The compositions of of many natural fluids are approximated by the ternary system H_2O -NaCl-CO₂. The PVTX properties of fluids in this ternary system can be used to interpret microthermometric data from many fluid inclusions from many different geologic environments.



When you look down the microscope at a fluid inclusion, you should <u>not</u> see this, but rather





.... you should see this!



Fluid inclusions represent chemical systems at constant volume (density) conditions. When you look at an Fl under the microscope, you should become the fluid inclusion and ask yourself:

- What chemical system am I in?
- What does the PT phase diagram for my chemical system look like?
- Where am I on that phase diagram?



The one-component system H₂O provides a basis for understanding the PVTX behavior of more complex fluid systems that are relevant to fluid inclusions.



The H₂O system, like other one-component systems, is characterized by a critical end point that terminates the liquid + vapor coexistence curve. At temperatures and pressures greater than the critical P&T, it is not possible for two fluid phases to coexist.



The Gibbs Phase Rule describes the number of phases that may coexist in equilibrium in a given chemical system, and is given by:

f =the number of degrees of freedom, or the number of variables (P, T, X) that can be varied arbitrarily without gaining or losing a phase;

- c = the number of components or chemical substances required to completely describe the compositions of all phases in the system;
- p = the number of phases, or substances with distinct physical and chemical properties.

So, according to the phase rule, what is the maximum number of phases that are possible in a one-component system?



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Note that the Gibbs Phase Rule describes the number of phases that can coexist **in equilibrium**, but does not constrain the total number of phases in the system. Thus, the system H_2O is characterized by at least 14 different phases, and multiple triple points where three different phases are in equilibrium.



<u>Triple Pt</u> (L+V+Ice(I)) 0.01°C, 0.00611 bar

<u>Critical Point</u> 373.946°C 220.64 bar 0.322 g/cc The density of fluid H_2O (liquid and vapor) is often plotted as isochores (lines of constant density or specific volume), especially for application to fluid inclusions.



The density of fluid H_2O (liquid and vapor) varies systematically with increasing temperature and pressure, as shown schematically below. Note that a discontinuity in density occurs for temperatures less than the critical temperature, whereas density varies smoothly and continuously with pressure at higher temperatures.





It is important to understand the relationship between fluid properties and phase behavior and microthermometric properties of fluid inclusions.

The critical density of H_2O is 0.31 g/cm³. If an FI traps H_2O with the critical density, what will be the volume percent vapor in the FI at room temperature?



The critical density of H_2O is 0.31 g/cm³. If an FI traps H_2O with the critical density, what will be the volume percent vapor in the FI at room temperature?

The easiest way to do these mass-volume balance calculations is to assume a volume for the FI – here we will assume 1 cm³ (the volume assumed does not affect the result).

So, if we have a 1 cm³ FI that traps H_2O with a density of 0.31 g/cm³, the FI contains:

 $(1 \text{ cm}^3) * (0.31 \text{ g/cm}^3) = 0.31 \text{ g of } H_2O.$

At room temperature the FI contains liquid and vapor. The vapor phase is essentially a vacuum (has no mass), so all of the 0.31 g of H_2O is contained in the liquid phase. If we assume a density of ~1 g/cm³ for the liquid, the volume of liquid is:

 $(0.31 \text{ g}) / (1 \text{ g/cm}^3) = 0.31 \text{ cm}^3 \text{ of } \text{H}_2\text{O}.$

The total volume of the FI is 1 cm³. If the liquid occupies 0.31 cm³, then the FI contains:

 $(0.31 \text{ cm}^3) / (1 \text{ cm}^3) = 0.31 \text{ volume fraction (31 volume %) liquid and, accordingly, 1.0 - 0.31 = 0.69 = 69 volume % vapor$



Knowing the density of the fluid that is trapped in the FI, and knowing the densities of the coexisting liquid and vapor phases at room temperature allows us to predict the liquid-to-vapor ratio for any homogenization temperature (or fluid density).



Modified from Fisher. 1976

According to the Gibbs Phase Rule:

$$f = c - p + 2$$

liquid + vapor (2 phases) coexist along a line in P-T space (one degree of freedom). Thus, if we measure the homogenization temperature of a fluid inclusion trapped in a 2-phase system, the pressure is known.



Knowing the density of the fluid that is trapped in the FI, and knowing the densities of the coexisting liquid and vapor phases at room temperature allows us to predict the liquid-to-vapor ratio for any homogenization temperature (or fluid density).



At room temperature, what is the liquid to vapor ratio of H_2O fluid inclusions trapped on the boiling curve at about 310°C?

The inclusion that traps the liquid phase will contain 70 volume % liquid and 30 volume % vapor at room temperature.

What are the phase ratios of the inclusion that traps the vapor phase?



The two phase diagrams below show the same fluid inclusion pairs, plotted in P-T and T – ρ space.



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Pure (or nearly pure) CO_2 fluid inclusions are common in upper mantle environments and in high-grade (granulite) metamorphic environments. What is the main difference between the phase diagram for CO_2 and that for H₂O discussed previously?



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Unlike the H_2O system which shows numerous solid polymorphs at elevated pressures, the CO_2 system contains no additional solid phases at higher pressures.



PT diagram for CO_2 to 800 MPa and 800°C with isochores in g/cm³ plotted.



PT diagram for CO_2 to 2 GPa and 1200°C with isochores in cm³/mole plotted.



Isochores (in molar volumes, cm³/mole) for pure CO₂ at high temperatures and pressures appropriate for deep crust and upper mantle conditions.



From Touret & Bottinga, 1979



Phase Equilibrium Properties of Fluids: H₂O-NaCl





Remember that in the one-component H_2O system, liquid and vapor can only coexist at PT conditions along the liquid+vapor equilibrium curve. So, what happens when we add a second component, such as NaCl?





The Gibbs Phase Rule describes the number of phases that may coexist in equilibrium in a given chemical system, and is given by:

$$f = c - p + 2$$

- f = the number of degrees of freedom, or the number of variables (P, T, X) that can be varied arbitrarily without gaining or losing a phase;
- c = the number of components or chemical substances required to completely describe the compositions of all phases in the system;
- p = the number of phases, or substances with distinct physical and chemical properties.

Now that we have added a second component, NaCl, to H_2O , the maximum number of phases that may coexist in equilibrium in this two-component system is four (4). Thus, triple points now become quadruple points.





From Souririjan & Kennedy 1962

In the two-component system H₂O-NaCI, 4 phases coexist at a PT point, 3 phases coexist along a line, 2 phases coexist in an area, and one phase is stable in a volume, corresponding to 0, 1, 2 and 3 degrees of freedom, respectively.





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From Driesner (web page)

To make it easier to visualize the phase behavior in the system H_2O -NaCl, we will look at PT projections of the phase equilibria. The diagram below shows the fields that are present at elevated temperatures, plotted to scale. Note the large region of PT space where liquid and vapor may coexist.



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The most significant difference between the H_2O system and the system H_2O -NaCl is the range of PT conditions over which liquid and vapor may coexist, shown schematically below.



The liquid-vapor coexistence curves in the system H_2O -NaCl extend to progressively higher temperature with increasing salinity, but do not end at the critical point as occurs in the one-component H_2O system.





The P-T region over which fluids may undergo immiscibility (boiling) expands and moves to higher temperatures and pressures with increasing salinity. Stated differently, as the bulk salinity of the fluid increases, the "size" of the PT region in which that fluid is stable as a single phase fluid decreases.



This salinity of two-phase aqueous FI can be determined by measuring the ice melting temperature and referring to the H_2O -NaCl system.



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The isopleth for a given salinity defines the region of P-T space in which fluid-fluid immiscibility is possible for that composition.



The temperature and mode of homogenization of fluid inclusions is defined by the density. If the density is greater than the critical density, the inclusion will homogenize by shrinkage and



The temperature and mode of homogenization of fluid inclusions is defined by the density. If the density is less than the critical density, the inclusion will homogenize by expansion of the vapor bubble to fill the inclusions at the homogenization temperature.





If the density equals the critical density, the inclusion will homogenize by disappearance of the meniscus between liquid and vapor at the critical temperature.





Note that as the salinity increases, the PT region in which fluidfluid immiscibility is possible expands to higher temperatures and pressures.



Note that as the salinity increases, the PT region in which fluidfluid immiscibility is possible expands to higher temperatures and pressures.



For halite-bearing FI, the PT path followed during heating depends on whether the halite dissolves before, after or at the same temperature as the bubble. In the example below, the halite daughter mineral dissolves first, followed by disappearance of the vapor bubble at the homogenization temperature.



We can determine the salinity of halite-bearing fluid inclusions by measuring the halite dissolution temperature and referring to the solubility of NaCI in the H_2O -NaCI system.



If the bulk composition is in the two-phase region, the fluid will undergo immiscibility and split into a higher salinity liquid in equilibrium with a lower salinity vapor.



Modified from Bodnar et al., 1985a

What happens to a fluid with a composition of 10 wt% NaCl at the P-T point represented by the **red** dot?

The fluid splits into two immiscible fluids.

What are the compositions of the coexisting fluids?





Modified from Bodnar et al., 1985a

The PX diagram shows the same information as shown on the previous PT diagram. At 700°C and 100 MPa an H₂O-NaCl fluid with a salinity of 10 wt% is not stable, and it will split into a liquid with a salinity of 50 wt% and a vapor with a salinity of 4 wt%.

Is the red dot in the one phase field or the two phase field?

If in the two phase field, what are the compositions of the coexisting phases?



When plotted in T-X space, the compositions of the liquid and vapor phases that are in equilibrium are defined by a tie line connecting the liquid and vapor compositions at the pressure and temperature of interest.



The TX diagram shows the same information as shown on the previous PT and PX diagrams. At 700°C and 100 MPa an H_2O -NaCl fluid with a salinity of 10 wt% is not stable, and it will split into a liquid with a salinity of 50 wt% and a vapor with a salinity of 4 wt%.

Is the red dot in the one phase field or the two phase field?

If in the two phase field, what are the compositions of the coexisting phases?



The system H_2O -NaCl exhibits a continuous critical curve that extends from the critical point of H_2O to the critical point of NaCl. Conversely, the system H_2O - CO_2 has a discontinuous critical curve.





The system $H_2O - CO_2$ exhibits a region of fluid immiscibility at low to moderate temperature and from low to very high pressure. In PTX space the two-phase region has the shape of a boot.





In a manner similar to the system H₂O-NaCI, phase relations in the system H₂O -CO₂ are easier to display and understand when isopleths are projected onto a PT diagram.



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From Burruss, 1981

The PT extent of the two-phase region in the system $H_2O - CO_2$ varies in a systematic and predictable manner with composition.



Bodnar unpublished, based on data from Takenouchi & Kennedy, 1964

Addition of CO₂ to H₂O causes the critical point to move to lower temperatures and higher pressures. For any given isopleth, the two-phase (liquid+vapor) field lies to the low temperature side of the isopleth. Fluid inclusions trapped in the one-phase field homogenize along the isopleth corresponding to the inclusion bulk composition.



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Bodnar unpublished, based on data from Takenouchi & Kennedy, 1964



Fluid immiscibility in the H₂O-CO₂ system



Bodnar unpublished, based on data from Takenouchi & Kennedy, 1964

As in the H₂O-NaCl system, the compositions of coexisting phases in the H₂O-CO₂ system are defined by the isopleths that intersect in PT space. Thus, at 250°C and 50 MPa (red dot), an H₂O-rich phase containing 6 mole % CO₂ is in equilibrium with a CO₂-rich phase containing 70 mole % CO₂. Is the green dot in the one-phase field or the twophase field?





From Sterner & Bodnar (1991)

The concept of "liquid" and "vapor" is ambiguous in the H_2O - CO_2 system because sometimes the H_2O -rich phase is more dense, and in other PT regions the CO_2 -rich phase is more dense.



Isochores in the H_2O-CO_2 system originate along the isopleth boundary that separates the one-fluid phase region from the two-fluid phase region.



Isochores in the H_2O-CO_2 system originate along the isopleth boundary that separates the one-fluid phase region from the two-fluid phase region.



Unpublished diagrams from Connolly & Bodnar, 1983



Isochores in the H_2O-CO_2 system originate along the isopleth boundary that separates the one-fluid phase region from the two-fluid phase region.



Unpublished diagrams from Connolly & Bodnar, 1983



H₂O-CO₂-NaCl



From Bodnar & Costain, 1991



The System H₂O-CO₂-NaCl





We can show phase relations in the ternary system H_2O-CO_2 -NaCl if we keep one variable, such as salinity or CO_2 concentration constant, or maintain a constant ratio between two of the components.



Limits of immiscibility and the critical point for H₂O-CO₂-NaCl solutions



Addition of NaCl and CO_2 to H₂O causes the critical point and region of immiscibility to migrate to higher temperatures and higher pressures.

As a result, fluid immiscibility in "real" geofluids containing significant amounts of both salts and gases is possible over a wide range of PT conditions encountered in the crust.



From Schmidt & Bodnar, 2000



From Heinrich, 2007 RIMG

Addition of both NaCl and CO₂ to H₂O causes the region of immiscibility to migrate to significantly higher temperatures and pressures. As a result, geofluids containing significant amounts of both salts and gases can undergo immiscibility (boiling) over a wide range of **PT** conditions encountered in the crust.



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Many studies have incorrectly interpreted microthermometric data obtained from H_2O-CO_2 -NaCl inclusions because of lack of understanding of fluid phase equilibria.



Modified from Hendel & Hollister, 1981

Microthermometric data obtained from fluid inclusions containing NaCl and CO₂ are often interpreted in a manner analogous to that used for two-component systems.

This approach has led to many incorrect interpretations of the PT conditions of trapping of multi-component fluid inclusions.

What are the compositions of the coexisting phases in the (H₂O-6 wt% NaCl) - CO₂ system indicated on the TX diagram?



Microthermometric data obtained from H_2O-CO_2 -NaCl inclusions should be evaluated using a ternary compositional diagram at fixed PT conditions (or an appropriate equation of state).



Bodnar, unpublished

If the bulk composition of the fluid is given by the white dot, at these same PT conditions, what are the compositions of the coexisting phases?

Ternary diagram showing the limits of the two-fluid-phase field (blue) at a fixed P&T for the system H_2O - NaCl - CO₂. Referring to the TX diagram on the previous slide, point "C" represents the bulk composition of the system, and points "A" and "B" represent the locations along the (H₂O-6 wt% NaCl) - CO₂ pseudobinary where the path enters ("A") and leaves ("B") the two-phase field. At this P&T, for a bulk composition "C" at 200°C and 1 kb, the compositions of the coexisting phases are given by "D" and "E".? Fluids Research Laboratory Tech BUBBLES 'A' US Virginia

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Bodnar, unpublished

The room temperature phase ratios of FI reflect the composition and density of the trapped fluid. As such, one can infer homogenization behavior (and trapping conditions) based on room temperature phase ratios.



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Phase relations at room temperature



temperature, density and composition, the expected room temperature phase ratios can be determined based on the PVTX properties of the fluid system.

For a given trapping

Why is it important to be able to infer PT trapping conditions based on room temperature phase relations?



Bodnar, unpublished

Summary of microthermometric data available from FI in different fluid systems.

H₂O: (see aqueous FI)

CO₂:

- Melting of solid CO₂; a melting T less than the triple point temperature (-56.6°C) indicates the presence of some other volatile species, such as N₂ or CH₄.
- Homogenization temperature; defines the isochore along which the FI was trapped; Th of FI that homogenize to the vapor phase is difficult to determine with high accuracy, and densities of such FI are often estimated from Raman analysis of the CO₂ vapor bubble (after homogenization).



Summary of microthermometric data available from FI in different fluid systems.

Aqueous-salt FI:

- Freezing temperature during cooling; Wilkinson (2017) reports relationship between metastable freezing T and final ice melting T
- First melting (eutectic) temperature; provides information on the chemical system; H₂O-NaCI = -21.2°C; H₂O-NaCI-CaCI₂ = -52.0°C
- Final melting temperature; provides information on the "salinity" of the aqueous phase; the final phase to melt could be H₂O ice, hydrohalite (NaCl • 2 H₂O), halite, sylvite, antarcticite (CaCl₂ • 6 H₂O), and others, depending on the chemical system
- Homogenization temperature; defines the isochore along which the FI was trapped



Summary of microthermometric data available from FI in different fluid systems.

 $H_2O-CO_2 \pm$ "salt":

- Melting of solid CO₂; a melting T less than the triple point temperature (-56.6°C) indicates the presence of some other volatile species, such as N₂ or CH₄.
- First melting (eutectic) temperature; usually not measured or reported for this type of FI
- Clathrate melting temperature; if clathrate melts in presence of both liquid and vapor CO₂ the salinity of the aqueous phase can be determined
- Homogenization of the CO₂ liquid and vapor phases; is used to calculate CO₂ density which, in turn, is used to estimate total CO₂ content of the FI.
- Total homogenization temperature; defines the isochore along which the FI was trapped

