



**Chemical equilibria and fluid flow during compaction
diagenesis of organic-rich geopressured sediments.**

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diagenesis of organic-rich geopressured sediments

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University of Arizona, 1988

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CHEMICAL EQUILIBRIA AND FLUID FLOW DURING COMPACTION
DIAGENESIS OF ORGANIC-RICH GEOPRESSURED SEDIMENTS

by

Regina Marie Capuano

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A Dissertation Submitted to the Faculty of the
DEPARTMENT OF GEOSCIENCES
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA

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Organic-Rich Geopressured Sediments

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NOMENCLATURE

A	interfacial area (m^2)
A_b	cross sectional area of the bulk elemental volume (cm^2)
C	concentration of a chemical component (mole cm^{-3})
H_i	Henry's law constant for component i ($\text{atm mole fraction}^{-1}$)
K	equilibrium constant
L	vertical length of elemental volume (cm)
M	mass of fluid in elemental volume (g)
P	total fluid pressure (bar)
P	total fluid pressure (atm)
P_H	hydrostatic pressure (bar)
P_L	lithostatic pressure (bar)
P^v	vapor pressure of pure water (bar)
R	gas constant ($82.053 \text{ atm cm}^3 \text{ }^\circ\text{K}^{-1} \text{ mole}^{-1}$)
R_v	volatility ratio
T	fluid temperature ($^\circ\text{C}$)
T	fluid temperature ($^\circ\text{K}$)
V	fluid volume in elemental volume (cm^3)
V_b	bulk-elemental volume (cm^3)
$V_{b,0}$	bulk-elemental volume at surface (cm^3)
V_r	rock volume in elemental volume (cm^3)
$\bar{V}$	molar volume of the fluid ($\text{cm}^3 \text{ mole}^{-1}$)
X_i	mole fraction of component i in the liquid phase

NOMENCLATURE—Continued

X_i^v	mole fraction of component i in the vapor phase
a	molecular attraction parameter ($\text{atm cm}^6 \text{ }^\circ\text{K}^{-5} \text{ mole}^{-2}$)
a°	molecular dispersion-molecular attraction force ($\text{atm cm}^6 \text{ }^\circ\text{K}^{-5} \text{ mole}^{-2}$)
a_i	activity of component i
b	molecular volume parameter ($\text{cm}^3 \text{ mole}^{-1}$)
f	coefficient in Equation 3.22
f_i	fugacity of the component i in the liquid phase
g	gravitational acceleration ($980.665 \text{ cm sec}^{-2}$)
j	coefficient in Athy's (1930) equation (km^{-1})
j_0	value of j at surface (km^{-1})
k^+	dissolution rate constant (sec^{-1})
k^-	precipitation rate constant (sec^{-1})
m_i	molality of component i in the liquid phase
m_i^v	molality of component i in the vapor phase
n_i	moles of component i
n_j	moles of all components other than i
q_z	volumetric flux in the z direction (mm yr^{-1})
r	grain radius (mm)
t	time (sec)
$v_{f,z}$	vertical fluid velocity relative to a stationary elevation datum (mm yr^{-1})
$v_{r,z}$	vertical rock velocity (mm yr^{-1})
v_z	vertical fluid velocity relative to the sediment (mm yr^{-1})
$\dot{v}$	burial rate (mm yr^{-1})
z	depth (km)

NOMENCLATURE—Continued

α	coefficient of thermal expansion of fluid ($^{\circ}\text{C}$)
β	coefficient of compressibility of fluid (bar^{-1})
γ_i	activity coefficient of component i
ρ	fluid density at T, P and X (g cm^{-3})
ρ_B	bulk density of rock (g cm^{-3})
ρ_R	average mineral density (2.65 g cm^{-3})
ϕ	total porosity
ϕ_0	total porosity at surface
ϕ_z	total porosity at depth z
φ	the volume fraction of a phase in the elemental volume

ABSTRACT

The effects of geopressuring and kerogen decomposition on mineral-fluid equilibria were calculated in order to predict the diagenetic-alteration mineralogy produced in equilibrium with kerogen-rich, geopressed sediments. These calculations indicate that several processes specific to kerogen-rich geopressed sediments contribute to the development of a characteristic alteration mineralogy. These processes are: 1) the upward flow of fluids in geopressed sediments, in contrast to the generally downward flow of fluids in normally-pressured sediments; 2) the coincidence of the depths of geopressuring (2-3 km; Fertl et al., 1976), with the geothermal temperatures necessary for CO₂ release (100°-135°C; Hunt, 1979), and CH₄ release (>90°C; Hunt, 1979); and 3) the opposing rates of sediment burial and CO₂ and CH₄ transfer into the upward-flowing fluids, which result in the geopressed pore fluids becoming enriched, and in some cases saturated, with respect to CO₂ and CH₄.

Three patterns of mineral deposition during diagenesis of kerogen-rich geopressed sediments are predicted. Quartz deposition should occur at the top of the geopressed zone and decrease rapidly with increased depth as a result of the decreased flux of upward fluid flow with increased depth. Carbonate deposition should occur above the zone of CO₂ release from kerogen degradation as a result of the upward flux of CO₂ saturated fluids and subsequent decreases in fluid temperature, pressure and CO₂ solubility. Kaolinite-carbonate could deposit within and above the zone of CO₂ release from kerogen as a result of silicate dissolution by CO₂-rich acid pore fluids, followed by the potential for albite-carbonate deposition upon CO₂ depletion.

In contrast, laumontite and anhydrite should not deposit during diagenesis of kerogen-rich geopressured sediments, but could deposit during diagenesis of normally-pressured or kerogen-poor geopressured sediments. An additional difference between these diagenetic environments is that quartz deposition would not be expected in normally-pressured sediments in which fluids are expected to be flowing downward.

These mineralogic relationships compare favorably with observed relationships in the kerogen-rich geopressured sandstones of the Frio formation from the Texas Gulf Coast.

CHAPTER 1

INTRODUCTION

Diagenetic reactions in kerogen-rich geopressured sediments are a function of the unique fluid pressures, temperatures, compositions and flow regimes common to these sediments. Sediment geopressing consists of the elevation of pore-fluid pressures to near-lithostatic pressures. These elevated fluid pressures are a product of low sediment permeability and thereby restricted flow conditions during sediment burial. Restricted flow in geopressured sediments results in a distinctive flow regime not expected in comparable normally-pressured sediments. Since the magnitude and direction of fluid flow govern the processes that result in mineral deposition and dissolution, the distinctive flow regime in geopressured sediments contributes to the deposition of characteristic alteration mineral assemblages and zoning patterns within these sediments.

In kerogen-rich geopressured sediments, the thermal degradation of kerogen that yields petroleum also yields CO_2 and CH_4 . Because of the addition of these gases, gas saturation and subsequent vapor separation may influence fluid-mineral equilibria in these sediments, particularly because the unusually low permeabilities limit gas mobility. In kerogen-poor sediments, insufficient quantities of gas are released to saturate the surrounding pore fluid, and in normally-pressured but kerogen-rich sediments, fluid flow allows dissipation of exsolved gases before saturation can occur. This is of practical geologic significance because it raises the possibility that kerogen-rich sediments, particularly geopressured sediments, may

develop a distinct suite of authigenic mineral assemblages that could serve as a useful petroleum-exploration guide.

In the calculation of diagenetic reactions in basin sediments the unique suite of conditions present in kerogen-rich geopressured sediments have not been considered. Bruton and Helgeson (1983) calculate the changes in mineral equilibria in basin sediments resulting from shifts in fluid pressures from hydrostatic to lithostatic. They do not address, however, the influence of other properties such as fluid composition and flow conditions which are also distinct in geopressured sediments. Merino (1975), Sverjensky (1984), Crossey, Frost and Surdham (1984), and Kaiser (1984) calculate mineral-fluid equilibria in sedimentary basins, but do not consider the effects of sediment geopressuring or liquid-vapor equilibria. The effect of CO₂ gas on the development of secondary porosity is discussed by Schmidt, McDonald and Platt (1977), Schmidt and McDonald (1979) and Franks and Forester (1984), but only in the context of the ability of CO₂ gas to acidify pore waters and thereby dissolve feldspar.

This study considers the combined effects of: 1) the direction and magnitude of fluid flow; 2) the addition of CO₂ and CH₄ to pore fluids and their solubility limits; and 3) the fluid temperature, pressure and composition, on mineral-fluid equilibria in kerogen-rich geopressured basins. Initially the physical conditions common in geopressured sedimentary basins are presented, as is the direction of fluid discharge from geopressured sediments during burial. Then the magnitude of fluid discharge is calculated. The conditions for CO₂ saturation of basin pore fluids and the consequences of vapor-liquid separation on mineral deposition are discussed. Activity/activity diagrams and relationships are calculated for the pressure and temperature conditions common to geopressured sediments for the

important authigenic minerals found in clastic sediments for which the necessary thermochemical data is available. These diagrams and relationships are then used to predict the alteration mineral assemblages and zoning patterns within the geopressured sediments, and the results are compared with the observed alteration mineralogy and fluid composition within the Frio Sandstone of the Texas Gulf Coast basins.

CHAPTER 2

GEOPRESSURED SEDIMENTARY BASINS

Sedimentary basins are generally oval to elongate in outline, very shallow relative to their horizontal extent, thin along distal edges, and are asymmetric in cross section (Halbouty et al., 1970; Selley, 1975, 1985; Conybeare, 1979; Klemme, 1980). They vary from a few tens of kilometers to several hundred kilometers in horizontal extent. These basins form during long periods of subsidence and lithification, and in some cases have been tilted, deformed, altered and eroded. Basin sediments tend to accumulate as either shale-sandstone or shale-carbonate-evaporite sequences (Chapman, 1983). Those basins composed of shale-sandstone sequences are the focus of this study.

Near-lithostatic fluid pressures, geopressures, develop during burial of basin sediments when fluid expulsion, in response to the combined effects of compaction and thermal expansion, is inhibited by low permeabilities (Bredehoeft and Hanshaw, 1968). Rapid sedimentation rates also contribute to the development of near-lithostatic fluid pressures by increasing the rate of fluid expulsion. Calculation of the hydrodynamic requirements for the maintenance of elevated-fluid pressures indicate that a sedimentation rate of 0.5 mm yr^{-1} will maintain near-lithostatic fluid pressures in sediments having permeabilities of less than $1 \times 10^{-15} \text{ cm}^2$ (Bredehoeft and Hanshaw, 1968).

A large component of marine shales is common in geopressured sediments (Dickinson, 1953) because their rapid sedimentation rates, averaging 0.1 to 0.3

mm yr⁻¹ (Berner, 1971; Smith, 1971), and low permeabilities, contribute to the maintenance of elevated fluid pressures. Marine shales are enriched in a type of kerogen that is a good source for petroleum (Tissot and Welte, 1978) and, therefore, petroleum resources are common in geopressed sedimentary basins (Fertl, Chilingarian and Rieke, 1976).

Basins with the rapid sedimentation rates and the high shale component required to generate geopressures, commonly form at continental margins (Selley, 1975, 1985). Basins occurring along the Texas and Louisiana Gulf Coast are an example of this depositional environment. Many of them are geopressed (Dickinson, 1953; Sharp, 1976), have rapid sedimentation rates of 0.1 to 10 mm yr⁻¹ (Sharp and Domenico, 1976), contain up to 85% marine shales (Boles and Franks, 1979) and contain considerable petroleum reserves.

Geopressed basins which contain petroleum reservoirs have normal thermal gradients, 20 to 30°C km⁻¹ (Fertl, Chilingarian and Rieke, 1976) (Figure 1). Thermal gradients are generally not constant throughout the sediment column, but will increase or decrease depending on the varying thermal conductivities and permeabilities of the sediments, the temperature of convecting fluid, and heat flow in the area. In geopressed sediments thermal gradients often increase in the overpressured zone by as much as 18°C km⁻¹ (Lewis and Rose, 1970; Fertl, Chilingarian and Rieke, 1976; Sharp, 1976). For example, thermal gradients in Louisiana Gulf Coast sediments range from approximately 30°C km⁻¹, in the near surface zone of hydrostatic fluid pressure, to 40°C km⁻¹, in the underlying sediments in which fluid pressures exceed hydrostatic (Schmidt, 1973; Sharp, 1976) (Figure 1).

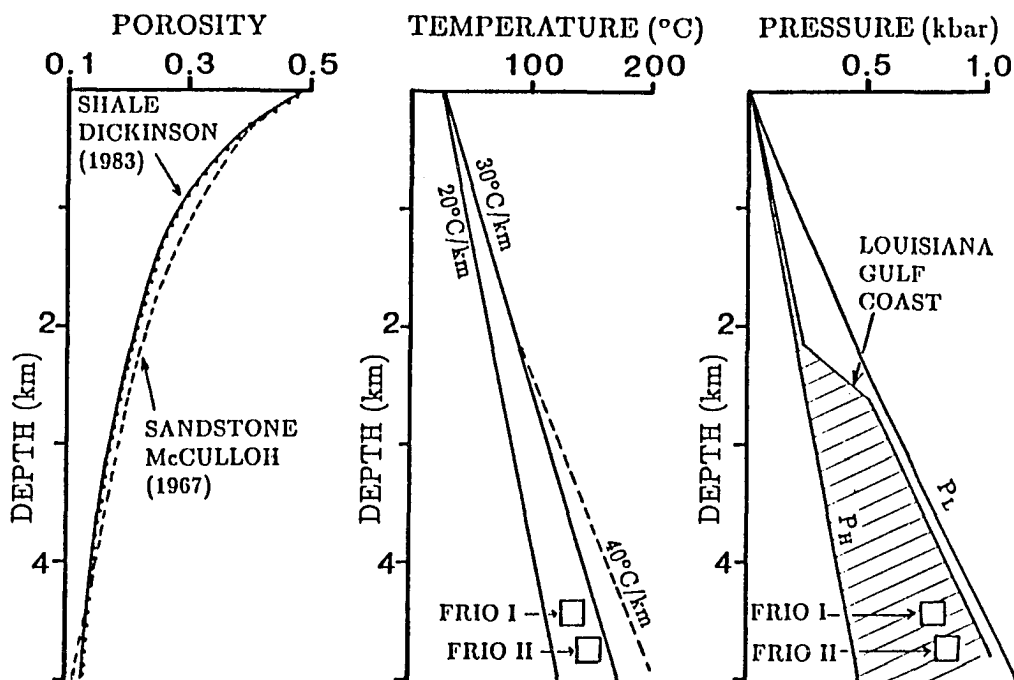


Figure 1: Porosity, temperature and pressure profiles for idealized geopressured basin.

The porosity profile for sandstone is from McCulloh (1967), dashed line, for shale is from Dickinson (1953), solid line, and calculated as described in text, dotted line. Hydrostatic pressure, P_H , and lithostatic pressure, P_L , profiles are calculated from equations discussed in the text and using porosity values from Dickinson's porosity profile. Fluid pressures from Louisiana Gulf Coast sediments (hatched area) are after Dickinson (1953). Fluid conditions in the Frio formation (FRIO) are from Kharaka et al. (1979).

Thus geopressed sedimentary basins are characterized by rapid sedimentation rates, low permeabilities, a large proportion of marine shale that act as a petroleum source material, and thermal gradients ranging from 30 to 40°C km⁻¹.

CHAPTER 3

FLUID-FLOW

The direction and magnitude of fluid flow in geopressured sediments govern the processes of mineral deposition and dissolution. Isotherms and isobars are nearly horizontal relative to the large vertical extent of sedimentary basins and therefore fluids with an upward component of vertical flow experience temperature and pressure decreases, whereas fluids flowing downward experience temperature and pressure increases. The magnitude of fluid displaced determines the amount of solute transport. Thus to calculate fluid-mineral equilibria in these sediments it is necessary to first determine the direction and magnitude of fluid flow.

Three driving forces contribute to flow in sedimentary basins: compaction, gravity and fluid density. Compaction-driven flow occurs as the superincumbent load on the subsiding sediments decreases porosity and expels fluid. Gravity-driven flow occurs in response to the recharge of ground water from the topographic highs surrounding a basin, or as a result of tectonic readjustments of the basin. Fluid-density-driven flow occurs in response to thermal perturbations imposed on the basin, and in response to fluid-density variations caused by the presence of compositionally distinct fluids.

In geopressured sedimentary basins that are large, depositionally-active, tectonically-stable and with thermal gradients of approximately $30^{\circ}\text{C km}^{-1}$, gravity-driven flow dominates above the geopressured zone, giving way to compaction-driven flow within the geopressured sediments (Galloway, 1984).

Compaction-driven flow contributes to flow above the geopressured zone, although permeabilities within these normally-pressured sediments are large enough to allow the downward influx of gravity-driven surface water to dominate. In contrast, within the geopressured zone low sediment permeabilities, less than approximately $1 \times 10^{-15} \text{ cm}^2$ (Bredehoeft and Hanshaw, 1968), limit surface water infiltration allowing fluid expulsion by compaction to dominate the flow regime. It follows then that in normally-pressured sedimentary basins, those in which geopressures do not develop at depth, permeabilities remain large enough at all depths to allow infiltration of gravity-driven fluids to dominate the flow regime. Results of numerical modeling of compaction-driven flow in normally-pressured sedimentary basins indicates that the potentials produced by compaction-driven flow are small and therefore are exceeded at all depths by the forces of gravity-driven fluids (Bethke, 1985).

Calculation of compaction-driven flow within a sedimentary basin indicates that fluids flow radially outward from the downwarped basin center with upward-vertical flow dominating at depths of less than 1 km (Bethke, 1986). A component of upward vertical flow remains at all depth with horizontal flow becoming increasingly more important with increased depth. Below 1 km horizontal flow dominates over upward vertical flow (Bethke, 1986). In work previous to Bethke's (1986) compaction-driven fluid in geopressured sediments has generally been assumed to flow either up or down into more permeable units (cf. Sharp, 1978; Cathles and Smith, 1983). The normally-pressured sedimentary basin to which Bethke's flow calculations apply, contains an underlying sandstone aquifer that is 500 m thick. Despite the presence of this permeable unit at the base of Bethke's (1986) hypothetical basin the vertical component of flow is always upward

rather than downward. The lack of a downward flow component for compaction-driven flow in normally-pressured sediments overlying a basal aquifer suggests that an upward rather than a downward flow component is expected in geopressured sediments, particularly in the upper portions of the geopressured zone where downward flow is inhibited by the presence of low permeability geopressured sediments below.

The possible effects of geopressuring on flow direction, however, are not considered by Bethke (1986). The lower permeabilities within geopressured sediments combined with the high pressure gradients present between geopressured sediments and the normally-pressured sediments above contributes to the increased importance of the upward flow component, particularly in the upper portions of the geopressured zone. Faults within geopressured sediments also contribute to the upward flow of fluids. Fluid pressure distributions measured around fault zones in geopressured sediments from the Texas Gulf Coast suggests the faults act as conduits for upward vertical discharge of geopressured fluids (Berg and Haybeck, 1982; Galloway, 1984).

Mass of Fluid Discharged

The dominance of compaction-driven flow in geopressured sediments indicates that the source of fluid flowing in these sediments is the fluid trapped within them at the time of geopressuring. This fluid is expelled from the sediments during burial as a result of compaction-induced pore-volume decreases. Thermal expansion of fluids resulting from temperature increases during burial also contributes

to fluid expulsion. The mass of fluid expelled from geopressed sediments as a result of burial compaction and thermal expansion are calculated below.

Flux Equations

The mass of fluid expelled from an elemental volume of geopressed sediment as a consequence of thermal expansion and pore-volume decrease during burial, is calculated from the definition of mass

$$M \equiv \rho V \quad (3.1)$$

where differentiation with respect to depth gives

$$\frac{dM}{dz} = V \frac{d\rho}{dz} + \rho \frac{dV}{dz} \quad (3.2)$$

and rearranging gives

$$\frac{1}{\rho V} \frac{dM}{dz} = \frac{1}{\rho} \frac{d\rho}{dz} + \frac{1}{V} \frac{dV}{dz} . \quad (3.3)$$

Substitution of the relationship between the volume of fluid in the elemental volume, V , to the bulk volume of the element, V_b ,

$$V = \phi V_b \quad (3.4)$$

into Equation 3.3, yields

$$\frac{1}{\rho \phi V_b} \frac{dM}{dz} = \frac{1}{\rho} \frac{d\rho}{dz} + \frac{1}{\phi V_b} \frac{dV}{dz} . \quad (3.5)$$

and rearranging

$$\frac{1}{\rho V_b} \frac{dM}{dz} = \frac{\phi}{\rho} \frac{d\rho}{dz} + \frac{1}{V_b} \frac{dV}{dz} . \quad (3.6)$$

allows calculation of the change in fluid mass relative to the bulk volume of the element.

The contribution of density change, $(1/\rho)d\rho/dz$, to the mass of fluid expelled is calculated assuming the pore volume remains constant and is fluid saturated. Consequently, all fluid expansion results in fluid removal from the pore and thus mass removal from the elemental volume. The change in density of the pore fluid in response to a temperature and pressure perturbation can be calculated by taking the total differential of the fluid volume with respect to pressure and temperature at constant mass of fluid

$$\bar{V} = \left(\frac{\partial \bar{V}}{\partial T} \right)_P dT + \left(\frac{\partial \bar{V}}{\partial P} \right)_T dP \quad (3.7)$$

(Knapp and Knight, 1977). Substituting the coefficients of thermal expansion

$$\alpha \equiv \frac{1}{\bar{V}} \left(\frac{\partial \bar{V}}{\partial T} \right)_P \quad (3.8)$$

and of compressibility

$$\beta \equiv -\frac{1}{\bar{V}} \left(\frac{\partial \bar{V}}{\partial P} \right)_T \quad (3.9)$$

for the fluid into Equation 3.7, and rearranging, gives

$$\frac{1}{\bar{V}} d\bar{V} = \alpha dT - \beta dP \quad (3.10)$$

(Knapp and Knight, 1977). The volume change at constant mass (Equation 3.10) is equal to negative the change in density (Equation 3.3), such that

$$\frac{1}{\rho} d\rho = \beta dP - \alpha dT \quad (3.11)$$

Although the density change is calculated with Equation 3.11 for a constant mass of fluid, the assumption that pore volume is constant allows a decrease in the fluid density to result in loss of mass, as fluid, from the elemental volume. Equation 3.11 is used to represent the change in mass of the elemental volume which results

from a decrease in fluid density. This change in mass represents expulsion of fluid from a constant pore volume, in Equation 3.6.

For the above calculations, values for α and β as a function of temperature and pressure for pure water are taken from Helgeson and Kirkham (1974). The effects of mineral expansion and compression on the volume of the fluid or of the bulk-elemental volume were not considered because mineral expansion and compression are two orders of magnitude less than that of H₂O liquid. The coefficients of expansion and compressibility for minerals are on the order of $1 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ and $1 \times 10^{-6} \text{ bars}^{-1}$, respectively, at the temperatures and pressures of interest (Clark, 1966). In contrast, the coefficient values for H₂O are on the order of $1 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$ and $1 \times 10^{-4} \text{ bars}^{-1}$, respectively (Helgeson and Kirkham, 1974). Therefore errors inherent in disregarding the contribution of the expansion and compression of the rock on the change in volume of the fluid, and therefore of the element, are small compared to other possible errors.

Fluid-density changes upon burial are calculated through differentiation of Equation 3.11 with respect to depth

$$\frac{1}{\rho} \frac{d\rho}{dz} = \beta \frac{dP}{dz} - \alpha \frac{dT}{dz} . \quad (3.12)$$

The factor $\alpha(dT/dz)$ accounts for expansion of pore fluid as temperature increases upon burial, with dT/dz taken as the thermal gradient. The factor, $\beta(dP/dz)$ accounts for fluid compression as a result of increased lithostatic pressure on the pore fluid in geopressured sediments. dP/dz is taken as the lithostatic pressure gradient, $\rho_b g$.

The contribution of volume change at constant density, $(1/V_b) dV/dz$, to the change in mass of the element (Equation 3.6) is calculated from the change in pore volume of the sediment. Pore-volume decrease, as a result of compaction of

water-saturated sediments, results in expulsion of fluid from the sediments. The volume of fluid expelled from an elemental volume of rock as a result of pore-volume decrease can be calculated given

$$V = \phi V_b = \frac{\phi V_r}{(1 - \phi)} \quad (3.13)$$

where the volume of rock in the elemental volume, V_r , is independent of the porosity. Integration of the relationship $(1/V)dV$ with respect to depth

$$\int_z^{z+1} \frac{1}{V} dV = \ln \frac{V_{z+1}}{V_z} \quad (3.14)$$

and substitution of Equation 3.13 gives

$$\ln \frac{V_{z+1}}{V_z} = \ln \frac{V_r \phi_{z+1} / (1 - \phi_{z+1})}{V_r \phi_z / (1 - \phi_z)} = \int_z^{z+1} \frac{1}{\phi(1 - \phi)} d\phi \quad (3.15)$$

Substitution of the relationship $V = \phi V_b$ and rearranging provides

$$\frac{1}{V_b} dV = \frac{1}{(1 - \phi)} d\phi \quad (3.16)$$

Finally, the mass of fluid expelled from an elemental volume of geopressed sediment upon burial is calculated through substitution of Equations 3.12 and 3.16 into Equation 3.6

$$\frac{1}{\rho V_b} \frac{dM}{dz} = \phi \beta \frac{dP}{dz} - \phi \alpha \frac{dT}{dz} + \frac{1}{(1 - \phi)} \frac{d\phi}{dz} \quad (3.17)$$

and rearranging gives

$$\frac{dM}{dz} = \rho V_b \left(\phi \beta \frac{dP}{dz} - \phi \alpha \frac{dT}{dz} + \frac{1}{(1 - \phi)} \frac{d\phi}{dz} \right) \quad (3.18)$$

The volumetric flux of fluid from an elemental volume of sediment, q_z , as a function of depth can then be calculated from Equation 3.18

$$\frac{dq_z}{dz} = \frac{\dot{v}_z}{\rho A_b} \frac{dM}{dz} = \dot{v}_z L_z \left(\phi \beta \frac{dP}{dz} - \phi \alpha \frac{dT}{dz} + \frac{1}{(1 - \phi)} \frac{d\phi}{dz} \right) \quad (3.19)$$

where, $\dot{v}$ is the sediment-burial rate taken as a function of depth, and A_b is the cross-sectional area of the bulk-elemental volume in the direction of flow, and L_z is the vertical dimension of the bulk elemental volume at depth z . Volumetric flux, q_z , is the volume of fluid flowing per unit time through a cross-sectional area (of the elemental volume) that is normal to the direction of flow. Flow in this case is in the z direction, vertically upward.

The velocity of vertical-fluid discharge from an elemental volume of sediment, v_z , is then calculated from the volumetric flux

$$v_z = \frac{q_z}{\phi}. \quad (3.20)$$

Porosity

Porosity in geopressed shales can be represented by the porosity profile from the petroleum-rich geopressed basin from the Louisiana Gulf Coast, presented by Dickinson (1953) (Figure 1). Sandstone porosity does not behave as consistently as shale porosity. Porosity in a single sandstone unit can vary locally by as much as 30 % (Maxwell, 1964). McCulloh (1967), however, provides a maximum-average-porosity profile for reservoir sandstones (Figure 1). Comparison of the sandstone and shale porosity profiles in Figure 1, shows them to be near coincident. Because of this similarity Dickinson's (1953) porosity profile is used to represent the sandstone-shale porosity profile in geopressed sediments for the calculation in this section.

Shale porosity profiles can be represented by Athy's (1930) exponential porosity equation

$$\frac{d\phi}{dz} = -j\phi. \quad (3.21)$$

The porosity profile of Dickinson's (1953) is calculated by taking Athy's equation as a superexponential, such that the coefficient 'j' varies exponentially with depth

$$\frac{dj}{dz} = -fj \quad (3.22)$$

giving

$$\phi = \phi_0 \left(e^{-j_0 z} (e^{-fz}) \right) \quad (3.23)$$

where $j_0 = 0.80 \text{ km}^{-1}$ and $f = 0.70$ for depths ranging from 0 to 2 km, and $j_0 = 0.27 \text{ km}^{-1}$ and $f = 0.25$ for depths ranging from 2 to 6 km. The porosity profile calculated using Equation 3.23 shown in Figure 1 almost exactly duplicates Dickinson's curve.

Bulk volume and burial rate

Both the bulk volume of the elemental volume, V_b , and the sediment burial rate, $\dot{v}$, decrease with increased depth as a result of the porosity decreases shown above. V_b and $\dot{v}$ decreases are calculated assuming porosity decreases are realized as a shortening in the vertical dimension, L , of the bulk-elemental volume at $z = 0$, $V_{b,0}$,

$$L_z = \frac{V_{b,0}(1 - \phi_0)}{(1 - \phi_z)} \quad (3.24)$$

where ϕ_0 is the porosity at the surface, and ϕ_z is the new porosity at depth z . Both V_b and $\dot{v}$ decrease as a function of depth directly proportional to the reduction in L such that

$$V_{b,z+1} = V_{b,z} \frac{L_{z+1}}{L_z} \quad (3.25)$$

and

$$\dot{v}_{z+1} = \dot{v}_z \frac{L_{z+1}}{L_z} \quad (3.26)$$

In calculation of the burial rate, the burial rate at the surface is assumed equal to the sedimentation rate of the basin, and the sedimentation rate is assumed constant during basin formation.

Changes in burial rate with depth calculated for sediments having a porosity profile equivalent to Dickinson's (1953) porosity profile (Figure 1) and for the sedimentation rate of 1 mm yr^{-1} used in the calculations below, are shown in Figure 2. At 2 km the surficial burial rate is reduced by 36 % to 0.64 mm yr^{-1} and at 4 km by 42 % to 0.58 mm yr^{-1} . Calculations using faster or slower sedimentation rates for the same porosity profile, resulted in a directly proportional increase or decrease, respectively, in the burial-rate profile.

Changes in the bulk volume of the element with depth are also shown on Figure 2. A bulk-elemental volume at the surface of 1 cm^3 is used in these calculations. The changes in bulk volume of the element with depth are similar to the changes in burial rate with depth discussed above. The similarity between bulk volume of the element and burial rate profiles should be expected because they are equally dependent on the height of the elemental volume, L .

Cross-Sectional Area

The cross-sectional area of the bulk-elemental volume, A_b , normal to vertical flow is calculated from the bulk volume of the element at the surface, $V_{b,0}$,

$$A_b = (V_{b,0})^{\frac{2}{3}} . \quad (3.27)$$

The cross-sectional area normal to vertical flow remains constant with increased burial depth. This is because the decrease in elemental volume upon compaction is assumed to shorten only the vertical dimension of the elemental volume. In this study a bulk-elemental volume at the surface of 1 cm^3 is used. Therefore the

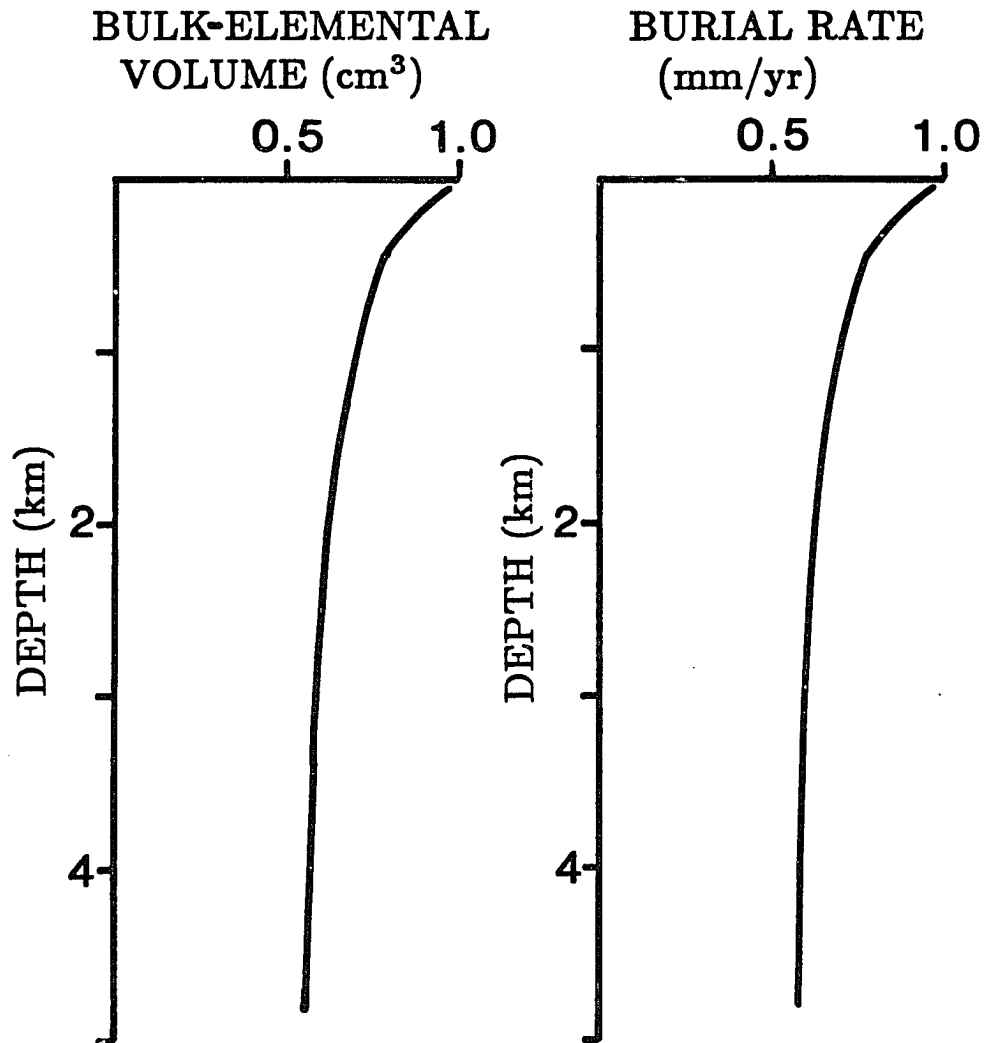


Figure 2: Bulk-elemental volume, V_b , and burial rate, $\dot{v}$.
 Calculated for Dickinson's (1953) porosity profile using Equations 3.24 and 3.26.

cross-sectional area normal to the vertical direction of flow is equal to 1 cm² at all depths.

Fluid Pressure

Lithostatic pressure is an upper limit on fluid pressure in geopressed sediments. Fluid pressure developed in excess of lithostatic is assumed to be relieved by fluid discharge in the calculations below. If pore-fluid pressure were to increase beyond the lithostatic pressure it would exceed the strength of the rock, expand pores, increase sediment permeability, and thereby release fluid (Hubbert and Rubey, 1959).

Lithostatic pressure, P_L , although a function of the local anisotropic stress field, can be approximated by:

$$\frac{dP_L}{dz} = g\rho_B \quad (3.28)$$

where g is gravitational acceleration, and z is positive downward. The bulk density of the rock, ρ_B , is calculated from Equation 3.29 with the assumption that the only phase filling the pores is pure H₂O liquid.

$$\rho_B = \rho\phi + \rho_R(1 - \phi) \quad (3.29)$$

where ρ is the density of H₂O calculated as a function of temperature and pressure from the equations of Helgeson and Kirkham (1974), and ρ_R is the mineral density taken as 2.65 g cm⁻³. A lithostatic pressure profile calculated for the porosity profile of Dickinson (1953), and a thermal gradient of 30°C km⁻¹, is shown in Figure 1. Because the density of water and of rock vary little over the temperatures and pressures considered, lithostatic pressures calculated for thermal gradients ranging from 20 to 40°C km⁻¹ differ by less than 10 bars. Lithostatic pressure

calculated for thermal gradients ranging from 20 to 40°C km⁻¹, therefore shows less than a 10 bar shift.

A hydrostatic pressure profile, calculated for a 30°C km⁻¹ thermal gradients, is also shown on Figure 1 for comparison. Hydrostatic pressure is a function of the fluid density, ρ , and is calculated using Equation 3.30.

$$\frac{dP_H}{dz} = g\rho \quad (3.30)$$

The depth of geopressuring within a sediment column depends on local conditions. The depth at which elevated fluid pressures approach lithostatic occurs between 1.5 and 4 km (Fertl, Chilingarian and Rieke, 1976). A depth of 2 km is used as the depth in which fluid pressures are equivalent to lithostatic in the calculations below.

Error Analysis

Calculation of mass of fluid expelled using the equations and data presented above and an integration interval of 100 m results in an integration error ranging from 1.1 % at 2.0 km to 0.2 % at 4.5 km. The integration error decreases with increased depth for each profile calculated, because the mass of fluid expelled from the sediments per 100 m interval decreases with increased depth. These integration errors are calculated by comparing the actual change in mass of fluid in the sediments over each 100 m interval with the change in mass over the same interval calculated through integration of Equation 3.18. The actual change in mass of fluid is taken as the difference in mass of the fluid in the sediments calculated using the relationship

$$M = \rho\phi V_b \quad (3.31)$$

Integration errors in the calculation of the volumetric flux, q_z , also range from 1.1 % at 2.0 km to 0.2 % at 4.5 km. These errors are calculated from the relationship between M and q_z ,

$$\frac{dq_z}{dz} = \frac{\dot{v}}{\rho A_b} \frac{dM}{dz} \quad (3.32)$$

Because of the linear relationship of V_b and $\dot{v}$ with L (Equation 3.25 and 3.26), the integration errors in calculating the bulk-elemental volume, V_b , and the burial rate, $\dot{v}$ are insignificant.

Results

The mass of fluid expelled from an elemental volume of sediments having a history of sediment porosity changes comparative to the porosity profile of Dickinson's (1953), and thermal gradients ranging from 0 to 100°C km⁻¹ are shown in Figure 3. Calculations of the mass of fluid expelled presented here, and of the volumetric flux presented below, are completed under the assumptions that fluid pressures in excess of lithostatic pressure develop below 2 km and that this pressure is relieved by fluid discharge from the pore space, that fluid mass and volume are unaffected by mineral transformations, and that each unit volume of sediment has undergone the same history of porosity and thermal changes as the unit volumes below.

Fluid mass discharged during burial of geopressed sediments as a result of porosity reduction alone is represented by the curve for a thermal gradient of 0°C km⁻¹ on Figure 3. Comparison of the 0°C km⁻¹ curve with that of higher thermal gradients allows prediction of the relative contribution of thermal expansion to the mass of fluid discharged.

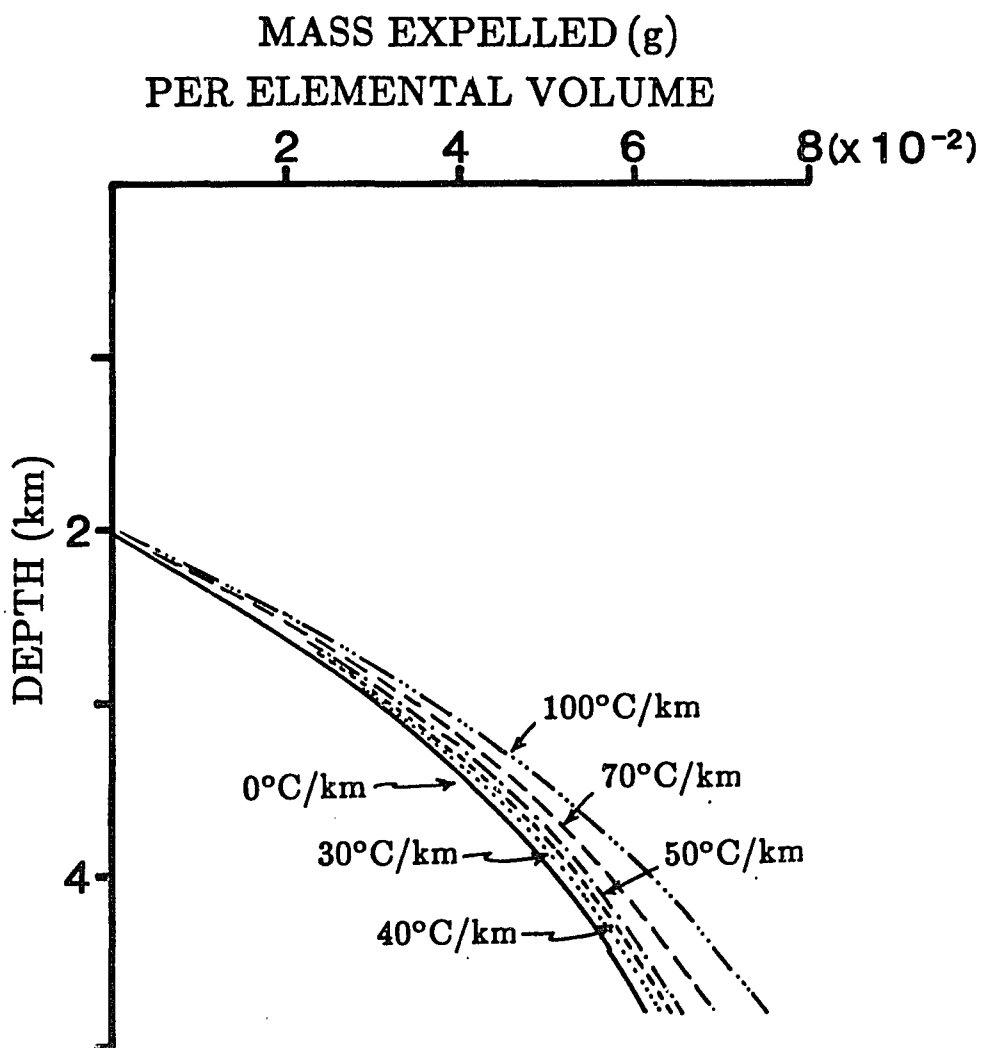


Figure 3: Mass of fluid expelled from an elemental volume of geopressed sediment during burial.

Calculated for sediments having Dickinson's (1953) porosity profile, a sedimentation rate of 1.0 mm yr^{-1} , and thermal gradients ranging from 0 to $100^\circ\text{C km}^{-1}$.

The mass of fluid released increases with increased thermal gradient. For thermal gradients of $40^{\circ}\text{C km}^{-1}$ and lower, which are common to geopressured sediments, the contribution of thermal expansion to fluid discharge is less than 1 %. The contribution of thermal expansion increases to approximately 20 % for a thermal gradient of $100^{\circ}\text{C km}^{-1}$. A thermal gradient of $100^{\circ}\text{C km}^{-1}$ would be encountered in a sedimentary basin with high heat flow such as found in the geothermal systems of the Salton trough of southern California and Mexico (Bird and Norton, 1981).

The change in volumetric flux of fluid from an elemental volume of sediment per 100 m of burial is shown on Figure 4. The volumetric flux per 100 m of burial, as a consequence of porosity reduction alone ($0^{\circ}\text{C km}^{-1}$), is largest at the top of the geopressured zone, at $-2.7 \times 10^{-3} \text{ mm yr}^{-1}$, decreasing to $-0.7 \times 10^{-3} \text{ mm yr}^{-1}$ at 4.5 km. This reduction in volumetric flux with increased depth occurs because of the reduction in the porosity gradient from $-2.5 \% \text{ km}^{-1}$ at 2 km to less than $-1.0 \% \text{ km}^{-1}$ at 4.5 km (Figure 1).

The contribution of thermal expansion to the volumetric flux, relative to the contribution of porosity reduction, increases with increased burial. For thermal gradients less than $40^{\circ}\text{C km}^{-1}$, less than 8 % of the volumetric flux is a result of thermal expansion at 2 km while up to 20 % of the volumetric flux is a result of thermal expansion at 4.5 km (Figure 4). In sediments with a thermal gradient of $100^{\circ}\text{C km}^{-1}$ the contribution to volumetric flux from thermal expansion of pore fluids exceeds the contribution from porosity reduction at depths greater than 3.5 km. This shift in the contribution of thermal expansion over that of porosity reduction for a thermal gradient of $100^{\circ}\text{C km}^{-1}$ is indicated by a change in the slope of the curve for volumetric flux on Figure 4.

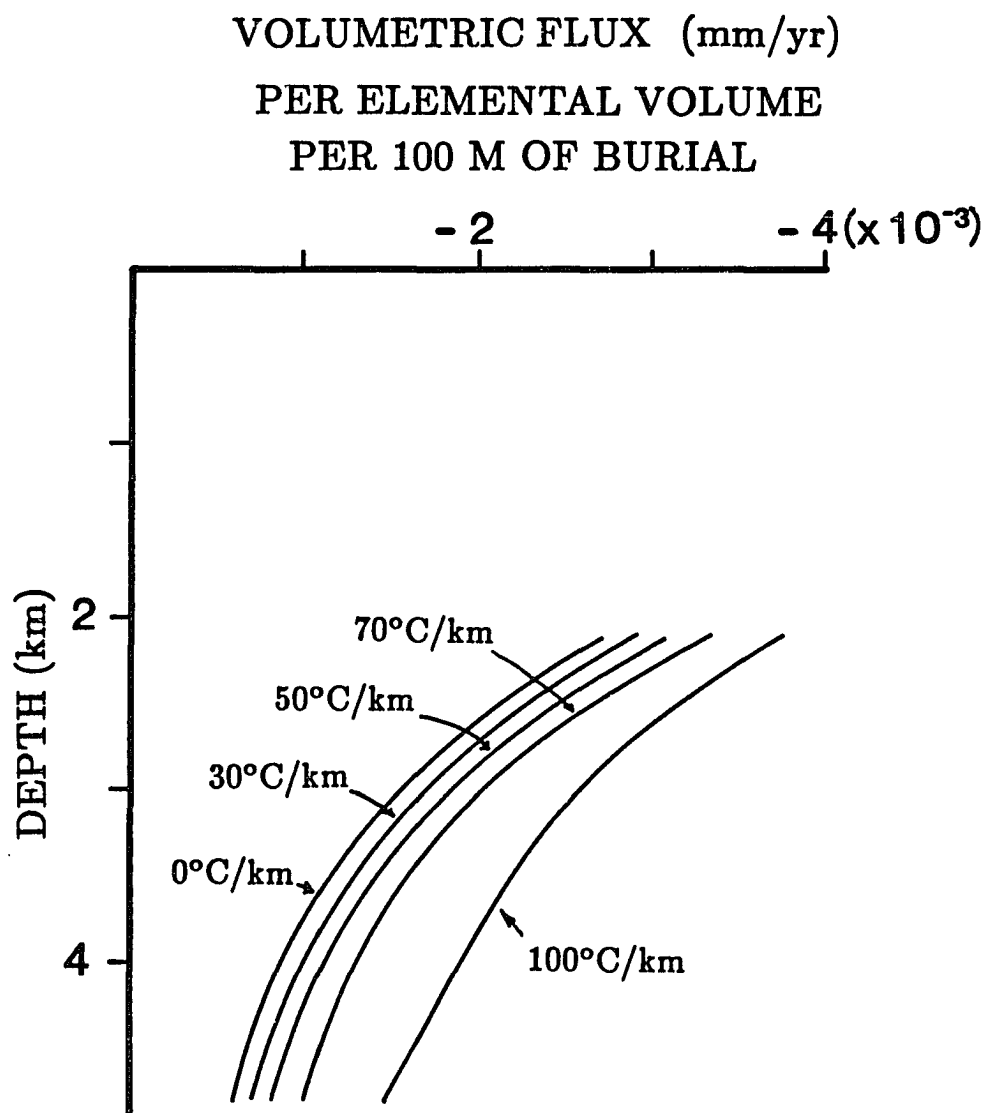


Figure 4: Volumetric flux per elemental volume.

For 100 m intervals of burial. Calculated for Dickinson's (1953) porosity profile, a sedimentation rate of 1.0 mm yr^{-1} , and thermal gradients ranging from 0 to $100^\circ\text{C km}^{-1}$.

It is apparent that a very small porosity gradient allows thermally induced density decreases to be more important than porosity decreases in governing discharge. The mass of fluid discharged by porosity gradients from -0.5 to -5.0 % km^{-1} , and by thermal gradients from 30 to $100^\circ\text{C km}^{-1}$ are compared on Figure 5. A porosity gradient of less than -0.5 % km^{-1} is necessary to allow thermal expansion to contribute more than compaction to the discharge of fluids from sediments having a thermal gradient of 40°C km^{-1} .

The calculation of discharge resulting from thermal expansion alone indicates that geopressed fluid can discharge from sediments during burial independent of porosity reduction. Thermal expansion in sediments with a thermal gradient of 40°C km^{-1} is responsible for discharge of 4×10^{-3} g of pore fluid per kilometer of burial (Figure 5). Although this contribution of density decreases to fluid discharge is small, it is adequate to result in flow in geopressed sediments in which porosity reduction is inhibited.

The cumulative fluid discharge from geopressed sediments resulting from pore volume decrease and thermal expansion, displaces pore fluid from the upper portions of geopressed sediments and ultimately flushes this fluid from the geopressed sediments. The depth of burial necessary to replace all the fluid from an elemental volume of sediment at the top of the geopressed zone, by fluids expelled from sediments below, is calculated. Sediments at 2 km, the top of the geopressed zone discussed above, with a porosity of 0.22 (Figure 1), an elemental volume of 0.63 cm^3 (Figure 2), and a fluid density of 0.99 g cm^{-3} , contain 0.14 g of fluid per elemental volume (Equation 3.31). In the upper 100 m of the geopressed zone, pore-volume decrease and thermal expansion result in expulsion of 4.3×10^{-3} g of fluid from an elemental volume of sediments per 100

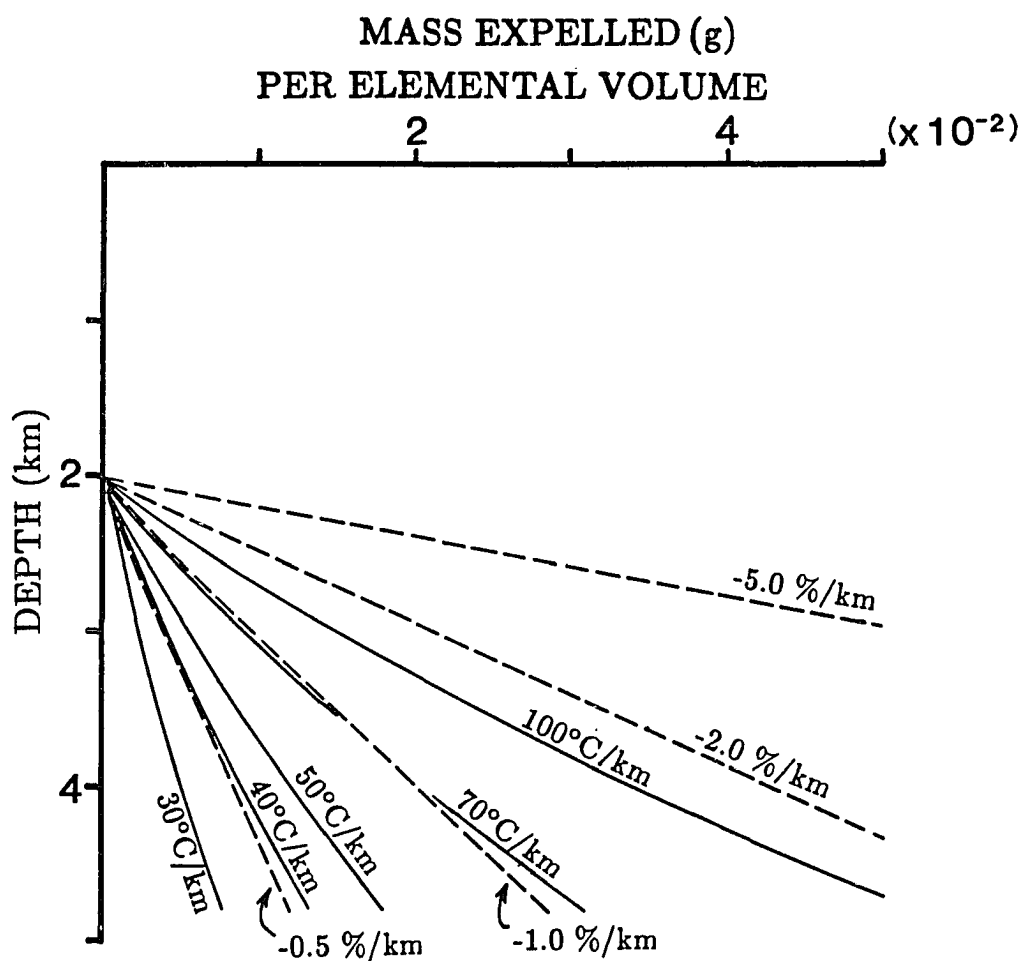


Figure 5: Mass of fluid discharged during burial as a result of thermal expansion and porosity reduction.

Calculated for thermal gradients ranging from 30 to 100°C km⁻¹, solid lines, and for porosity gradients ranging from -0.5 to -5 % km⁻¹, dashed lines. Initial conditions at 2 km are porosity = 0.22, temperature = 85°C, fluid pressure = lithostatic pressure = 418 bar, and sediment burial rate = 0.64 mm yr⁻¹. These conditions are set for a sediment column above 2 km that has a thermal gradient of 30°C km⁻¹ and porosity profile of Dickinson's (1953).

m of burial (Figure 3). Given an average elemental volume of 0.63 cm^3 (Figure 2) and assuming flow is vertically upward, all 0.14 g of fluid in the top-most elemental volume is displaced, after approximately 20 cm of burial, by the accumulated discharge of fluid from a 100 m column of sediment below. If the direction of fluid flow is only 10° from horizontal, fluid from the top-most elemental volume is displaced after 200 cm of burial. These calculations indicate that fluids in the upper portions of geopressured sediments are readily flushed up and out of the geopressured zone by pore fluids expelled from geopressured sediments below.

Calculation of the velocity of upward-vertical fluid discharge indicates that it is greater than the rate of sediment burial. The velocity of fluid discharged from an elemental volume of sediment buried from 2.1 to 2.2 km is $-1.4 \times 10^{-2} \text{ mm yr}^{-1}$ (Equation 3.20). The velocity of fluid discharge accumulated from a 100 m column of sediment, over the same burial distance, is -200 mm yr^{-1} . The velocity of fluid discharge exceeds negative the rate of sediment burial at 2.1 km of -0.63 mm yr^{-1} (Figure 2) by over 3 orders of magnitude. This large difference in the magnitudes of upward flow and burial indicates that even if only a small fraction of the flow direction is vertical, upward vertical flow will still exceed the rate of burial. Therefore, as the sediments are moving downward the fluids are flowing up and out of the geopressured zone.

Predicted Hydrologic Conditions

Fluid flow in geopressured sediments is dominantly compaction-driven. The source of fluid is, therefore, the fluid present in pore spaces at the time of geopressuring. These geopressured pore fluids are then discharged from the

pore volume as a result of compaction-induced pore-volume decreases and thermal expansion during sediment burial.

Flow in the upper portion of the geopressured zone has both a horizontal and upward-vertical component. The volumetric flux is the largest at the top of the geopressured zone, at $-2.7 \times 10^{-3} \text{ mm yr}^{-1}$ at 2 km, and decreases with increased depth to $-0.7 \times 10^{-3} \text{ mm yr}^{-1}$ at 4.5 km. This decrease in the volumetric flux is a result of the decrease in porosity gradient with increased depth. The cumulative fluid discharge from geopressured sediments is adequate to replace pore fluids in the upper portions of the geopressured zone with fluids expelled from geopressured sediments below. The velocity of fluid discharge that is vertically upward, exceeds the rate of sediment burial, and, therefore, fluids are flowing up and out of the geopressured zone.

Thermal expansion makes a lesser contribution to flow than porosity reduction because of the high porosity gradients and low thermal gradients, of less than 40°C km^{-1} , in the sediments of interest. When porosity reduction is inhibited, however, thermal expansion of pore fluids is adequate to maintain flow in geopressured sediments. This situation could occur, for example, when high fluid pressures inhibit compaction in the upper portions of the geopressured zone (cf. Magara, 1968; Schmidt, 1973). These zones of inhibited compaction are marked by reversals in the porosity gradient. Another situation occurs in sediments in which deposition of authigenic cements, such as silica and carbonate, strengthen the pore matrix and prevent compaction. In this case, fluids trapped in pores or fractures by authigenic cement or as inclusions within the cement expand fracturing the cement and reopening flow paths (Hubbert and Rubey, 1959).

Flow in normally-pressured sediments is distinctly different from that in geopressured sediments. In normally-pressured sediments the downward influx of gravity-driven fluids dominates over the relatively small upward component of compaction-driven flow. In contrast, compaction-driven flow with an upward component dominates in geopressured sediments. These differences in flow between geopressured and normally-pressured sediments contribute to differences in the location and composition of authigenic mineral deposition. An exception to this contrast in flow between normally-pressured and geopressured sediments is the case in which fluid in normally-pressured sediments flows upward as a result of thermally-driven flow. Thermally-driven flow, however, is the exception in basin sediments having thermal gradients less than $40^{\circ}\text{C km}^{-1}$.

CHAPTER 4

CO₂ and CH₄ IN GEOPRESSURED FLUIDS

Thermal decomposition of organic material in shales produces CO₂ and CH₄. Recent work by Tannenbaum and Kaplan (1985) indicates that during the pyrolysis of kerogen, up to 6 wt % converts to CO₂ and up to 1 wt % to CH₄. Unpublished experimental work by L. L. Lundell and A. Brown (Franks and Forester, 1984) indicates that up to 22 wt % CO₂ is released from the more oxygen-rich kerogen composed of humic material. Temperatures at which CO₂ is released suggest that the largest CO₂ generation occurs at approximately 100°C, and is completed at 135°C (Hunt, 1979). In contrast, CH₄ release occurs continuously at temperatures greater than 90°C (Hunt, 1979).

Gases released during thermal degradation of kerogen dissolve in surrounding pore fluids. In normally-pressured sediments pore fluids are readily flushed and renewed by the influx of gravity-driven fluids. If the rate of flow is fast relative to the rate of CO₂ and CH₄ release from kerogen, then this process prevents the buildup of high concentrations of these gases in the pore fluids. In geopressured sediments, however, the pore fluids are not replaced by the influx of new fluids, but are essentially isolated with the only flow being that of fluid out of the sediments. The competing processes of upward fluid flow and downward burial of sediments with accompanied CO₂ and CH₄ release, result in high concentrations of CO₂ and CH₄ accumulating in geopressured pore fluids.

In the following section CO_2 and CH_4 solubilities are reviewed. It is then calculated whether the amounts of CO_2 and CH_4 released during kerogen maturation are sufficient to saturate upwardly mobile geopressured pore fluids. Calculations also indicate that upon saturation continued upward fluid flow results in separation of a CO_2 - CH_4 -rich vapor.

CO_2 and CH_4 Solubility

The addition of small amounts of CO_2 to an H_2O -rich solution results in large shifts in the vapor-liquid equilibria surface of the solution. Vapor-liquid equilibria surfaces for the system $\text{CO}_2 - \text{H}_2\text{O}$ are shown in Figure 6. The isocompositional curves in Figure 6 represent the mole % CO_2 in the liquid phase at vapor-liquid equilibria. Comparison of these equilibria surfaces with the temperature and pressure conditions of geopressured fluids with a thermal gradient of 30°C km^{-1} indicates that as little as 2 mole % CO_2 results in their intersection.

CH_4 has a similar effect on vapor-liquid equilibria. Vapor-liquid equilibria surfaces for the system $\text{CH}_4 - \text{H}_2\text{O}$ are shown in Figure 7. The isocompositional curves in Figure 7 represent the mole % CH_4 in the liquid phase. Less than 0.25 mole % CH_4 is necessary for CH_4 saturation at the temperature and pressure conditions common to petroleum-bearing basins.

The addition of solutes to H_2O -rich solutions enhances the effects of CO_2 and CH_4 on lowering of the vapor-liquid equilibria surfaces into the range of temperatures and pressures of interest. This relationship is shown through comparison of the vapor-liquid equilibria surfaces for the systems $\text{CO}_2 - \text{H}_2\text{O}$ and $\text{CO}_2 - \text{H}_2\text{O} - \text{NaCl}$ shown in Figures 8. Addition of 2 mole % NaCl , to a 2 mole % CO_2 solution at 150°C , drops the vapor saturation surface over 200 bar.

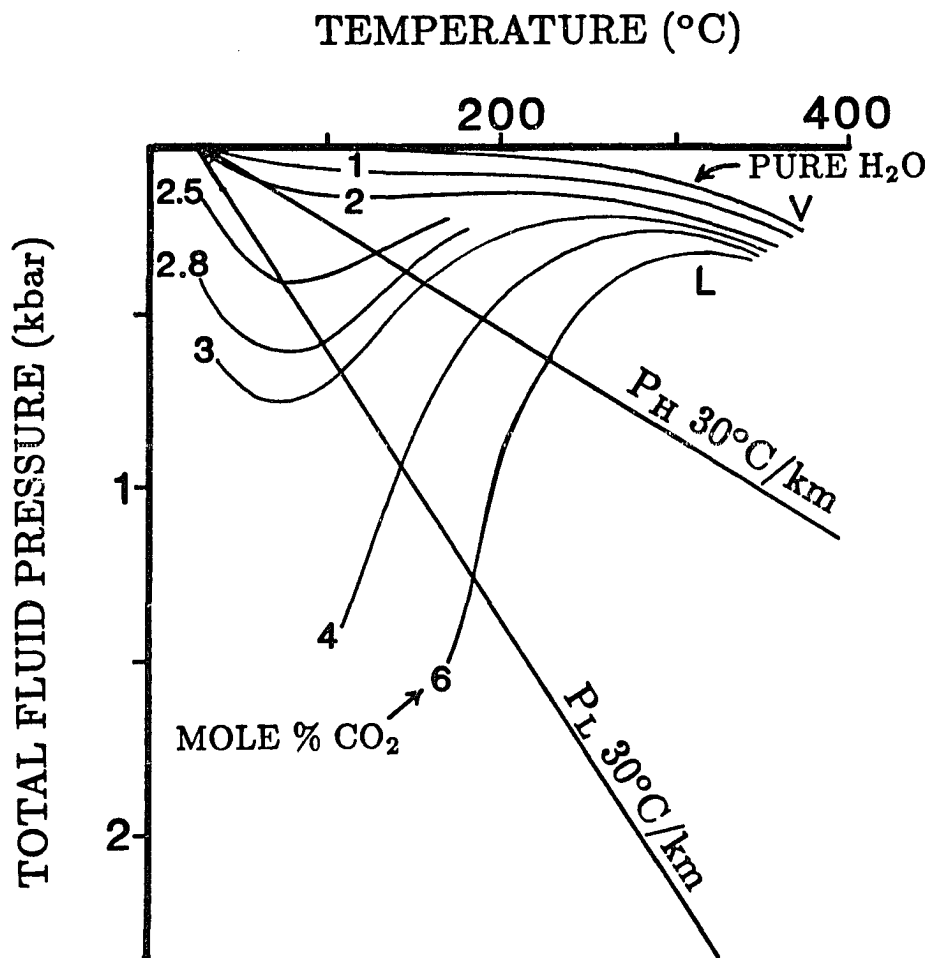


Figure 6: Isocompositional curves of CO₂ in the liquid phase at vapor-liquid equilibria for the system CO₂ - H₂O.

Data from Takenouchi and Kennedy (1964). Hydrostatic, P_H, and lithostatic, P_L, pressures for 30°C km⁻¹ taken from Figure 1.

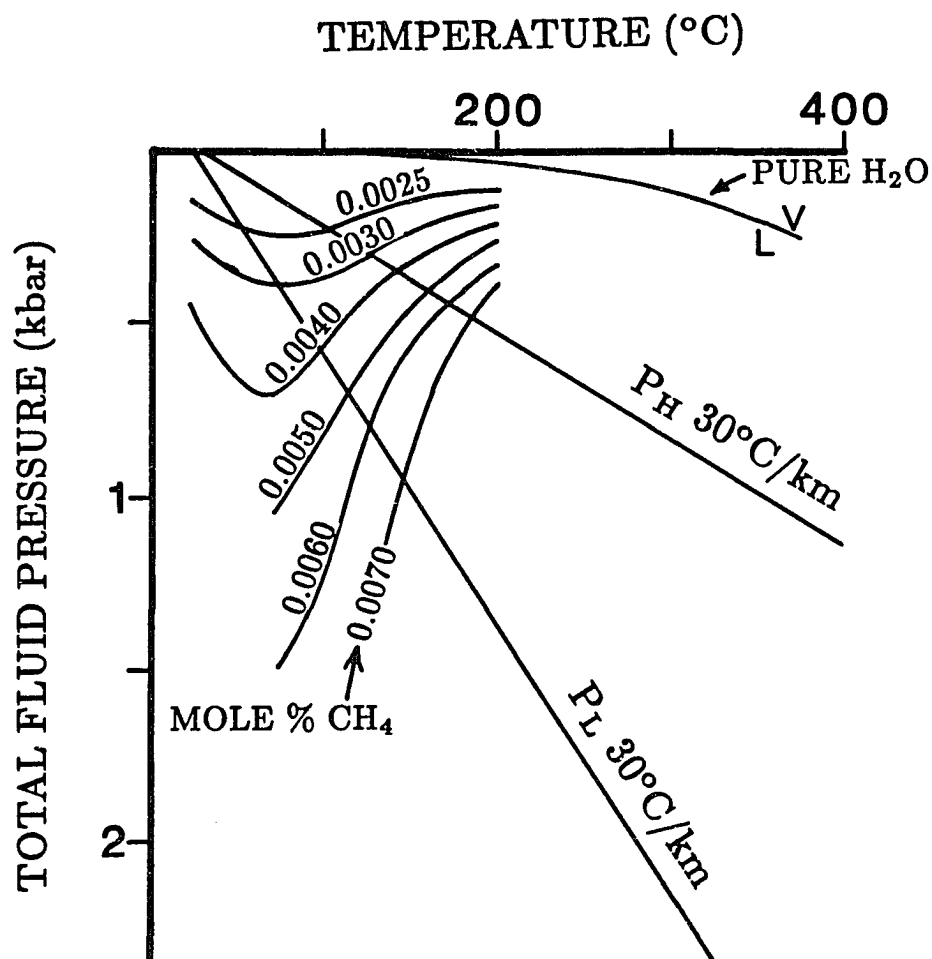


Figure 7: Isocompositional curves of CH_4 in the liquid phase at vapor-liquid equilibria for the system $\text{CH}_4 - \text{H}_2\text{O}$.

Data from Jarsen and Prausnitz (1984). Hydrostatic, P_H , and lithostatic, P_L , pressures for 30°C km^{-1} taken from Figure 1.

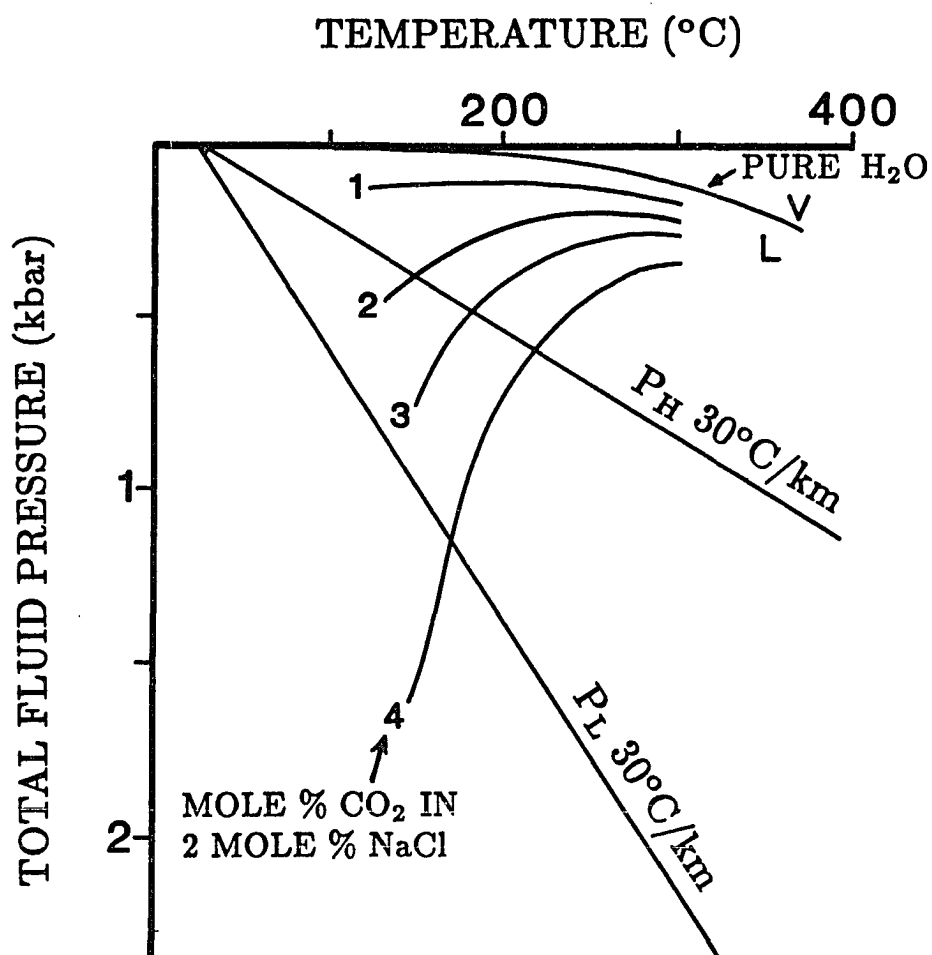


Figure 8: Isocompositional curves of CO_2 in the liquid phase at vapor-liquid equilibria for the system $\text{CO}_2 - \text{H}_2\text{O} - \text{NaCl}$ for 2 mole % NaCl.

Data from Takenouchi and Kennedy (1964, 1965). Hydrostatic, P_H , and lithostatic, P_L , pressures for 30°C km^{-1} taken from Figure 1.

Vapor in equilibrium with $\text{CO}_2 - \text{H}_2\text{O}$, $\text{CO}_2 - \text{H}_2\text{O} - \text{NaCl}$, and $\text{CH}_4 - \text{H}_2\text{O}$ solutions is enriched in the more volatile components. The mole % CO_2 and CH_4 in the vapor phase at vapor-liquid equilibria are shown in Figures 9 and 10. Under 150°C the vapor phase contains over 90 % CO_2 or CH_4 and less than 10 % H_2O . Vapor separation tends, therefore, to deplete the remaining liquid of these gases.

Experimental solubility data for the combined systems $\text{CO}_2 - \text{CH}_4 - \text{H}_2\text{O}$ or $\text{CO}_2 - \text{CH}_4 - \text{H}_2\text{O} - \text{NaCl}$ are not available over the temperature and pressure range of interest. Therefore, solubility data for the binary systems $\text{CO}_2 - \text{H}_2\text{O}$ and $\text{CH}_4 - \text{H}_2\text{O}$ are used in this study. Equilibrium properties of the binary systems, however, do not accurately represent the more complex systems because of the additional intermolecular attractions resulting from the presence of both CO_2 and CH_4 in H_2O . Addition of small amounts of CH_4 to the binary system $\text{CO}_2 - \text{H}_2\text{O}$ slightly increases the activity of H_2O and significantly decreases the activity of CO_2 (Jacobs and Kerrick, 1981). Data for the binary systems used in this study, therefore, represent maximum solubilities (Prausnitz, Lichtenthaler and DeAzevedo, 1986).

Calculation of $\text{CO}_{2(\text{vapor})} - \text{CO}_{2(\text{liquid})}$ Equilibria

Equation-of-State

The compositions of coexisting vapor and liquid phases at vapor-liquid equilibria can be calculated if an equation-of-state is available that adequately describes a system over the range of temperatures and pressures of interest. The Redlich-Kwong equation-of-state (Equation 4.1) (Redlich and Kwong, 1949),

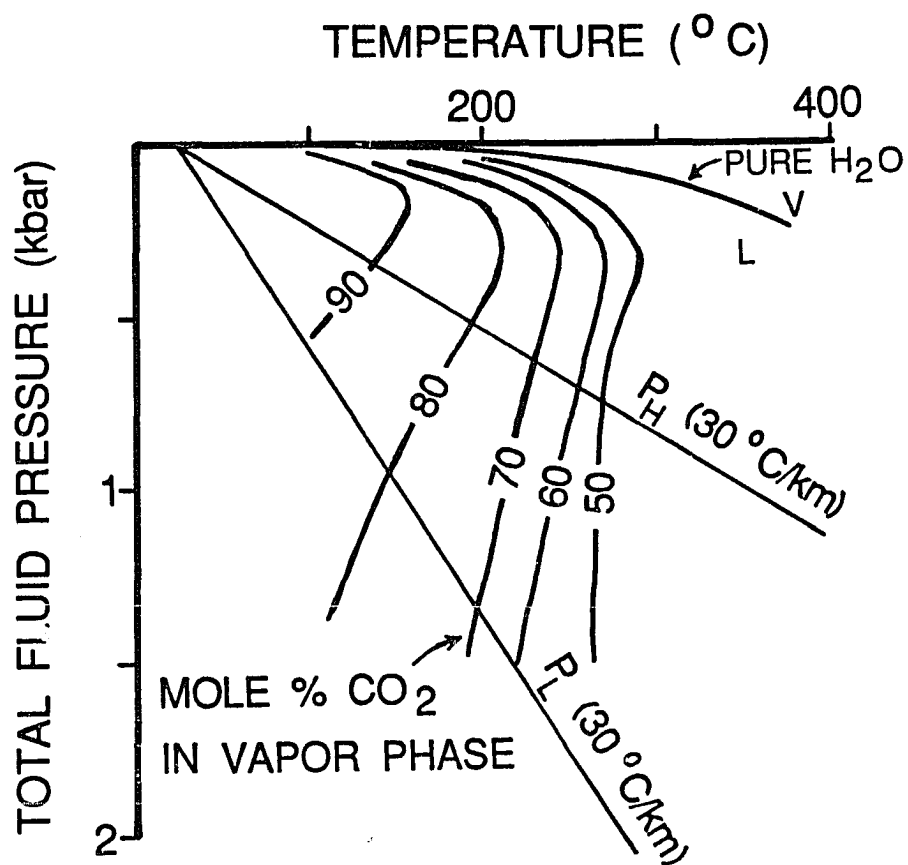


Figure 9: Isocompositional curves of CO_2 in the vapor phase at vapor-liquid equilibria for the system $\text{CO}_2 - \text{H}_2\text{O}$.

Data from Takenouchi and Kennedy (1964). Hydrostatic, P_H , and lithostatic, P_L , pressures for $30^{\circ}\text{C km}^{-1}$ taken from Figure 1.

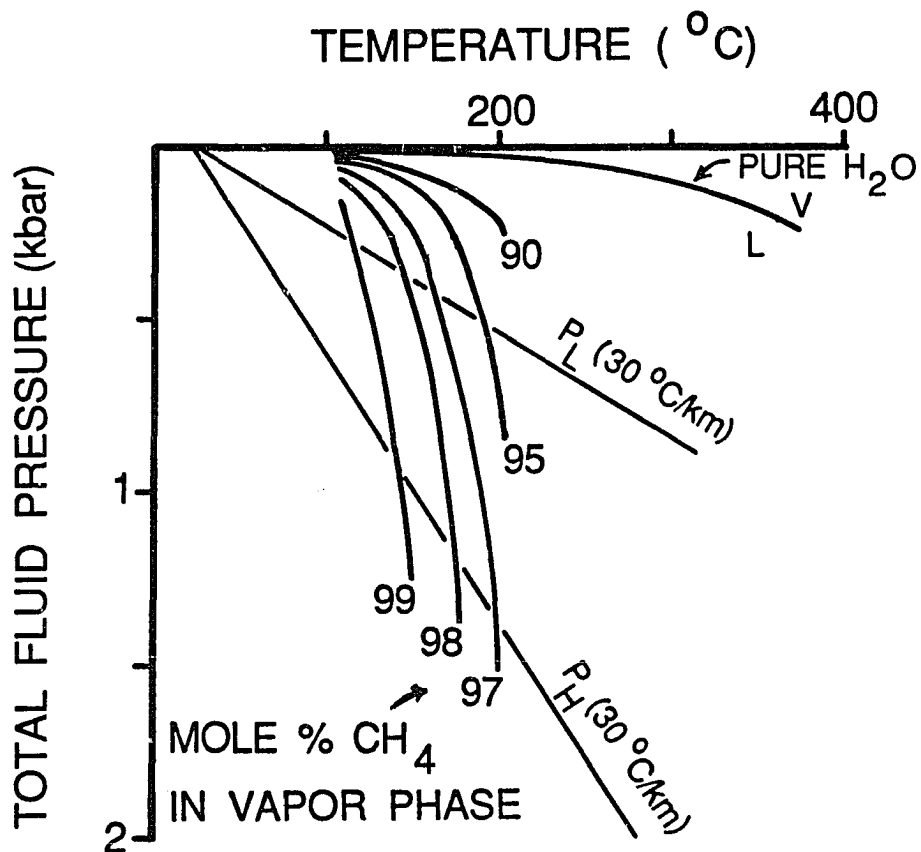


Figure 10: Isocompositional curves of CH_4 in the vapor phase at vapor-liquid equilibria for the system $\text{CH}_4 - \text{H}_2\text{O}$.

Data from Larsen and Prausnitz, 1984). Hydrostatic, P_H , and lithostatic, P_L , pressures for $30^{\circ}\text{C}/\text{km}^{-1}$ taken from Figure 1.

which is the most widely used in chemical process design (Van Ness and Abbott, 1982) and geologic applications (cf. Holloway, 1977, Flowers, 1979, Kerrick and Jacobs, 1981, Bottinga and Richet, 1981, Bowers and Helgeson, 1983), does not adequately describe vapor-liquid equilibria in the system $\text{CO}_2\text{-H}_2\text{O}$ at temperatures below the critical isotherm.

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{T^{\frac{1}{2}}\bar{V}(\bar{V} + b)} \quad (4.1)$$

Inconsistencies between experimentally derived vapor-liquid equilibria surfaces and those calculated for the system $\text{CO}_2\text{-H}_2\text{O}$ using the Redlich-Kwong equation-of-state with the a and b parameters selected by the methods of DeSantis, Breedveld and Prausnitz (1974) and Holloway (1977) are discussed below.

Mixing rules for calculation of the a and b parameters of the Redlich-Kwong equation for the system $\text{H}_2\text{O} - \text{CO}_2$ are presented by DeSantis, Breedveld and Prausnitz (1974). The linear mixing relationships originally presented by Redlich and Kwong (1949) do not apply to the system $\text{CO}_2 - \text{H}_2\text{O}$ because CO_2 is a strong quadrupole molecule and H_2O a strong dipole molecule. Using the mixing rules of DeSantis, Breedveld and Prausnitz (1974) the parameter a for a fluid mixture is calculated using Equation 4.2.

$$a = \sum_i \sum_j X_i X_j a_{ij} \quad (4.2)$$

For the system $\text{H}_2\text{O} - \text{CO}_2$, Equation 4.2 is written as

$$a = X_{\text{H}_2\text{O}}^2 a_{\text{H}_2\text{O}} + X_{\text{CO}_2}^2 a_{\text{CO}_2} + 2X_{\text{CO}_2} X_{\text{H}_2\text{O}} a_{\text{CO}_2\text{-H}_2\text{O}} , \quad (4.3)$$

$a_{\text{H}_2\text{O}}$ = molecular attraction parameter for pure H_2O

a_{CO_2} = molecular attraction parameter for pure CO_2

$$a_{\text{CO}_2\text{-H}_2\text{O}} = (a_{\text{CO}_2}^{\circ} a_{\text{H}_2\text{O}}^{\circ})^{\frac{1}{2}} + \frac{R^2 T^{\frac{5}{2}} K}{2}. \quad (4.4)$$

Parameters $a_{\text{CO}_2}^o$ and $a_{\text{H}_2\text{O}}^o$ are temperature independent and represent molecular attraction forces arising only from molecular dispersion. K is the equilibrium constant accounting for the association of CO_2 and H_2O in either the gas or liquid phase,



$\ln K$ is represented as a power function of temperature ($^\circ\text{K}$),

$$\ln K = -11.071 + \frac{5953}{T} - \frac{2746 \times 10^3}{T^2} + \frac{464.6 \times 10^6}{T^3}, \quad (4.6)$$

where K is in reciprocal atmospheres. The value for a is then calculated essentially as a linear change between the two end member a values with a correction for the association of CO_2 and H_2O as the complex H_2CO_3 .

The parameter b for a fluid mixture is calculated by DeSantis, Breedveld and Prausnitz (1974) using Equation 4.7.

$$b = \sum_i X_i b_i \quad (4.7)$$

For the system $\text{H}_2\text{O} - \text{CO}_2$, Equation 4.7 is written as

$$b = X_{\text{CO}_2} b_{\text{CO}_2} + X_{\text{H}_2\text{O}} b_{\text{H}_2\text{O}}. \quad (4.8)$$

This equation shows that b changes linearly between the pure end member values for a fluid mixture.

Pressure-volume-temperature properties in the system $\text{H}_2\text{O} - \text{CO}_2$ are calculated using the Redlich-Kwong equation-of-state and the mixing equations from DeSantis, Breedveld and Prausnitz (1974) (Figures 11 through 16). Isotherms on Figures 11 through 16 are calculated using values for a , a^o and b for end member compositions given in DeSantis, Breedveld and Prausnitz (1974).

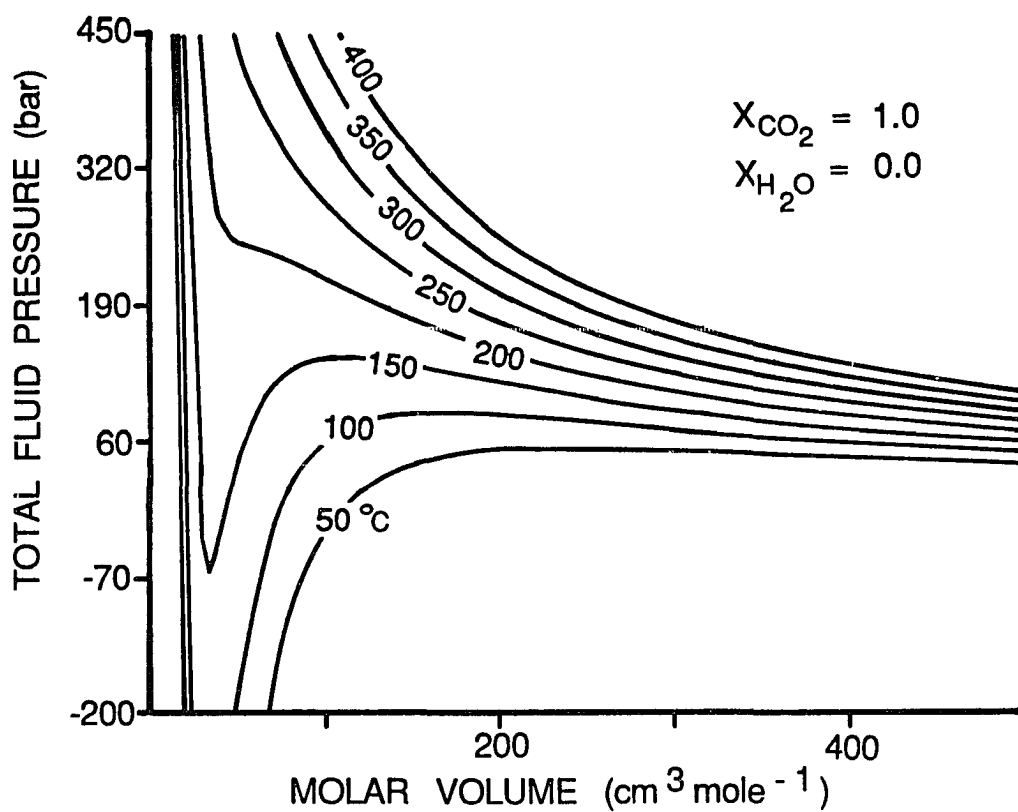


Figure 11: Isotherms for a fluid of composition $X_{\text{CO}_2} = 1.0$ and $X_{\text{H}_2\text{O}} = 0.0$. Calculated using the Redlich-Kwong equation of state with the mixing equations and data presented in DeSantis, Breedveld and Prausnitz (1974).

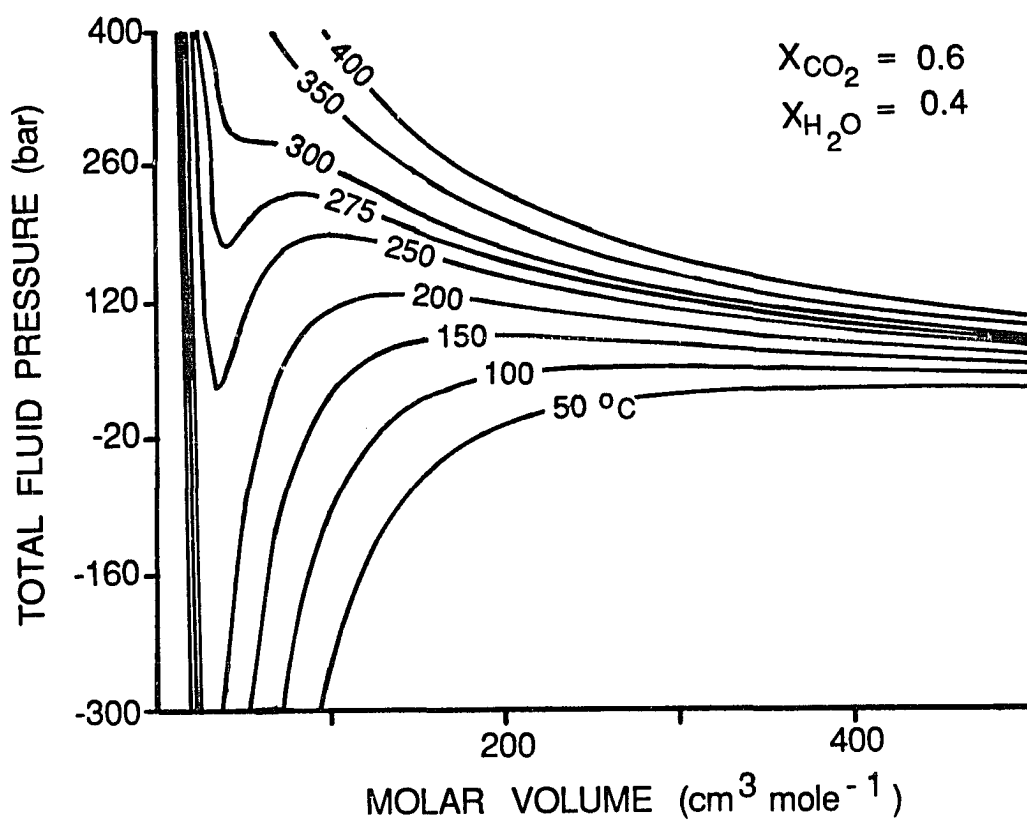


Figure 12: Isotherms for a fluid of composition $X_{\text{CO}_2} = 0.6$ and $X_{\text{H}_2\text{O}} = 0.4$. Calculated using the Redlich-Kwong equation of state with the mixing equations and data presented in DeSantis, Breedveld and Prausnitz (1974).

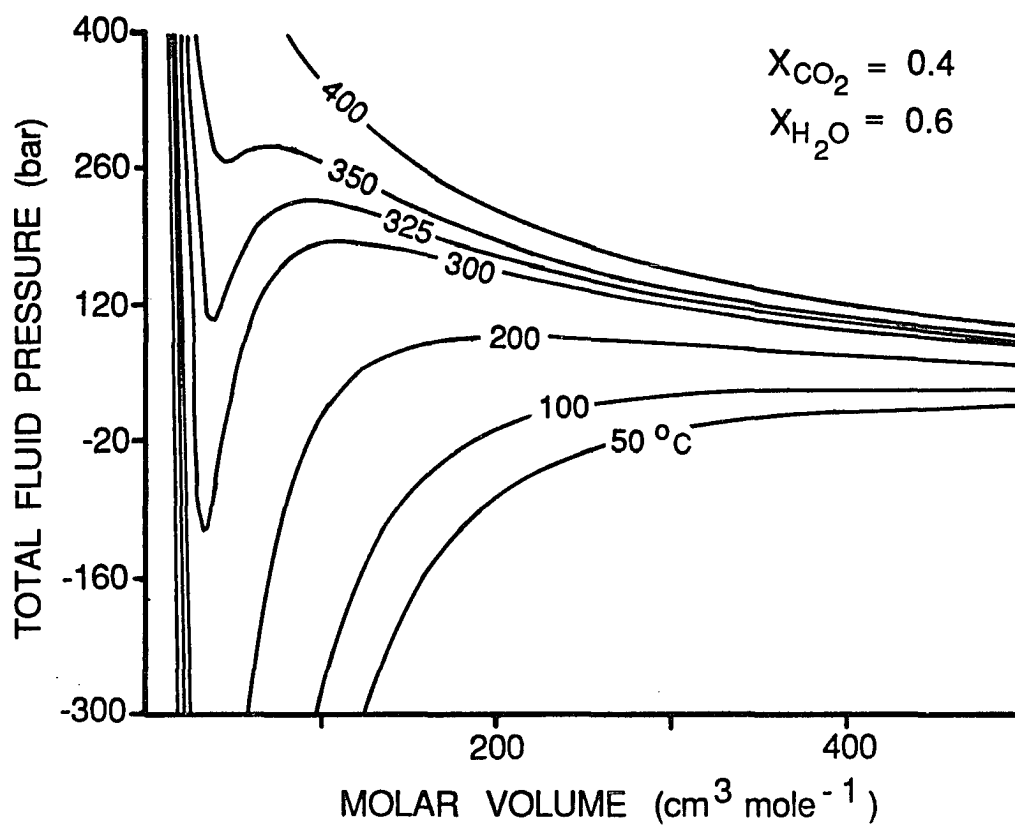


Figure 13: Isotherms for a fluid of composition $X_{\text{CO}_2} = 0.4$ and $X_{\text{H}_2\text{O}} = 0.6$. Calculated using the Redlich-Kwong equation of state with the mixing equations and data presented in DeSantis, Breedveld and Prausnitz (1974).

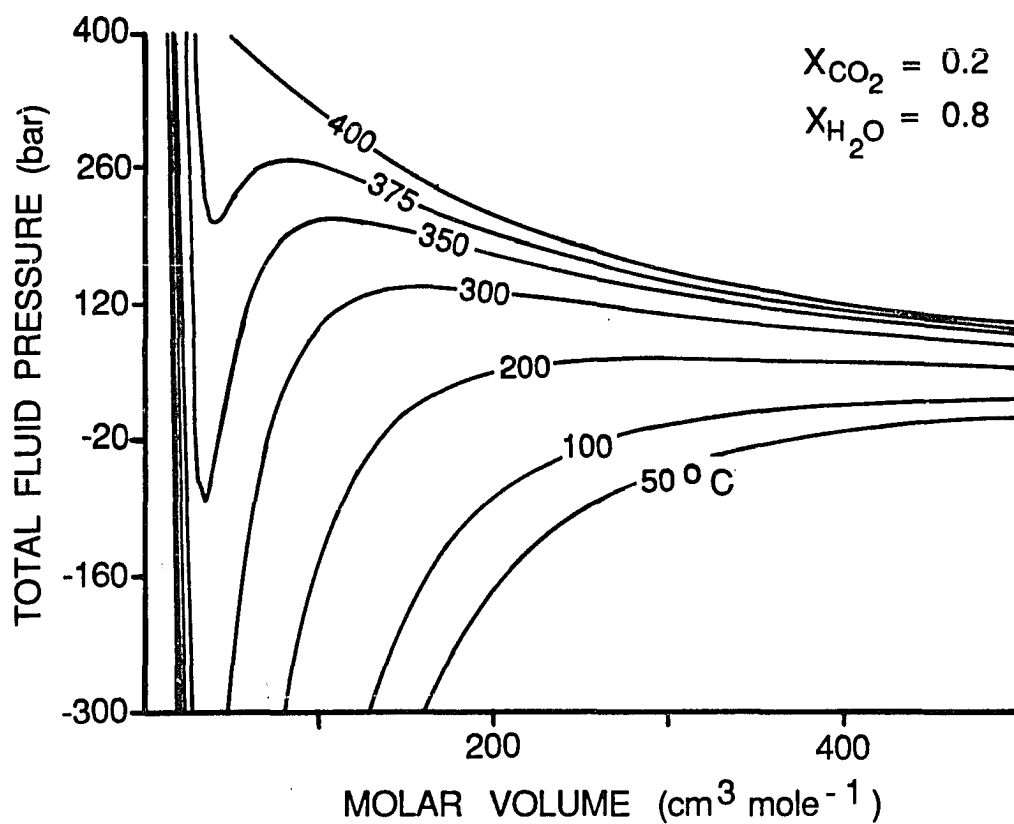


Figure 14: Isotherms for a fluid of composition $X_{\text{CO}_2} = 0.2$ and $X_{\text{H}_2\text{O}} = 0.8$. Calculated using the Redlich-Kwong equation of state with the mixing equations and data presented in DeSantis, Breedveld and Prausnitz (1974).

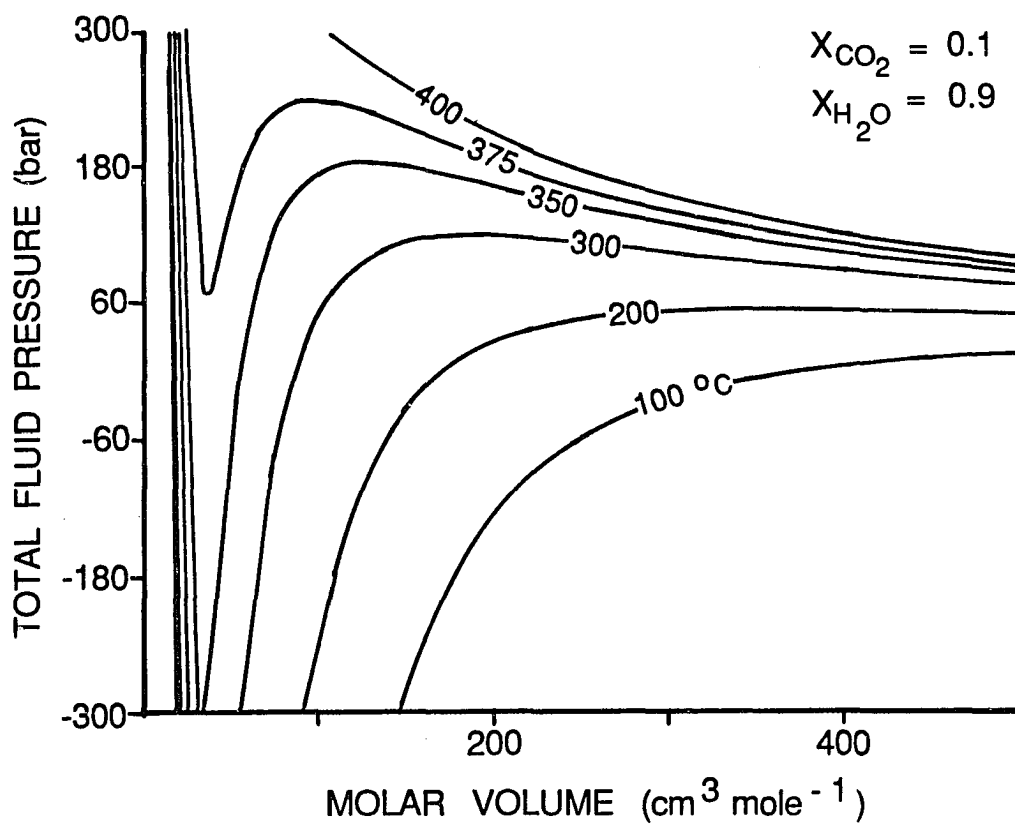


Figure 15: Isotherms for a fluid of composition $X_{\text{CO}_2} = 0.1$ and $X_{\text{H}_2\text{O}} = 0.9$. Calculated using the Redlich-Kwong equation of state with the mixing equations and data presented in DeSantis, Breedveld and Prausnitz (1974).

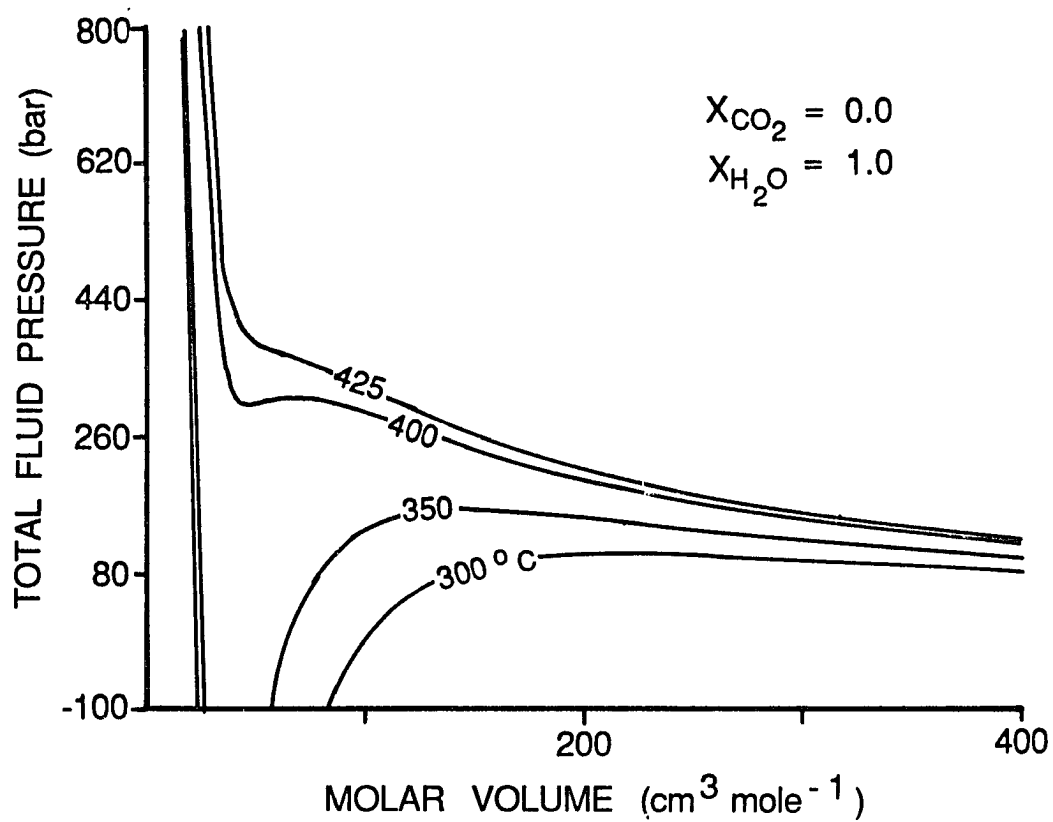


Figure 16: Isotherms for a fluid of composition $X_{\text{CO}_2} = 0.0$ and $X_{\text{H}_2\text{O}} = 1.0$. Calculated using the Redlich-Kwong equation of state with the mixing equations and data presented in DeSantis, Breedveld and Prausnitz (1974).

Graphical analysis of the Redlich-Kwong equation, Figure 17, demonstrates its utility as a cubic equation in representing the P-V-T behavior of a fluid (Prigogine and Defay, 1954). Rearrangement of the Redlich-Kwong equation (Equation 4.1) reveals the cubic nature (Equation 4.9) of this equation.

$$\bar{V}^3 - \left(\frac{RT}{P}\right)\bar{V}^2 - \left(b^2 + \frac{bRT}{P} - \frac{a}{T^{\frac{1}{2}}P}\right)\bar{V} - \frac{ab}{T^{\frac{1}{2}}P} = 0 \quad (4.9)$$

At or above the critical isotherm, a cubic equation has only one real root. This value is the fluid volume. The remaining two roots are imaginary. At the critical point the solution with respect to volume gives three real roots, two of which are equal. The two equal roots have no physical significance, whereas the remaining root represents the volume of the fluid.

Below the critical isotherm, solution of the Redlich-Kwong equation with respect to volume for each temperature gives three real, but unequal, roots within the pressure range represented by the pressure extrema M1 and M2 for each isotherm in Figure 17. M1 and M2 represent the extrema of the polynomial solution of Equation 4.9. Of these three real roots, the smallest is the volume of the liquid phase; the largest is the volume of the vapor phase. The median root is the volume of a metastable fluid. For pressures outside the pressure interval marked by the pressure extrema, M1 and M2, solution of the Redlich-Kwong equation with respect to volume gives one real and two imaginary roots. The real root is equivalent to the volume of the vapor or liquid, depending on the region in which it occurs. The intersection of the saturation surface with each isotherm is defined by the pressure at which areas A and B on Figure 17 are equal (Prigogine and Defay, 1954).

The critical curve for the system CO₂-H₂O determined using the Redlich-Kwong equation-of-state is shown in Figure 18. The critical values on this critical

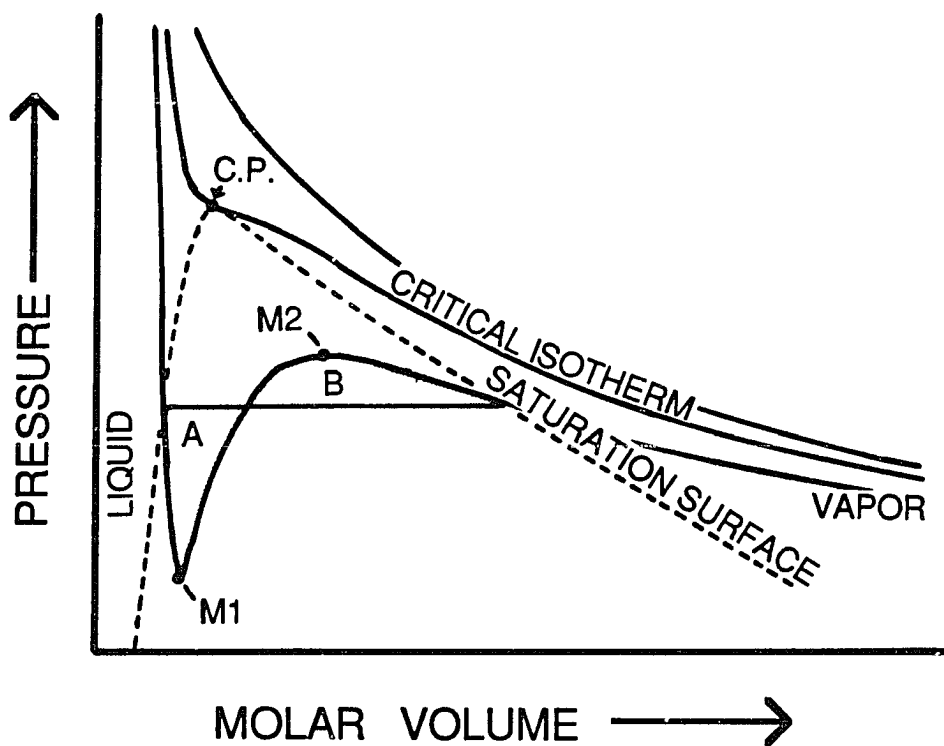


Figure 17: Schematic showing isotherms on a pressure-volume projection as defined by a cubic equation of state.

See text for discussion.

curve are obtained from the series of isotherms presented on Figures 11 through 16 and using the graphical relationships discussed above. Experimentally derived critical curves of Takenouchi and Kennedy (1964) and Todheide and Franck (1963) are also plotted on Figure 18.

Calculated and experimental critical curves are in poor agreement (Figure 18). The calculated curve shows a linear decrease in pressure and a continuous nonlinear decrease in temperature of the critical point as the CO_2 content of the solution increases. In contrast, the experimentally derived critical curve indicates the critical pressure increases and the critical temperature decreases as the CO_2 content of the solution increases.

Comparison of the experimentally derived vapor-liquid equilibria surfaces in Figure 6 with those derived from the calculated curves in Figures 11 to 16, shows large differences in experimental and calculated surfaces. The calculated vapor-liquid equilibria surfaces would limit vapor-liquid separation to pressures of less than 400 bar at all temperatures. In contrast the experimentally derived surfaces indicate that vapor-liquid equilibria at temperatures less than 250°C occur at pressures well over 1000 bar.

Other modifications of the Redlich-Kwong equation-of-state by Bowers and Helgeson (1983) for the system $\text{CO}_2 - \text{H}_2\text{O} - \text{NaCl}$, by Kerrick and Jacob (1981) for the system $\text{CO}_2 - \text{H}_2\text{O}$ and by Jacob and Kerrick (1981) for the system $\text{CO}_2 - \text{CH}_4 - \text{H}_2\text{O}$ were derived to fit experimental data at temperatures above the critical isotherm. No effort was made by these researchers to improve the agreement in the two phase region between calculated and experimental results. Furthermore, Bowers and Helgeson (1985) state the equations of Bowers and Helgeson (1983) should not be applied at temperatures below the critical isotherm. Because

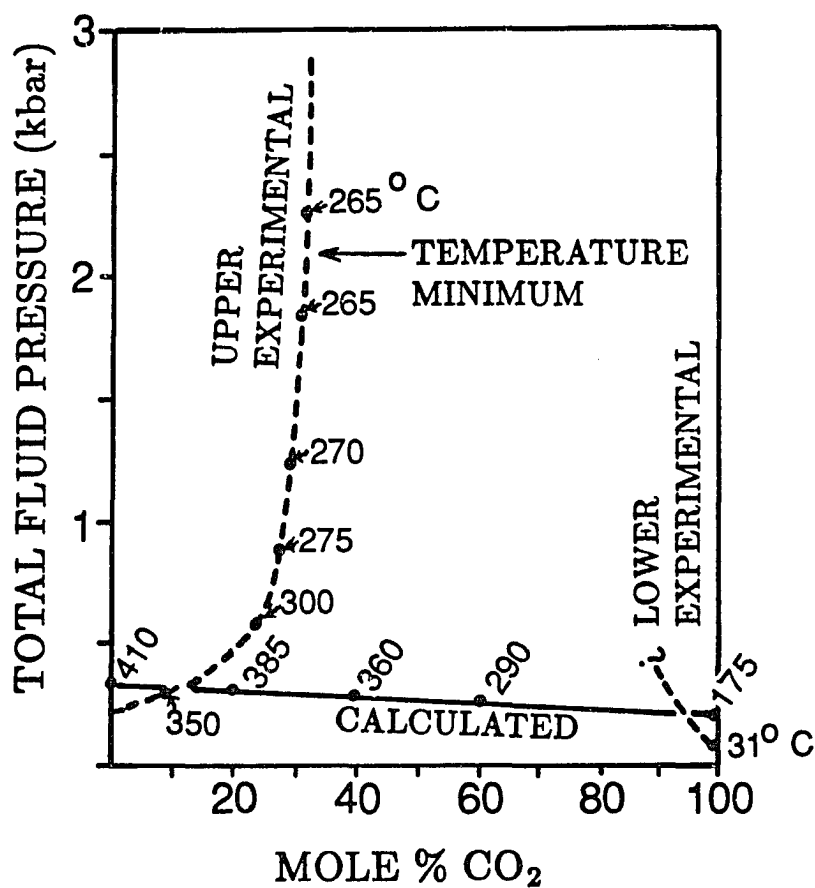
CRITICAL CURVES: SYSTEM $\text{CO}_2 - \text{H}_2\text{O}$ 

Figure 18: Critical curves for the system $\text{CO}_2 - \text{H}_2\text{O}$.

The dashed curves are from Takenouchi and Kennedy (1964) and Todheide and Franck (1963), the solid curve is calculated in this study.

of this poor agreement between calculated and experimental data, the experimental data from Takenouchi and Kennedy (1964) are used directly in the calculations of fluid-mineral equilibria presented in the following chapter.

Volatility Ratio

Vapor-liquid equilibria in near-surface hydrothermal systems are calculated by Drummond (1981) and Drummond and Ohmoto (1985) using a volatility ratio rather than an equation-of-state. The volatility ratio, R_v , defines the partitioning of a component between the liquid and vapor phase upon equilibrium separation.

$$R_v = m_i^v / m_i \quad (4.10)$$

They consider R_v to be a function of temperature but not a function of pressure, at pressures less than 150 bar.

Large errors in calculation of vapor-liquid equilibria at high pressures result from using this pressure-independent volatility ratio. For example, a volatility ratio for CO_2 at 200°C in the system $\text{CO}_2 - \text{H}_2\text{O}$ is given as 400 by Drummond and Ohmoto (1985). The volatility ratio is equated to the mole ratio by Equation 4.11.

$$\frac{X_i^v}{X_i} = \frac{R_v(1 + 55.508)}{R_v + 55.508} \quad (4.11)$$

Using this relationship the volatility ratio of 400 is found equivalent to a mole ratio (X_i^v/X_i) of 50. In contrast, mole ratios for CO_2 taken from the experimental work of Takenouchi and Kennedy (1964) (Figures 6 and 9) for the system $\text{H}_2\text{O} - \text{CO}_2$ at 200°C vary from 31 at 200 bars to 11 at 1000 bars. This large variation in mole ratio over the pressure interval expected in geopressured sediments demonstrates

that the method of calculation presented by Drummond (1981) and by Drummond and Ohmoto (1985) is not applicable to this study.

Gas Saturation in Geopressured Fluids

Gases released by the thermal decomposition of organic material present in downwardly mobile sediments are adsorbed by advecting pore fluids. The transfer of gases released from the sediments to the advecting pore fluids can be calculated from the equation for conservation of mass,

$$\sum_{i=1}^I \left(\frac{\partial(\varphi_i C_i)}{\partial t} + \bar{v}_i \cdot \nabla \bar{C}_i \right) = 0 \quad . \quad (4.12)$$

Equation 4.12 allows calculation of the change in concentration of a chemical component, C , in the i^{th} phase, $i = 1, \dots, I$, as a result of advection, where φ is the volume fraction, and v is the velocity of the i^{th} phase in the elemental volume. Expansion of Equation 4.12 for a system containing fluid, f , and rock, r , gives

$$\frac{\partial(\varphi_f C_f)}{\partial t} + \bar{v}_f \cdot \nabla \bar{C}_f + \frac{\partial(\varphi_r C_r)}{\partial t} + \bar{v}_r \cdot \nabla \bar{C}_r = 0 \quad . \quad (4.13)$$

For the system of interest the total concentration of each chemical component in the elemental volume equals the sum of the concentrations in the rock and the fluid such that

$$\frac{\partial(\varphi_f C_f)}{\partial t} + \frac{\partial(\varphi_r C_r)}{\partial t} = 0 \quad . \quad (4.14)$$

Substitution of this relationship into Equation 4.13 gives,

$$\bar{v}_f \cdot \nabla \bar{C}_f + \bar{v}_r \cdot \nabla \bar{C}_r = 0 \quad . \quad (4.15)$$

Equation 4.15 is further simplified by considering only the vertical components of concentration gradient and velocity

$$v_{f,z} \frac{\partial C_f}{\partial z} + v_{r,z} \frac{\partial C_r}{\partial z} = 0 \quad . \quad (4.16)$$

A vertical control on gas transfer is assumed because gas release from sediments is a temperature dependent process. Isotherms on a basin-wide scale are near horizontal, resulting in vertical thermal gradients that are at least an order of magnitude greater than horizontal thermal gradients. Therefore, the vertical flow component results in the greatest changes in gas concentration. In contrast, the horizontal component results in a relatively insignificant contribution.

Vertical fluid velocity, $v_{f,z}$, as used in Equation 4.16 describes fluid flow relative to an arbitrary-elevation datum that is stationary. In contrast, the velocity of vertical fluid flow from an elemental volume of sediment, v_z as calculated in the previous chapter by Equation 3.20, describes fluid flow relative to the downwardly mobile sediment. Fluid velocity relative to a stationary-elevation datum, $v_{f,z}$ (Equation 4.16), therefore, is equivalent to sum of the fluid velocity relative to the sediments, v_z (Equation 3.20), and the sediment burial rate, $\dot{v}$,

$$v_{f,z} = v_z + \dot{v} \quad . \quad (4.17)$$

Substitution of this relationship between $v_{f,z}$ and v_z (Equation 4.17), and the assumption that the vertical rock velocity, $v_{r,z}$, is equivalent to the sediment burial rate, $\dot{v}$, into Equation 4.16 gives

$$(v_z + \dot{v}) \frac{\partial C_f}{\partial z} + \dot{v} \frac{\partial C_r}{\partial z} = 0 \quad . \quad (4.18)$$

Rearranging Equation 4.18,

$$\frac{\partial C_f}{\partial z} = - \frac{\dot{v}}{(v_z + \dot{v})} \left(\frac{\partial C_r}{\partial z} \right) \quad , \quad (4.19)$$

demonstrates that the change in concentration of a chemical component in the fluid with change in depth is dependent on the sediment burial rate, the concentration

of the component released from the sediment with change in depth, and the velocity of fluid flow.

Inspection of this simplified mass-conservation equation (Equation 4.19) indicates that for the unique case of fluids flowing upward relative to the downwardly mobile sediments that contain them there are two domains that define gas accumulation. A lower domain exists in which the velocity of upward fluid flow is less than negative the velocity of downward sediment transport,

$$0 \leq v_z \leq -\dot{v} , \quad (4.20)$$

such that fluids have a net flow that is downward relative to arbitrary-elevation datum, although upward relative to the downwardly mobile sediments. In contrast, an upper domain exists in which the velocity of upward fluid flow is greater than the negative the velocity of downward sediment transport,

$$-\dot{v} \leq v_z \leq \infty , \quad (4.21)$$

such that fluids have a net flow that is upward relative to the arbitrary-elevation datum.

The limits on these two domains define minimum and maximum gradients of gas accumulation in the pore fluids. Maximum possible gas accumulation occurs under the condition shared by the lower and upper domains,

$$v_z = -\dot{v} , \quad (4.22)$$

such that

$$v_z + \dot{v} = 0 . \quad (4.23)$$

This condition represents fluid that has an upward velocity relative to the sediments that is exactly equal to negative the sediment velocity. These fluid are,

therefore, stationary relative to an elevation datum. Substitution of the relationship in Equation 4.23 into the simplified mass-conservation equation (Equation 4.19) gives

$$\frac{\partial C_f}{\partial z} = -\frac{\dot{v}}{0} \left(\frac{\partial C_r}{\partial z} \right) = \infty \left(\frac{\partial C_r}{\partial z} \right) , \quad (4.24)$$

Thus pore fluids that are stationary relative to an elevation datum, accumulate the gas released from each volume of sediment transported past it during burial. The concentration of gas accumulated by stationary pore fluids, therefore, can accumulate to infinity, limited only by the amount of sediment buried, the quantity of gas released from the sediments, and the solubility of the gas. This case results in the maximum possible gas-accumulation gradient for the pore fluid.

Pore fluids with velocities either slower or faster than the case of the stationary pore fluids have increasingly lower gas-accumulation gradients. Within the lower domain where pore fluid velocities are slower than the stationary fluids, a lower limit on gas accumulation is defined by stagnant pore fluids which have zero velocity relative to the sediments,

$$v_z = 0 . \quad (4.25)$$

Substitutions of this relationship into Equation 4.19,

$$\frac{\partial C_f}{\partial z} = -\frac{\dot{v}}{(0 + \dot{v})} \left(\frac{\partial C_r}{\partial z} \right) \quad (4.26)$$

gives

$$\frac{\partial C_f}{\partial z} = - \left(\frac{\partial C_r}{\partial z} \right) . \quad (4.27)$$

Thus each volume of stagnant pore fluid accumulates only the gas released from the volume of sediment in which it is contained during the entire burial event. Stagnant fluids, therefore, define the minimum gas-accumulation gradient within the lower domain.

In contrast, in the upper domain pore-fluid velocities are greater than those of the stationary fluids. In this upper domain a lower limit on the gas-accumulation gradient is defined by fluids that are flowing upward infinitely fast,

$$v_z \rightarrow \infty . \quad (4.28)$$

Substitutions of this relationship into Equation 4.19,

$$\frac{\partial C_f}{\partial z} = -\frac{\dot{v}}{(\infty + \dot{v})} \left(\frac{\partial C_r}{\partial z} \right) \quad (4.29)$$

gives

$$\frac{\partial C_f}{\partial z} \approx 0 . \quad (4.30)$$

Thus if fluid is flowing upward infinitely fast it accumulates an infinitesimally small amount of gas. Fast flowing fluid essentially flushes the gas from the system.

It is apparent from this analysis that if adequate gas is released from the sediments to result in saturation of stationary pore fluid, then minimum and maximum velocities exist that establish upper and lower limits on the conditions necessary to achieve gas saturation. Fluids flowing too slow are not exposed to enough sediment to achieve saturation, whereas, fluids flowing too fast are not exposed to the sediment long enough to achieve saturation. Rearranging the simplified-mass conservation equation (Equation 4.19) to solve for fluid velocity,

$$v_z = -\dot{v} \left(\frac{\frac{\partial C_r}{\partial z}}{\frac{\partial C_f}{\partial z}} + 1 \right) , \quad (4.31)$$

permits calculation of the range in fluid velocities that result in the accumulation of a gas to the limits of saturation. For these calculations $\frac{\partial C_r}{\partial z}$ is taken as the change in concentration of gas in the sediment over the depth interval of gas release, $\frac{\partial C_f}{\partial z}$ is taken as the change in concentration of the gas in solution that is necessary to

achieve saturation over the same depth interval in which the gas is released from the sediment, and $\dot{v}$ is taken as the average sediment burial rate over the same depth interval.

The range in fluid velocities that could result in CO₂ saturation in upwardly mobile pore fluids is calculated, given that the majority of CO₂ is released from kerogen between the temperatures of 100 and 135°C, and that from 6 to 22 wt % of the kerogen present in the sediment converts to CO₂ (Hunt, 1979; Franks and Forester, 1984; Tannenbaum and Kaplan, 1985). Given the amount of kerogen in the sediments as 1.4 wt %, an amount common to shales in petroliferous basins (Ronov, 1958), the concentration of CO₂ available for release from these sediments, having a density of 2.65 g cm⁻³, ranges from 0.5×10^{-4} to 1.8×10^{-4} moles of CO₂ per cm³ of rock.

The concentration of CO₂ necessary for CO₂ saturation of the pore fluids is not only dependent on temperature but also pressure. For sediments with a thermal gradient of 30°C km⁻¹ a temperature of 100°C occurs at 2.5 km where the lithostatic pressure is 590 bar, and a temperature of 135°C occurs at 3.7 km where the lithostatic pressure is 860 bar (Figure 1). Under these conditions the pore fluids would need from 1.6×10^{-3} moles of CO₂ per cm³ of fluid at 100°C and 590 bar, to 2.1×10^{-3} moles of CO₂ per cm³ of fluid at 135°C and 860 bar (Figure 6), in order to achieve saturation with CO₂. These are maximum concentrations, calculated assuming that the initial pore fluid contains essentially no CO₂ and no NaCl, which are both unlikely conditions.

The average sediment burial rate over this depth interval is 0.6 mm yr⁻¹ (Figure 2), and the average porosity is 0.17 (Figure 1). Using this porosity a

volumetric ratio of rock to fluid of 4.9, is accounted for in the calculation of the transfer of CO_2 from rock to fluid.

For the conditions summarized above, the maximum fluid velocity, v_z , that allows for CO_2 saturation is calculated to range from -0.67 to -0.93 mm yr^{-1} , and the minimum fluid velocity that allows for CO_2 saturation is calculated to range from -0.28 to -0.53 mm yr^{-1} . Because CH_4 saturates more readily than CO_2 it is assumed that the velocities that allow for CH_4 saturation encompass the same or a wider range.

Comparison of these velocities with those calculated in the previous chapter as resulting from sediment compaction and fluid thermal expansion during sediment burial suggests that the range in velocities required for CO_2 saturation is possible. The velocity of vertical fluid flow from each elemental volume calculated for sediments having a thermal gradient of 30°C km^{-1} , and for other conditions as described in the previous chapter, ranges from $-0.012 \text{ mm yr}^{-1}$ at 2.5 km to $-0.0079 \text{ mm yr}^{-1}$ at 3.7 km (Figures 1, 2 and 4). From this same data a vertical fluid velocity accumulated from each pore volume within a 100 m column of sediment from 2.5 to 2.6 km is calculated as approximately -200 mm yr^{-1} . As discussed in the previous chapter, these fluid velocities overestimate actual fluid velocities because they are calculated assuming that fluid expelled from the sediments flows only vertically upward. The horizontal flow component, however, dominates over the vertical at depths over 1 km and becomes even more dominant with increased depth and at the margins of the basin (Bethke, 1986). Although these calculated fluid velocities are maximum velocities, they bracket the range in velocities calculated as necessary to achieve CO_2 saturation in the pore fluids.

Additional temperature and pressure decreases as the CO₂ and CH₄ enriched fluids continue to flow upward act to bring the fluids closer to CO₂ and CH₄ saturation, or even to exceed saturation and release these gases, because of decreased gas solubility. For example, a decrease in temperature from 100° to 80°C with the accompanied decrease in pressure from 750 to 500 bar, results in a 10 % decrease in CO₂ solubility in pure H₂O and a 16 % decrease in CH₄ solubility in pure H₂O. Furthermore, as these CO₂- and CH₄-rich pore fluids are discharged out of the geopressured sediments the drop in pressure from hydrostatic to lithostatic results in a large drop in CO₂ and CH₄ solubilities. At 100°C the drop in fluid pressure from lithostatic, at 750 bar, to hydrostatic, at 200 bar, decrease CO₂ solubility by 33 % and CH₄ solubility by 50 % , both in pure H₂O.

Actual flow velocities in geopressured sediments vary widely rather than being uniform and constant. Flow can range from very restricted and thus slow, under which conditions fluid pressures increase in excess of lithostatic at which time the rock can fracture. Upon fracturing fluid velocity increases allowing rapid release of fluid, which results in fluid pressure reduction to well below lithostatic and subsequent reduction in fluid velocity. This crack-healing process can be repeated at different scales throughout the lifetime of geopressuring and in different regions of the basin. During periods of restricted flow CO₂ saturation is favored, whereas during periods of rapid flow CO₂ loss by excess saturation is possible.

In addition, the amount of kerogen and CO₂ content of the kerogen also varies widely within basin sediments such that some sediments may release much greater quantities of CO₂ than others. Therefore fluids within particular sedimentary units or portions of a unit where CO₂-rich kerogen is abundant will become saturated with CO₂, whereas fluids elsewhere may only be enriched in CO₂.

Thus geopressured pore fluids within kerogen-rich sediments near or above the 100°C isotherm will become enriched and potentially saturated with respect to CO₂ and CH₄. The upward flow of this gas-enriched fluid along temperature and pressure gradients further decreases the gas solubilities and ultimately could result in separation of a CO₂- and CH₄-rich vapor. In normally-pressured sediments CO₂ or CH₄ enrichment of the sediments is unlikely, unless there is another outside source for these gases, because in normally-pressured sediments fluids are most likely flowing downward rather than upward and at velocities that exceed those generally found in geopressured sediments. Similarly, kerogen-poor geopressured sediments are unlikely to have CO₂- or CH₄-enriched pore fluids because they lack a source of these gases.

CHAPTER 5

FLUID-MINERAL EQUILIBRIA

The predicted hydrologic and chemical conditions present in the upper portions of kerogen-rich geopressured sediments should produce a distinct alteration mineralogy and a distinct zoning pattern. An important factor in the development of this characteristic mineralogy is the coincidence of geopressures, which commonly occur at depths greater than 2 to 3 km where sediments have temperatures on the order of 85° to 100°C, with the release of CO₂ and CH₄ during kerogen decomposition between approximately 100° and 135°C. These mineralogic distinctions are, therefore, the result of the combined effects of the upward flow of geopressured fluids to regions of lower temperature and pressure and the enrichment of these fluids in CO₂ and CH₄ from the decomposition of kerogen within the downwardly mobile sediments.

Authigenic-mineral equilibrium relationships expected in geopressured fluid-rock systems as compared to those expected in normally-pressured or kerogen-poor fluid-rock systems are described in the following section by phase relations in chemical subsystems. Equilibrium relationships within each subsystem are represented within the context of changes in fluid composition, temperature and pressure.

Thermochemical Data

Thermochemical equilibrium constants for minerals and gases are calculated using data and retrieval equations reported by Helgeson et al. (1978, with updates through 1984) with the aid of the program SUPCRIT (written by D.H. Kirkham, J. V. Walther and G. C. Flowers). Consequently, the standard states used in the derivation of the data set of Helgeson et al. (1978) and as outlined by Bowers, Jackson and Helgeson (1984) apply in this study. The standard state for H_2O and the intercrystalline standard state for solids are consistent with unit activity of the pure component at any pressure and temperature. The standard state for gases is one of unit fugacity of the hypothetical ideal gas at one bar and any temperature. Accordingly, the gas fugacities are equal to their activities at all pressures and temperatures.

The standard state for aqueous species is unit activity of the species in a hypothetical one molal solution referenced to infinite dilution at any pressure and temperature. The activity coefficients of aqueous species thus approach one at both high and low temperatures and pressures as the activity of the solvent, in the liquid standard state, approaches unity. In contrast the fugacity coefficients of the components of gas mixtures approach the fugacity coefficients of the pure gases as the mole fractions of the gases approach unity at any pressure and temperature.

The presence of appreciable quantities of gases such as CO_2 and CH_4 in solution decreases the $a_{\text{H}_2\text{O}}$ measurably from unity. Methods for correcting for the effects of CO_2 impurities in equilibrium calculations are outlined by Walther and Helgeson (1980) and Bowers, Jackson and Helgeson (1984). Fugacities of H_2O

and CO_2 gas are calculated from the mole fraction of the gas present, the fugacity coefficient and the total fluid pressure. To calculate the fugacity coefficients an equation of state is needed. As previously discussed, an equation of state is not available that adequately represents the properties of the system $\text{CO}_2 - \text{H}_2\text{O}$ at the temperatures and pressures of interest. It is not possible, therefore, to calculate the decrease in the $a_{\text{H}_2\text{O}}$ that results from increased gas concentrations in the solution.

As an alternative, the effect of CO_2 impurities on the fugacity of H_2O in higher temperature solutions, for which an equation of state is available to calculate fugacity coefficients, was calculated. This allows an estimate of the magnitude of possible errors which result from using the $a_{\text{H}_2\text{O}}$ as unity. Fugacity coefficients for the system $\text{CO}_2 - \text{H}_2\text{O}$ for temperatures in excess of 400°C and pressures in excess of 500 bar are presented by Bowers, Jackson and Helgeson (1984). Using these fugacity coefficients, the fugacity of H_2O gas for fluids having CO_2 contents up to 6 mole % were calculated. The fugacity of H_2O was found to shift less than 1 % over this compositional range. Using an $a_{\text{H}_2\text{O}}$ of unity to represent equilibrium in solution with up to 6 mole % CO_2 results in only small shifts in equilibrium calculations for reactions in which the coefficient for water is small. In contrast, increased gas concentrations result in large shifts in gas fugacities that must be accounted for.

Based on these calculated errors, the effect of gas impurities on the fugacity of H_2O , and therefore the $a_{\text{H}_2\text{O}}$, are not considered for the systems of interest in this study. Errors resulting from this assumption are less than errors in the Henry's law constants used to calculate f_{CO_2} and f_{CH_4} , and in the experimental-solubility data for these gases.

The effect of salts on the activity of water is important, particularly for the high NaCl concentrations common to basin waters. Aqueous fluids in sandstones from the Louisiana Gulf Coast sediments have concentrations of NaCl ranging from less than 1 mole % at shallow depths to 6 mole % at 3 km (Schmidt, 1973). In shales the NaCl concentration stays below 2.5 mole % at all depths (Schmidt, 1973; Osmaston, 1975). NaCl concentrations in geopressured fluids, occurring at depths greater than 3 km, decrease to less than 1.2 mole %. At the high concentrations of 6 mole % NaCl the a_{H_2O} is reduced by as much as 5 % (Helgeson, Brown and Leper, 1969). In this range of NaCl concentrations aqueous ion solubilities tend to increase, whereas, gas solubilities decrease. At NaCl concentrations on the order of 1.2 mole % these effects are not as important. The effect of this decrease in a_{H_2O} on the prediction of mineral stabilities, is most important for reactions in which the coefficient for H_2O is greater than one. For the reactions important in high CO_2 solutions with the system considered the coefficient for H_2O is generally unity. Therefore the simplification of a_{H_2O} equals unity does not result in large shifts in the equilibrium surfaces calculated.

Gas fugacities, f_i , are calculated using the Henry's law relation

$$f_i = H_i X_i . \quad (5.1)$$

Henry's law constants, H_i , for CO_2 as a function of temperature and NaCl content of the solution are taken from Ellis and Golding (1963). Henry's law constants for CH_4 as a function of temperature are taken from Naumov, Ryzhenko and Khodakovsky (1974) and Cramer (1982).

CO₂

When CO₂ released from kerogen degradation dissolves into surrounding pore fluids it shifts the fluid-mineral equilibria of these solutions. Upon reaching saturation in the solution, further addition of CO₂, or a temperature or pressure decrease, results in separation of a CO₂-rich vapor from the solution. Removal of CO₂ by vapor separation also results in a shift in fluid-mineral equilibria of the pore fluids. These relationships are discussed below.

When CO₂ dissolves into solution it not only increases the total carbon content of the solution, but it also results in changes in the concentrations of aqueous carbonate complexes. Shifts in the concentration of aqueous carbonate complexes can result in large changes in solution pH. Sedimentary basin fluids from sandstone reservoirs are generally near neutral (White, Hem and Waring, 1963). In near-neutral solutions HCO₃⁻ and H₂CO₃ are the dominant carbonate complex in solution between 100° and 150°C (Barnes, 1979). Dissolving CO₂ into a solution in which a dominant carbonate complex is HCO₃⁻, releases hydrogen ions as described in Reaction 5.2.



This reaction results in a decrease in the solution pH to more acid conditions.

This acidified fluid will react with minerals in the host sediments, such as feldspars and biotite. Because of the high carbonate content of this CO₂-rich fluid it is readily saturated with calcite after only minor dissolution of calcite or Ca- feldspar in the sediment. Thus, this acid pore fluid may or may not dissolve

calcite. Reaction of this acidified pore fluid with feldspars, and possibly calcite, is suggested as a contributing factor in the development of secondary porosity (Siebert, Moncure and Lahann, 1984; Franks and Forester, 1984). When the source of CO_2 is depleted the continued hydrolysis of feldspars neutralizes the solution increasing its pH. The results of this process and the authigenic minerals deposited as a result of it are discussed in a later section.

The upward flow of fluids discharged from geopressured sediments during burial, to regions of lower temperature and pressure, results in a decrease in CO_2 solubility. If these displaced pore fluids are near saturation or saturated with CO_2 , as would be expected in kerogen-rich geopressured sediments, a decrease in temperature or pressure results in separation of a CO_2 -rich vapor.

The loss of CO_2 from near-neutral pore fluids as a result of vapor separation causes a shift in aqueous complexing opposite to that caused by the addition of CO_2 to solution (Reactions 5.2). These shifts in equilibrium of aqueous species result in an increase in solution pH. Calculation of the effects of separation of a CO_2 -rich vapor from near-neutral solutions indicates that these changes are often accompanied by the deposition of calcite and possibly other minerals from the solution (Drummond and Ohmoto, 1985). These calculations, combined with the evidence of calcite deposition as a result of vapor separation in well bores (cf. Arnorsson, 1978; Michels, 1980), indicate that carbonate mineral deposition is an expected consequence of vapor separation of geopressured fluids if these fluids are initially near carbonate mineral equilibrium.

SiO₂ – H₂O

The SiO₂ – H₂O system includes quartz, the most common authigenic cement (Krauskopf, 1959), as well as other SiO₂ polymorphs, such as chalcedony and amorphous silica, which are also common cements, and α - and β -cristobalite, which are uncommon as a cementing material. Quartz, chalcedony and amorphous silica have well defined stability fields under equilibrium conditions. Variations in their stability fields with changing temperature are shown on Figure 19. Quartz and amorphous silica define the extremes in solubility, with quartz being the least soluble, and amorphous silica the most soluble. Solubility variations for quartz, chalcedony and amorphous silica have similar trends with changing temperature. Generally the equilibrium value of $a_{(\text{SiO}_2)}$ decreases as temperature decreases.

The stability relationships of two other SiO₂ polymorphs, α - and β -cristobalite, are also included in Figure 19. Their solubilities are intermediate between those of quartz and chalcedony. Neither α - nor β -cristobalite is a common sedimentary cement, but their high solubilities and presence in volcanic rock fragments account in part for the high silica concentrations in fluids from volcanoclastic sediments (Marshall, 1961; White, Hem and Waring, 1963). Thermochemical data was not available for tridymite another SiO₂ polymorph found as a common volcanoclastic component.

Variations in the stability fields of quartz and amorphous silica with changing pressure are shown on Figure 20. Solubilities of both quartz and amorphous silica increase as pressure increases.

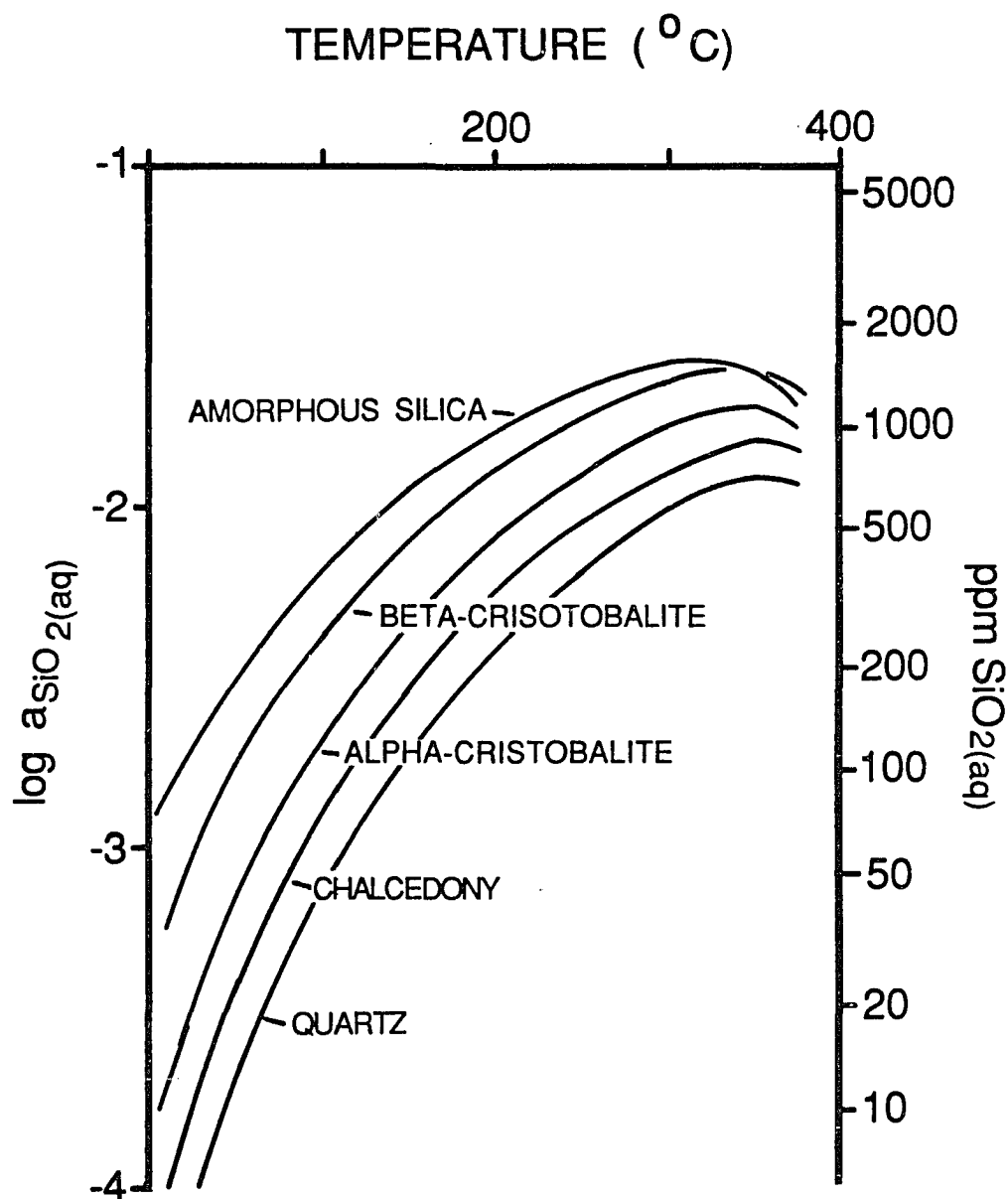


Figure 19: Solubility of silica polymorphs as a function of temperature.

At pressures corresponding to the vapor pressure of pure H_2O (after Walther and Helgeson, 1977).

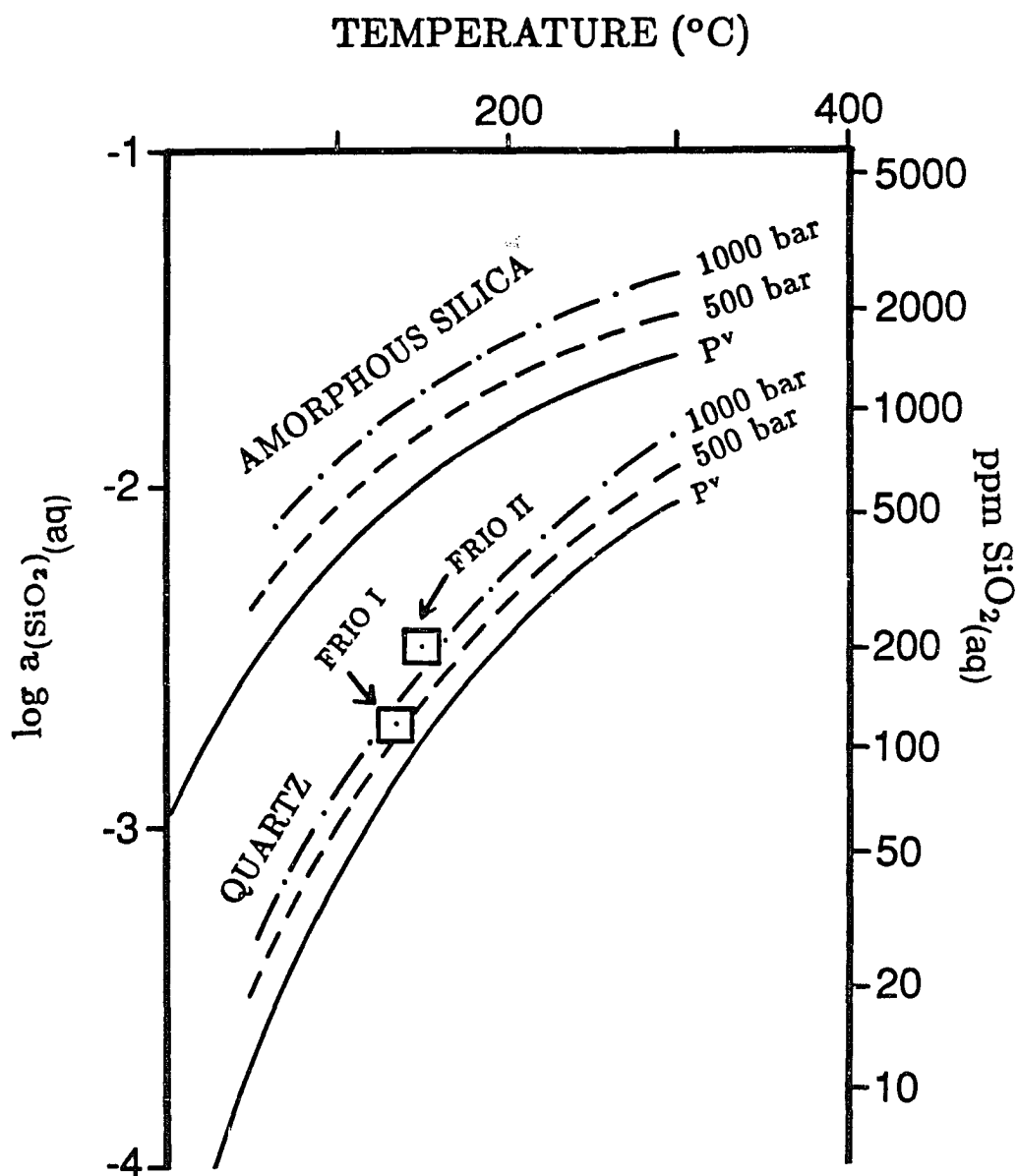


Figure 20: Quartz and amorphous silica solubility as a function of temperature at P_v , 500 and 1000 bars

P_v (the vapor pressure of pure H_2O) = solid, 500 bars = dashed, and 1000 bars = dot-dashed.

Reaction kinetics, rather than solubility control quartz deposition at temperatures below 150°C. Quartz precipitation is very slow at temperatures less than 150°C, which allows near-surface fluids to maintain high levels of a_{SiO_2} , well above quartz saturation (Rimstidt and Barnes, 1980). The highest values of a_{SiO_2} , generally equivalent to amorphous silica saturation, are found in fluids from volcanoclastic sediments. Volcanoclastics are generally rich in amorphous silica and cristobalite, which have rapid dissolution rates (Marshall, 1961) and, as discussed above, high solubilities.

Temperatures of fluids of interest in this study are below 150°C and therefore can become supersaturated with respect to quartz because of slow precipitation rates. The calculation below, however, indicates that sediment burial rates on the order of 1 mm yr⁻¹ are slow enough to allow quartz to reach saturation at low temperatures. The time necessary for fluids to achieve quartz equilibrium is calculated using the differential rate equation for the system SiO₂-H₂O derived by Rimstidt and Barnes (1980) (Equation 5.3).

$$\left(\frac{\partial a_{\text{SiO}_2(\text{aq})}}{\partial t} \right)_{P,T,M,\gamma} = \gamma_{\text{SiO}_2(\text{aq})} \frac{A}{M} \left(k^+ a_{\text{SiO}_2(s)} a_{\text{H}_2\text{O}}^2 - k^- a_{\text{SiO}_2(\text{aq})} \right) \quad (5.3)$$

The A/M ratio relates the area of mineral surfaces to the mass of solution and is calculated using the relationship (Rimstidt and Barnes, 1980):

$$\frac{A}{M} = \frac{8.55}{10^6 \rho r} \quad (5.4)$$

where r is the grain radius in mm. The derivation of Equation 5.3 assumes a near neutral solution, that the total mass of the system is constant during the reaction, and that the total fluid pressure is below 500 bar. The pH of ground waters in sandstones are generally within 1 log unit from neutral (White, Hem and Waring, 1963), although fluids from volcanoclastic sandstones can be much more basic, on

the order of 2 log units above neutral. The assumption that the solution is dilute allows the $\gamma_{\text{SiO}_2(\text{aq})}$, $a_{\text{SiO}_2(\text{s})}$ and $a_{\text{H}_2\text{O}}$ to be taken as equal to unity (Walther and Helgeson, 1977).

Under the above conditions Equation 5.3 can be integrated with respect to time:

$$t_1 - t_0 = -\frac{1}{(k^-) \left(\frac{A}{M}\right)} \ln \left(\frac{k^+ - k^- \left(a_{\text{SiO}_2(\text{aq})}\right)_1}{k^+ - k^- \left(a_{\text{SiO}_2(\text{aq})}\right)_0} \right) \quad (5.5)$$

with the dissolution rate constant, k^+ , for quartz equal to

$$k^+ = 1.174 - 2.028 \times 10^{-3} T - \frac{4158}{T} \quad (5.6)$$

and the precipitation rate constant for all SiO_2 polymorphs, k^- , equal to

$$k^- = -0.707 - \frac{2598}{T} \quad (5.7)$$

(Rimstidt and Barnes, 1980).

To estimate the maximum time necessary to precipitate quartz, a minimum A/M ratio is used to solve Equation 5.5. Equation 5.4 predicts the A/M ratio for cubic-close packed spheres having a porosity of 0.26. An A/M ratio calculated with Equation 5.4, therefore, is lower than the actual A/M ratio of sediments composed of nonspherical grains with a porosity less than 0.26. Using a grain radius of 2 mm, the upper limit on sand sized particles, a minimum A/M ratio of 4.3 $\text{m}^2 \text{kg}^{-1}$ is calculated.

The rate of quartz precipitation from a 50°C solution initially in equilibrium with amorphous silica, and with a concentration of SiO_2 of 0.0032 molal, was calculated. The initial solution which starts out saturated with amorphous silica takes less than 16 years to deposit over 0.0028 molal of SiO_2 to bring it into equilibrium with quartz at 50°C. When compared to the burial rate of less than

1 mm yr⁻¹ (Figure 2), the time necessary for deposition of this amount of quartz is relatively short and occurs while the sediments subside less than 16 mm.

The increase in temperature and pressure of pore waters with increased burial increases the solubility of quartz. Fluids retained in geopressed sediments during burial, therefore, dissolve quartz and maintain the a_{SiO_2} at quartz saturation. Fluid expulsion from geopressed sediments as a result of porosity reduction and thermal expansion, however, can reverse these temperature and pressure changes resulting in decreased quartz solubility and precipitation.

As discussed in Chapter 3, porosity reduction and thermal expansion during burial of geopressed sediments results in upward fluid flow. In addition, the cumulative mass of fluid expelled is sufficient to completely replace pore fluids in the upper portions of the geopressed zone with fluids from below after only a small amount of burial.

Transport of quartz-saturated pore fluid to shallower depths, with subsequent temperature and pressure decreases, results in quartz deposition to maintain equilibrium with the solution (Figure 20). The time necessary for quartz deposition, at less than 16 years, is considerably faster than the rate of fluid discharge to shallower depths. As calculated in Chapter 3, it takes more than 20 cm of burial and therefore over 200 years at a burial rate of 1 mm yr⁻¹, to displace the pore fluid in a single elemental volume at the top of the geopressed zone. The upward flow of geopressed fluids is therefore slow enough to give the solution sufficient time to maintain equilibrium with quartz through quartz precipitation.

Because of these competing effects on quartz solubility the largest mass of authigenic quartz forms in the upper portions of the geopressed zone where

the cumulative flow of silica-rich fluids from below is the greatest. In contrast, in the lower portions of the geopressured zone quartz dissolution prevails.

Porosity reduction from quartz precipitation, as a result of compactive displacement of pore fluids, is calculated by Walder and Nur (1984). They suggest that quartz deposition plays a role in the crack-healing process, and thereby in the maintenance of elevated fluid pressures in crystalline rocks. The crack-healing process is one in which quartz deposition seals fractures that constitute fluid-flow paths. Then when thermal expansion of fluids trapped in these fractures causes the fluid pressures to exceed lithostatic, the fractures reopen to flow. This process is then repeated.

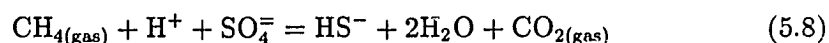
Silicate-Carbonate System

To facilitate the study of this complex geologic system activity diagrams (Garrels and Christ, 1965; Helgeson, 1969, 1970a; Helgeson, Brown and Leper, 1969; Bowers, Jackson and Helgeson, 1984) with more than one balancing cation are used (Johnson and Norton, 1985). These diagrams are constructed by writing the hydrolysis reactions for all minerals of interest in the multicomponent system. Through a series of balanced mineral-mineral reactions all but two of the aqueous-complex hydrogen-ion activity ratios are cancelled, eliminated or assigned values based on geologic constraints. On these diagrams, the a_{SiO_2} is set at the equilibrium concentration for quartz, and the $\log a_{\text{HS}^-} \cdot a_{\text{H}^+}$ and $\log a_{\text{SO}_4^{2-}} \cdot a_{\text{H}^+}^2$ are determined by gas equilibrium or mineralogic buffers (see discussion in the following section).

Oxidation-Reduction

The insitu-redox state of a basin solution can be inferred from mineralogic relationships. The $\log a_{\text{SO}_4=} \cdot a_{\text{H}^+}^2$ and $\log a_{\text{HS}^-} \cdot a_{\text{H}^+}$ of ground water can be estimated from the equilibrium reactions between hematite-pyrite, magnetite-pyrite and pyrrhotite-pyrite. The presence of these mineral assemblages represents a line on Figure 21 which defines the $\log a_{\text{SO}_4=} \cdot a_{\text{H}^+}^2$ and $\log a_{\text{HS}^-} \cdot a_{\text{H}^+}$ in the solution. The oxidation state of the solution in equilibrium with each of these assemblages decreases as equilibrium shifts from hematite-pyrite to magnetite-pyrite and on to pyrrhotite-pyrite.

Equilibrium between mineral assemblages, however, does not predict the oxidation state of pore waters that contain large amounts of CO_2 and CH_4 . The release of CO_2 , and lesser CH_4 , during kerogen maturation, at temperatures of 100°C and higher, is adequate to allow the oxidation state of the solution to be controlled by equilibrium between these gases. This occurs because in these CO_2 and CH_4 saturated solutions the concentrations of CO_2 and CH_4 are orders of magnitude greater than the concentrations of HS^- and SO_4^- . The relationship between these two gases and $\log a_{\text{SO}_4=} \cdot a_{\text{H}^+}^2$ and $\log a_{\text{HS}^-} \cdot a_{\text{H}^+}$ are described by Equation 5.8,



The fugacities of CO_2 and CH_4 in a saturated fluid at 100°C and 590 bar, calculated using the data and relationships discussed above, are nearly equivalent at 116 and 128, respectively. Calculation of the oxidation state of the solution using Equation 5.8 and the condition that $f_{\text{CO}_2} = f_{\text{CH}_4}$, gives a $\log a_{\text{SO}_4=} \cdot a_{\text{H}^+}^2 / \log a_{\text{HS}^-} \cdot a_{\text{H}^+}$ of

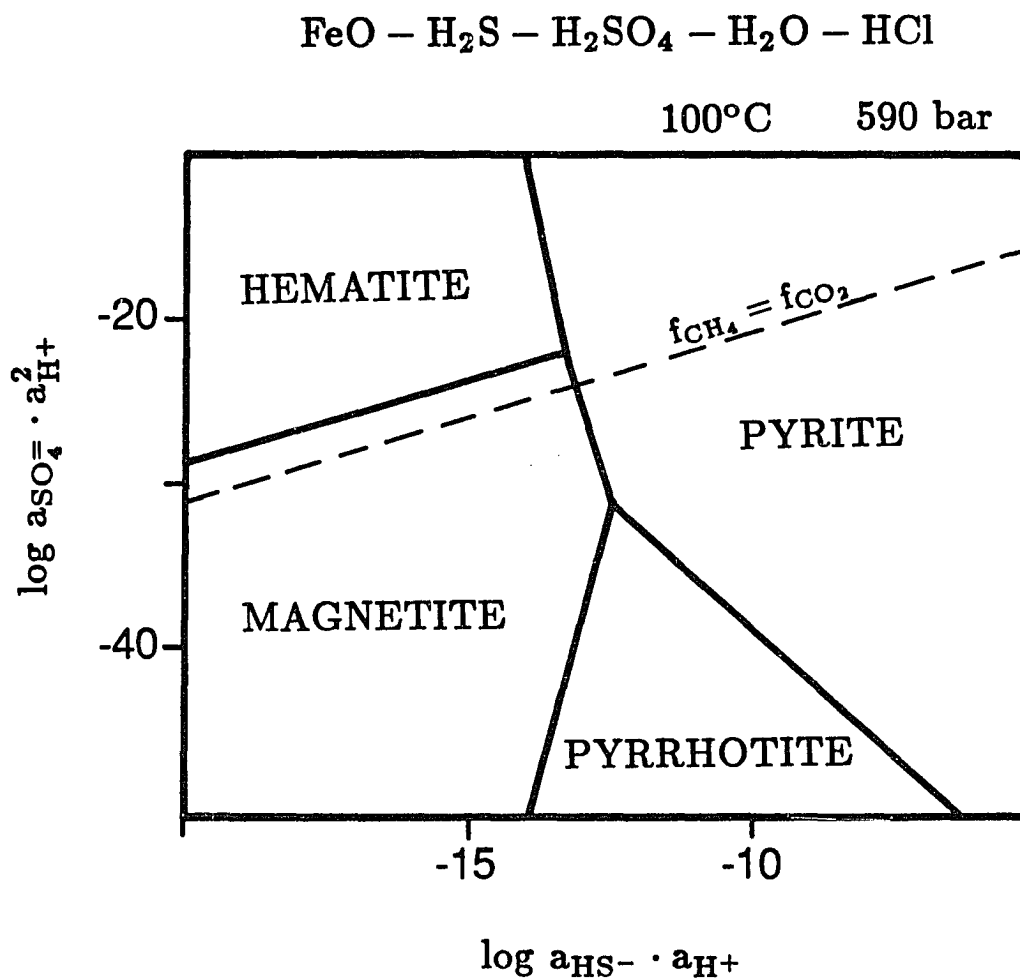
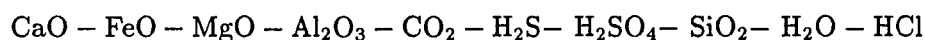


Figure 21: Chemical equilibrium diagram for the system $\text{FeO} - \text{H}_2\text{S} - \text{H}_2\text{SO}_4 - \text{H}_2\text{O} - \text{HCl}$

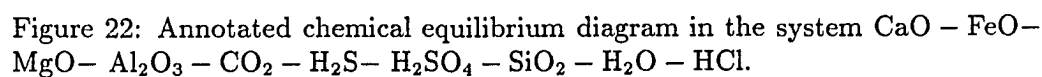
At 100°C and 590 bar with $\log a_{\text{Fe}^{++}}/a_{\text{H}^+}^2$ conserved. $f_{\text{CO}_2} = f_{\text{CH}_4}$ dashed line.

-10.8 (Figure 21). Large shifts in the $\text{CO}_2\text{-CH}_4$ ratio, to $2f_{\text{CO}_2}=f_{\text{CH}_4}$ and $f_{\text{CO}_2}=2f_{\text{CH}_4}$, result in only small changes, less than a tenth of a log unit, in the predicted $\log a_{\text{SO}_4=} \cdot a_{\text{H}+}^2 / \log a_{\text{HS}-} \cdot a_{\text{H}+}$.

For fluid-mineral equilibrium calculations, discussed in later sections, hematite-pyrite, magnetite-pyrite and pyrrhotite-pyrite equilibrium are assumed to limit the oxidation state of the solution in sediments lacking organics. The condition that $f_{\text{CO}_2}=f_{\text{CH}_4}$ is assumed to limit the oxidation state of the solution in sediments rich in organics.



This system contains almost all the common authigenic minerals deposited in clastic sediments during diagenesis; calcite, dolomite, magnesite, ankerite, siderite, kaolinite, pyrophyllite, laumontite, magnetite, hematite, pyrite, quartz, chalcedony, amorphous silica, and anhydrite. Equilibrium relationships among minerals in this subsystem can be graphically represented as a function of $\log a_{\text{Mg}++}/a_{\text{H}+}^2$ and $\log a_{\text{Fe}++}/a_{\text{H}+}^2$ on a single diagram (cf. Figures 22 and 23) by writing conservative reactions between minerals for $\log a_{\text{CO}_3=} \cdot a_{\text{H}+}^2$, $\log a_{\text{Ca}++}/a_{\text{H}+}^2$ and $\log a_{\text{Al}+3}/a_{\text{H}+}^3$ (Tables 1 and 2). The $\log a_{\text{SO}_4=} \cdot a_{\text{H}+}^2$ and $\log a_{\text{HS}-} \cdot a_{\text{H}+}$ are set by either equilibrium between the gases CO_2 and CH_4 , or between pyrite and hematite, magnetite or pyrrhotite, as discussed above. The $a_{(\text{SiO}_2)}$ is determined by the assumption of quartz equilibrium. This diagram allows prediction of equilibrium-mineral assemblages by the relationships between adjacent and overlapping stability fields. All the minerals in the SUPCRIT data base (Helgeson et al., 1978, with updates through 1984) are considered in preparation of these activity diagrams. This includes all the common authigenic minerals listed above except ankerite, whose thermochemical data are not available.



Circled numbers correspond to the equation numbers in Tables 1 and 2. MT = magnetite, PY = pyrite, $\log a_{\text{SiO}_2}$ is equal to quartz saturation, $\log a_{\text{SO}_4} = \cdot a_{\text{H}^+}^2 / \log a_{\text{HS}^-} \cdot a_{\text{H}^+}$ are set by the condition that $f_{\text{CH}_4} = f_{\text{CO}_2}$, and $\log a_{\text{CO}_3} = \cdot a_{\text{H}^+}^2$, $\log a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$ and $\log a_{\text{Al}^{+3}}/a_{\text{H}^+}^3$ are conserved. Bold dashed lines are saturation surfaces. Fine dashed lines represent equilibrium relationships at hydrostatic pressure (245 bar).

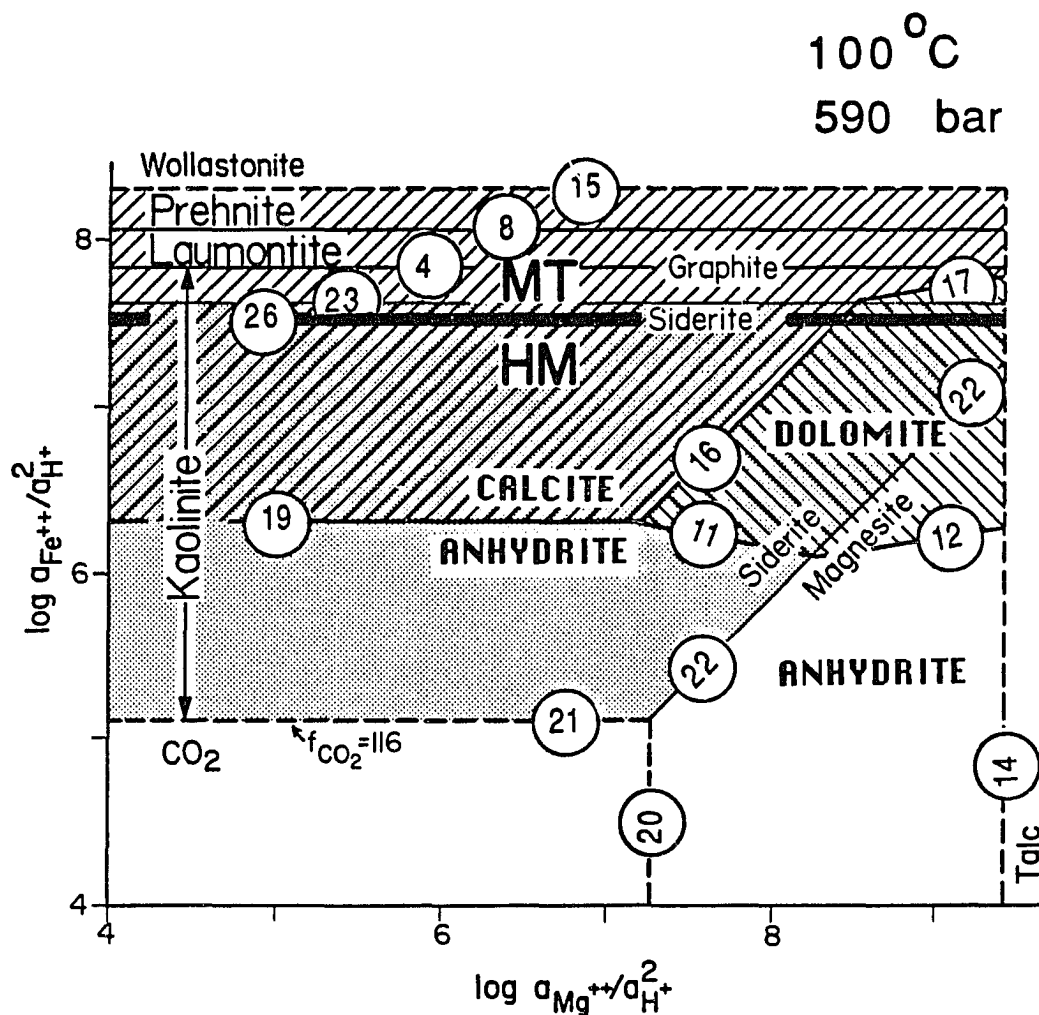


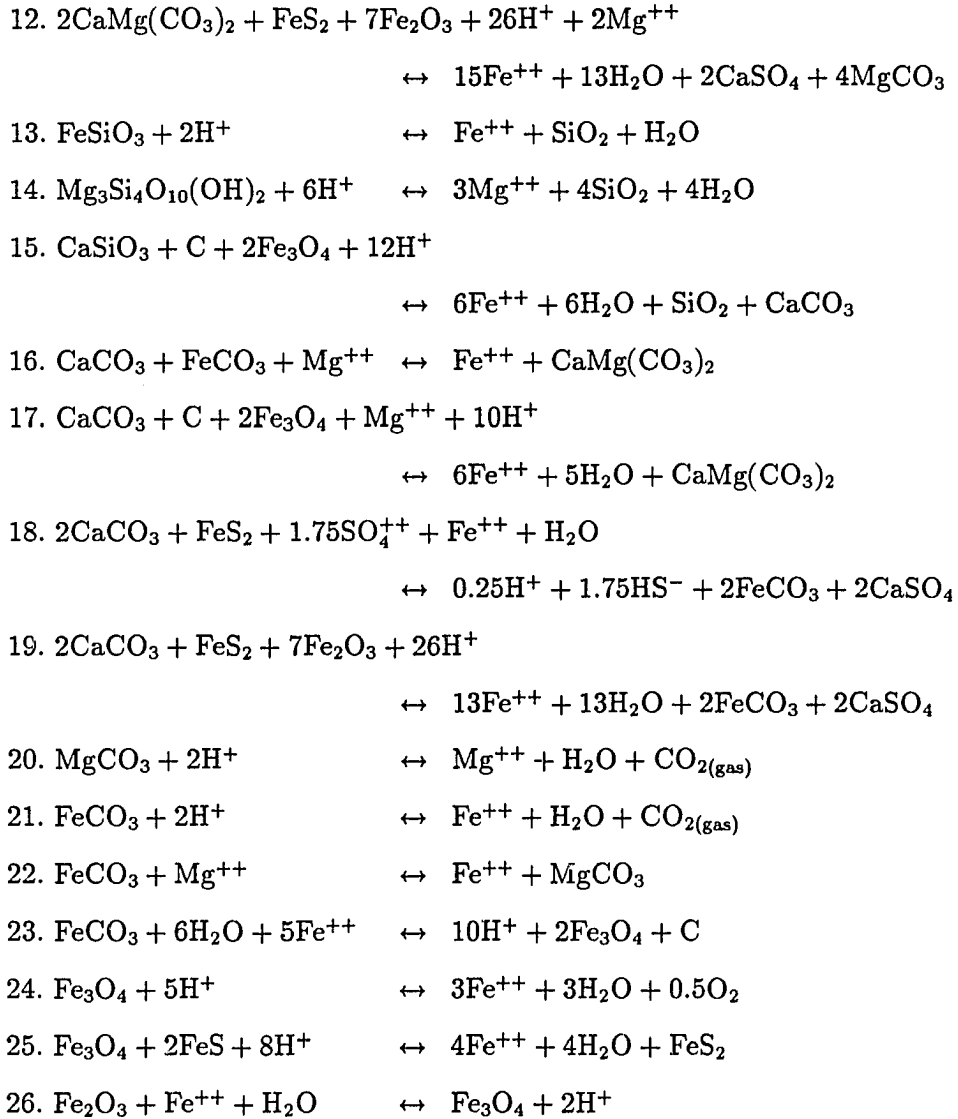
Figure 23: Annotated chemical equilibrium diagram in the system $\text{CaO} - \text{FeO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{CO}_2 - \text{H}_2\text{S} - \text{H}_2\text{SO}_4 - \text{SiO}_2 - \text{H}_2\text{O} - \text{HCl}$ (organic-poor system).

Circled numbers correspond to equation numbers in Tables 1 and 2. MT = magnetite, HM = hematite, the $\log a_{\text{SiO}_2}$ = quartz saturation, and $\log a_{\text{CO}_3} = a_{\text{H}^+}^2$, $\log a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$ and $\log a_{\text{Al}^{3+}}/a_{\text{H}^+}^3$ are conserved. Pyrite is in equilibrium everywhere on this diagram, allowing pyrite-hematite or pyrite-magnetite equilibria to determine the $\log a_{\text{SO}_4} \cdot a_{\text{H}^+}^2$ and $\log a_{\text{HS}^-} \cdot a_{\text{H}^+}$ which vary across the figure. Dashed lines are saturation surfaces.

Table 1: Mineral reactions for activity diagrams.

1. $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{SiO}_2 + \text{CaCO}_3 + 3\text{H}_2\text{O} + \text{Fe}^{++}$
 $\leftrightarrow 2\text{H}^+ + \text{FeCO}_3 + \text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$
2. $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{SiO}_2 + \text{CaMg}(\text{CO}_3)_2 + 3\text{H}_2\text{O} + 2\text{Fe}^{++}$
 $\leftrightarrow \text{Mg}^{++} + 2\text{H}^+ + 2\text{FeCO}_3 + \text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$
3. $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{SiO}_2 + \text{CaMg}(\text{CO}_3)_2 + 3\text{H}_2\text{O} + \text{Mg}^{++}$
 $\leftrightarrow 2\text{H}^+ + 2\text{MgCO}_3 + \text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$
4. $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{SiO}_2 + \text{CaCO}_3 + 6\text{Fe}^{++} + 8\text{H}_2\text{O}$
 $\leftrightarrow 12\text{H}^+ + 2\text{Fe}_3\text{O}_4 + \text{C} + \text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$
5. $\text{Ca}_2\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 + \text{FeCO}_3 + \text{SiO}_2 + 2\text{H}^+ + 2\text{H}_2\text{O}$
 $\leftrightarrow \text{Fe}^{++} + \text{CaCO}_3 + \text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$
6. $\text{Ca}_2\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 + 2\text{FeCO}_3 + \text{SiO}_2 + 2\text{H}^+ + 2\text{H}_2\text{O} + \text{Mg}^{++}$
 $\leftrightarrow 2\text{Fe}^{++} + \text{CaMg}(\text{CO}_3)_2 + \text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$
7. $\text{Ca}_2\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 + 2\text{MgCO}_3 + \text{SiO}_2 + 2\text{H}^+ + 2\text{H}_2\text{O}$
 $\leftrightarrow \text{Mg}^{++} + \text{CaMg}(\text{CO}_3)_2 + \text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$
8. $\text{Ca}_2\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 + \text{C} + 2\text{Fe}_3\text{O}_4 + 12\text{H}^+ + \text{SiO}_2$
 $\leftrightarrow 6\text{Fe}^{++} + 3\text{H}_2\text{O} + \text{CaCO}_3 + \text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$
9. $2\text{CaMg}(\text{CO}_3)_2 + \text{FeS}_2 + 1.75\text{SO}_4^{++} + 3\text{Fe}^{++} + \text{H}_2\text{O}$
 $\leftrightarrow 0.25\text{H}^+ + 2\text{Mg}^{++} + 1.75\text{HS}^- + 4\text{FeCO}_3 + 2\text{CaSO}_4$
10. $2\text{CaMg}(\text{CO}_3)_2 + \text{FeS}_2 + 1.75\text{SO}_4^{++} + 2\text{Mg}^{++} + \text{H}_2\text{O}$
 $\leftrightarrow 0.25\text{H}^+ + \text{Fe}^{++} + 1.75\text{HS}^- + 4\text{MgCO}_3 + 2\text{CaSO}_4$
11. $2\text{CaMg}(\text{CO}_3)_2 + \text{FeS}_2 + 7\text{Fe}_2\text{O}_3 + 26\text{H}^+$
 $\leftrightarrow 11\text{Fe}^{++} + 2\text{Mg}^{++} + 13\text{H}_2\text{O} + 2\text{CaSO}_4 + 4\text{FeCO}_3$

Table 2: Mineral reactions (continued).



Mineral stability relationships between pore fluids and kerogen-rich sediments at 100° and 150°C are shown in Figures 24 and 25. These figures were constructed for fluids in sediments having a thermal gradient of 30°C km⁻¹. Fluid at 100°C, therefore, occur at 2.5 km, in the upper portion of the geopressured zone in Gulf Coast sediments, and fluids at 150°C occur at 4.2 km, well within the geopressured zone (Figure 1). The pressure selected for each figure is the lithostatic pressure at the above depths (Figure 1). Fluid-pressure changes from hydrostatic to lithostatic at 100° and 150°C shift the location of the equilibrium surfaces in Figures 24 and 25 only slightly as represented by the fine dashed lines, and therefore equilibrium relationships at hydrostatic pressures are not discussed further.

Oxidation-reduction within pore-fluids from kerogen-rich sediments, as represented in Figures 24 and 25, is assumed controlled by CO₂-CH₄ equilibria, with the ratio of $f_{\text{CO}_2}/f_{\text{CH}_4}$ equal to unity. This choice of oxidation-reduction accounts for the release of CO₂, and lesser CH₄, from kerogen maturation at temperatures on the order of 100°C, as discussed above. The $\log a_{\text{SO}_4=} \cdot a_{\text{H}+}^2 / \log a_{\text{HS}-} \cdot a_{\text{H}+}$ at 100°C in Figure 24, therefore, is constant at -10.8 and in Figure 25 is constant at -11.1.

Stability relations on Figure 24 are divided into two fields, pyrite at lower $\log a_{\text{Fe}++} / a_{\text{H}+}^2$ and magnetite at higher $\log a_{\text{Fe}++} / a_{\text{H}+}^2$. As $\log a_{\text{Fe}++} / a_{\text{H}+}^2$ increases, the values of $\log a_{\text{SO}_4=} \cdot a_{\text{H}+}^2$ and $\log a_{\text{HS}-} \cdot a_{\text{H}+}$ decrease in the pyrite stability field, although the ratio of $\log a_{\text{SO}_4=} \cdot a_{\text{H}+}^2 / \log a_{\text{HS}-} \cdot a_{\text{H}+}$ remains constant. For example at 100°C and 590 bar (Figure 26) the $\log a_{\text{SO}_4=} \cdot a_{\text{H}+}^2$ decreases from -22.0 at the base of the pyrite field to -23.8 at the pyrite-magnetite equilibria surface. Within the same region, $\log a_{\text{HS}-} \cdot a_{\text{H}+}$ decreases from -11.2 to -13.0. In the magnetite

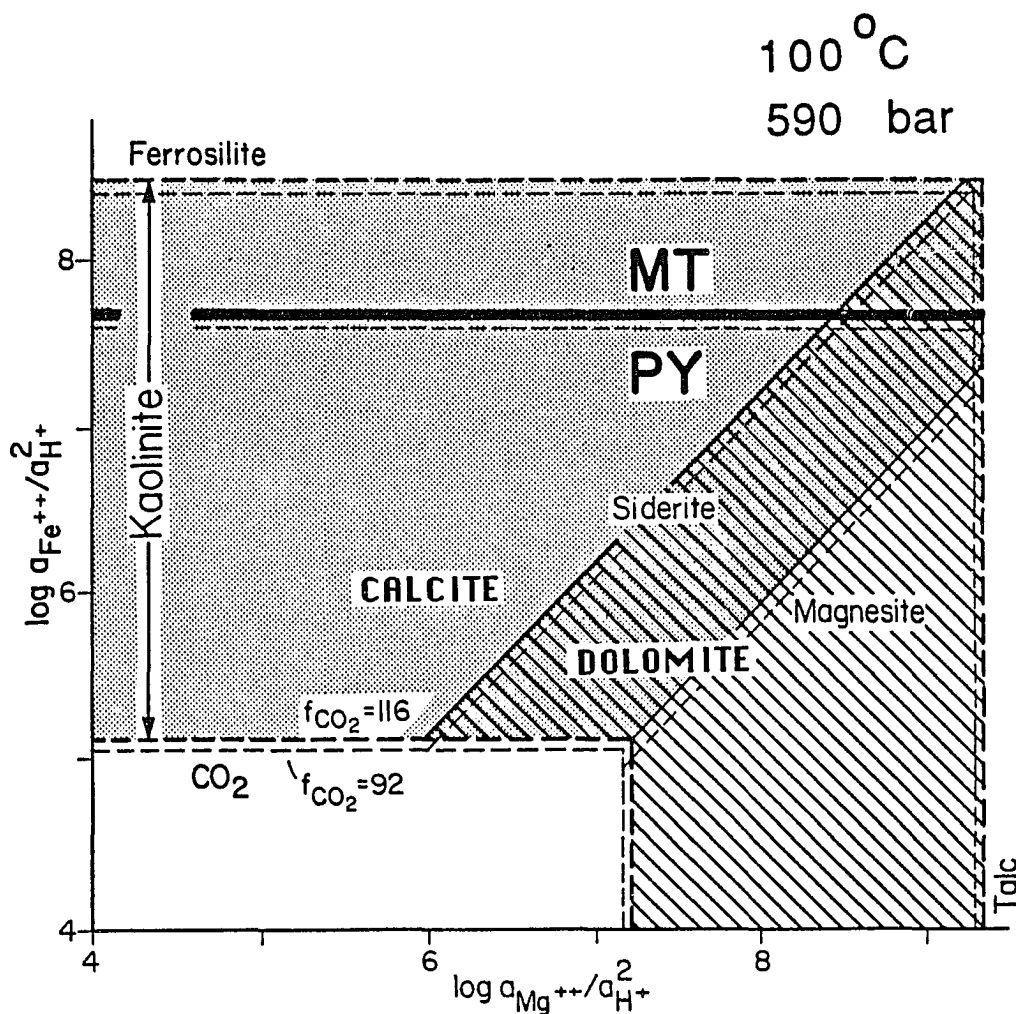


Figure 24: Chemical equilibrium diagram in the system $\text{CaO} - \text{FeO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{CO}_2 - \text{H}_2\text{S} - \text{H}_2\text{SO}_4 - \text{SiO}_2 - \text{H}_2\text{O} - \text{HCl}$ at 100°C and 590 bar (lithostatic pressure).

MT = magnetite, PY = pyrite, $\log a_{\text{SiO}_2}$ is equal to quartz saturation, $\log a_{\text{SO}_4} = \log a_{\text{HS}^-} \cdot a_{\text{H}^+}^2 / \log a_{\text{H}_2\text{S}} \cdot a_{\text{H}^+}$ are set by the condition that $f_{\text{CH}_4} = f_{\text{CO}_2}$, and $\log a_{\text{CO}_3} = \log a_{\text{Ca}^{++}} / a_{\text{H}^+}^2$, $\log a_{\text{Ca}^{++}} / a_{\text{H}^+}^2$ and $\log a_{\text{Al}^{+3}} / a_{\text{H}^+}^3$ are conserved. Bold dashed lines are saturation surfaces. Fine dashed lines represent equilibrium relationships at hydrostatic pressure (245 bar).

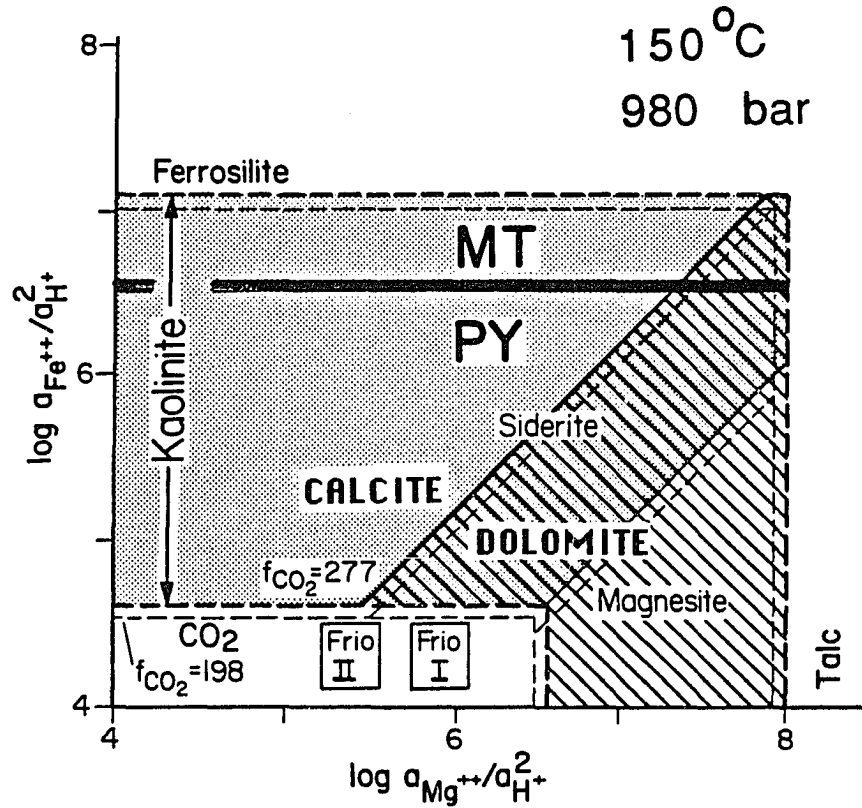


Figure 25: Chemical equilibrium diagram in the system $\text{CaO} - \text{FeO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{CO}_2 - \text{H}_2\text{S} - \text{H}_2\text{SO}_4 - \text{SiO}_2 - \text{H}_2\text{O} - \text{HCl}$ at 150°C and 980 bar (lithostatic pressure).

MT = magnetite, PY = pyrite, $\log a_{\text{SiO}_2}$ is equal to quartz saturation, $\log a_{\text{SO}_4} = \log a_{\text{HS}^-} \cdot a_{\text{H}^+}$ is set by the condition that $f_{\text{CH}_4} = f_{\text{CO}_2}$, and $\log a_{\text{CO}_3} = \log a_{\text{H}^+}^2$, $\log a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$ and $\log a_{\text{Al}^{+3}}/a_{\text{H}^+}^3$ are conserved. Bold dashed lines are saturation surfaces. Fine dashed lines represent equilibrium relationships at hydrostatic pressure (400 bar).

field both $\log a_{\text{SO}_4=} \cdot a_{\text{H}+}^2$ and $\log a_{\text{HS}-} \cdot a_{\text{H}+}$ remain constant at -23.8 and -13.0, respectively. Under these chemical conditions, anhydrite and graphite stability fields, which are present on later figures, are outside the range of fluid composition.

Conservation of $\log a_{\text{CO}_3=} \cdot a_{\text{H}+}^2$ and $\log a_{\text{Ca}++}/a_{\text{H}+}^2$ also results in compositional gradients which are governed by equilibrium reactions between the stable minerals. Compositional gradients for $\log a_{\text{CO}_3=} \cdot a_{\text{H}+}^2$ and $\log a_{\text{Ca}++}/a_{\text{H}+}^2$ at 100°C and 590 bar, are shown in Figure 27. The $\log a_{\text{CO}_3=} \cdot a_{\text{H}+}^2$ decreases radially from a high of -17.7 at CO_2 saturation to a low of -20.3 at ferrosilite saturation. The position of $\log a_{\text{CO}_3=} \cdot a_{\text{H}+}^2$ contours are shifted by the position of the siderite-magnesite stability surface. The $\log a_{\text{Ca}++}/a_{\text{H}+}^2$ increases asymmetrically from a low of 5.1 at CO_2 saturation to a high of 9.5 at ferrosilite saturation, with the position of the contours shifted by the position of the siderite-magnesite and calcite-dolomite stability surfaces.

Conservation of $\log a_{\text{Al}+3}/a_{\text{H}+}^3$ also allows consideration of aluminum silicate minerals in construction of Figure 24, with aluminum being conserved. The kaolinite stability field fills the region between the CO_2 saturation surface and ferrosilite and talc saturation surfaces. Concentrations of $\log a_{\text{Ca}++}/a_{\text{H}+}^2$ are too low for laumontite and prehnite equilibrium, present on later figures, and concentrations of $\log a_{\text{SiO}_2}$ are too low (at quartz saturation) for pyrophyllite equilibrium.

At higher temperatures as depicted in Figure 25, the mineral stability relationships are similar, particularly for the carbonate minerals. The only marked changes are shifts, ranging from 0.5 to 1.0 log units, in the saturation surfaces for CO_2 , ferrosilite and talc, and in the equilibrium surface of magnetite-pyrite, to lower values of $\log a_{\text{Fe}++}/a_{\text{H}+}^2$ and $\log a_{\text{Mg}++}/a_{\text{H}+}^2$.

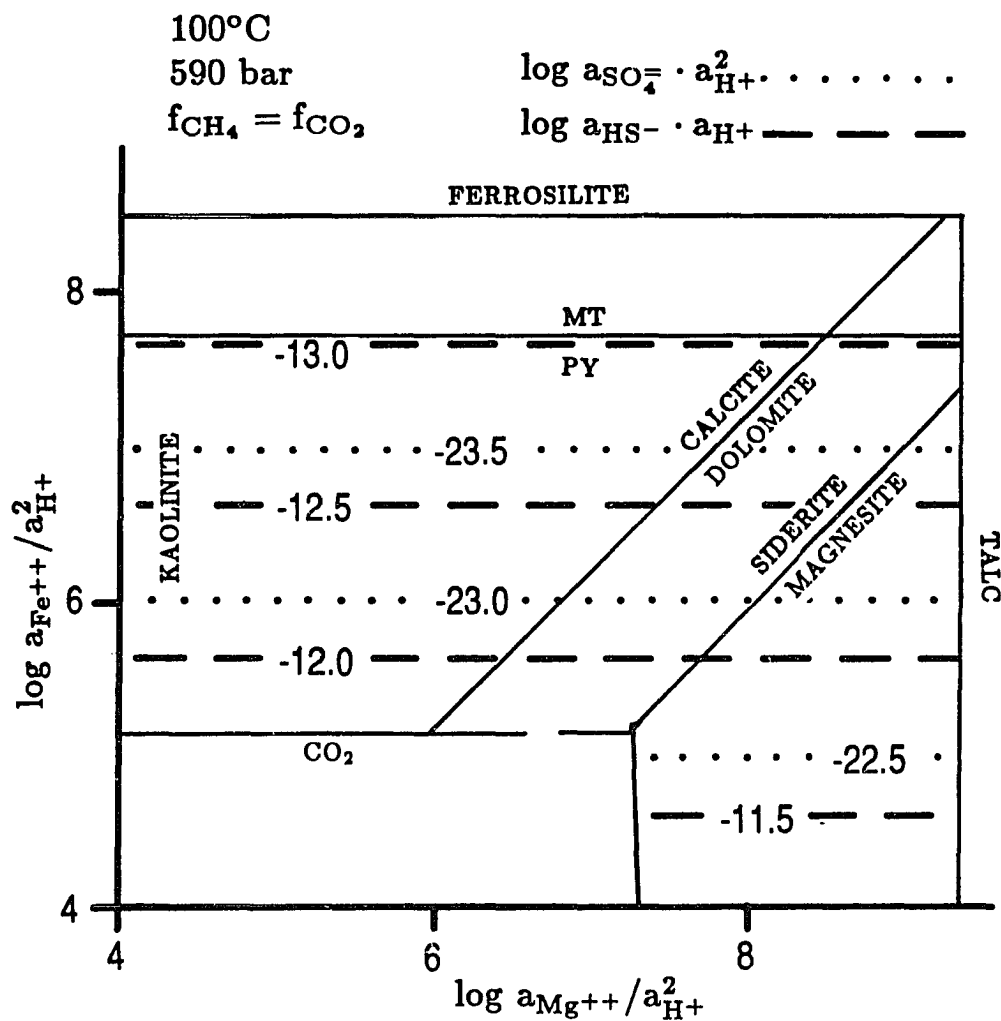


Figure 26: Contours of $\log a_{\text{SO}_4^{2-}} \cdot a_{\text{H}^+}^2$ and $\log a_{\text{HS}^-} \cdot a_{\text{H}^+}$.

$\log a_{\text{SO}_4^{2-}} \cdot a_{\text{H}^+}^2$ = dot-dashed and $\log a_{\text{HS}^-} \cdot a_{\text{H}^+}$ = dotted at 100°C and 590 bar. Mineral stability surfaces (solid) are from Figure 24.

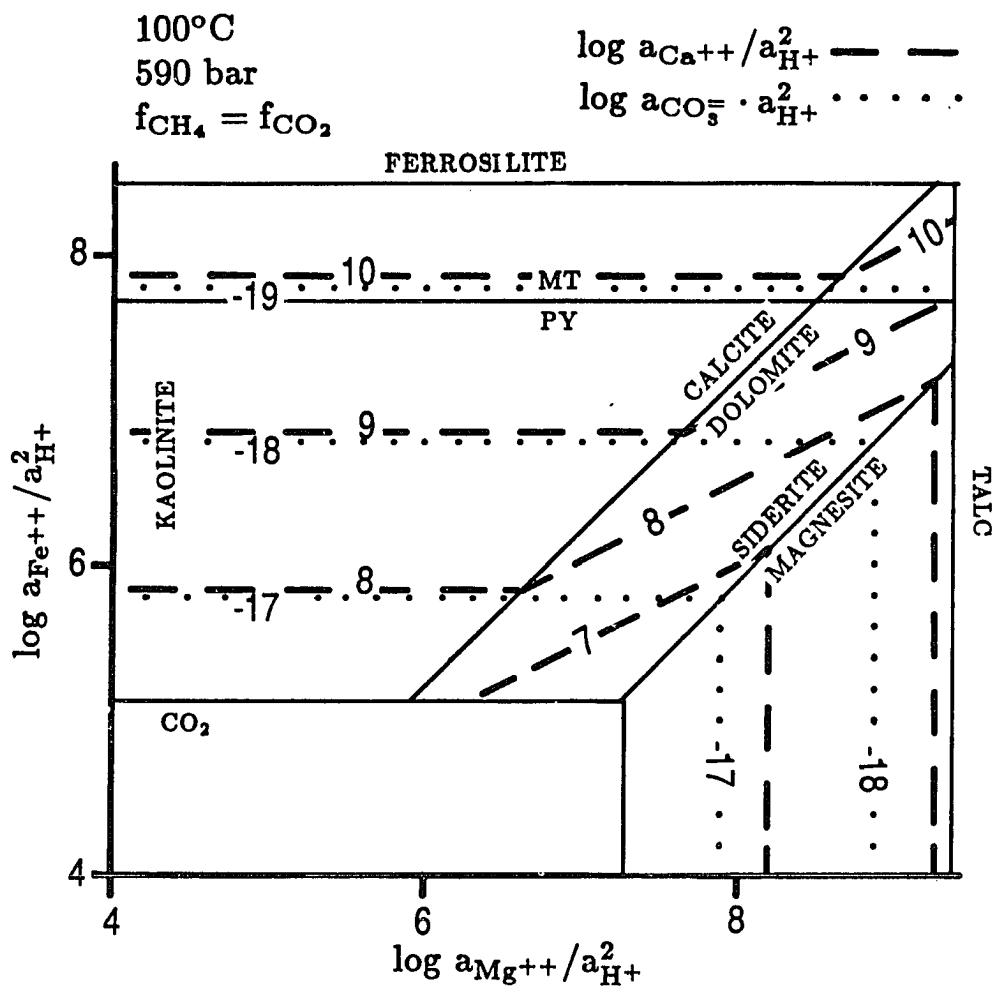


Figure 27: Contours of $\log a_{\text{CO}_3} \cdot a_{\text{H}^+}^2$ and $\log a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$.

$\log a_{\text{CO}_3} \cdot a_{\text{H}^+}^2$ = dot-dashed and $\log a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$ = dotted at 100°C and 590 bar. Mineral stability surfaces are from Figure 24.

Mineral assemblages that could deposit from CO_2 -saturated solution, as would be found in kerogen-rich geopressured sediments, can be predicted from equilibrium relationships on Figures 24 and 25. The predicted mineral assemblage includes a carbonate mineral, kaolinite and pyrite.

In contrast, solutions from either organic-poor or normally-pressured sediments are represented by a different set of activity diagrams. Pore fluids in these sediments are not enriched in gases such as CO_2 or CH_4 , because of the lack of thermally-degrading organic material to contribute the gas, or because pore fluids are not adequately isolated to allow the buildup of gases. In gas-poor solutions such as these, oxidation-reduction is mineralogically controlled rather than controlled by CO_2 - CH_4 equilibrium, as discussed above. To represent equilibrium in these gas-poor fluids, activity diagrams were constructed for 100° and 150°C for a fluid composition following the pyrite-hematite, pyrite-magnetite and pyrite-pyrrhotite saturation surfaces (Figures 28 and 29). The pressures represented on Figures 28 and 29 are the lithostatic pressures.

A shift from lithostatic to hydrostatic pressure results in small shifts in the equilibrium surface on Figures 28 and 29, similar to the shifts displayed on Figures 24 and 25. Therefore these figures are used to represent equilibrium relationships for both geopressured sediments, and normally-pressured sediments.

Mineral stability relationships in Figures 28 and 29 are similar over the temperature range studied. Equilibria between all phases, excepting the carbonate minerals, shift by 1 to 1.5 log units to lower values of $\log a_{\text{Fe}^{++}}/a_{\text{H}^+}^2$ with the temperature increase from 100° to 150°C.

Oxidation on Figures 28 and 29 decreases from the bottom of the hematite-pyrite field to the top of the magnetite-pyrite field. In the oxidized

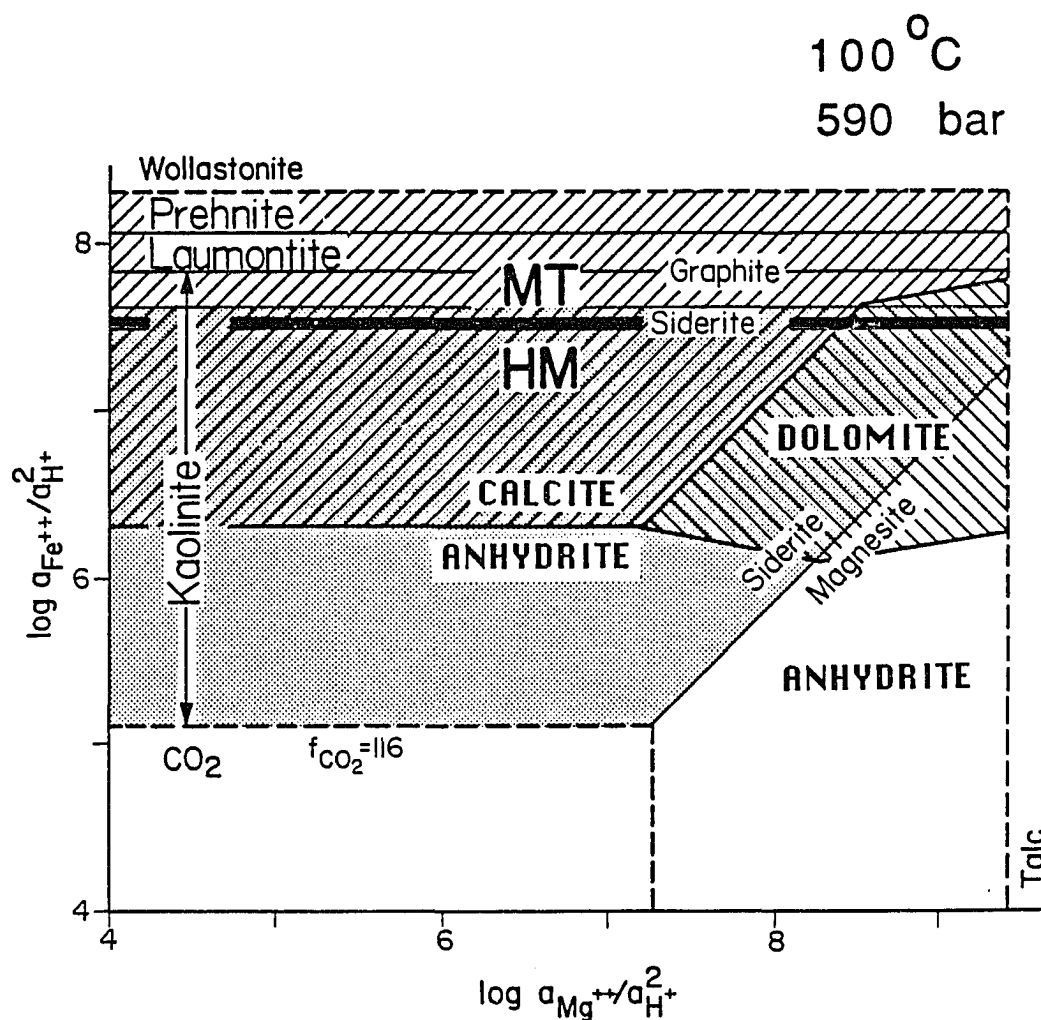


Figure 28: Chemical equilibrium diagram in the system $\text{CaO} - \text{FeO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{CO}_2 - \text{H}_2\text{S} - \text{H}_2\text{SO}_4 - \text{SiO}_2 - \text{H}_2\text{O} - \text{HCl}$ at 100°C and 590 bar (organic-poor system).

MT = magnetite, HM = hematite, the $\log a_{\text{SiO}_2}$ is equal to quartz saturation, and $\log a_{\text{CO}_3} = \log a_{\text{H}^+}^2$, $\log a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$ and $\log a_{\text{Al}^{+3}}/a_{\text{H}^+}^3$ are conserved. Pyrite is in equilibrium everywhere on this diagram, allowing pyrite-hematite or pyrite-magnetite equilibria to determine the $\log a_{\text{SO}_4} = \log a_{\text{H}^+}^2$ and $\log a_{\text{HS}^-} \cdot a_{\text{H}^+}$ which vary across the figure. Dashed lines are saturation surfaces.

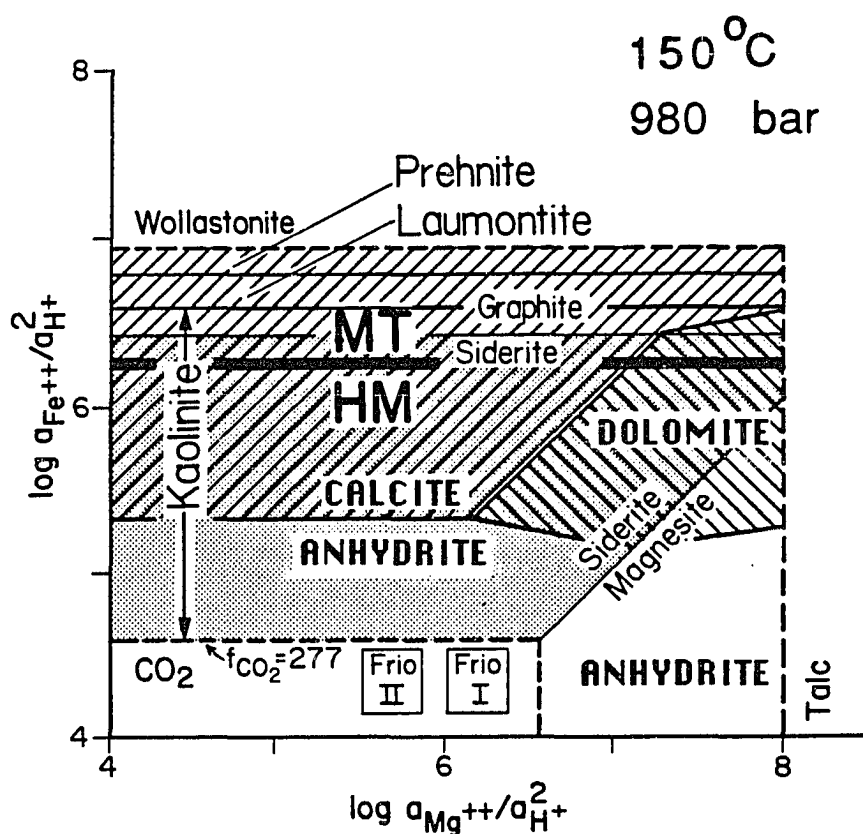


Figure 29: Chemical equilibrium diagram in the system $\text{CaO} - \text{FeO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{CO}_2 - \text{H}_2\text{S} - \text{H}_2\text{SO}_4 - \text{SiO}_2 - \text{H}_2\text{O} - \text{HCl}$ at 150°C and 980 bar (organic-poor system).

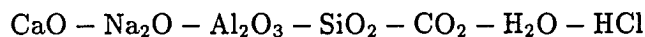
MT = magnetite, HM = hematite, the $\log a_{\text{SiO}_2}$ is equal to quartz saturation, and $\log a_{\text{CO}_3} \cdot a_{\text{H}^+}^2$, $\log a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$ and $\log a_{\text{Al}+3}/a_{\text{H}^+}^3$ are conserved. Pyrite is in equilibrium everywhere on this diagram, allowing pyrite-hematite or pyrite-magnetite equilibria to determine the $\log a_{\text{SO}_4} \cdot a_{\text{H}^+}^2$ and $\log a_{\text{HS}^-} \cdot a_{\text{H}^+}$ which vary across the figure. Dashed lines are saturation surfaces.

solution the stability field for calcite and dolomite is limited by anhydrite equilibrium at low values of $\log a_{\text{CO}_3} \cdot a_{\text{H}^+}^2$. In the reduced solution the stability field of siderite is limited by graphite equilibrium, at high values of $\log a_{\text{CO}_3} \cdot a_{\text{H}^+}^2$. The calcium-aluminum silicates, laumontite and prehnite are also stable, limiting the kaolinite stability in the graphite-magnetite stability field, at high values of $\log a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$. In addition, the upper limit on $\log a_{\text{Fe}^{++}}/a_{\text{H}^+}^2$ is set by wollastonite saturation, rather than ferrosilite as in Figures 24 and 25.

Comparison of equilibrium mineral relationships in the low f_{CO_2} and f_{CH_4} solutions, as represented in Figures 28 through 29, with those in the high f_{CO_2} and f_{CH_4} solutions, as represented in Figures 24 and 25, suggests that distinctly different alteration mineral assemblages would be in equilibrium with and, therefore, could deposit from these different solutions. The common sandstone cement, laumontite, can only deposit from the low f_{CO_2} solution represented by the reduced, low $\log a_{\text{CO}_3} \cdot a_{\text{H}^+}^2$, solution at the top of Figures 28 and 29. Laumontite in this solution is in equilibrium with the assemblage calcite-graphite-magnetite-pyrite-quartz. Under the conditions of these figures laumontite cannot coexist in equilibrium with the other carbonate minerals, dolomite, siderite, and magnesite, nor with anhydrite or hematite. In contrast, kaolinite rather than laumontite is in equilibrium with CO_2 -rich solutions in organic-rich geopressured sediments. Kaolinite could, furthermore, coexist in equilibrium with dolomite, siderite or magnesite, and under conditions of low f_{CO_2} with anhydrite and hematite.

In addition comparing equilibrium relationships on Figures 24 and 25 with those on 28 and 29 suggests that anhydrite is in equilibrium with solutions with high f_{CO_2} but low f_{CH_4} . The absence of CH_4 from solutions not affected by kerogen maturation, permits the oxidation state of the solution to become oxidized as a

result of processes such as temperature and pressure changes or mineral reactions. Oxidation of pore fluids could shift the solution to equilibrium with anhydrite. Whereas, anhydrite could not be in equilibrium with the CO_2 - CH_4 -rich pore fluids present in kerogen-rich geopressed sediments. This is because the presence of CH_4 keeps the oxidation state of the solution reduced.



This subsystem contains the common sandstone cements, calcite, kaolinite, laumontite, albite, and paragonite. Equilibrium relationships among minerals in this subsystem are represented as a function of $\log a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$ and $\log a_{\text{Na}^+}/a_{\text{H}^+}$ in Figures 30 and 31 at lithostatic pressure. From the relationships on these figures it is apparent that kaolinite is more stable than laumontite, paragonite or albite in a more acid solution. In addition, laumontite stability increases in a solution rich in Ca^{++} , and paragonite and albite stability increases in a solution rich in Na^{++} . An increase in temperature from 100° to 150°C lowers the stability field of laumontite by 2 log units of $\log a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$, and the stability field of both paragonite and albite by 1 log unit of $\log a_{\text{Na}^+}/a_{\text{H}^+}$. A shift from lithostatic to hydrostatic pressures shifts the equilibrium surfaces on Figures 30 and 31 less than two tenths of a log unit.

The calcite saturation surface is also drawn on Figures 30 and 31. Calcite saturation in solution places an upper limit on the $\log a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$ in solution. The calcite saturation surfaces are for an f_{CO_2} at CO_2 saturation. Equilibrium relationships on Figures 30 and 31 indicate that calcite equilibrium limits the $\log a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$ in a solution saturated with CO_2 or near CO_2 saturation well below laumontite equilibrium. Furthermore these equilibrium relationships indicate that

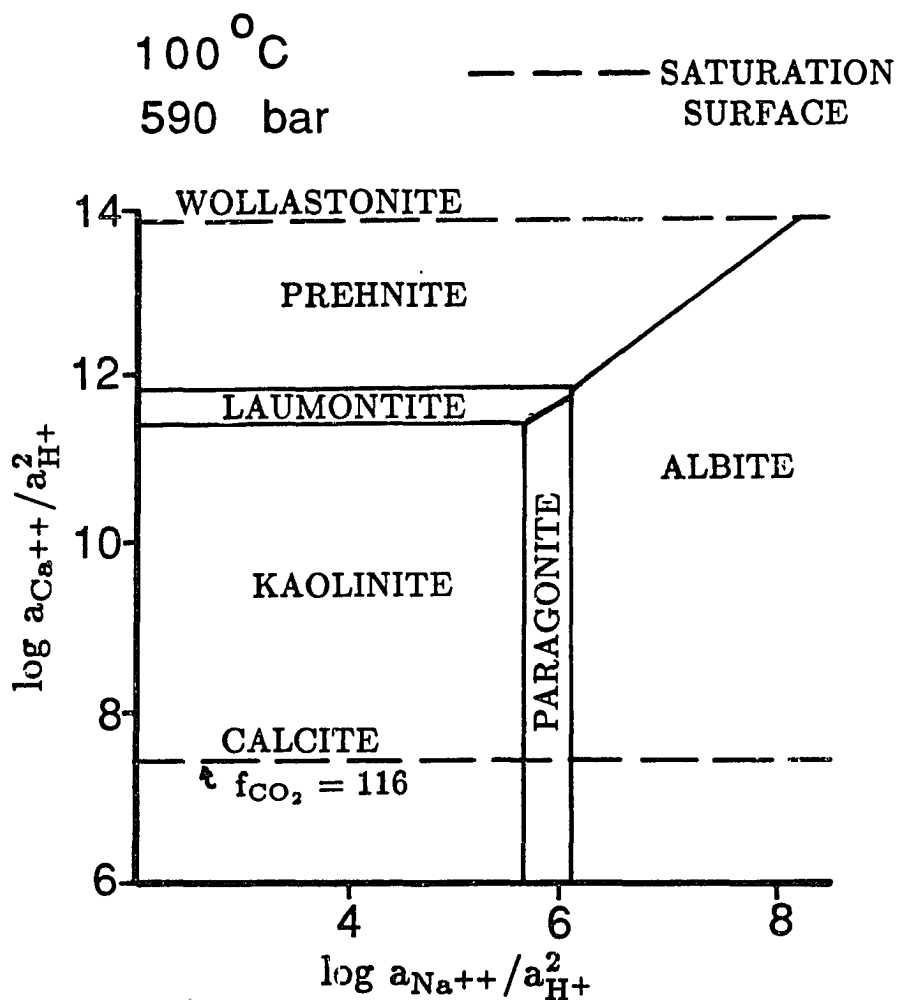


Figure 30: Chemical equilibrium diagram in the system $\text{CaO}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CO}_2-\text{H}_2\text{O}-\text{HCl}$ at 100°C and 590 bar.

Calcite saturation surface is for f_{CO_2} at CO_2 saturation. In construction of this figure $\log a_{\text{Al}+3}/a_{\text{H}^+}^3$ is conserved and $\log a_{\text{SiO}_2}$ is set at quartz saturation. Dashed lines are saturation surfaces.

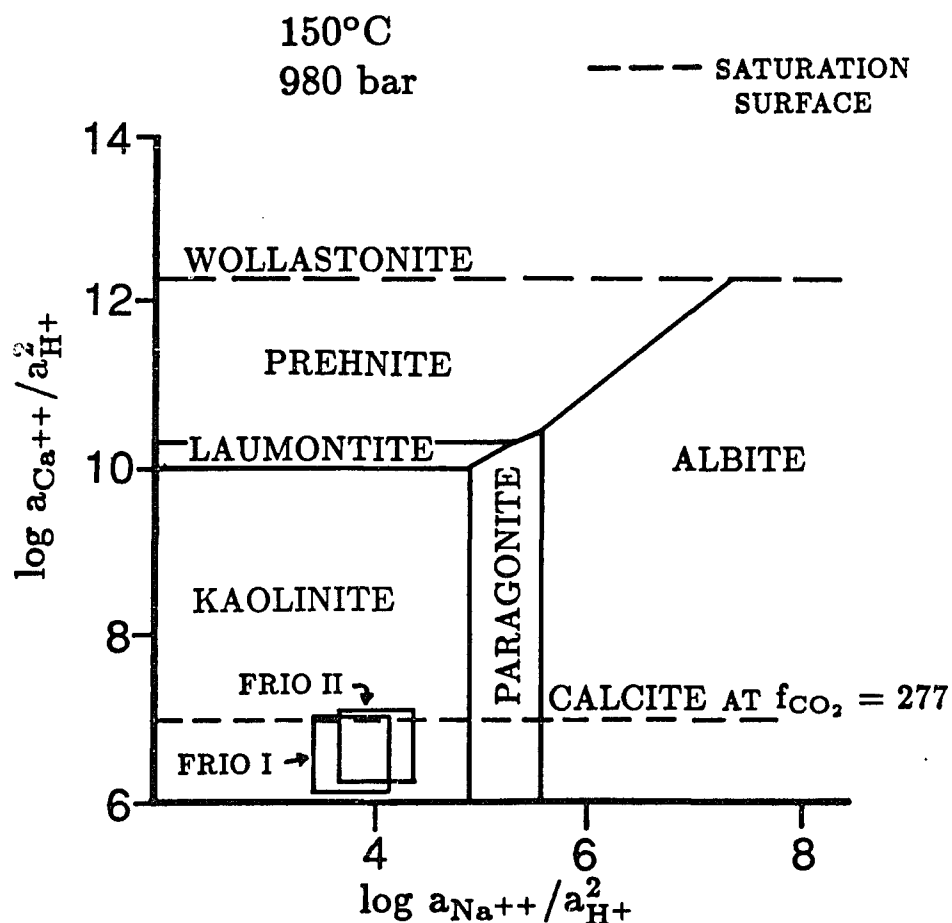


Figure 31: Chemical equilibrium diagram in the system $\text{CaO} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{CO}_2 - \text{H}_2\text{O} - \text{HCl}$ at 150°C and 980 bar.

Calcite saturation surface is for f_{CO_2} at CO_2 saturation. In construction of this figure $\log a_{\text{Al}+3}/a_{\text{H}+}^3$ is conserved and $\log a_{\text{SiO}_2}$ is set at quartz saturation. Dashed lines are saturation surfaces.

kaolinite-calcite could deposit from acid, high f_{CO_2} pore fluid, and paragonite-calcite or albite-calcite, rather than laumontite or prehnite, could deposit from more basic, high f_{CO_2} pore fluid.

Phase Relations Relevant to the Silicate-Carbonate System

The chemical conditions present in kerogen-rich geopressed sediments provide the mechanisms for feldspar dissolution and kaolinite-carbonate deposition at temperatures ranging from approximately 100° to 135°C, followed by albite-carbonate deposition at higher temperatures. The majority of CO_2 released during kerogen maturation occurs at approximately 100°C with the highest temperature of release at approximately 135°C (Hunt, 1979). CO_2 dissolves in the geopressed pore fluids resulting in a shift in aqueous carbonate complexing which releases hydrogen ions and acidifies the pore fluid (Reaction 5.2). Reaction of a pore fluid with a large a_{H^+} (acid) and small a_{K^+} , a_{Na^+} and $a_{\text{Ca}^{++}}$ with the sediments causes dissociation of detrital K-feldspars, Na-Ca plagioclase and biotite. This mechanism has been predicted to contribute to the development of secondary porosity in basin sandstones (Siebert, Moncure and Lahann, 1984; Franks and Forester, 1984).

Detrital and authigenic carbonate minerals are not in all cases dissolved by this pore fluid with a large a_{H^+} (acid) and small $a_{\text{Ca}^{++}}$ because its high $a_{\text{CO}_3=}$ maintains the solution near or in equilibrium with carbonate minerals. This mechanism is suggested by Siebert, Moncure and Lahann (1984) to explain the persistence of calcite clasts and early calcite cement in the zone of acid alteration and secondary porosity development.

Once the source of CO_2 is exhausted, continued feldspar dissolution decreases the a_{H^+} . CO_2 depletion occurs at approximately 135°C, the maximum temperature of CO_2 release from the thermal degradation of kerogen. This de-

crease in a_{H+} , along with the continued increase in a_{K+} , a_{Na+} and a_{Ca++} from feldspar dissolution, shifts the fluid equilibrium from kaolinite, through the narrow paragonite stability field, and ultimately on to albite equilibrium.

Reaction path calculations (Helgeson, Brown and Leper, 1969) completed by Helgeson (1970b) and Sverjensky (1984) predict similar effects for the reaction of acid pore fluids with the minerals commonly present in arkosic sandstones. Helgeson (1970b) calculated the reaction of a sodium-chloride solution with an initial pH of 3, at 100°C and 1 bar with K-feldspar, biotite and albite. Sverjensky (1984) calculated the effect of the reaction of a sodium-chloride solution with an initial pH of 4.5, at 125°C and 2.3 bar with quartz, K-feldspar, muscovite and pyrite. The results of their calculations indicate that the reaction of an acid sodium-chloride solution with the mineral assemblage commonly present in arkosic sandstones results in an increase a_{Na+} , a_{K+} , and a_{SiO_2} and decrease in the a_{H+} . The relative change in the a_{H+} is much greater than the change in the cation concentrations. The decrease in the a_{H+} , therefore, results in large increases in the $\log a_{Na+}/a_{H+}$, $\log a_{K+}/a_{H+}$, and $\log a_{Ca++}/a_{H+}^2$ of the solution. Sverjensky's (1984) reaction path calculation indicate that these shifts in the solution composition result in kaolinite-dolomite deposition. The work of Helgeson (1970b) further suggests that continued reaction of the solution with K-feldspar, biotite and albite ultimately results in the deposition of biotite, muscovite, K-feldspar and paragonite and finally to albite equilibrium.

Predicted Authigenic Mineral Assemblages

Three distinct environments of alteration in kerogen-rich geopressured sediments are: 1) Quartz deposition should occur primarily in the upper portions of geopressured sediments as a result of the upward flow of fluids, and temperature and pressure decreases. Also, the largest proportion of quartz deposition should occur at the top of the geopressured zone, and decreases rapidly with increased depth. This is because the largest upward flux of fluid occurs in the upper portions of the geopressured zone as a result the cumulative upward flow from below and because the large porosity gradients in these shallower sediments results in greater fluid fluxes.

2) Carbonate minerals should deposit above the zone of CO_2 release from kerogen decomposition. This occurs as a result of the upward flow of fluids saturated with CO_2 or near saturated with CO_2 to lower temperatures and pressures resulting in the separation of a CO_2 rich vapor and subsequent carbonate deposition.

3) Feldspar dissolution and kaolinite-carbonate deposition occurs in the zone of CO_2 generation. CO_2 dissolves in pore fluids, producing an acid solution which reacts with the sandstone. After CO_2 generation by kerogen degradation ceases, dissolution of feldspars by these acid solutions causes the pH of the solution to increase. The solution subsequently equilibrates with K-feldspar, and continued dissolution of primary Ca-Na plagioclase shifts the solution equilibrium toward that of albite resulting in albite-carbonate equilibrium. Despite the continued addition of calcium to solution the high f_{CO_2} of the solution causes calcite equilibrium

to limit the $\log a_{\text{Ca}^{++}}/a_{\text{H}^{+}}^2$ below that necessary for laumontite equilibrium and precipitation.

In contrast, alteration minerals that should not deposit from pore fluid in kerogen-rich geopressured sediments include laumontite and anhydrite. These minerals could deposit from pore fluids within kerogen-poor geopressured sediments. They could also deposit from pore fluids within kerogen-rich normally pressured sediments in which CO_2 and CH_4 from kerogen maturation are flushed from the sediments before accumulating in amounts approaching saturation in solution.

Quartz deposition as described above should be characteristic of geopressured sediments independent of the kerogen content of the sediments. In contrast the deposition of quartz by upward flowing fluids would not be expected in normally-pressured sediments in which gravity-driven fluid dominate the flow regime.

CHAPTER 6

Frio Sandstone

The above predictions are typical of observed relationships in the kerogen-rich Frio formation of the Texas Gulf Coast. Conditions in Texas Gulf Coast basins are similar to those assumed for the geopressed basin studied above. They have extensive development of geopressed sediments, at depths in excess of approximately 2.5 km, as well as thermal gradients ranging from 30 to 40°C km⁻¹ (Sharp, 1976). Sandstone-shale ratios in Texas Gulf Coast sediments are typically 10 to 1 (Siebert, Moncure and Lahann, 1984). The original concentration of organic matter in Gulf Coast shales is typically 0.6 wt % (Siebert, Moncure and Lahann, 1984). The Frio formation in particular was chosen for comparison because the alteration mineralogy and pore fluids are well studied.

The sandstones of the Frio formation range in composition from feldspathic litharenites to quartz-rich arkoses or subarkoses (Loucks, Dodge and Galloway, 1984). Rock fragments in the Frio sandstones are predominantly volcanic and compose from 10 to 50 volume % of the rock. Alteration in the Frio sandstone, as described by Loucks, Dodge and Galloway (1984), Franks and Forester (1984), Land (1984) and Kaiser (1984), is dominated by quartz, carbonate, kaolinite and albite. A zone of secondary porosity has developed in the Frio sandstone at approximately 3.4 km (Loucks, Dodge and Galloway (1984). This zone is marked by an increase in porosity by more than 30 % through dissolution of primary K-feldspar, Na-Ca feldspar, volcanic rock fragments and, in some locations, calcite. Overlying

Vicksburg and Wilcox sandstones have compositions and alteration mineralogies similar to those of the Frio (Loucks, Dodge and Galloway, 1984).

Analyses of liquid and gas sampled from 4462 m, at 137°C, and 4740 m, at 150°C, within the Frio sandstone are reported by Kharaka et al. (1979) and are listed in Tables 3 and 4. These fluid samples were collected from the Pleasant Bayou no. 2 well from Brazoria County, Texas. The fluid pressure is 787 bar, at 4450 m, and 843 bar, at 4740 m. These pressures approach lithostatic pressures (Figure 1). The fluids are sodium-chloride rich, and high in dissolved solids, 132,000 and 108,000 ppm. A deep reservoir pH of 4.1, corrected for CO₂ loss, was calculated for both these fluid samples by Kharaka et al. (1979). Although, there are many potential errors in doing these calculations and in collecting and analyzing for the gases lost from solution, the calculated pH is at best within a log unit of the actual subsurface pH.

Under subsurface conditions Frio fluid is enriched in CO₂. This is apparent from the high CO₂ content of up to 10 mole % in the gas phase separate. Under subsurface conditions Frio fluid is saturated with respect to CH₄ (Kharaka et al., 1979).

Quartz

The log a_{SiO_2} in the Frio fluid samples plotted on Figure 20 shows both fluids to be very close to equilibrium with quartz at the subsurface temperatures and pressures of each sample. Authigenic quartz in the Frio sandstone is generally rare above 2.5 km (Miliken, Land and Loucks, 1981; Land, 1984). Below 2.5 km authigenic quartz averages 2.5 volume % of the rock (Land, 1984). The $\delta^{18}\text{O}$ of quartz cement from the Frio formation averages +31‰ ±1.5 ‰ at all depths

Table 3: Analyses of Pleasant Bayou 2 liquid samples.

	I ^a	II ^a		I ^a	II ^a
Depth (m)	4462	4740	SiO ₂	120	200
Temperature (°C)	138	150	B	32	32
Pressure (bar)	787	843	HCO ₃ ^c	365	498
T.D.S. ^b	132,000	108,000	NH ₃	78	118
Na	38,00	32,100	SO ₄	5.4	21
K	840	1,900	H ₂ S	0.5	2.0
Ca	9,100	6,500	Cl	80,600	64,700
Mg	660	210	Br	82	61
Fe	62	68	I	30	16
Sr	1020	867	F	1.4	1.1
Ba	760	700	pH(field)	6.5	6.2
Mn	25	15	pH(calculated) ^d	4.1	4.1
Cs	50	49	$\delta^{18}\text{O}(\text{‰})$	5.4	4.9
Li	39	34	$\delta\text{D}(\text{‰})$	-20.8	-25.8

a)Data from Karaka et al. (1979). Units in mg/liter unless otherwise noted.

b)Total dissolved solids.

c)Field titrated alkalinity.

d)Corrected for CO₂ lost to gas separate at surface.

Table 4: Analyses of Pleasant Bayou 2 gas samples.

	I ^a	II ^a
Gas Produced	3.7 ^b	4.8 ^b
CH ₄	84.51	88.93
C ₂ H ₆	2.97	4.65
CO ₂	10.54	5.24
N ₂	0.57	0.67
H ₂ S	nd ^c	<0.01
SO ₂	nd	<0.05
O ₂	nd	<0.02
Ar	nd	<0.02

a)Data from Karaka et al. (1979). Units mole % unless otherwise noted.

b)Units m³gas/m³water.

c) nd = analysis not available.

(Land, 1984). Deposition of this authigenic quartz in isotopic equilibrium with the Pleasant Bayou well fluid samples from the Frio formation, which have a $\delta^{18}\text{O}$ of +4.9 and +5.4‰ (Table 3), occurs at approximately 60° to 80°C. These values indicate that authigenic quartz within the Frio deposited below 100°C at all depths.

The occurrence and isotopic composition of quartz in the Frio sandstone are consistent with the mechanism of quartz deposition in geopressed sediments presented above. The occurrence of quartz cement only below 2.5 km and its isotopic equilibrium with the geopressed formation fluids at approximately 70°C suggests it deposited from upward flowing fluids (Miliken, Land and Loucks, 1981; Land, 1984) in the geopressed zone. In addition, Land (1984) indicates it is unlikely that the quartz deposited in equilibrium with the isotopically low $\delta^{18}\text{O}$ fluids from above.

The low temperature of quartz deposition of 70°C $\pm$ 10°C also supports the conclusion that the majority of quartz cement deposits in the upper portion of the geopressed zone. Since the $\delta^{18}\text{O}$ of quartz is an average value in each sample and there are large errors in its determination (Land, 1984), small additions of quartz deposited at higher temperatures cannot be discerned from the overall average and may not be adequate in volume to shift the average $\delta^{18}\text{O}$ of quartz with depth. These data, therefore, do not preclude the deposition of some quartz at greater depths in the geopressed zone. The rapid decrease in cumulative fluid flux with increased depth results in a large decrease in the amount of quartz deposition relative to that deposited above.

Calcite

The $\log a_{\text{Ca}^{++}}/a_{\text{H}^{+}}^2$ in the Frio fluid samples plotted on Figure 31 shows them to be very near equilibrium with calcite. There is conflicting information as to the occurrence and deposition of authigenic carbonate in the Frio sandstone. Land (1984) describes authigenic carbonate as comprising an average of 5.3 volume % of the rock with no trend in the degree of cementation with depth, and as composed predominantly of calcite and less than 10 % dolomite. Land (1984) also found that the $\delta^{18}\text{O}$ of the carbonate cement and its trace element composition are uniform with depth, and interprets this to suggest that carbonate cement in the Frio formation deposited as a consequence of a homogeneous event under a restricted range of $\delta^{18}\text{O}$ and temperature. Lindquist (1977) found petrographic evidence that calcite cementation in all cases preceded the development of secondary porosity. In contrast, Loucks, Dodge and Galloway (1984) describe several events of carbonate cementation. These include carbonate deposition during the development of secondary porosity as an Fe-rich dolomite or ankerite deposited with kaolinite, and carbonate deposition after secondary porosity development as an Fe-rich calcite deposited with albite.

The multiple events of carbonate deposition make it difficult to evaluate if indeed carbonate cement deposited as a result of vapor separation above the zone of CO_2 generation in geopressed sediments. These multiple events could be indicative, however, of carbonate deposition as a result of a series of repeated incidents of pore-fluid pressure building up to lithostatic and then rock failure releasing the pressure. Carbonate cementation in the fracture could then seal it

allowing the pore-fluid pressure exceed lithostatic and reopen the flow paths to release the pressure.

The $\delta^{18}\text{O}$ analyses of these authigenic carbonates also support the possibility that these carbonates are deposited above the zone of CO_2 generation. The average $\delta^{18}\text{O}$ of carbonate of $-7.2^\circ/\text{‰} \pm 2^\circ/\text{‰}$ (Land, 1984), gives a temperature of calcite precipitation from the Frio fluid samples with a $\delta^{18}\text{O}$ of -4.9 and $-5.4^\circ/\text{‰}$ (Table 3) of $95^\circ\text{C} \pm 10^\circ\text{C}$. This temperature corresponds to the temperature of solutions above the zone of CO_2 generation from kerogen degradation at 100° to 135°C .

Kaolinite-Albite

Values of $\log a_{\text{Mg}^{++}}/a_{\text{H}^+}^2$ and $\log a_{\text{Fe}^{++}}/a_{\text{H}^+}^2$ for the Frio fluid samples show it to plot beyond the CO_2 saturation surface on Figures 25 and 29. Considering the potential error in calculating the subsurface pH of these fluids, it can be assumed that the $\log a_{\text{Mg}^{++}}/a_{\text{H}^+}^2$ and $\log a_{\text{Fe}^{++}}/a_{\text{H}^+}^2$ are limited by CO_2 saturation. With this assumption mineralogic stabilities can be determined by projecting the fluid compositions onto the CO_2 saturation surface.

Oxidation-reduction in the Frio fluid samples, which are enriched in the gases CO_2 and CH_4 , is then governed by CO_2 - CH_4 equilibrium rather than being mineralogically controlled. This allows equilibrium in these solutions to be best represented by the mineralogic relationships shown on Figure 25 rather than Figure 29. Values of $\log a_{\text{Fe}^{++}}/a_{\text{H}^+}^2$ and $\log a_{\text{Mg}^{++}}/a_{\text{H}^+}^2$ show the Frio sandstone fluid to plot in the stability fields for kaolinite-pyrite-quartz-dolomite (bordering the calcite stability field)-siderite on Figure 25, when projected onto the CO_2 saturation surface.

Kaolinite deposited as a cement and as a replacement product of feldspars in the zone of secondary porosity development at approximately 3400 m. Iron-rich dolomite and ankerite are also deposited in this zone in association with the kaolinite (Loucks, Dodge and Galloway, 1984). Isotopic data suggest kaolinite was deposited at temperatures between 100° and 140°C (Land, 1984). As discussed above, the composition of the Frio fluid plots in the kaolinite-pyrite-quartz-dolomite (on the border of the calcite stability field)-siderite stability field at CO₂ saturation (Figure 25). Ankerite, a calcium-iron carbonate, is not represented on Figure 25, and therefore siderite-calcite stability fields occur on Figure 25 where ankerite should be stable. Thus deposition of kaolinite and iron-calcium-magnesium carbonates in this zone is consistent with the mineral assemblage predicted to be in equilibrium with the CO₂-charged reservoir water (Figure 25). This deposition is also consistent with the mechanism for mineral deposition discussed in the previous chapter.

Albitization of feldspars occurs below the zones of kaolinite deposition and development of secondary porosity, at depths greater than 3400 m (Loucks, Dodge and Galloway, 1984). Isotopic data suggest albite deposits at temperatures ranging from 100° and 150°C (Franks and Forester, 1984). The deposition of albite after kaolinite and after secondary porosity development is consistent with the equilibrium relationship between kaolinite and albite described in the previous chapter.

Mineral fluid reactions described in the previous chapter also suggest that K-feldspar, muscovite, biotite and paragonite could potentially deposit during diagenesis of kerogen-rich geopressured sediments. None of these minerals, however, is described as an authigenic mineral in the Frio sandstone.

CHAPTER 7

CONCLUSION

Chemical and hydrologic conditions present within kerogen-rich geopressured sediments during diagenesis are uniquely different from those present within normally-pressured or kerogen-poor sediments. In geopressured sediments compaction-driven flow dominates such that fluids are transported upward to regions of lower temperature and pressure. In contrast flow in normally-pressured sediments is generally gravity-driven and therefore downward to regions of higher temperature and pressure. Calculation of the magnitude of fluid flow in geopressured sediments resulting from burial compaction and fluid thermal expansion indicates that the greatest magnitude of upward flow is at the top of the geopressured zone decreasing rapidly with increase depth.

Kerogen present within geopressured sediments decomposes releasing CO_2 and CH_4 at temperatures over 90° to 100°C , temperatures generally present in the upper portions of the geopressured zone. Calculation of the opposing rates of sediment burial with subsequent CO_2 and CH_4 release, and absorption of these gases by the upward flowing fluids indicates that this process can result in gas enrichment to or near to saturation in geopressured fluids within petroleum-source rock. Gas saturation is further enhanced by the temperature and pressure decreases and subsequent decreases in gas solubilities experienced by the fluids as they move upward. In contrast, in kerogen-rich normally-pressured sediments fluids flow downward, thereby diluting gases released from the sediments into the

fluid. In addition, downward fluid flow results in temperature and pressure increases and subsequent increases in gas solubilities. In kerogen-poor geopressured sediments pore fluids generally lack a source of CO_2 and CH_4 and, therefore, do not become enriched in these gases.

The unique chemical and hydrologic conditions present during diagenesis of kerogen-rich geopressured sediments could produce alteration mineral assemblages having both distinctive mineralogies and depositional patterns. Authigenic quartz deposition should occur at the top of the geopressured zone and decrease rapidly with increased depth as a result of the decreased flux of upward fluid flow with increased depth. Carbonate minerals should deposit primarily above the zone of maximum CO_2 generation from kerogen decomposition. Carbonate mineral deposition results from the upward flux of CO_2 saturated fluids and subsequent decreases in fluid temperature and pressure and CO_2 solubility. Feldspar dissolution and kaolinite-carbonate deposition occur within and above this zone of maximum CO_2 generation. Albite-carbonate precipitation could occur below the zone of CO_2 generation. These predictions are in part borne out by observation as compared with authigenic mineral deposition within the Frio sandstone of the Texas Gulf Coast.

These mineral assemblages and their patterns of occurrence could differ from mineral alteration produced in kerogen-poor geopressured sediments of normally pressured sediments. The minerals laumontite and anhydrite could deposit from pore fluids in these sediments, but should not deposit from fluid in kerogen-rich geopressured sediments. In addition, quartz deposition by upwardly mobile fluids would not be expected in normally-pressured sediments in which gravity-driven fluids dominate the flow regime.

The history of mature sedimentary basins is complex and during that time the sediments undergo a number of changing conditions. The predicted mineralogic relationships presented in this text, therefore, should prove useful in reconstructing geologic conditions in older basins, and ultimately assist in the prediction of petroleum formation, migration and entrapment.

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