CHAPTER 8. REEQUILIBRATION OF FLUID INCLUSIONS

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INTRODUCTION

A fluid inclusion provides microthermo-
metric data that can be used to infer trapping
conditions only if the inclusion satisfies several
criteria (Roedder 1984). First, the inclusion must
trap a single, homogeneous phase. Secondly, the
inclusion must remain a constant volume system
after trapping (excluding reversible elastic
volume changes) and, thirdly, nothing can be
added to, or removed from the inclusion follow-
ing trapping. These criteria are here referred to as
"Roedder's Rules", and must be met if one wishes
to use inclusions to reconstruct the thermobaric
history of the host rocks. If the inclusion volume
changes, or if anything is added to or lost from
the inclusion following trapping, the inclusion is
said to have reequilibrated. Reequilibration can
occur in nature during continued burial or uplift
of the rock to the surface, or reequilibration may
occur during sample preparation and/or data
collection in the laboratory. Less often considered
by inclusionists is the possibility that fluid
inclusions in samples collected from surface
outcrops may have experienced elevated tempera-
tures during exposure to the sun or to forest fires,
or may have undergone freezing in colder
climates. Especially for low temperature
inclusions, these temperature fluctuations may
have been sufficient to cause reequilibration.

As a result of numerous studies of both
natural and synthetic fluid inclusions over the past
few decades, we now have a fairly comprehensive
understanding of the reequilibration process.
Before I discuss the physical and chemical factors
that affect the reequilibration process, it is first
necessary to introduce the various terms that are
used to describe fluid inclusion reequilibration. In
the fluid inclusion literature, reequilibration is a
general term that has been used to describe fluid
inclusions that have changed volume, or have lost
or gained components, or both. Stretching is a
term that is generally used to describe fluid
inclusions whose volume has changed with little
or no discernible loss of fluid from the inclusion
(Fig. 8-1). The term was first introduced by
Larson et al. (1973) to describe permanent,
nonelastic deformation of the walls of inclusions
in fluorite and sphalerite as a result of
overheating. Stretching usually results when an
inclusion reequilibrates in a low strain rate
environment in which the host phase deforms
plastically, and is more common in softer
minerals than in harder minerals. Any material
that is lost from the inclusion occurs as a result of
diffusion or leakage along dislocations (Wilkins
et al. 1981, Bodnar & Bethke 1984, Wilkins

With increasing strain rate, fractures may
develop in the host adjacent to inclusions, with
partial loss of fluid by advection along the
microfractures. This type of reequilibration is
referred to as leakage or partial decrepitation.
Sometimes, the extent of fracturing is so intense
that all fluid is lost, leaving an empty, dark cavity
in the host phase. This is referred to as
decrepitation. Note that the resulting inclusions
are probably not sensu stricto empty but, rather,
likely contain a low-density version of the
original fluid (water vapor or CO₂ gas, for
example). The inclusions are referred to as being
empty because no fluid phase is observed during
petrographic or microthermometric examination.

The term decrepitation was introduced
by researchers in the former Soviet Union to
describe the explosive release of inclusion
contents during heating. In the early days of fluid
inclusion research, before the development of
microscope heating/cooling stages and high-
quality long-working distance microscope
objectives, workers would heat mineral samples
in a furnace with a sensitive microphone attached.
The microphone records acoustic emissions (e.g.,
noise) associated with decrepitating fluid
inclusions, and the decrepitation temperatures
would be related to inclusion trapping
temperatures (incorrectly, in many cases!).
FIG. 8-1 Schematic representation of the relationship between different types of fluid inclusion reequilibration (stretching, leakage, decrepitation) and the environment of deformation (strain rate), the mechanisms of deformation (plastic vs. brittle) and fluid loss (diffusion vs. advection), and the amount of fluid lost from the inclusion during deformation (undetectable to complete). According to these relationships, stretching is associated with plastic deformation in a low strain environment, where undetectable amounts of fluid may be lost from the inclusion by diffusion. Conversely, decrepitation is associated with brittle deformation in a high strain environment, with partial to complete loss of fluid by advection along fractures. (from Vityk et al. 2000).

Related to this, Hall & Bodnar (1989) showed that energy detected during acoustic emission studies of natural rocks and minerals is directly related to decrepitation of fluid inclusions in the sample.

An additional type of reequilibration sometimes occurs when the fluid in the inclusion reacts with the host phase after trapping to generate a new mineral assemblage. For example, Kleinefeld & Bakker (2002) report the presence of calcite, paragonite and pyrophyllite crystals in fluid inclusions in plagioclase, and relate their origin to reaction of the CO$_2$-rich fluid with the calcite host. Similarly, Heinrich & Gottschalk (1995) observed inclusions containing calcite and quartz crystals in wollastonite. These phases were generated by the reaction of the wollastonite host with the CO$_2$-bearing fluid during retrogression. Kodera et al. (2003) reported the occurrence of ferropyrosmalite [(Fe,Mn)$_8$Si$_6$O$_{15}$(OH,Cl)$_{10}$] in fluid inclusions in magmatic quartz. These workers attribute the origin of this phase to reaction of an original clinopyroxene daughter mineral with the saline solution in the inclusion during cooling, and were able to reverse this process during laboratory heating. In this chapter, these somewhat specialized cases of reequilibration will not be considered further.

The type of reequilibration that occurs is a function of many factors, and in a given fluid inclusion assemblage some inclusions may show evidence of significant reequilibration, while others may show no evidence of reequilibration. Below I outline some of the many factors that affect the reequilibration process. Of particular importance is the effect of time on the reequilibration process, because this may affect the applicability of laboratory-based studies to reequilibration of fluid inclusions in nature. The intent of this chapter is to provide information that inclusionists might gain from petrographic and microthermometric analyses of inclusions, and excludes detailed theoretical discussions of the reequilibration process. Note, however, that the empirical observations presented below are generally consistent with theoretical models for mineral deformation. For a more detailed discussion of the theoretical basis for mineral deformation.
deformation, the reader is referred to Poirier (1985) and to Küster & Stöckhert (1997) for a discussion of rock deformation theory applied to fluid inclusion reequilibration.

WHAT DETERMINES HOW EASILY AN INCLUSION WILL REEQUILIBRATE?

Mineralogy

The most important factor that determines the ease with which fluid inclusions reequilibrate is the structure and composition of the host phase. As fluid inclusion reequilibration involves the breaking or modification of bonds within the host mineral, the ease with which a mineral reequilibrates can be correlated with the weakest bond in that mineral. While there are many ways of characterizing bond strength, one of the most basic is related to the hardness of the mineral. Minerals with small atoms that are tightly packed and involve covalent bonds are harder than those containing larger atoms that are held together by van der Waals or metallic bonds.

Among the first to recognize the relationship between mineral hardness and the ease with which fluid inclusions reequilibrate were Tugarinov & Naumov (1970), who noted a linear relationship between Mohs hardness and the pressure required to decrepitate fluid inclusions in several minerals (Fig. 8-2). Thus, fluid inclusions in soft minerals such as orpiment and stibnite (Mohs hardness ~ 2) will reequilibrate (decrepitate) when the internal pressure reaches only a few hundred bars, whereas about 800 bars of internal pressure is required to initiate reequilibration of inclusions in quartz (Mohs hardness ~ 7). Faiziev & Alidovov (1976) also noted that inclusions in soft minerals with perfect cleavage (e.g., fluorite, calcite, sphalerite, and scheelite) show an increase in measured homogenization temperature during repeated measurements. These workers attributed reequilibration to the presence of weak bonds between cleavage layers, consistent with observations by Tugarinov & Maumov (1970). The consistent

![Graph](image)

**Fig. 8-2.** Relationship between the internal pressure necessary to initiate reequilibration of fluid inclusions and the Mohs hardness of the host mineral (modified from Tugarinov & Naumov, 1970). Ranges in pressure for calcite, barite, sphalerite, fluorite and quartz represent the variation in pressure as a function of inclusion size. Size data for quartz are from Bodnar *et al.* (1989); data for fluorite and sphalerite are from Bodnar & Bethke (1984); data for barite are from Ulrich & Bodnar (1988); data for calcite are estimated from Hall *et al.* (1993) and Prezbindowski & Larese (1987).
relationship between Mohs hardness and the pressure required to cause reequilibration of fluid inclusions makes it possible to estimate the suitability of a given mineral for fluid inclusion studies. Thus, one would expect that gypsum, with a Mohs hardness of 2, might not be the best host for fluid inclusion studies, whereas corundum, with a Mohs hardness of 9, would be an ideal mineral for fluid inclusion studies. It should be recognized that Mohs hardness is not a quantitative scale but, rather, a qualitative scale that makes it convenient to compare the relative hardness or tensile strength of two minerals. The absolute hardness (or tensile strength) of a mineral is not a linear function of Mohs hardness. Thus, the difference in absolute hardness between quartz (Mohs hardness = 7) and topaz (Mohs hardness = 8) is about the same as the difference in absolute hardness between talc (Mohs hardness = 1) and quartz. As such, Figure 8-2 shows the relationship between pressure required to initiate reequilibration and Mohs hardness over the range of experimental observations (Mohs hardness ~1-7), but should not be applied to minerals with a Mohs hardness greater than that of quartz (=7). It is expected that in the future additional empirical data will become available for minerals with Mohs hardness above that of quartz, allowing the trend shown on Figure 8-2 to be extended to higher values of Mohs hardness.

The type of reequilibration that occurs is also somewhat related to mineral hardness. As noted above, soft minerals tend to reequilibrate by stretching to produce a gradual increase in homogenization temperature as reequilibration proceeds, whereas harder minerals such as quartz tend to maintain their original homogenization temperature until the inclusion decrepitates with complete loss of fluid. It should be emphasized, however, that many exceptions to this general trend have been reported. For example, Ulrich and Bodnar (1988) observed decrepitation of inclusions in the soft mineral barite (Mohs hardness ~3), and Bodnar et al. (1989) noted that some fluid inclusions in quartz reequilibrated by stretching (followed by later decrepitation). Additionally, minerals that reequilibrate by brittle failure (decrepitation) in the laboratory may reequilibrate by stretching or leakage under the higher confining pressures and much lower strain rates common in nature. Thus, Guilhaumou et al. (1987, 1988) found that fluid inclusions in fluorite decrepitated with complete loss of fluid when overheated in the laboratory at one atmosphere confining pressure, whereas inclusions from the same sample that were overheated under 200 or 400 bars of confining pressure reequilibrated by stretching.

Inclusion Size

Whereas the mineralogy of the inclusion host appears to be the most important factor controlling the pressure required to reequilibrate fluid inclusions, the "average" pressure can vary significantly depending on inclusion size. Naumov et al. (1966) and Tugarinov & Naumov (1970) determined that fluid inclusions larger than about 35 µm in quartz decrepitate when the internal pressure reaches about 850 bars. Leroy (1979) reported that this pressure increases to 1.2 kbar for 12-13 µm fluid inclusions, and that inclusions smaller than 12 µm did not decrepitate even when the internal pressure reached 2.7 kbars. Swanenburg (1980) reported that approximately 1 µm inclusions were able to maintain internal pressures of 5-7 kbars before decrepitating.

Bodnar et al. (1989) conducted an experimental study of the decrepitation behavior of fluid inclusions in quartz and combined their results with those of Leroy (1979) and Swanenburg (1980) to produce the following relationship between inclusion size and the internal pressure required to initiate reequilibration (Fig. 8-3):}

\[
\text{Pressure (kbar)} = 4.26 \times D^{0.423}
\]

where \(D\) is the inclusion diameter in micrometers. According to equation (1), the internal pressure required to reequilibrate inclusions in quartz varies from 0.8 kbar for a 50 µm inclusion, to 1.6 kbars for a 10 µm inclusion, to 4.3 kbars for a 1 µm inclusion (Fig. 8-3).

Bodnar and Bethke (1984) found a similar relationship between inclusion size and the minimum pressure required to initiate stretching of fluid inclusions in fluorite. According to these workers, the internal pressure required to initiate stretching decreases with inclusion size according to:

\[
\text{Pressure (bars)} = 900 - 147 \log_{10} V
\]
where $V$ is the inclusion volume in $\mu m^3$. Assuming a spherical geometry, this translates to about 635 bars for a 5 $\mu m$ inclusion, and 200 bars for a 50 $\mu m$ inclusion. Bodnar & Bethke (1984) also observed a clear relationship between inclusion size and the internal pressure required to stretch fluid inclusions in sphalerite, but were unable to accurately calculate the inclusion volumes because the vapor bubbles were not spherical at room temperature, precluding application of the technique described by Bodnar (1983). According to their data, the pressure necessary to stretch an inclusion smaller than about 5-10 $\mu m$ in sphalerite is about 800 bars, whereas an inclusion 50 $\mu m$ in diameter requires about 300-400 bars of internal pressure (Fig. 8-2).

The relationship between inclusion size and the pressure required to initiate stretching is less well defined for inclusions in barite (Ulrich & Bodnar 1988), although the trend indicates higher pressures for smaller inclusions, consistent with other minerals studied. Prezbindowski & Tapp (1991) showed that the size-pressure relationship observed in fluid inclusions is consistent with theoretical models of crack propagation and stress concentration surrounding flaws (fluid inclusions) in minerals.

Prezbindowski & Larese (1987) conducted an experimental study of stretching of fluid inclusions in calcite and found that larger inclusions stretch more ($i.e.$, the homogenization temperature increases by a larger amount) than smaller inclusions subjected to the same P-T history. Based on the results of Bodnar & Bethke (1984), which indicate that the amount of stretching (change in the homogenization temperature) for a group of inclusions that initially had the same homogenization temperature can be related to the temperature at which stretching begins, the results of Prezbindowski & Larese (1987) would suggest that the larger inclusions began to stretch before the smaller inclusions. Goldstein (1986) observed a similar size-pressure relationship for naturally reequilibrated inclusions in low temperature calcium carbonate cements. However, Hall et al. (1993) found no correlation between inclusion size and ease of stretching during an experimental study of calcite, although they did notice that inclusions closer to the mineral surface were more...
prone to stretching compared to those deeper in the sample.

**Inclusion shape**

A secondary factor that determines how easily a fluid inclusion will reequilibrate is inclusion shape. Bodnar et al. (1989) noted that the average pressure required to reequilibrate fluid inclusions in quartz increased by about 400 bars as the inclusion shape varied from very irregular, with many reentrants or "tentacles", to one that was spherical or negative-crystal shaped. Goldstein (1986) noted a similar dependence on inclusion shape for calcite, as did Bodnar & Bethke (1984) for inclusions in fluorite and sphalerite. The relationship between inclusion shape and the amount of pressure required to initiate reequilibration is generally consistent with theoretical deformation models which indicate that stress is concentrated at sharp corners, and that the stress approaches infinity at crack tips (ends of tentacles in irregularly-shaped inclusions) or at the corners of angular inclusions (Prezbindowski & Tapp, 1991). However, the fact that most angular inclusions do not spontaneously stretch or decrepitate during heating suggests that while theoretical models of deformation provide valuable insights into the reequilibration process, they may be less useful than empirical models for predicting the reequilibration behavior of fluid inclusions.

**Fluid Composition**

Little information is available concerning the role of fluid composition in the reequilibration process. However, one would expect that fluid inclusions containing water might reequilibrate more easily than those that are water-free, owing to the presumed higher solubilities of host minerals in aqueous fluids compared to, for instance, carbon dioxide. Hall & Wheeler (1992) conducted a preliminary study of the relationship between fluid composition and inclusion decrepitation and found that 3 µm diameter inclusions containing H₂O-NaCl required a lower pressure (3.0 kbars), and inclusions containing H₂O-CO₂ a higher pressure (4.2 kbar), compared to pure H₂O inclusions (3.4 kbars) of the same size. The role that fluid composition plays in reequilibration is an area of research that should be given high priority in future studies.
Just as an FIA with real or apparently consistent phase ratios is possible even if inclusions have reequilibrated, a range in liquid-to-vapor ratios is not always indicative of reequilibration. If the inclusions were trapped in a boiling (or immiscible fluid) system, a bimodal distribution of phase ratios will result, with a complete range between the end-member ratios from trapping mixtures of the two phases present. Fortunately, the range of possible phase ratios is not entirely random, and is controlled by the PVTX properties of the two immiscible fluids, and the possible phase ratios that might result from trapping mixtures may be calculated using PVTX data (see Bodnar et al. 1985, their Fig. 5.5).

Textural features in the host mineral surrounding fluid inclusions perhaps provide the most diagnostic evidence for reequilibration. When inclusions reequilibrate, the host phase surrounding the inclusions is deformed to produce a variety of features that are visible using conventional optical microscopy or more sophisticated techniques such as cathodoluminescence, transmission electron microscopy (TEM), or X-ray tomography. Moreover, the textures that result may be diagnostic of the P-T path followed during reequilibration. Most experimental studies, as well as studies of naturally reequilibrated inclusions have focused on the mineral quartz, and the discussion of fluid inclusion textures below is limited to this mineral. It is expected that petrographic features observed for quartz may not always apply to other minerals that have significantly different crystallographic and rheological properties or solubility in the inclusion fluid.

Before discussing the various textural features associated with reequilibrated fluid inclusions in quartz, it is first necessary to consider the various P-T histories under which fluid inclusions may be reequilibrated, because each produces slightly different and, in some cases, diagnostic textural features. Following trapping, fluid inclusions may follow a P-T path that maintains an internal pressure in the inclusion equal to the confining (or lithostatic) pressure, or may follow paths such that the internal pressure is greater than or less than the confining pressure (Fig. 8-4). If the inclusion follows an isochoric path such that the confining pressure and the internal pressure are always equal, reequilibration is unlikely to occur. This type of cooling path is a special case that occurs only rarely in nature. In most natural systems the rocks do not follow a P-T path that approximates the inclusion isochore. Rather, the confining (geologic) pressure is either greater than, or less than, the internal pressure in the inclusions. In these cases the inclusion is not in equilibrium with the surrounding rock and reequilibration may occur (see Diamond 2003, Fig. 3-5).

If the inclusion follows a P-T path that results in internal overpressure, the first modification that inclusions experience is a change in shape, often without a measurable change in volume. Specifically, the inclusions become more regularly shaped, and elongated inclusions become more rounded or equant (Fig. 8-5) (Grattier & Jenatton 1984, Pêcher & Boullier 1984, Bodnar et al. 1989, Bakker & Jansen 1991). The evolution from less to more regular or negative-crystal shape represents the normal maturation process that all fluid inclusions undergo as they try to minimize their surface area, as discussed by Bodnar et al. (1985). Given sufficient time, all inclusions should approach an equant or negative-crystal shape. Thus, the evolution from irregular to more-regular inclusion shape that occurs under conditions of internal overpressure is not diagnostic of this type of
Fig. 8-5. Evolution in the shape of fluid inclusions in quartz during reequilibration at conditions of $P_{\text{internal}} > P_{\text{confining}}$. The length/width ratio of the inclusion indicated by the arrow gradually decreases with time to produce an equant negative-crystal-shaped fluid inclusion after being held at a temperature of 370°C and an internal pressure of 400 bars for 5621 hours. The scale bar equals 50 µm. (modified from Bodnar et al., 1989).
FIG. 8-6. Relationship between the intensity of reequilibration features and the size and pressure differential ($P_{\text{internal}} - P_{\text{confining}}$) for methane inclusions in quartz from the Ukrainian Carpathian Mountains. At low pressure differential (top row) none of the inclusions show reequilibration textures. With increasing departure of the confining pressure and internal pressure in the inclusions, the largest inclusions begin to reequilibrate, while the smaller inclusions show no reequilibration textures. Progressively smaller inclusions begin to reequilibrate as the pressure differential increases. All inclusions in samples with the largest pressure differential (bottom row) show evidence of fracturing and development of haloes of secondary inclusions surrounding the original inclusion. (from Vityk et al., 1996)

FIG. 8-7. TEM photomicrographs showing microstructures produced during reequilibration at 625°C and 2 kbar. The inclusions were originally formed at 700°C and 5 kbar, resulting in an internal overpressure ($P_{\text{internal}} - P_{\text{confining}}$) of about 2.1 kbar at the reequilibration conditions. Fluid inclusions in "A" and "B" are surrounded by poorly healed fractures (arrow 1), a few dislocations connected to the inclusion walls (arrows labeled 2), and a Dauphine twin (arrow #4 in "B"). Note the high density of water bubbles in the healed fracture in "A". Also note that some dislocations are pinned with bubbles (arrows #3 in "A"). (from Vityk et al., 2000).
Fig. 8-8. Evolution of fluid inclusions in quartz after reequilibration at conditions of internal underpressure (Fig. 8-9) (Hurai & Horn 1992, Vityk \textit{et al.} 1994). Careful petrographic observations to determine whether the smallest or the largest inclusions in a given sample show the most intense reequilibration features may provide a means of determining whether the sample experienced an initially isobaric cooling path, or an initially isothermal unroofing path, following formation.

Microthermometric Evidence

As the inclusion volume or composition changes, the microthermometric behavior of inclusions will change in a somewhat predictable manner. An increase in volume without fluid loss results in a lower density and concomitant increase in the homogenization temperature. Based on numerous laboratory studies, when a group of inclusions with initially uniform homogenization temperatures is overheated by a certain amount, the amount of stretching (percent volume increase) of the inclusions in the FIA is highly variable, resulting in a wide range of homogenization temperatures. For example, Vityk \& Bodnar (1998) reported that 160 fluid inclusions in quartz that were trapped at 700°C and 5 kbars all homogenized within a three degree range from 282-285°C. Another sample was formed at the same conditions and then cooled to 625°C and 2 kbar and held at these conditions for 30 days, resulting in an initial internal overpressure in the inclusions of about 2.1 kbars. After 30 days the sample was quenched and the homogenization temperatures of the inclusions were measured. Not only had the temperatures been shifted to higher values compared to the original Th, but also the original three degree Celsius range in Th (282-285°C) had expanded to about 65 degrees Celsius (~310-375°C).

The relationship between the range in Th and extent of stretching observed in laboratory studies may not be applicable to reequilibration in nature, as noted in the introduction to this chapter. While it is true that stretching results in a wide range in Th during laboratory reequilibration studies, if these same samples were held at the reequilibration conditions for durations approaching geologic time scales (10⁷ - 10⁶ years), it is likely that the homogenization temperatures of all the inclusions would approach some new "equilibrium" homogenization temperature. Results presented by Vityk &
Fig. 8-9. Relationship between the intensity of reequilibration features and the size and pressure differential (\(P_{\text{confining}} - P_{\text{internal}}\)) for aqueous inclusions in quartz from the Bayanovoo granite in central Mongolia. The inclusions were reequilibrated at 500°C and pressures of 1 (A-C), 2 (D-F), 3 (G-I), 4 (J-L) and 5 (M-O) kbar for 7 days. At run conditions, all of the inclusions had an internal pressure of about 500 bars. With increasing pressure differential the smaller inclusions begin to reequilibrate first, followed by increasingly larger inclusions as the pressure differential increased from about 500 bars (A-C) to 4.5 kbar (M-O). (from Vityk et al. 1994).

Bodnar (1995a, 1998) are consistent with this suggestion.

Goldstein (1986) examined fluid inclusions from recent calcium carbonate cements that had formed at the surface and were never deeply buried. He compared these to inclusions in similar cements that had formed at the surface but were later buried to significant depths and exposed to temperatures well above 100°C. The recent samples that had never been buried contained mostly all-liquid inclusions, in addition to liquid + vapor inclusions that had trapped water plus air. Deeply buried samples showed a wide range in homogenization temperatures and salinities, reflecting continued reequilibration during burial and exposure to fluids of different salinities as burial progressed. Goldstein (1986) concluded that the deeply buried cements were unlikely to provide any useful information concerning original formation conditions, but could prove useful for interpreting burial pore fluid history. Barker & Goldstein (1990) used the fact that inclusions in calcite reequilibrate relatively easily to suggest that inclusions in calcite from sedimentary basins and geothermal fields might be used to estimate the maximum burial conditions.

One misconception that many workers have concerns the reproducibility of microthermometric data as a means of testing whether or not reequilibration has occurred. Workers often report that homogenization temperatures of inclusions are reproducible when measured multiple times. These workers then interpret this to indicate that the inclusions have not reequilibrated. However, a reproducible Th is necessary but not sufficient to prove that an inclusion has not reequilibrated. As noted by Bodnar & Bethke (1984), stretched fluid inclusions in fluorite gave reproducible (±0.2°C) homogenization temperatures, even though these temperatures were ~40°C higher than the Th before the inclusions were stretched by laboratory heating. Larson et al. (1973) also noted that some inclusions in fluorite gave reproducible Th after four heating runs, even though some of these temperatures were as much as 70 degrees Celsius too high (i.e., the inclusions had been stretched by 70 degrees Celsius). Thus, reproducibility of homogenization temperatures is a necessary criterion to confirm that inclusions have not reequilibrated, but is not in itself sufficient to prove that reequilibration has not occurred.

**Compositional Reequilibration**

Compared to volumetric reequilibration, compositional reequilibration is less well understood and more difficult to recognize. Most
compositional reequilibration involves the loss (or gain) of hydrogen or water (OH) from the inclusion (Hall & Sterner, 1995). In melt inclusion studies, other components, including sodium and some trace elements, can be lost from inclusions during heating. Melt inclusion reequilibration is not considered here.

Pure carbon dioxide (or carbon dioxide-rich) inclusions are common in medium to high-grade metamorphic environments. Based on thermodynamic considerations, water-free (or water-poor) fluids often are not in equilibrium with the mineral assemblage in the rocks, and this has led many workers to invoke post-trapping reequilibration of the inclusions to explain the high CO₂ contents. Hollister (1990) has suggested that CO₂ inclusions in metamorphic rocks are produced when water leaks out of originally water-rich inclusions during plastic deformation, to produce pure CO₂ or CO₂-rich, inclusions. Bakker & Jansen (1991) were able to reproduce this process experimentally. Water was lost from H₂O-CO₂ inclusions during reequilibration, resulting in inclusions more CO₂-rich than the original inclusions. Alternatively, Lamb et al. (1987) and Lamb (1990) suggested that the "primary appearing" CO₂ inclusions in granulites were actually trapped during retrogression and are not associated with peak granulite grade conditions.

Owing to the small size of the hydrogen ion, hydrogen is able to diffuse through most mineral structures very easily. Mavrogenes & Bodnar (1994) showed experimentally that fluid inclusions several tens of micrometers beneath the surface of a quartz crystal will reequilibrate to the external hydrogen fugacity in only a few hundred hours at 600-800°C, or in only a few tens of thousands of hours (several years) at temperatures of 400°C. As part of this work, these workers were able to confirm that the common failure of sulfide daughter minerals to dissolve during heating is the result of post-entrapment hydrogen loss from the inclusions. These workers were able to reverse this process experimentally and dissolve chalcopyrite daughter minerals - these phases did not dissolve before hydrogen was experimentally diffused into the inclusion at high temperature and pressure. Hall et al. (1991) attributed the presence of methane in fluid inclusions from the Ducktown, Tennessee, USA, massive sulfide deposits to hydrogen diffusion into the inclusions during uplift and cooling. The extremely negative hydrogen isotopic (D/H) composition of the fluid inclusions was consistent with enrichment in the hydrogen isotope, as the larger deuterium diffuses through quartz at a much slower rate. Hall & Bodnar (1990) suggested that the small amount of methane often reported in fluid inclusions from granulites is the result of hydrogen diffusion into the inclusions following trapping, consistent with thermodynamic properties in the C-O-H system.

Hall & Sterner (1993) conducted experimental studies of water loss from aqueous fluid inclusions. As a result of water loss, the salinity of the inclusions increased by 22 %. Vityk et al. (2000) conducted similar experiments and were able to increase the salinity by a few tenths of a weight percent NaCl as a result of water loss. Audétat & Günter (1999) noted characteristic reequilibration textures associated with fluid inclusions in quartz from the Mole Granite, Australia, and attributed variable and high salinities in the inclusions to loss of water to produce "sweat haloes" around deformed inclusions. It is likely that ranges in salinities of apparently coeval inclusions in some magmatic hydrothermal ore deposits, such as the porphyry copper deposits, are due at least in part to water loss from the inclusions following entrapment.

One could interpret the discussion above to indicate that inclusions reequilibrate by an increase in volume with no fluid loss (stretching) or by loss of fluid through leakage or decrepitation. In practice, these various mechanisms of reequilibration likely operate together, with perhaps one or the other dominating, depending on the environment in which reequilibration is occurring. Thus, Vityk et al. (2000) note that stretching of fluid inclusions in quartz requires the diffusive loss of fluid from the inclusion into the surrounding quartz host to initiate the stretching process. However, normal petrographic observations would not reveal the presence of water-bearing dislocations, and one might assume that the change in homogenization temperature was due solely to volume change. Based on our experience and observations, we believe that in all, or certainly most, examples of reequilibration, both volume change and fluid loss (or gain) occur. Possible exceptions might include, for example, the reequilibration of "pure" CO₂ inclusions. Wanamaker & Evans (1989)
noted that following heating to generate high internal pressures, the density of CO₂ inclusions in olivine had decreased. Assuming that CO₂ cannot diffuse through olivine at these conditions, these workers attributed the density decrease to stretching (volume increase), in agreement with their measurements of inclusion diameters before and after heating.

**Necking Down**

Most fluid inclusions that we observe today do not have the same shape as when the fluid was originally trapped in the mineral. Following entrapment in the host phase, most inclusions change shape through a process referred to as "necking down" that involves dissolution and re-precipitation of the host phase to reduce the surface area and produce many smaller inclusions from the original larger inclusion. For example, when a mineral fractures during or after growth, some fluid may enter the fracture as shown in Figure 8-10a. As necking down proceeds, the fluid in the fracture becomes isolated into progressively more and smaller fluid inclusions. During this process, the inclusion shape tends to become more regular. This process is often referred to as maturation in the fluid inclusion literature (cf. Bodnar et al., 1985). If this process goes to completion, the former fracture plane will be decorated by numerous spherical or negative-crystal shaped fluid inclusions, often showing a decrease in inclusion size towards the original fracture tip (Fig. 8-10d).

If necking down occurs at the temperature and pressure of trapping of the original fluid, the resulting inclusions will all show similar phase relations as well as microthermometric behavior that is consistent with the PTX trapping conditions. Indeed, the process described above and illustrated in Figure 8-10 is identical to that used to trap synthetic fluid inclusions according to the technique of Sterner & Bodnar (1984). Accordingly, fractured quartz cores are placed into high temperature autoclaves along with a fluid of known composition. During the constant-temperature experiment, fluid enters the fracture and the fracture heals as shown in Figure 8-10 to produce numerous synthetic fluid inclusions trapped at constant and known PTX conditions. The microthermometric behavior of the resulting inclusions is consistent with the known formation conditions. In this case, necking down is simply the process by which inclusions mature and does not involve reequilibration of the type discussed in this chapter.

Inclusions that undergo necking down at constant temperature and pressure, and in the one-phase fluid field, are of no concern in discussions.
of reequilibration processes that lead to incorrect microthermometric results. However, if the temperature and/or pressure change during the reequilibration process, or if two or more fluids ± solids are present in the fracture during necking down, the resulting inclusions likely will provide incorrect compositional and microthermometric data. Figure 8-11 is a schematic representation of necking down in a decreasing temperature system in which phase separation to produce a vapor bubble occurs during cooling. The original inclusion at time $T_0$ contains only liquid. During cooling to temperature $T_1$, a vapor bubble nucleates in the inclusion. During cooling from temperature $T_1$ to $T_2$, the original inclusion necks down to produce two inclusions. One inclusion (inclusion a) contains the larger vapor bubble that formed during initial cooling, and the other inclusion contains only a small vapor bubble that formed after the two inclusions were separated. With continued cooling, the larger inclusion undergoes necking down again to produce two smaller inclusions, one containing the bubble that was present at the moment necking occurred (inclusion b) and the other (inclusion c) containing a smaller bubble that nucleated after necking during cooling from $T_2$ to $T_3$. At room temperature ($T_4$) the three inclusions show very different liquid to vapor ratios, and would homogenize at different temperatures. Thus, if an FIA is comprised of inclusions that have undergone necking down in a changing temperature and/or pressure system, or in the presence of two or more phases, the fluid inclusions will show variable phase relations and a range in homogenization temperatures. Such inclusions should be avoided during microthermometric studies if the goal is to determine the original PT formation conditions.

**REEQUILIBRATION OF MELT INCLUSIONS**

Compared to fluid inclusions, compositional reequilibration of melt inclusions is much more common. Anderson (1974) was one of the first to consider the reliability of melt inclusions and the various post-entrapment changes that might lead to reequilibration. Nielsen et al. (1998) address the relative advantages of microscope heating versus batch heating of mineral grains to homogenize melt inclusions, and also discuss volatile loss and contamination of melt inclusions from alteration products. Manley (1996) discussed the use of melt inclusion morphology as an indicator of the timing of inclusion formation during the eruption event. Qin et al. (1992) developed a general theoretical model for diffusive reequilibration of melt inclusions, and applied this model to evaluate water loss from melt inclusions following entrapment, as well as reequilibration of trace element concentrations in melt inclusions. Gaetani & Watson (2000) evaluated Fe-Mg exchange between melt inclusions and host olivine, and Danyushevsky et al. (2000) provide data from natural melt inclusions in olivine that have reequilibrated by Fe-loss.

A complete consideration of the melt inclusion reequilibration process is beyond the scope of this chapter. The reader is referred to the sources listed above, as well as references therein, for a more complete discussion of this problem.

**HOW TO AVOID LABORATORY REEQUILIBRATION OF FLUID INCLUSIONS**

For most fluid inclusions, compositional reequilibration during laboratory studies is unlikely if care is taken during data collection. Exceptions include hydrogen loss (or gain) by the inclusions during microthermometry and compositional reequilibration of melt inclusions during heating. The main type of reequilibration that one has to be concerned with during laboratory studies of most fluid inclusions is...
volumetric reequilibration. Fluid inclusions tend to reequilibrate volumetrically when the internal pressure exceeds the strength of the host mineral and, as noted above, this value depends on the mineral hardness as well as the inclusion size and shape and fluid composition. In most cases, heating to some temperature above room temperature (and above the homogenization temperature) is required to generate pressures sufficiently high to cause most inclusions to reequilibrate. Low temperature (Th =150°C) aqueous inclusions may also reequilibrate during cooling studies to measure ice-melting temperatures. In this case, formation of ice during cooling, which occupies approximately 9 % more volume than the liquid water it formed from, can generate high pressures and cause the inclusion to stretch. Lawler & Crawford (1983) coined the term "freeze stretching" to describe this phenomenon.

In the early days of fluid inclusion studies, most polished sections were prepared using Canada balsam or Lakeside cement or some other adhesive that required the sample to be heated to temperatures approaching 100°C. In many cases, little care was taken to control this temperature and samples may have been heated to several hundred degrees to mount the sample on a glass slide. Such high temperature would cause fluid inclusions to stretch before they were placed into the fluid inclusion stage, resulting in erroneous microthermometric data. Today, most workers take care to minimize heating of the sample during polishing, and often use adhesives such as Superglue™ that sets at room temperature and requires no heating. In some extreme cases involving very low temperature inclusions, the samples must be stored in a temperature-controlled room and transported in ice to avoid stretching of the inclusions (cf. Wilson et al., 2003).

Most workers believe that reequilibration in the laboratory is not a problem as long as the inclusions are not heated above the homogenization temperature. This is because the rate of pressure increase in the inclusion during heating is much lower before the inclusion has homogenized than it is after homogenization occurs. And, for gas-free aqueous inclusions in most minerals, the internal pressure is unlikely to exceed a few hundred bars during heating, as long as the homogenization temperature is below about 400°C. For higher homogenization temperatures, the internal pressure can become sufficiently high to reequilibrate inclusions in even some of the more resistant minerals, such as quartz. For example, a fluid inclusion containing a 25 wt. % NaCl solution will have an internal pressure of about 900 bars at a homogenization temperature of 600°C (Bodnar & Vityk, 1994). According to equation (1) above, this pressure is sufficient to cause decrepitation of inclusions in quartz larger than about 25 micrometers (Bodnar et al., 1989).

Many who study fluid inclusions from medium- to high-grade metamorphic environments have experienced inclusion decrepitation before homogenization occurs. This happens because most inclusions from this environment contain significant amounts of carbon dioxide, resulting in elevated pressure in the inclusions, even at room temperature. As an example, an H2O-CO2 inclusion containing 37 mole percent CO2 and homogenizing at 263°C would have an internal pressure of 2880 bars at homogenization (Sterner & Bodnar, 1991). This pressure would cause decrepitation of all inclusions larger than about 3 µm in quartz (equation (1) above), and any inclusions larger than this would decrepitate during heating, before the homogenization temperature is reached. Schmidt et al. (1999) described application of the Hydrothermal Diamond Anvil Cell as a pressurized fluid inclusion stage to eliminate (or minimize) decrepitation of high pressure inclusions during heating to homogenization.

In some cases it may simply not be possible to heat (or cool) a fluid inclusion without causing reequilibration to occur. Not every fluid inclusion is able to provide useful microthermometric data. What is most important to the fluid inclusionist is to be able to recognize inclusions that reequilibrate during laboratory studies. This can best be accomplished by following one simple rule during microthermometric analysis: Thou shalt collect no data from any fluid inclusion that has not been observed continuously during the very first heating (or cooling) run. If one obeys this rule, the probability of collecting data from inclusions that have reequilibrated during laboratory analysis is significantly reduced.
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ACKNOWLEDGEMENTS

Much of the information presented in this chapter represents studies by former students and post-doctoral researchers and visitors to the Fluids Research Laboratory. I wish to acknowledge Don Hall, Mike Sterner and Max Vityk for their many contributions that helped me to better understand the reequilibration process. I also give special thanks to Phil Bethke and Ed Roedder for encouraging me as a student to pursue this important area of fluid inclusion research. Alan Anderson, Will Lamb, Iain Samson and one anonymous reviewer are thanked for their comments and suggestions for improving the manuscript. The National Science Foundation, Department of Energy, NASA, and the American Chemical Society have supported work in the Fluids Research Laboratory over the years. NSF Grants EAR-0001168 and EAR-0125918 provided support during preparation of this manuscript.


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