Fluid Inclusion Introduction

Introduction to Fluid Inclusions

What is a Fluid Inclusion?

Cavity in a mineral that may contain 1 or more phases

- vapor - H_2O (P<<1 atm), CO_2, CH_4, N_2, H_2S, …
- liquid - H_2O, CO_2, petroleum, …
- solid - NaCl, KCl, hematite, anhydrite, muscovite, cpy, magnetite, carbonates, ...

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Introduction to Fluid Inclusions

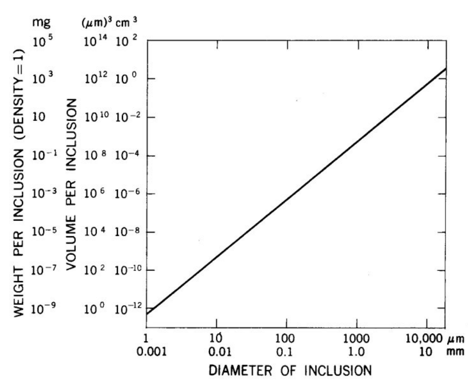
What are the sizes?

> mm are museum specimens

3-20μm; typical range for microthermometry

1.5μm; smallest workable size for H_2O or CO_2 inclusions

5 μm; smallest workable size for H_2O+CO_2 inclusions



Volume and weight of spherical inclusions assuming a fluid of density 1.0 g/cc.

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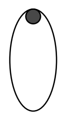
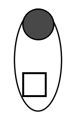
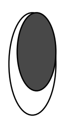
Types of Inclusions



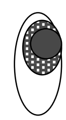
undersaturated, liquid-rich H_2O



saturated H_2O, daughter likely NaCl or KCl



undersaturated, vapor-rich (must heat to be sure Th → Vap)



CO_2-bearing (below Th_{L-V})

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Introduction to Fluid Inclusions

Major Textural Criteria

- Primary:
  formed during the mineral growth
  - growth zones; overgrowths defined by inclusions
- Pseudo-secondary:
  formed in healed fracture in mineral during original mineral growth
- Secondary:
  developed after the crystallization of the host

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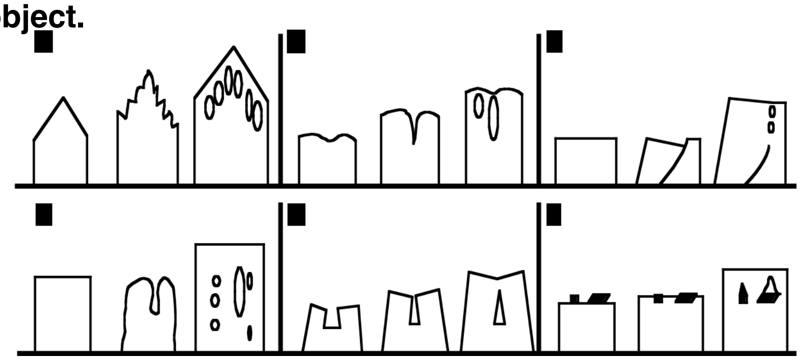
Introduction to Fluid Inclusions

Mechanisms of Trapping

(a) dendritic growth, (b) partial solution, (c) between growth spirals, (d) sub-parallel block growth, (e) fracture during growth, (f) foreign object.



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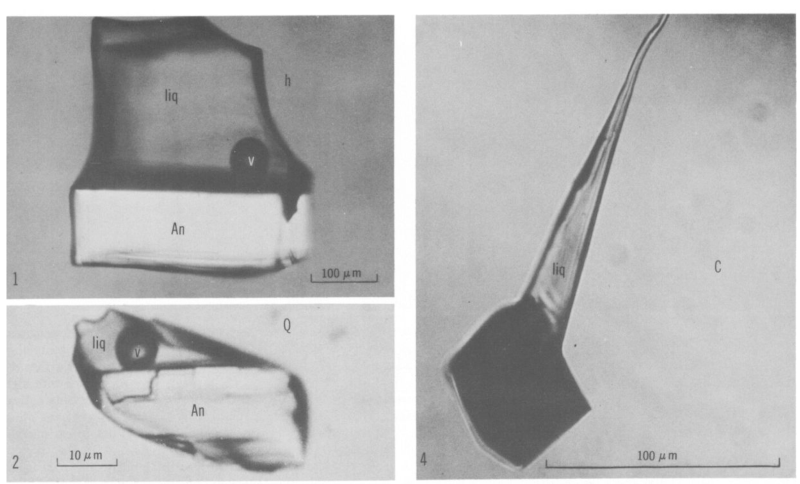
Accidental Trapping



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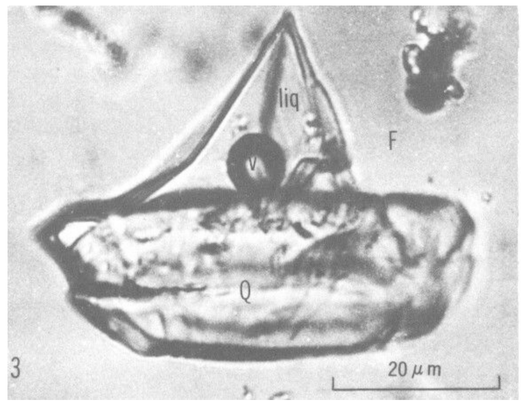
Trapping

- Quartz in Fluorite
- Certainly not a daughter crystal



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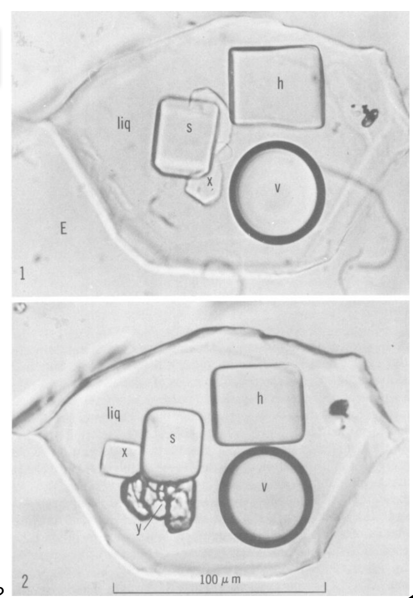
Daughter Crystals

- Before (top) and after freezing
- Both photos at room temp.



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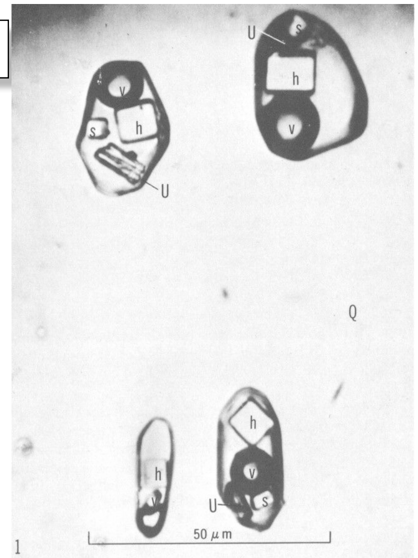
Constancy of Ratios

- For these inclusions:

- Sylvite dissolves at 145°C
- Halite dissolves at 400°C
- Vapor disappears at 440°C
- U is strongly birefringent, parallel extinction, and refuses to dissolve



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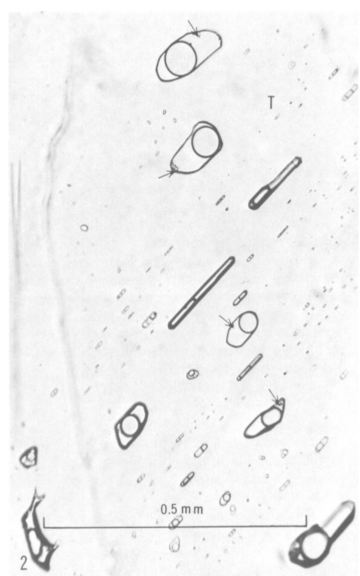
Introduction to Fluid Inclusions

Constancy of Ratios

- L-V ratios
- Tiny daughter crystal visible in largest inclusions



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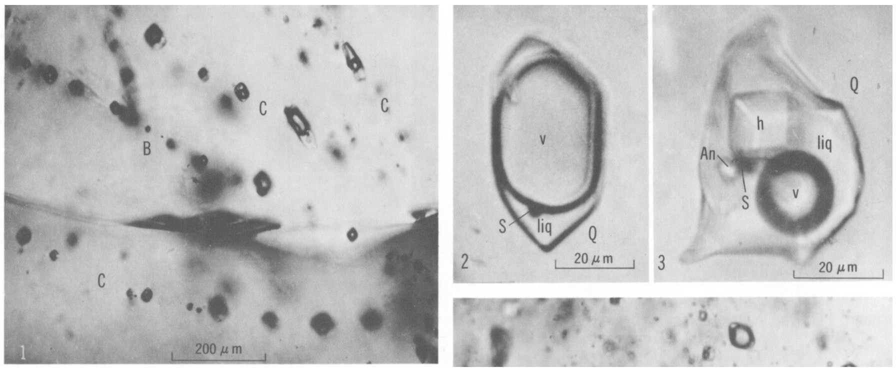
Immiscible Fluids



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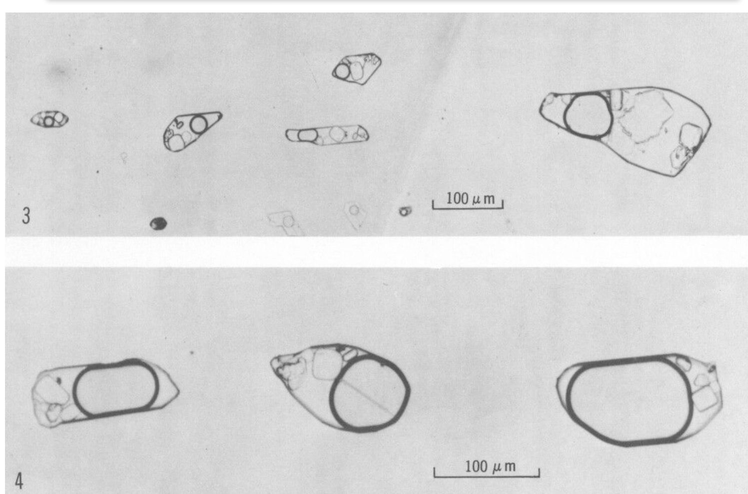
Adjacent planes of inclusions



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Secondary Inclusions

- Look at essentially any sandstone/quartzite samples in the lab

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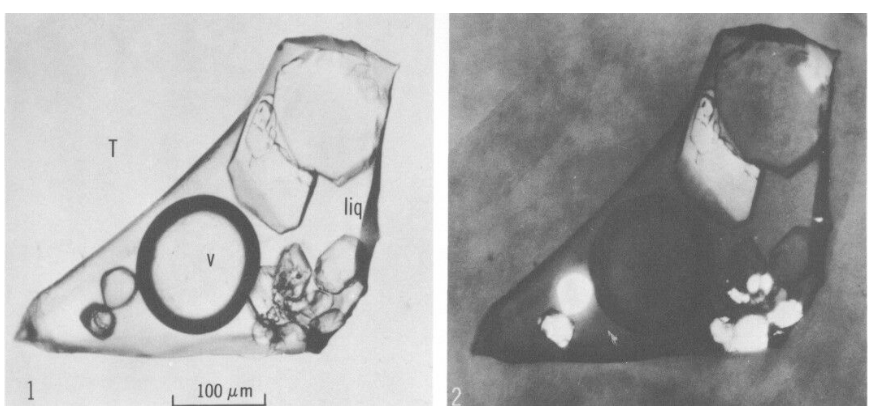
Anisotropic Daughters



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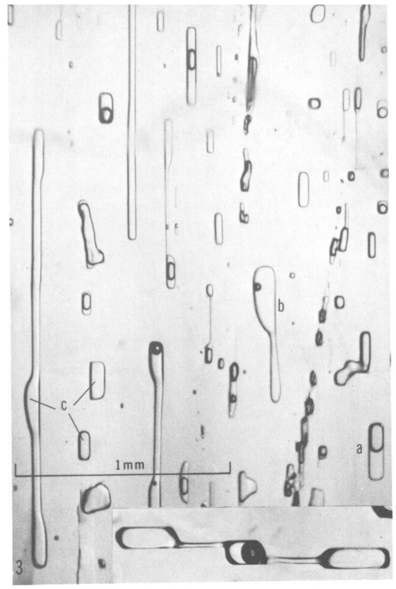
Fluid Inclusion Introduction

Necking

- Why does this happen?
- How can you tell?
- What data can still be measured?



Roedder, 1972

Basic Assumptions:

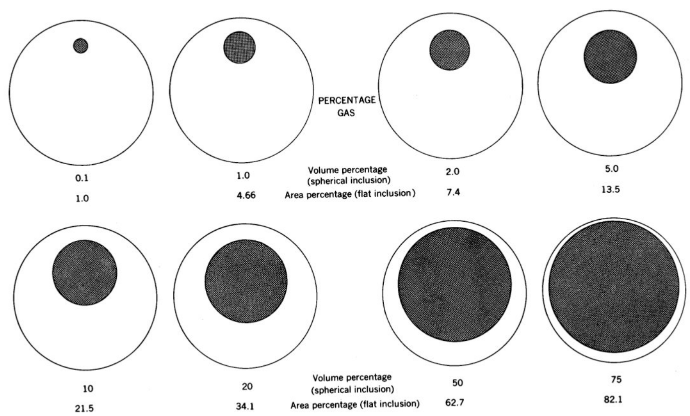
These form the basis of geothermometry and geobarometry

- Trapped fluid was a single homogeneous phase
- The cavity has not changed in volume
- Nothing is added or lost after sealing
- Effects of pressure are insignificant or known
- The origin of the inclusion is known
- The determinations of Th are both precise and accurate

Introduction to Fluid Inclusions

Phase Ratio Estimation

Inclusion appearance for various volume percentages of the gas phase assuming both the gas bubble and inclusion are spherical. The area percentages assume flat circular disks.



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Introduction to Fluid Inclusions

Terms and Abbreviations

- **Th - Temperature of total homogenization**
- **Th L-V, Th CO_2 L-V, etc. - Temperature of homogenization of the stated pair of phases only. The phase into which homogenization occurs should also be stated [e.g. Th CO_2 L-V (L)]**
- **Tt - Temperature of trapping**
- **Td - Temperature of decrepitation**
- **Tm - Temperature of melting**
- **Te - Temperature of eutectic**
- **Tn - Temperature of nucleation in fluid**

(Roedder, 1984)

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Transitions on Cooling

<u>Phase transitions on Cooling</u>:

- Heterogenization (Tb)

  A single phase becoming immiscible [F → L+V]

  for non-isochoric systems:

  condensation [V → L+V]

  boiling [L → L+V]

- Sublimation (Tsc)

  Transition [F → S+F] and [S+F → F] (cont.)

Terms and Abbreviations (van den Kerkhof, 1988)

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Cooling (cont)

- Freezing (Tf)

  (or solidification) forming of a solid phase from a liquid and a vapor [L+V → S+F]

- Crystallization (Tx)

  (or precipitation) nucleation of a crystal in a liquid coexisting with a vapor [L+V → S+L+V]

- Partial heterogenization (Tbs)

  the forming of a bubble in the presence of solid CO_2

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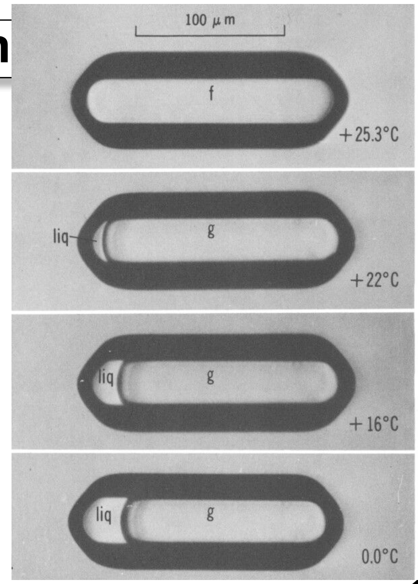
Cooling Observation

- CO_2 Inclusion



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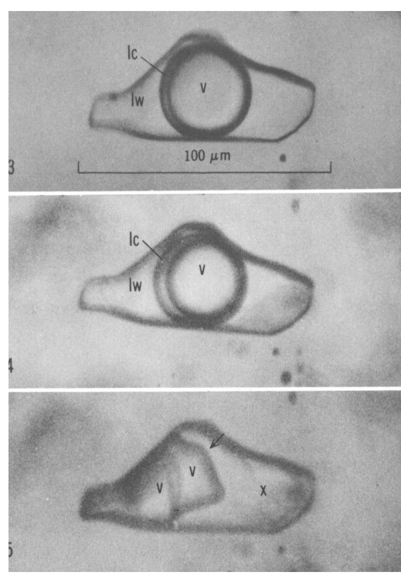
Cooling

- Room temp
- Cooled quickly to -5°C
- Cooled to -78°C then equilibrated at -8°C



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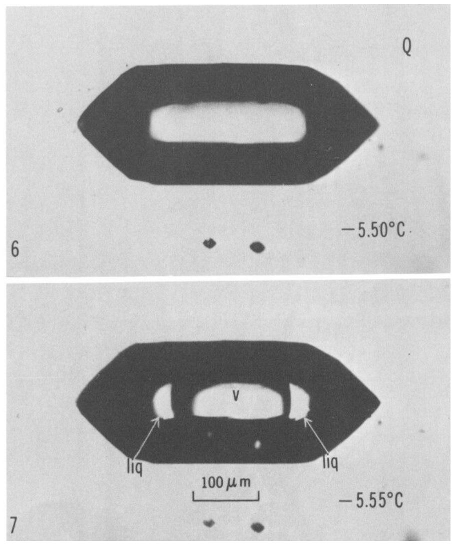
Easy Does It!

- Notice the temperatures



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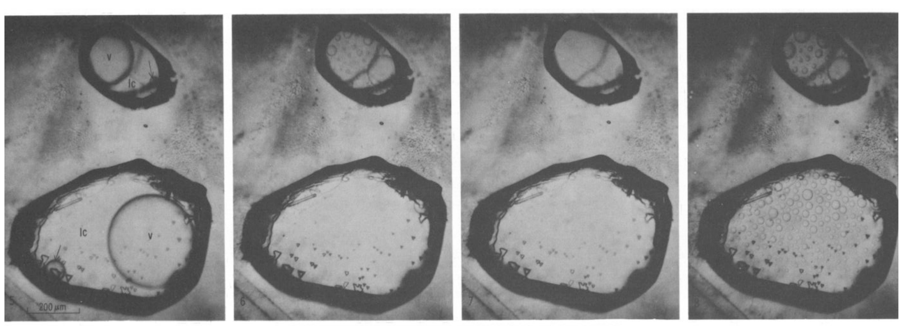
Near Critical Behavior



BEHAVIOR OF LARGE CO_2 INCLUSIONS IN SAPPHIRE

Roedder, 1972

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Transitions on Warming

Phase transitions on Warming:

- Partial homogenization (Ths)

  homogenization of liquid and vapor in the presence of solid CO_2 [S+L+V → S+L] or [S+L+V → S+V]

- Incipient melting (Ti)

  solid coexisting with liquid or vapor to 3-phase equilibrium [S+L → S+L+V] or [S+V → S+L+V]

(cont.)

Terms and Abbreviations (van den Kerkhof, 1988)

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Warming (cont)

- Melting (Tm)

  (or final melting) 3-phases to liquid and vapor [S+L+V → L+V]

- Homogenization (Th)

  (normal or stable) [L+V → L or → V] or [L+V → L=V]

- Metastable homogenization (Thm)

  homogenization of a metastable liquid and vapor

- Sublimation (Ts)

  transition of solid directly to vapor or liquid

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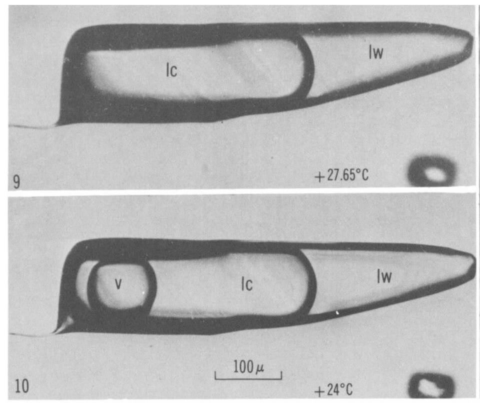
Heating in 3-phase inclusion

- CO_2 L-V homogenizes here at 27.65°C



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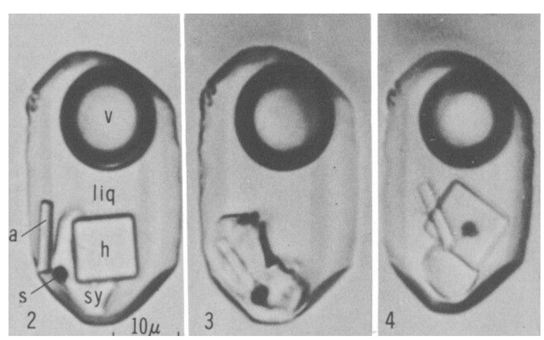
Time Passes

- Room temp
- Room temp. after 4 days at 410°C
- 8 months later



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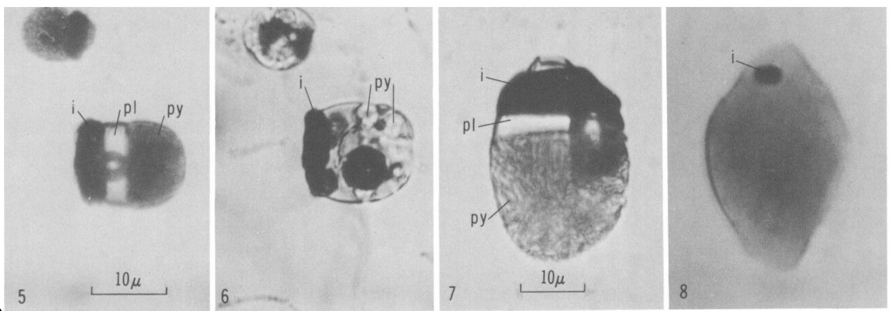
Silicate Melt Inclusions

- Apollo 11 lunar olivines
- Heated to over 1100°C, then quenched



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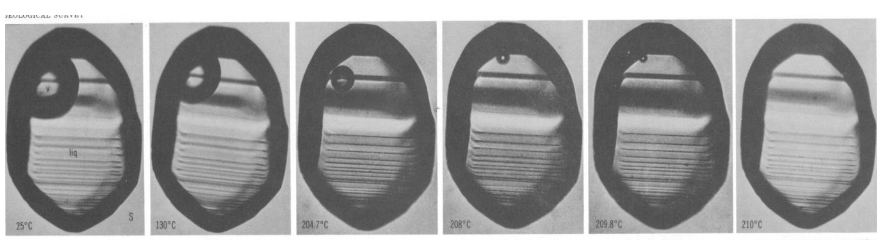
Homogenization

- Creede ZnS



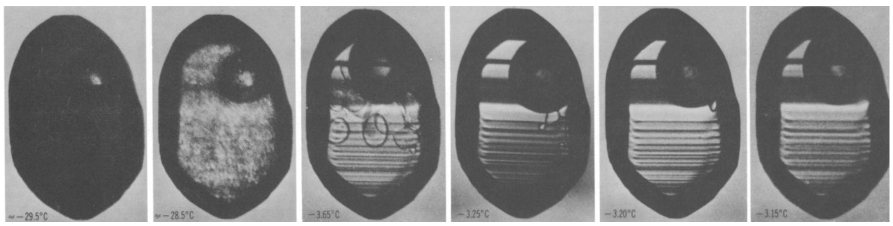
25° C | 130° | 204.7° | 208° | 209.8° | 210°

Roedder, 1972

Introduction to Fluid Inclusions

Melting

- Creede ZnS



-29.5° -28.5° -3.65° -3.25° -3.20° -3.15°

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Introduction to Fluid Inclusions

Outline

What, Why, How?

Phase equilibria: H_2O; H_2O-NaCl; CO_2; CO_2-CH_4; H_2O-CO_2, H_2O-CO_2-NaCl

Pressure determinations

Post-entrapment changes

Decrepitation

H_2O-CO_2 details

Analytical methods

Miscellaneous

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Introduction to Fluid Inclusions

What, Why, How?-1

The single most important step in interpreting fluid inclusions is the selection of appropriate inclusions for analysis. The 5 fundamental steps in setting up a fluid inclusion study are shown below.

[1] What can be learned? Fluid inclusions record information on temperature, pressure, composition and density of a fluid. Inclusions may also provide records of deformation events and both relative and absolute age relationships.

[2] Goal of study? The first order question is "What lead you to consider a fluid inclusion study in the first place?" In other words, what hypothesis can be formulated that fluid inclusion evidence will bear on, at least theoretically? What are you trying to learn? A fluid inclusion study is seldom an end in itself- the data you derive almost certainly must be interpreted in the context of other geochemical parameters.

[3] What is needed? On the basis of the question or hypothesis formulated in the previous step, what kinds of inclusions need to be present to answer the question or address the hypothesis?

primary inclusions? secondary inclusions? both? one or the other?

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Introduction to Fluid Inclusions

What, Why, How?-2

[3] What is needed (cont.)? e.g. (a) diagenesis or dolomitization of carbonate rocks might be recorded in primary inclusions in the cements but in secondary inclusions in pre-existing grains that were fractured or partially dissolved during either tectonic movements or slumping/ karstification.

(b) epithermal vein quartz may contain both primary and secondary inclusions related to quartz growth and cracking (respectively) associated with hydraulic fracturing and pressure cycling between lithostatic and hydrostatic conditions.

[4] Reconnaissance study. MOST IMPORTANT STEP! In all cases, one should do a broad reconnaissance survey of many selected samples. The sample selection criteria will vary with the question to be answered and with the amount of time the researcher has available. As many samples as possible should be surveyed using preparation techniques that don't necessarily require perfect doubly polished chips.

[5] Will the study work? As a result of the survey, the careful and thoughtful researcher will have to decide whether the study as originally conceived is still feasible. More likely, the original research plan will need to be modified in light of what has been discovered during the reconnaissance survey.

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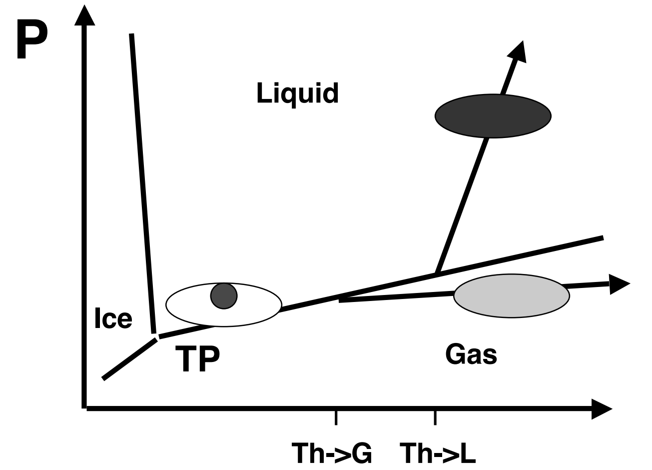
Introduction to Fluid Inclusions

Schematic H_2O Diagram



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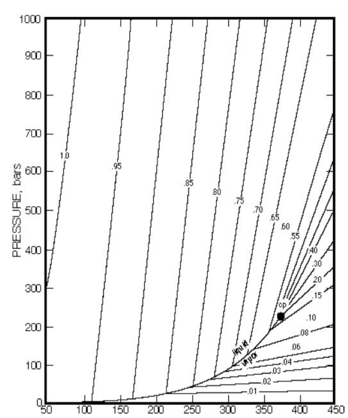
Introduction to Fluid Inclusions

P-T Diagram: H_2O

This diagram shows the liquid-vapor line, critical point, and a variety of isochores for the H_2O system. Heating an inclusion until the liquid and vapor phase homogenize (become one) will determine a point on the L-V curve. The inclusion was trapped somewhere along the isochore that emanates from that point; the steep isochores correspond to homogenization to the liquid by vapor shrinkage. Inclusions that exhibit Th → V were trapped along the flatter isochores.



Fisher et al., 1974

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Salinity Determinations

- *freezing point depressions*

  traditional microthermometry
- *observations of first melting*

  difficult, may or may not be eutectic
- *crushing*

  followed by leaching; bulk, contamination
- *Raman spectroscopy*

  new technique, H_2O peak shape details

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First Melting

- used to determine Te (eutectic temperature)

• NaCl	-21.2°C
• KCl	-10.7°C
• $CaCl_2$	-49.8°C
• $MgCl_2$	-33.6°C
• NaCl-KCl	-22.9°C
• NaCl-$CaCl_2$	-52.0°C
• NaCl-$MgCl_2$	-35°C

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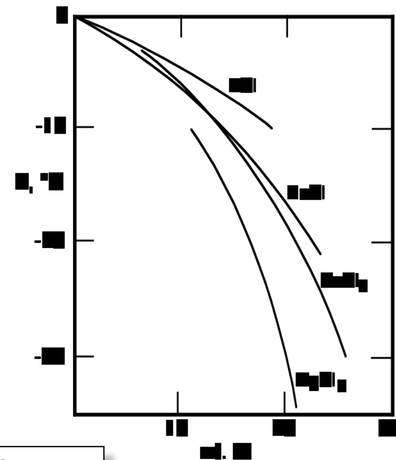
Freezing Point Depressions

- Note how well the NaCl system serves as a model for the other salts.
- There is a lot of experimental data available for the NaCl-H_2O system.
- Pure $MgCl_2$ solutions are not likely so the maximum error in modeling observations as NaCl will be less than 5%.



- Thus we commonly express salinity as weight percent NaCl equivalent.

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System H_2O - NaCl

- *undersaturated case* (<23.3 wt% NaCl):

  wt% NaCl eq = 1.76958T - 4.2384E-2 T^2 + 5.2778E-4 T^3 ± 0.028 wt%

  T = °C of last ice melt (-21.2°c < T < 0°C)
- *saturated case* (>23.3 wt% NaCl):

  wt% NaCl eq = 26.218 + 0.0072 T + 0.000106 T^2 ± 0.5 wt%

  T = °C at which NaCl crystal disappears
- *see figure which follows*

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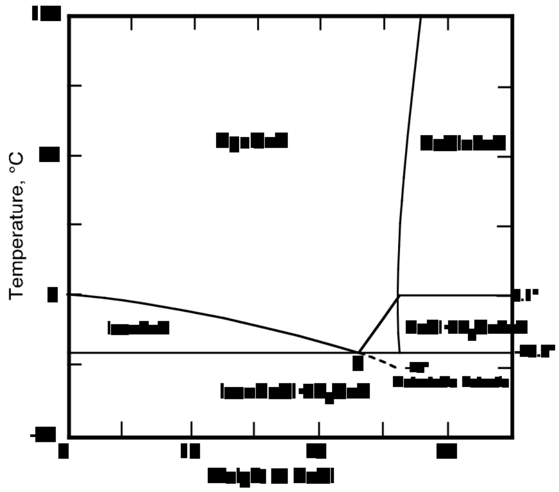
T-X Relations: H_2O-NaCl



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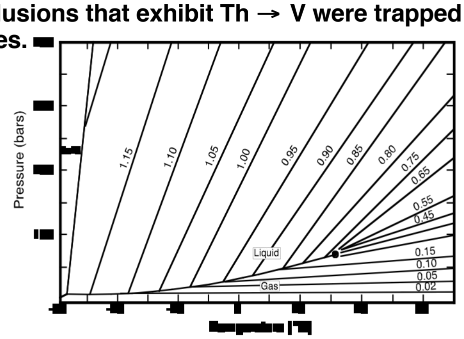
Introduction to Fluid Inclusions

P-T Diagram: CO_2

This diagram shows the liquid-vapor line, critical point, and a variety of isochores (labeled with density) for the CO_2 system. Heating an inclusion until the liquid and vapor phase homogenize (Th L+V) determines a point on the L-V curve. The inclusion was trapped somewhere along the isochore that emanates from that point; the steep isochores correspond to homogenization to the liquid by vapor shrinkage. Inclusions that exhibit Th → V were trapped along the flatter isochores.



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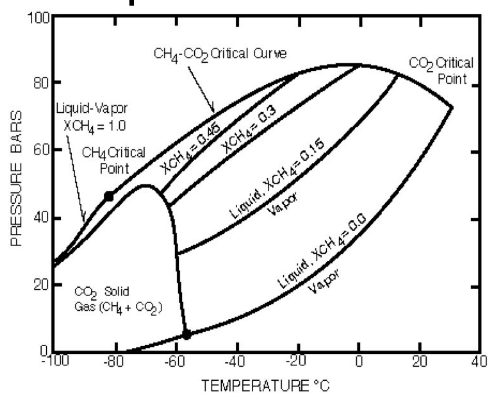
CO_2-CH_4

The basic phase diagram showing CO_2 triple point, critical points, critical curve, S+L+V curve and several bubble point curves.



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H_2O-CO_2 Determinations

- ***gas chromatography***

  bulk, reasonably sensitive

- ***vacuum line manometer***

  crush and separate cryogenically, bulk

- ***FTIR?***

  good peak shapes, questions about optics and resolution

- ***Raman?***

  new instruments have decent H_2O peak shape

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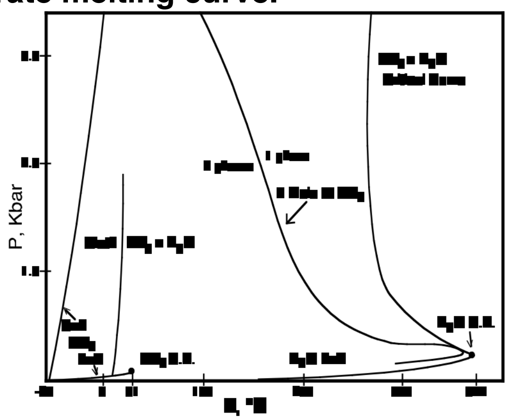
Basic CO_2-H_2O System

Note critical curve and 7 mole % solvus as well as clathrate melting curve.



H_2O-CO_2-NaCl:

On freezing:

- **clathrate formation** **-30 to -40°C**
- **water ice formation** **-40 to -60°C**
- **CO_2 freezing** **-90 to -110°C**

On warming:

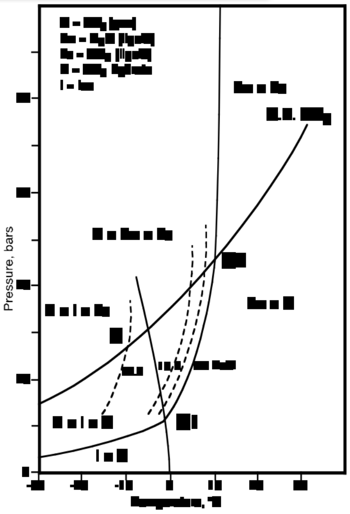
- **CO_2 melting** **-60 to -56.6°C**
- **H_2O ice melt** **not quantitative**
- **clathrate melt** **+10 to 0°C**
- **Th CO_2 L-V → L(V)**

Introduction to Fluid Inclusions

H_2O-CO_2-NaCl Clathrates-1

Phase diagram for H_2O-CO_2 at low T. The dashed lines indicate the shift to lower temperatures of the decomposition of CO_2 hydrate in equilibrium with 5 and 10 wt. % NaCl solutions and a saturated NaCl solution (24.2%).

Note also the difference between being along C-Q2 and being off this univariant curve.



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Introduction to Fluid Inclusions

Pressure Determinations

To derive information on the pressure at the time of trapping of a group of fluid inclusions, one needs:

- Good control on time of trapping
- Good evidence of freedom from secondary effects
- Good thermometric data
- Good compositional data
- Good P-V-T-X data covering the range of conditions

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Introduction to Fluid Inclusions

Pressure Correction Diagrams

"Pressure correction" for H_2O-NaCl inclusions assuming:

- **– pure NaCl solution – salinity determined**
- **– pressure known – Th–> liquid**

Figure from Potter (1977) who has diagrams for 1, 5, 10, 15, 20 & 25% NaCl solutions in large (10 x15 cm) format.

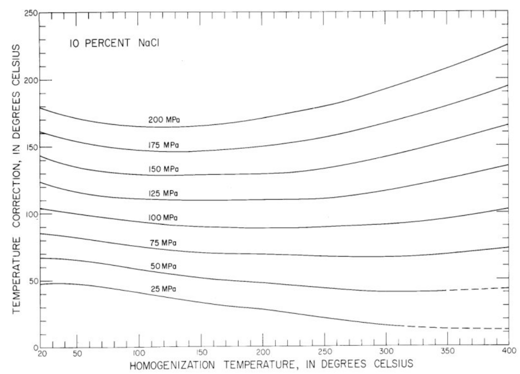

FIGURE 3.—Temperature correction for a 10-percent NaCl solution as a function of homogenization temperature and pressure.

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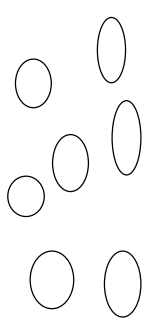
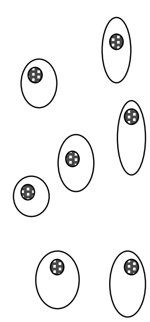
Introduction to Fluid Inclusions

Secondaries and Necking-1



If a plane of secondary inclusions neck down before hitting the L-V curve:

- ***correct* Th**
- ***correct* salinity**



cooling to L-V curve

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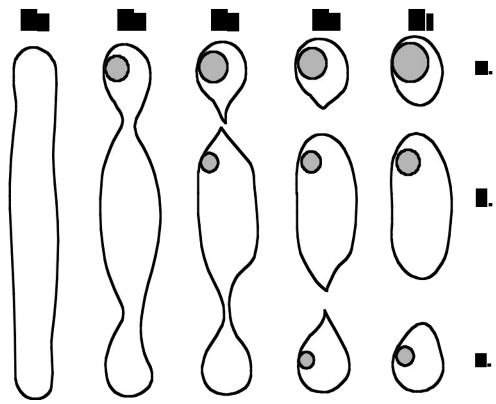
Introduction to Fluid Inclusions

Secondaries and Necking-2

If a plane of secondary inclusions is necking down when it hits the L-V curve:

- *incorrect* Th
- *correct* salinity



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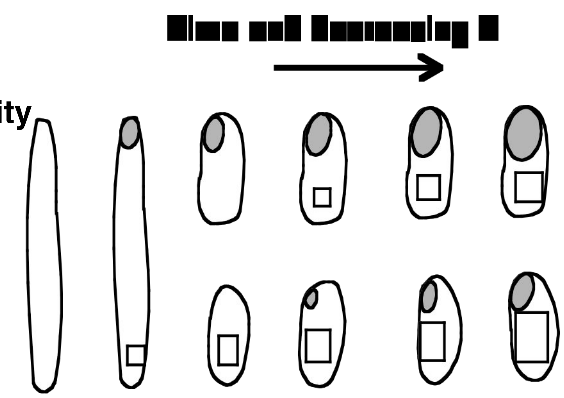
Introduction to Fluid Inclusions

Secondaries and Necking-3

If a plane of inclusions contains a saturated solution and is necking down when it hits the L-V curve:

- *incorrect* Th
- *incorrect* salinity



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Introduction to Fluid Inclusions

Decrepitation: P vs. Size-1

As determined by Naumov et al. (1966), Leroy (1979), and Swanenberg (1980), size strongly effects the maximum internal pressure that an inclusion can withstand. For quartz, this ranges from ≈ 850 bars for 30μm inclusions to 1200 bars at 12 μm and 5000-6000 bars for 1μm diameters.

Recently, Bodnar and others have done experiments attempting to quantify these relations.

Lacazette (1990) has calculated, using fracture mechanics, the strengths of various sized inclusions in quartz and calcite. Results of these calculations agree well with the observed and experimental data and are presented on the following slide.

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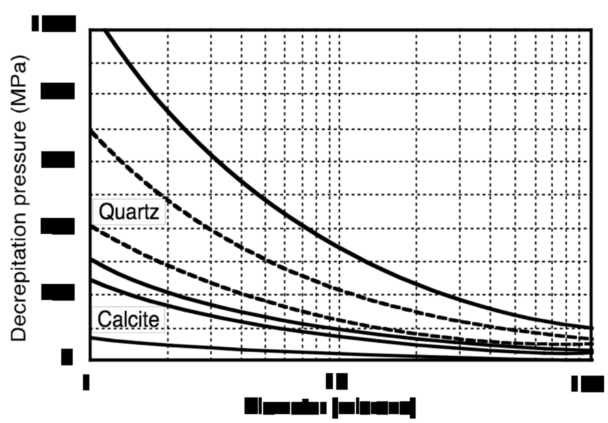
Introduction to Fluid Inclusions

Decrepitation: P vs. Size-2

The 4 curves for quartz (only 2 are shown for calcite) are for different shape factors and represent the size vs pressure relationship for inclusions of a given shape. All inclusions should decrepitate at pressures above the upper boundaries of a field; none should decrepitate at pressures below the lower boundary.



Lacazette, 1990

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