formation. These workers found that cracks ~ 100 μm long and 10 μm wide will heal in 4 hours at 600°C and 2 kbars in the presence of pure water. At 200°C, these same cracks can heal in about 40 days to 1,000 years, depending on the activation energy. Brantley (1992) also showed that cracks will heal faster in the presence of H₂O-salt solutions, and slower in the presence of H₂O-CO₂ solutions, both compared to rates in pure water. The variation in homogenization temperature that is acceptable within an FIA is thus a function of the actual temperature of formation (which, to a large extent controls how fast crystals can grow), the fluid composition (which controls mineral solubility) and on the geological environment (which generally controls the rate and magnitude of temperature and pressure fluctuations).

Determination that all of the inclusions in a group were trapped “at the same time” is based on petrographic analysis of the sample (see Goldstein & Reynolds 1994). A group of inclusions along an easily-recognizable growth zone in the host mineral may generally be assumed to have all been trapped at the same time and thus represent an FIA. Similarly, inclusions along a fracture that

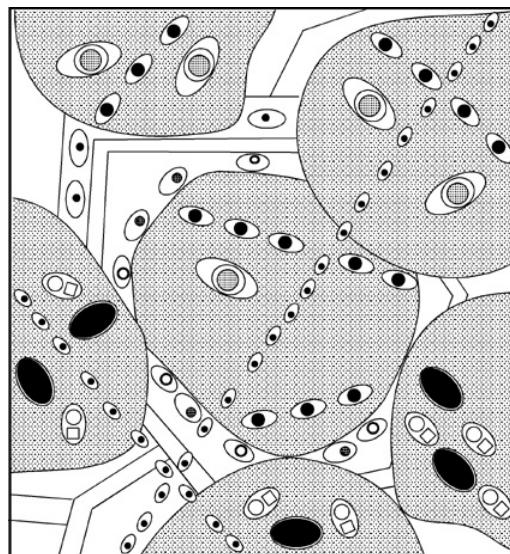


FIG. 1-3. Schematic representation of the various FIAs that might be observed in a well-cemented sandstone from a hydrocarbon basin. The original detrital grains are shaded. A description of the various FIAs and information available from those inclusions is shown in Figure 4. (from Bodnar 1994).

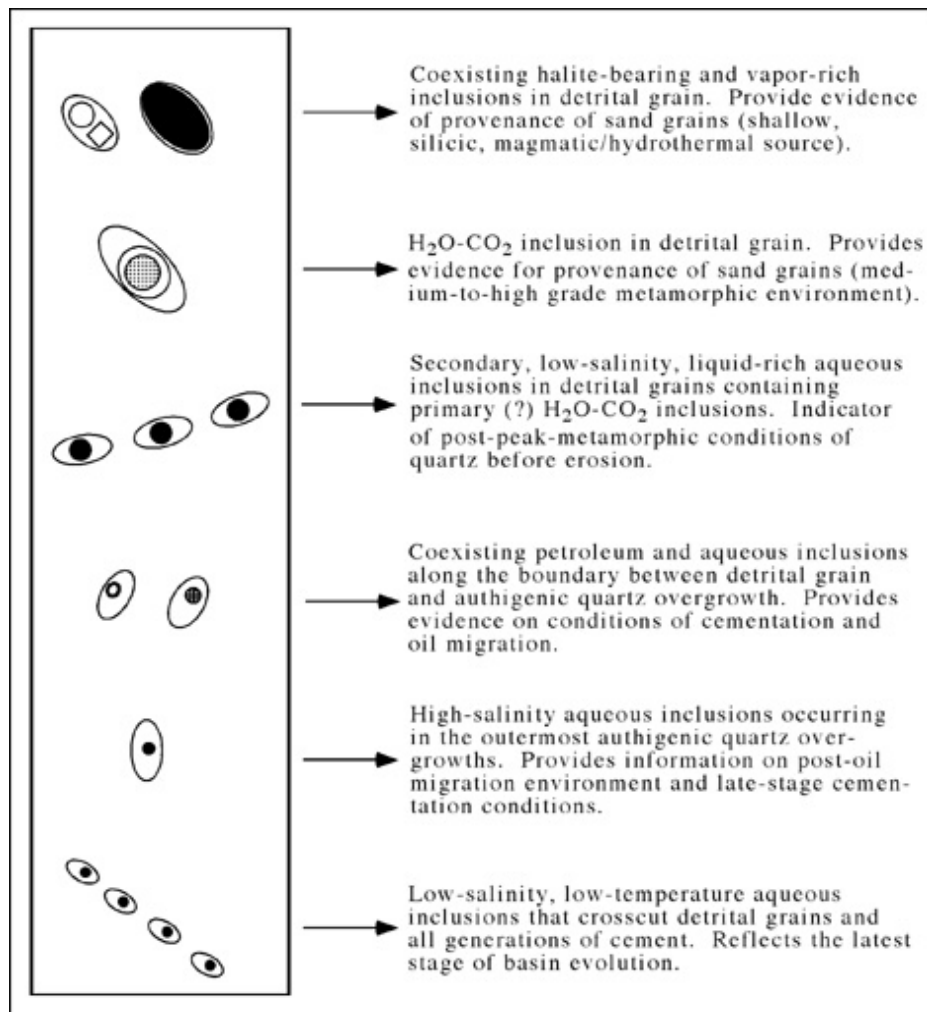


FIG. 1-4. Description of the various FIAs shown in Figure 3, along with a summary of information available from each FIA. (from Bodnar 1994).

crosscuts a mineral grain were probably all trapped at the same time as the fracture healed. Inclusions that are distributed randomly in three dimensions within the core of a host crystal provide less convincing evidence that a group of inclusions represents an FIA.

An Example of the use of FIAs

Most samples contain numerous fluid inclusion assemblages, only some of which may be relevant to the problem being considered. Figure 1-3 is a schematic representation of a well-cemented sandstone from a hydrocarbon reservoir, showing several different FIAs. Figure 1-4 describes the various FIAs shown on Figure

3, and briefly summarizes the type of information each FIA might provide. The geological problem that is being investigated will dictate which of the many FIAs should be studied. For example, if the major focus of the study is to understand the tectonic history of the area, then an important question concerns the source(s) of sediments in the basin and the directions of sediment transport. To address this question, one would be interested in the geology of the source region(s). Thus, inherited inclusions in the detrital quartz grains suggest at least two sources for the quartz - a medium-to-high grade metamorphic environment (as evidenced by H₂O-CO₂ inclusions containing both liquid and vapor CO₂) and a shallow granitic

intrusive source (as evidenced by coexisting halite-bearing and vapor-rich fluid inclusions). By determining the relative amounts of the two different types of detrital grains and their variation within a given stratigraphic horizon, it may be possible to determine relative distances to the two different source regions. Variations in the two different detrital FIAs vertically within the sandstone unit may reflect changing tectonic conditions (rates of exhumation?) in the two different source regions with time.

A petroleum geologist studying the same sample might not be interested in the source of the sediments, but rather with the timing of hydrocarbon migration relative to cementation and porosity loss or gain. In this case, one would not study FIAs containing inherited inclusions in the detrital grains, but instead would focus on FIAs containing petroleum inclusions and occurring in authigenic quartz near the detrital grain/overgrowth interface. Similarly, analysis of the very latest FIA that contains (secondary) aqueous inclusions and crosscuts all generations of cement as well as the detrital grains might help to determine the thermal history following oil migration. Such information is crucial to (1) understanding the post-migration history of the basin, and (2) whether the original liquid hydrocarbons that filled pore spaces in the rock were subsequently buried beyond the oil window, resulting in degradation of the liquid petroleum into methane and other light gaseous hydrocarbons.

Before any FIA can be used to study the thermal and chemical evolution of a geologic system, one must be certain that the inclusions have trapped a fluid representative of that present at the time of inclusion formation and have not reequilibrated following formation (Bodnar, 2003a). To accomplish this, one must test the inclusions for adherence to "Roedder's Rules", which state that:

1. the inclusions trapped a single, homogeneous phase.
2. the inclusions represent an isochoric (constant volume) system.
3. after trapping, nothing has been added to, or removed from, the inclusions.

That the inclusions do adhere to "Roedder's Rules" may be confirmed based on petrographic (Bodnar, 2003a; Goldstein, 2003) and microthermometric analysis (Bodnar, 2003b).

Finally, it should be emphasized that many of the geological problems one might be trying to resolve using fluid inclusions can be solved without the need for microthermometric or chemical data for the inclusions. For example, if one wants to know if hydrocarbons ever migrated through a given lithologic unit, the simple presence, or absence, of petroleum inclusions in the sample may answer the question. Similarly, if one wishes to know if the fluids in an epithermal precious metal exploration target were boiling, the presence, or absence, of FIAs with coexisting liquid-rich and vapor-rich inclusions may provide the answer, without the need for time-consuming and expensive microthermometric analysis.

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