

Phase relations in model fluid systems

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ABSTRACT. — Phase relations in geologic fluids are described by a general P-T-X model in which the relationships among solids, liquids, vapours and supercritical fluids are developed in a manner consistent with the phase rule and the principles of phase theory. The general P-T-X model is described for a binary system with a single critical endpoint and involving two solid phases that show no mutual solubility as well as a liquid and vapour that are completely miscible in the two components. A binary system of this type describes the behaviour of the geologically important system, NaCl-H₂O. Isothermal, isobaric and isocompositional sections through the P-T-X model are used to illustrate the behaviour of fluids as, for example, under a heating-cooling stage on the petrographic microscope.

Key words: binary, phase relations, P-T-X, fluid inclusions, NaCl-H₂O.

Introduction

The study of geologic fluids within the Crust has been greatly advanced by a knowledge of the phase relations in simple systems. These systems are used to model the behaviour of more complex natural fluids. Important model system are the unaries, CO₂, H₂O, the binaries, CO₂-H₂O (TAKENOCHI and KENNEDY, 1964) and H₂O-NaCl (SOURIRAJAN and KENNEDY, 1962), as well as the ternary, CO₂-H₂O-NaCl (TAKENOCHI and KENNEDY, 1965; GEHRIG, 1980). In this paper, we examine certain aspects of the phase relations in these systems and their application to geologic problems such as the interpretation of fluid inclusions.

Unary Phase Relations

The phase rule indicates the number of phase elements that must exist on a phase diagram. Each element can be stable or metastable although it is not unusual to show only the stable elements. All of the possible elements must exist somewhere on a phase diagram.

The phase rule is written as,

$$f = c + 2 - \phi$$

where f is the variance, (the number of variable parameters such as pressure, temperature, or the chemical potential of each

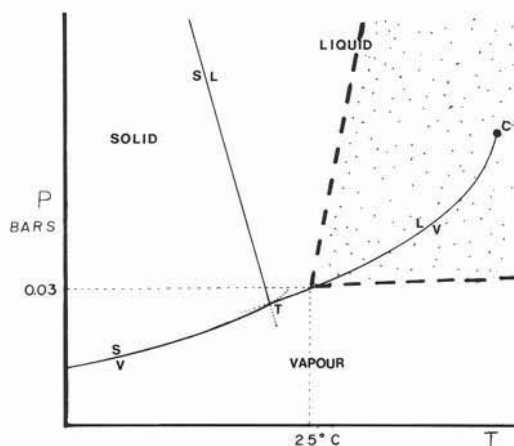


Fig. 1. — Pressure-Temperature diagram for a typical unary system such as H₂O. Inclusions of H₂O trapped initially within the stippled area will exhibit two phases at 25°C., S, solid; L, liquid; V, vapour. T indicates the triple point and C indicates the critical point.

compotent); c is the number of components; ϕ is the number of phases present. Unary phase relations are illustrated on Figure 1. The maximum of three phases exists at the triple point, T , where the variance is zero. Along a univariant curve such as liquid + vapour ($L + V$), two phases coexist in stable equilibrium. Within the divariant fields of a single fluid phase, either liquid or vapour, it is possible to draw lines of constant volume (isochors) or constant density as shown by the dashed curves on Figure 1. Fluid inclusions that initially trapped pure H_2O at a pressure and temperature within the stippled area will consist of a liquid and vapour under 0.03 bars of pressure at $25^\circ C$. Other conditions of entrapment result, after cooling to $25^\circ C$, in a single liquid phase at a pressure greater than 0.03 bars or a single vapour phase at a pressure less than 0.03 bars. All fluid inclusions are, of course, constrained to room temperature under the normal petrographic microscope. The pressure of such inclusions can have a range of values up to a limit determined by the strength of the crystal; beyond this limit, the fluid inclusion decrepitates.

The $L + V$ curve ends at the critical point. Above the critical point, the liquid and vapour phases become indistinguishable and a single phase, the supercritical fluid, is involved in phase relations.

Binary Phase Relations

The application of the phase rule to binary systems is summarised in Table 1. For a binary system consisting of a relatively volatile component such as H_2O (component A) and

a relatively involatile component such as NaCl (component B) the maximum number of phases that can coexist at stable or metastable equilibrium is four as for the element, ice (A)-halite (B)-liquid (L)-vapour (V). If the phase relations among these four phases plus one additional phase such as hydrohalite ($NaCl \cdot 2H_2O$) were under consideration, then five invariant elements would exist on the phase diagram to depict stable and metastable phase relations. Further consideration is only given here to phase relations among two immiscible solid phases, with compositions of the pure components, A and B, as well as L and V that are miscible in the two components. These four phases result in the single invariant point on Table 1.

Univariant phase relations in a binary system require that three phases coexist along a phase element with a variance of unity. The combination of four into groups of three produces four such univariant elements as indicated in Table 1. Each of these elements plots as a line in P-T space. In a similar manner, it is possible to define six divariant phase elements in Table 1; these elements occupy an area in P-T space. Four trivariant elements are possible. The two solid phases, A and B, exhibit no mutual solid solution and are therefore confined to the planes for the unary system in the P-T-X diagram. The elements, L and V, are binary solutions that require three dimensions to illustrate geometrically; these two elements therefore appear as projected volumes in P-T space.

Projected Binary Phase Relations

Figure 2 presents the phase relations of

TABLE 1
Phase Elements in a Binary System of Two Components

Variance	Number of Phases	Phase Elements	Geometry in P-T Space
0	4	A + B + V	point
1	3	A + B + L, A + B + V, A + L + V, B + L + V	line
2	2	A + B, A + L, A + V, B + L, B + V, L + V	area
3	1	A, B, L, V	projected volume

Table 1 on P-T, T-X and P-X projections. The two unary systems with compositions, A and B, are shown as described above for Figure 1. The points, T and C, are the triple point and critical point in the indicated unary. The triple point for A is at much lower temperature than

which both solids are stable on the P-T diagram. The curves along which either solid coexists with two fluids ($A + L + V$ or $B + L + V$) are bounded by the unary and binary invariant points. Two solids coexist with liquid ($A + B + L$) along a steep melting

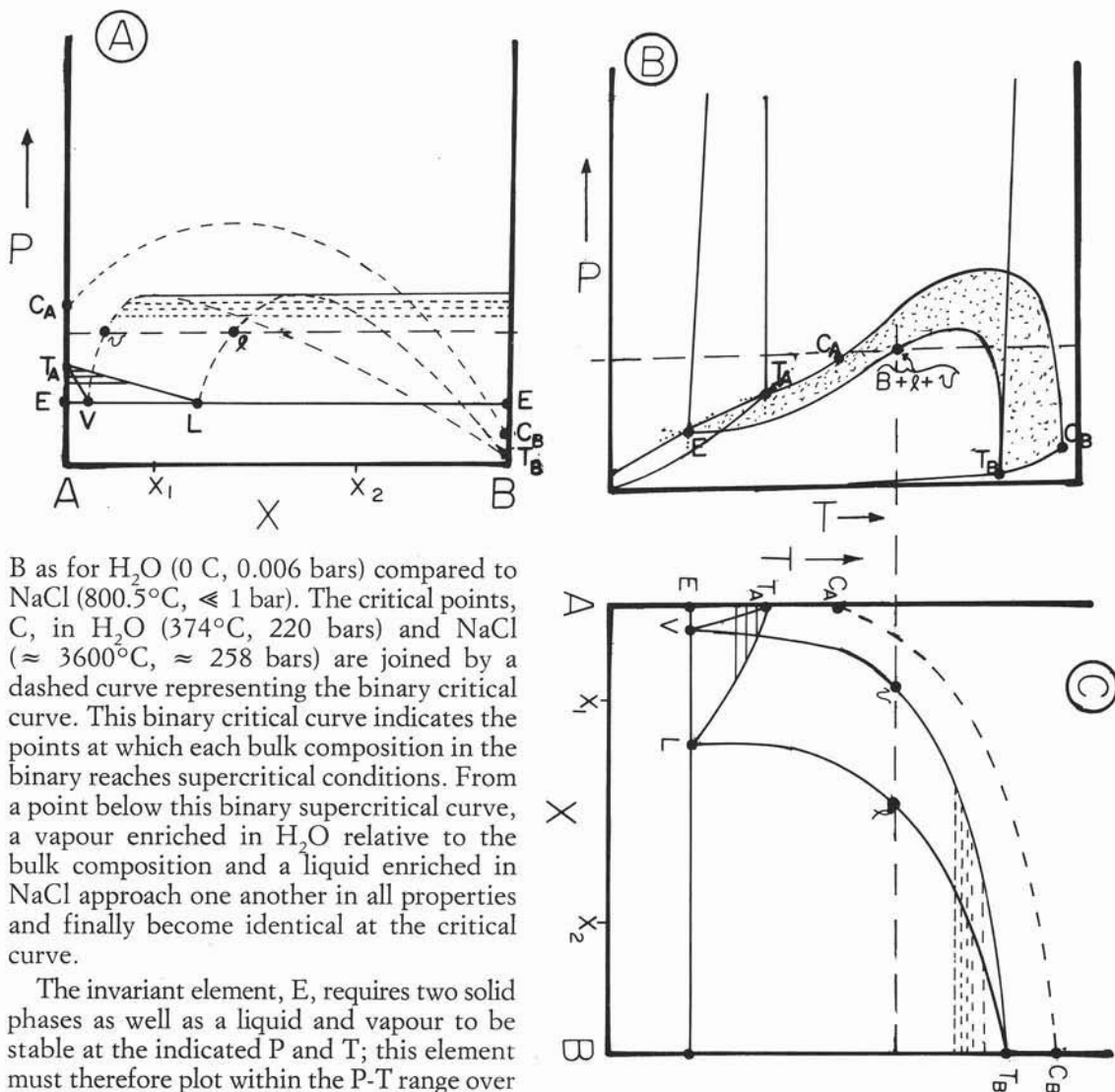


Fig. 2. — Phase relations on pressure (P), temperature (T), composition (X), projections for a typical binary system such as H_2O -NaCl with solid phases showing no mutual solid solution and a liquid and vapour phase with complete miscibility of the two components, A and B. T, triple point in the subscripted binary. C, critical point in the subscripted binary. E, binary invariant point along which the two solid phases as well as a liquid, L, and a vapour, V, coexist. C_A - C_B indicates the binary critical curve. The stippled area indicates the projected two-phase element, $L + V$. The composition of the liquid and vapour coexisting with solid B is fixed at a specified P and T as indicated by the points, V and L, along the same dashed tie-line on the three-phase element, $B + L + V$. The points, X_1 and X_2 , indicate the compositions for which the sections on Figure 5 have been drawn. 2a: Pressure-composition projection. 2b: Temperature-pressure projection. 2c: Temperature-composition projection.

curve originating at point E in P-T space. Two solids and a vapour ($A + B + V$) coexist along a shallow curve in P-T space that originates at the invariant point, E.

The $A + L + V$ and $B + L + V$ curves are further illustrated in Figures 2a and 2c as P-X and T-X projections. The elements $A + B + L$ and $A + B + V$ are omitted from Figures 2a and 2c for clarity. Dashed tie-lines parallel to the X axis have been included on 2a and 2c to emphasize that the composition of the vapour and liquid that coexist with solids are fixed at a particular temperature and pressure. For example, along the element $B + L + V$, the temperature and pressure at which B coexists with saturated liquid, L, and saturated vapour, V, are indicated on the three diagrams of Figure 2.

The two-phase element, $L + V$, is of considerable interest in the geological study of fluids. This element plots as an area on a P-T diagram (the stippled area on Figure 2a) and expands into a volume when the compositional dimension, X, is considered in addition to P and T. The $L + V$ volume is illustrated in a P-T-X block diagram in Figure

3. It is bounded by the three-phase surfaces (stippled) on which the two fluids, L and V, are simultaneously saturated in either solid A or solid B. It is also bounded by the unary $L + V$ curves and the binary critical curve, C_A-C_B . A series of isothermal sections through the $L + V$ volume is sketched into Figure 3 with a series of isothermal, isobaric tielines joining coexisting liquid and vapour. The vapour is more A-rich and the liquid more B-rich than any bulk composition along a tie-line. The tie-lines become shorter as the binary critical curve is approached and finally decrease to a point at the critical curve. If B is added to a typical bulk composition within the $L + V$ region, then the bulk composition will eventually shift into the L only field; as more B as added, the liquid will reach saturation and the bulk composition will enter the $L + B$ volume. Addition of H_2O to a bulk composition within the $L + V$ field eventually shifts the system into the V only field.

To gain familiarity with the phase elements listed in Table 1 and illustrated on Figures 1 to 3, it is helpful to draw isotherms, isobars

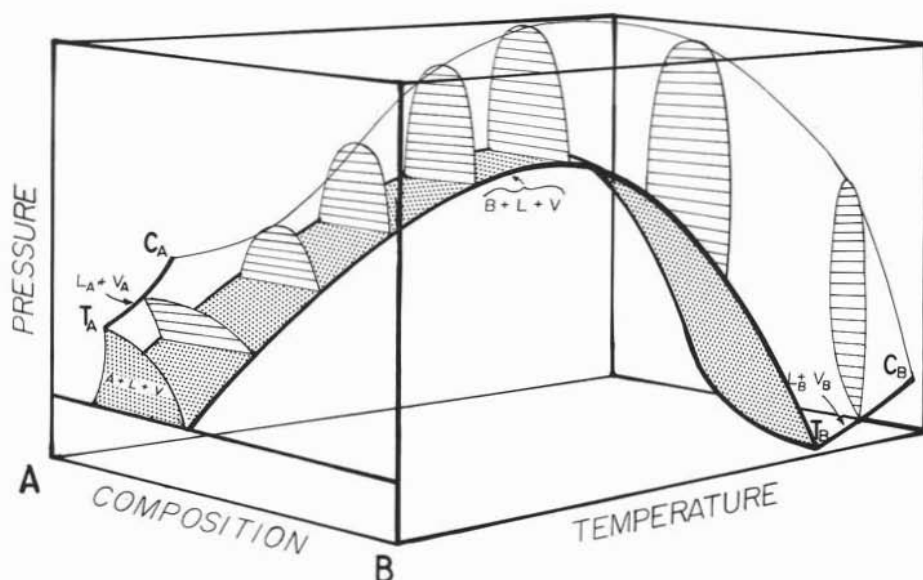


Fig. 3. — The liquid (L)-vapour (V) volume for a binary system such as H_2O -NaCl. T, triple point for the subscripted unary. C, critical point in the subscripted unary. C_A-C_B indicates the binary critical curve. Unary $L + V$ curves are also indicated. The three-phase surfaces, $A + L + V$ and $B + L + V$, are shown in a stippled pattern. Typical isothermal sections through the volume are indicated with tie-lines parallel to composition plane. The tie-line becomes shorter as the binary critical curve is approached and eventually becomes a single point along the binary critical curve. Above the critical curve, only one fluid phase, the supercritical fluid, exists.

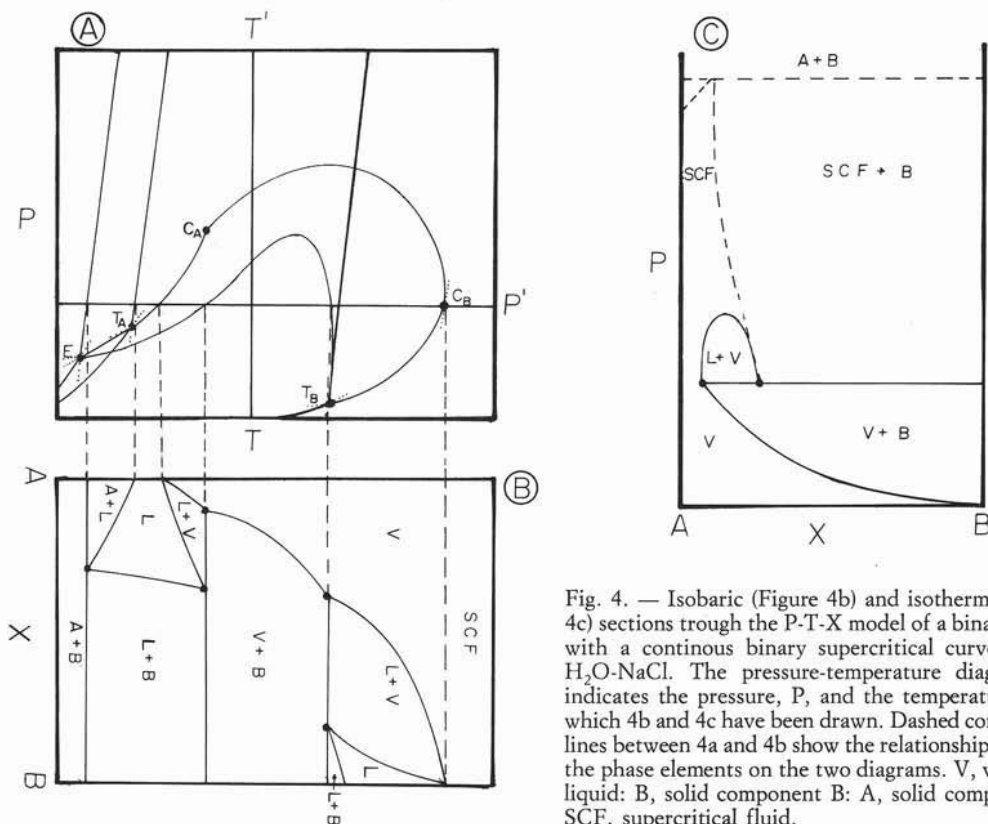


Fig. 4. — Isobaric (Figure 4b) and isothermal (Figure 4c) sections through the P-T-X model of a binary system with a continuous binary supercritical curve such as H_2O -NaCl. The pressure-temperature diagram (4a) indicates the pressure, P , and the temperature, T , at which 4b and 4c have been drawn. Dashed construction lines between 4a and 4b show the relationships between the phase elements on the two diagrams. V, vapour; L, liquid; B, solid component B; A, solid component A; SCF, supercritical fluid.

and isocomposition sections (isopleths) through the binary P-T-X space. Figure 4b is an isobar drawn for the pressure indicated on Figure 4a. The dashed lines between 4a and 4b emphasise that the temperature at which each phase element is intersected by the isobar, P_1 , on 4a can be transferred to 4b. A similar method is used to construct the isotherm, T_1 , drawn on 4c for the temperature indicated on 4a.

Isotherm and isobars such as shown in Figures 4b and 4c are helpful in understanding the phase relations in fluid systems. It should be emphasized, however, that fluids in natural systems are not generally constrained to an isobaric or isothermal plane. Isobars such as drawn on Figure 4 are, nevertheless, widely used in the study of fluids inclusions; the curve representing the composition of liquid saturated with halite, L (H), can be used to determine the salinity of the liquid from the temperature at which the halite crystal

disappears by rehomogenisation. A similar diagram is given in many reference sources for microthermometry (see for example, CRAWFORD, 1981, Figure 4.2; ROEDDER, 1984; Figures 8-11a, 8-14). The suggestion in these references that a vapour phase coexists with liquid and salt at 1 bar of pressure is not meant to imply that the pressure within the inclusion is, in fact, 1 bar; rather, the pressure within the inclusion is that indicated by the three-phase curve, $L+V+H$, for the temperature of interest. The composition of the homogenised liquid is normally a close approximation to the bulk composition of the fluid inclusion in H_2O -NaCl since the vapour phase has much lower density than the liquid and solid phases. The influence of pressure on the position of the curve, liquid in equilibrium with halite, is sufficiently low that pressure variations within inclusions are assumed to have negligible effect on salinity determinations by the above method.

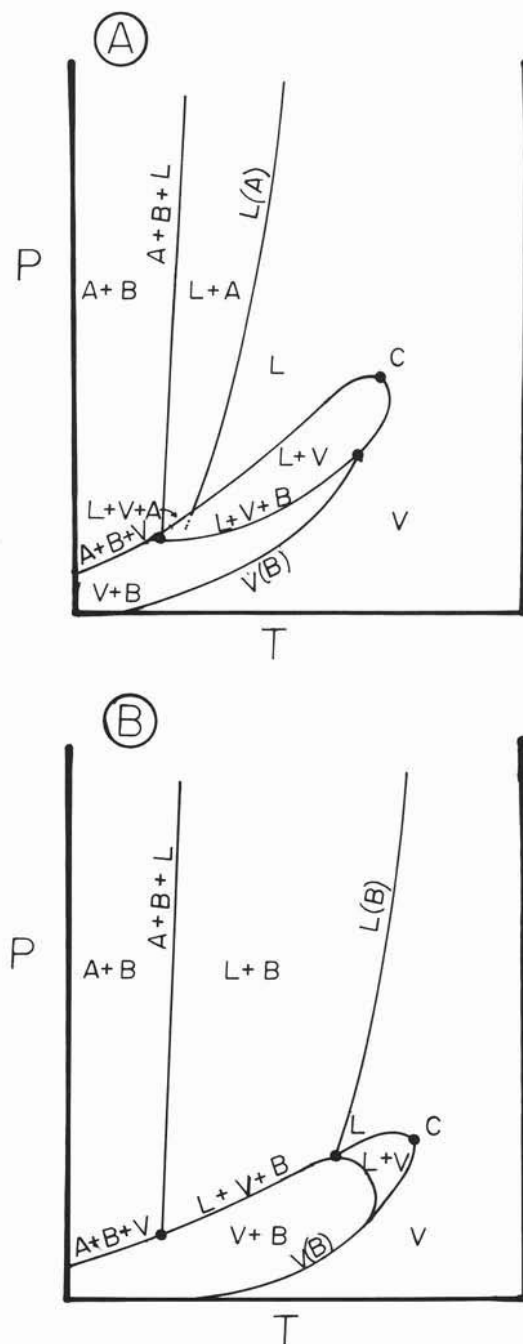


Fig. 5. — Constant composition sections through the binary P-T-X model. 5a for a composition such as X_1 and 5b for X_2 , as shown on Figure 2. Liquid, L; vapour, V; 5A, solid component A; B, solid component B; C, critical point; L(A), L(B) liquid in equilibrium with solid phase in parenthesis; V (A), V (B), vapour in equilibrium with the solid phase in parenthesis.

Isocomposition sections through the P-T-X model are also useful in the study of fluid inclusions that can be modeled by the system, NaCl-H₂O. Two representative sections are given in Figure 5 for the two compositions, X_1 and X_2 , that are shown on Figure 2. The invariant element, E, and the univariant elements with three coexisting phases are constant in P-T space as well as for all isopleths. The three-phase curves for a solid coexisting with liquid and vapour terminate at the appropriate temperature and pressure for that composition, as can be seen on Figures 2a and 2c. The saturated liquid and vapour shown by the points on the three-phase elements on Figure 5 do not coexist; each of these fluids is in equilibrium with a coexisting fluid that plots outside of the plane of the section.

The bulk composition of a fluid inclusion is taken, as a first approximation, to be constant over the history of an inclusion (excluding problems such as diffusion, chemical reaction with the crystal, necking down). The liquid or the vapour obviously have this composition when a single phase is present and can be plotted within the plane of a constant composition section such as 5a and 5b. In a two-phase region such as L + V, L + B or V + B, the compositions of the two phases lie outside of the plane of the constant composition section. The compositions of the liquid and vapour in multiphase inclusions must be read for a specific temperature and pressure from quantitative projections such as those determined by SOURIRAJAN and KENNEDY (1962, Figure 13 or 19 etc.).

A fluid inclusion trapped at a P and T above the two-fluid element, L + V, can eventually reach the two-fluid element on cooling; the P and T at which two phases appear are dependent on the bulk composition and density of the inclusion (see Figure 5). The inclusion will subsequently follow a P-T trajectory through the L + V volume with the composition of the L and V phases plotting outside of the plane of the isocomposition section. Many fluid inclusions that were initially trapped above the two-phase region are sufficiently dense that they become saturated in one of the two solid phases and

subsequently follow a three-phase curve to lower temperatures.

Ternary Phase Relations

Few experimental data are available for important ternary fluid systems. One of the best studied is the system $\text{CO}_2\text{-H}_2\text{O-NaCl}$ that is discussed elsewhere in this volume in more detail. GEHRIG (1980) has measured P-V-T data for this ternary to pressures of 3000 bars and temperatures to 500°C . BOWERS and HELGESON (1983a, 1983b) have fitted an equation of state to the measured data and provided a discussion of the phase relations in the ternary system. BOWERS and HELGESON (1985) have also written a Fortran computer code, DENFIND, that uses the equation of state to calculate isochors in P-T space for ternary fluids of a specified composition.

The computer code, DENFIND, has been used to calculate a representative series of isochors as shown on Figure 6. All of these isochors pass through 500°C and 2000 bars and continue to the point at lower P and T where a single fluid enters the two-phase region; the lower limit for each curve on

Figure 6 corresponds to the point that would be measured as the homogenisation temperature in microthermometry.

The isochor for pure H_2O has a density of 0.69 and terminates at the L + V curve in the unary system as illustrated on Figure 1. The isochor for pure water has been calculated from an equation given by HAAR and COWORKERS (1979). The addition of 10 weight per cent NaCl to the pure water results in a fluid with a density of 0.80; this isochor on Figure 6 is similar in slope to that for pure water. The isochor for pure CO_2 as calculated from the BOWERS and HELGESON computer code has a density of 0.77 and is much flatter than that for water and brine; the isochor for CO_2 continues to the lowest temperatures shown on Figure 6 due to the low critical temperature and pressure for this gas.

The addition of 20 mole per cent CO_2 to pure water results in a density of 0.70. The addition of 20 mole per cent CO_2 to the 10 weight per cent NaCl solution produces a solution with a density of 0.73 and a higher homogenisation temperature than pure water or the CO_2 -free brine.

Concluding Statement

The isochors shown on Figure 6 provide a general illustration of the influence of salinity and volatile content on the slope of isochors and the homogenisation temperature to be expected under the microscope. The computer code, DENFIND, can be used on personal type computers and is a valuable tool for understanding the geologic behaviour of fluids in the ternary $\text{CO}_2\text{-H}_2\text{O-NaCl}$ and its constituent binary and unary systems.

There is, of course, a continuing and important need to obtain more P-V-T data for fluids that model the relationships among liquids, vapours and supercritical fluids in geologic processes.

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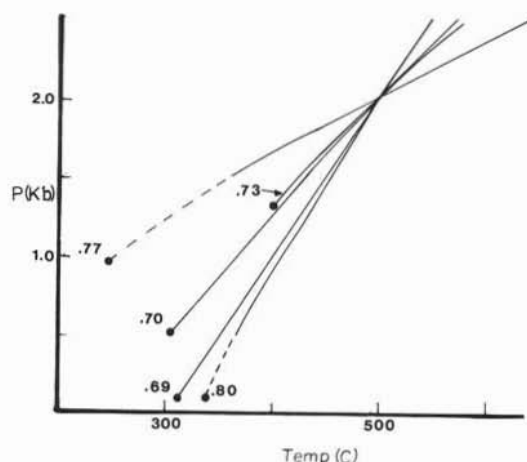


Fig. 6. — Representative isochors for fluids passing through 500°C and 2000 bars. Numerical values correspond to densities calculated for the following fluids: 0.69, pure H_2O ; 0.80, brine with 10 weight per cent NaCl; 0.77, pure CO_2 ; 0.70, H_2O with 20 mole per cent CO_2 ; 0.73, ternary fluid with 10 weight per cent NaCl, 20 mole per cent CO_2 with the remainder, H_2O .

REFERENCES

- BOWERS T.C., HELGESON H.C. (1983a) - *Calculation of thermodynamic and geochemical consequences of nonideal mixing in the system H_2O-CO_2-NaCl on phase relations in geologic systems: Equation of state for H_2O-CO_2-NaCl fluids at high temperatures and pressures.* Geochim. e Cosmochim. Acta, v. 47, p. 1246-1275.
- BOWERS T.C., HELGESON H.C. (1983b) - *Calculation of the thermodynamic and geochemical consequences of nonideal mixing in the system H_2O-CO_2-NaCl on phase relations in geologic systems. Metamorphic equilibria at high pressures and temperatures.* Am. Mineralogist., v. 68, p. 1059-1075.
- BOWERS T.C., HELGESON H.C. (1985) - *Fortran programs for generating fluid inclusion isochors and fugacity coefficients for the system H_2O-CO_2-NaCl at high pressures and temperatures.* Computers and Geosciences, v. 11, No. 1.
- CRAWFORD M.L. (1981) - *Phase equilibria in aqueous fluid inclusions.* In HOLLISTER L.S. and CRAWFORD M.L. eds., *Fluid inclusions: Applications to Petrology.* Mineral. Assoc., Canada Short Course handbook, v. 6, p. 75-100.
- GEHRIG M. (1980) - *Phasengleichgewichte und P-V-T-Daten ternärer Mischungen aus Wasser, Kohlendioxid und Natriumchlorid bis 3 kbar und 550 C.* Dissertation Univ. Karlsruhe Hochschule Verlag, Freiberg, 149 pp.
- HAAR L., GALLAGHER J., KELL G. (1979) - *Thermodynamic properties of fluid water.* In STRAUD J. and SCHEFFLER K.S., eds. *Water and steam, their properties and current industrial applications.* Proc. of the 9th Int'l Conf. on the properties of steam, Sept. 10-14, 1979, Technische Univ. München, F.R.G. Ferguson Press, New York, p. 69-82.
- ROEDDER E. (1984) - *Fluid inclusions.* Mineral Society America Reviews in Mineralogy, v. 12. Bookcrafters Inc., Chelsea Michigan, 644 pp.
- SOURIRAJAN S., KENNEDY G.C. (1962) - *The system $H_2O-NaCl$ at elevated temperatures and pressures.* Am. Jour. Sci., v. 260, p. 115-141.
- TAKENOUCHI S., KENNEDY G.C. (1964) - *The binary system CO_2-H_2O at high temperature and pressures.* Am. Jour. Sci., v. 262, p. 1055-1074.
- TAKENOUCHI S., KENNEDY G.C. (1965) - *The solubility of Carbon dioxide in $NaCl$ solutions at high temperatures and pressures.* Am. Jour. Sci., v. 263, p. 445-454.