

Hydrochemical constraints on fluid-mineral equilibria during compaction diagenesis of kerogen-rich geopressed sediments

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Abstract—Hydrochemical conditions characteristic of kerogen-rich geopressed sediments contribute to the development of a predictable alteration mineralogy. The following conditions result in the geopressed fluid becoming enriched, and in some cases, saturated with CO_2 and CH_4 : (1) the upward and generally restricted flow of fluids in geopressed sediments, in contrast to the generally more rapid flow of fluids in nongeopressed sediments; (2) the coincidence of the depths of geopressing with the geothermal temperatures necessary for CO_2 and CH_4 release; and (3) the opposing rates of sediment subsidence and CO_2 and CH_4 transfer into the upward-flowing fluid. Calculation of the phase relations in the system $\text{CaO-FeO-MgO-Na}_2\text{O-Al}_2\text{O}_3\text{-CO}_2\text{-H}_2\text{S-H}_2\text{SO}_4\text{-SiO}_2\text{-H}_2\text{O-HCl}$, as constrained by the above hydrochemical criteria, allows prediction of three patterns of mineral deposition during diagenesis of kerogen-rich geopressed sediments. Quartz deposition is favored in the upper portions and margins of the geopressed section and at the contact between geopresses and normal pressures because of increased fluid flux at shallower depths within the geopressed section. Carbonate deposition could occur above the zone of CO_2 release from kerogen degradation, as a result of the upward flux of CO_2 - and CH_4 -enriched (and possibly saturated) fluids, and the subsequent decrease in fluid temperature, pressure, and CO_2 solubility. Kaolinite-carbonate could deposit within and above the zone of CO_2 release from kerogen as a result of silicate dissolution by CO_2 -rich acid pore fluids, followed by the potential for illite-carbonate and albite-carbonate deposition upon CO_2 depletion. In contrast, laumontite and anhydrite should not deposit during diagenesis of kerogen-rich geopressed sediments but could deposit during diagenesis of nongeopressed or kerogen-poor geopressed sediments. These mineralogic relationships compare favorably with observed relationships in the kerogen-rich geopressed sediments of the Frio Formation from the Texas Gulf Coast.

INTRODUCTION

DIAGENETIC REACTIONS in kerogen-rich geopressed sediments are a function of the distinct 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 as a result of the combined effects of low sediment permeabilities and high sedimentation rates, which restrict the expulsion of compaction-driven and, to a lesser extent, thermally-driven fluids from the geopressed sediments (BREDEHOEFT and HANSHAW, 1968; BETHKE, 1986b). Geopressing develops in positionally active immature basins with high sedimentation rates and large shale components (BREDEHOEFT and HANSHAW, 1968; BETHKE, 1986b). Basins with the high sedimentation rate and the large shale component required to generate geopresses commonly form at continental margins (SELLEY, 1975, 1985). Marine shales deposited at continental margins are enriched in kerogen II, which is a good source for petroleum (TISSOT and WELTE, 1984). The dominance of marine shales in geopressed sediments, therefore, probably results in the common occurrence of petroleum resources in geopressed sedimentary basins (FERTL et al., 1976). The Texas and Louisiana Gulf Coast is an example of this depositional environment. It is geopressed (DICKINSON, 1953; SHARP, 1976), has high sedimentation rates of 0.1 to 10 mm a^{-1} (SHARP and DOMENICO, 1976), contains up to 85% marine shales (BOLES and FRANKS, 1979), and contains considerable petroleum reserves.

Fluid pressures in excess of hydrostatic begin to develop in the onshore portions of basins at continental margin between the depths of 2 to 3 km (FERTL et al., 1976) where lithostatic pressures range from 470 to 710 bars. Basins containing petroleum resources generally have low thermal gradients ranging from 20 to 30°C km^{-1} (FERTL et al., 1976). At these low thermal gradients the top of geopressing coincides with temperatures of 70 to 110°C. Thermal decomposition of kerogen during sediment subsidence releases CO_2 between 100 and 135°C, and CH_4 above 90°C (HUNT, 1979), temperatures that generally fall within the upper portions of the geopressed section. The temperature range of CO_2 from kerogen release is within the temperature range that the majority of kerogen transforms to petroleum, approximately 60 to 120°C (NORTH, 1985).

At the low temperatures and elevated pressures of geopressed pore fluids in the upper portions of the geopressed section, relatively small amounts of CO_2 and CH_4 are necessary to achieve saturation. These low saturation limits, combined with the restricted flow conditions present in geopressed sediments, may result in these gases approaching saturation in geopressed fluids within kerogen-rich sediments. In this case the solubilities of these gases provide a limit on the fluid composition and thereby constrain the diagenetic mineralogy. In contrast, in kerogen-poor sediments, insufficient quantities of gas are released to enrich surrounding pore fluids, and in nongeopressed but kerogen-rich sediments, fluid flow regimes differ and may allow dissipation of exsolved gases such that fluids do not approach gas saturation.

This is of practical geologic significance because it suggests that kerogen-rich sediments, particularly geopressed sediments, may develop a characteristic suite of authigenic mineral assemblages that could serve as a useful petroleum-exploration guide by providing information on fluid flow during petroleum generation.

In the calculation of diagenetic reactions in basin sediments, the distinct suite of conditions present in kerogen-rich geopressed sediments has 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 conditions characteristic of geopressed sediments, such as fluid composition and the magnitude and direction of fluid flow. MERINO (1975), SVERJENSKY (1984), CROSSEY et al. (1984), and KAISER (1984) calculated mineral-fluid equilibria in sedimentary basins, but did not consider the effects of geopressing or liquid-vapor equilibria. The effect of CO_2 gas on the development of secondary porosity is discussed by SCHMIDT et al. (1977), SCHMIDT and McDONALD (1979), and FRANKS and FORESTER (1984) but only in the context of the ability of CO_2 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 CO_2 and CH_4 to pore fluids and their solubility limits, and (3) the effect of the predicted range in fluid temperature, pressure, and composition in kerogen-rich geopressed basins on mineral-fluid equilibria and diagenetic mineralogy. The direction and magnitude of fluid flow in geopressed sediments are compared with those expected in nongeopressed sediments. The conditions for CO_2 enrichment in geopressed pore fluids and the consequences of separation of a CO_2 -rich gas on mineral deposition are then discussed. Equilibrium activity diagrams for possible authigenic minerals are calculated for the pressure and temperature conditions common in geopressed sediments. These phase relations are then used to predict the alteration mineral assemblages and zoning patterns within the geopressed sediments, and the results are compared with the observed alteration mineralogy and fluid composition within the Frio Formation of the Texas Gulf Coast.

FLOW IN GEOPRESSED SEDIMENTS

The rate and direction of fluid flow will govern whether the gases released during kerogen thermal maturation are concentrated in the sediment pore fluids. Compaction-driven flow dominates within geopressed sediments, while gravity-driven or thermal-density driven flow dominate in nongeopressed sediments (GALLOWAY, 1984; BETHKE, 1985; GARVEN and FREEZE, 1984a and b). Thermal-density driven flow could contribute to flow in geopressed sediments, but under the low thermal gradients commonly associated with petroleum basins, the contribution of thermal-density changes on flow is small relative to the contribution resulting from compaction (BETHKE, 1986b).

Numerical simulations of compaction-driven flow within a sedimentary basin indicate that fluids flow radially outward and upward from the downwarped basin center (BETHKE,

1985). The rates of compaction-driven flow are calculated to range from approximately 0.3 to 2.2 millimeters per year in basins with subsidence rates on the order of 0.02 to 0.03 mm a^{-1} (BETHKE, 1985, 1986a). The vertical component of flow in these simulations was predicted to be upward for all cases, even when a 500 m thick permeable sandstone unit is present at the base of the hypothetical basin (BETHKE, 1985). The rate of upward vertical flow in these calculations is predicted to be on the order of 0.03 to 0.06 mm a^{-1} , slightly larger but similar in magnitude to the subsidence rate.

At the depths of geopressing, horizontal flow dominates over vertical flow. However, vertical temperature and pressure gradients greatly exceed horizontal temperature and pressure gradients in sediments having the low thermal gradients on the order of 20 to 30°C km^{-1} (BETHKE, 1985). Thus it is the vertical component of flow, whether it is up or down, and its rate, that will have the larger effect on fluid and mineral equilibria and, therefore, is significant to this discussion.

The possible effects of geopressing on flow direction and magnitude are not predicted in BETHKE's (1985) numerical simulations of compaction-driven flow. The lower permeabilities within geopressed sediments combined with the high pressure gradients present between geopressed sediments and the nongeopressed section above, however, should increase the possibility of upward rather than downward flow, particularly in the upper portions of the geopressed zone. Faults within geopressed sediments also contribute to the upward flow of fluids. Fluid-pressure distributions measured around fault zones in geopressed sediments from the Texas Gulf Coast suggest that the faults act as conduits for upward vertical discharge of geopressed fluids (BERG and HAYBECK, 1982; GALLOWAY, 1984). This is in contrast to the general assumption used prior to BETHKE's (1985) numerical simulation, that compaction-driven fluid in geopressed sediments would flow either up or down into more permeable units (cf. SHARP, 1978; CATHLES and SMITH, 1983).

In contrast, flow in nongeopressed sediments may differ widely from the conditions predicted for geopressing. Simulations of gravity-driven flow predict that the vertical component of flow may be either up or down and can achieve velocities on the order of meters per year (GARVEN and FREEZE, 1984a,b; BETHKE, 1986a), three orders of magnitude greater than those of compaction-driven fluids. Under the relatively unrestricted flow conditions present in nongeopressed sediments, a wide range in fluid velocities is possible, such that the flow can be fast as predicted above or in some cases may be slow and possibly duplicate flow in geopressed sediments. Generally, however, the larger permeabilities of nongeopressed sediments will permit much higher flow rates compared to those expected in geopressed sediments.

CO_2 AND CH_4 IN GEOPRESSED FLUIDS

The addition of small amounts of CO_2 and CH_4 to an H_2O -rich solution results in large shifts in the vapor-liquid equilibria surface of the solution at the temperatures and pressures common to geopressed fluids. Vapor-liquid equilibria surfaces for the system $\text{CO}_2\text{-H}_2\text{O}$ and $\text{CH}_4\text{-H}_2\text{O}$

are shown in Fig. 1. These diagrams are constructed from the experimental data of TAKENOUCHI and KENNEDY (1964, 1965) and LARSEN and PAUSNITZ (1984). The isocompositional curves in these figures represent the mol% CO_2 and CH_4 in the liquid phase at vapor-liquid equilibria. Comparison of these equilibria surfaces with the temperature and pressure conditions of geopressed fluids with a thermal gradient of 30°C km^{-1} indicates that as little as 2 mol% CO_2 and 0.25 mol% CH_4 can result in saturation in the upper portions of the geopressed section.

The addition of solutes to H_2O -rich solutions enhances the effects of CO_2 and CH_4 , shifting the vapor-liquid equilibria surfaces into even lower ranges of temperature and pressure. This relationship is shown through comparison of the vapor-liquid equilibria surfaces for the systems CO_2 - H_2O and CO_2 - H_2O - NaCl shown in Fig. 1. Addition of 2 mol% NaCl to a 2 mol% CO_2 solution at 150°C drops the vapor-saturation surface over 200 bar.

Experimental solubility data for the combined systems CO_2 - CH_4 - H_2O or CO_2 - CH_4 - H_2O - NaCl are not available over the temperature and pressure range of interest. Therefore, solubility data for the binary systems CO_2 - H_2O and CH_4 - H_2O are used in this study. Because of the additional intermolecular attractions resulting from the presence of both CO_2 and CH_4 in H_2O , the data for the binary systems represent maximum solubilities (PRAUSNITZ et al., 1986). Addition of small amounts of CH_4 to the binary system CO_2 - H_2O slightly increases the activity of H_2O and significantly decreases the activity of CO_2 (JACOBS and KERRICK, 1981).

Gas enrichment in geopressed fluids

During the pyrolysis of kerogen, up to 6 wt% of the total kerogen converts to CO_2 and up to 1 wt% to CH_4 (TANNENBAUM and KAPLAN, 1985). Unpublished experimental work by L. L. Lundell and A. Brown (FRANKS and FORESTER, 1984) indicated that up to 22 wt% CO_2 is released from the more oxygen-rich kerogen composed of humic material.

Temperatures at which CO_2 is released suggest that the largest CO_2 generation occurs at approximately 100°C and is completed at 135°C (HUNT, 1979). In contrast, CH_4 release occurs continuously at temperatures greater than 90°C (HUNT, 1979).

Although it has long been recognized that hydrocarbon gas accumulations, of predominantly CH_4 , are associated with petroleum occurrences (TISSOT and WELTE, 1984), the CO_2 content of these accumulations in the Gulf Coast are reported to be generally less than 4 mol% (FRANKS and FORESTER, 1984). Thus it might be inferred that pore waters associated with these hydrocarbon gas accumulations are enriched and possibly saturated with respect to CH_4 , while the enrichment or saturation of these associated pore fluids with CO_2 is less obvious. Between 100 and 135°C , however, CO_2 is released during kerogen maturation in amounts greater than CH_4 . Consequently, it is proposed that the competing processes of the slow upward flow of fluids and the slow downward mobility of the sediments with accompanied CO_2 release may result in the enrichment and saturation of CO_2 in geopressed pore fluids between the 100 to 135°C isotherms.

Maximum possible gas concentrations should result from the case in which the vertical component of flow is opposite and equal to the subsidence rate. In this case upward fluid movement is stationary relative to an elevation datum and thus stationary relative to the 100 to 135°C isotherm. Under this condition the concentration of gas accumulated in the "stationary" pore fluids could approach infinity, limited only by the amount of sediment buried, the quantity of gas released from the sediments, and the solubility of the gas. Thus if adequate CO_2 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 CO_2 saturation. Fluids flowing downward, too slowly upward, or upward too fast relative to the sediments may not have adequate residence time between the 100 to 135°C isotherm to achieve CO_2 saturation. Similarly, CH_4 which is released in smaller

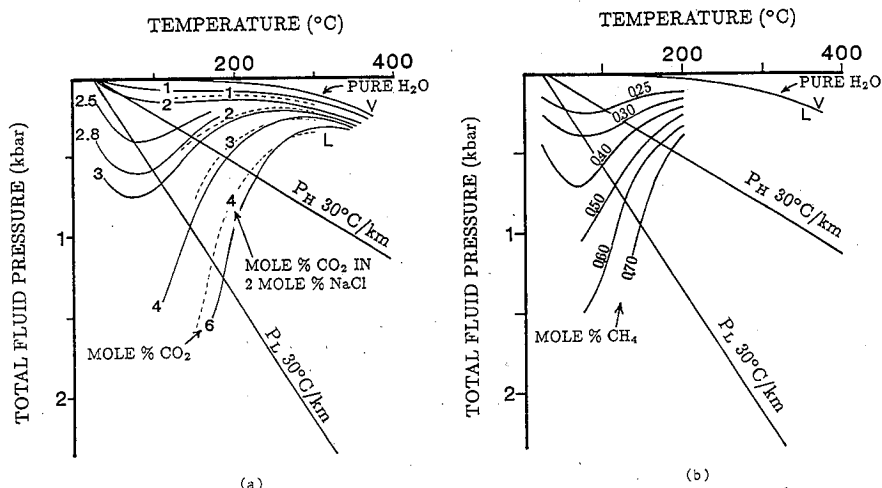


FIG. 1. Isocompositional curves of (a) CO_2 in the liquid phase at vapor-liquid equilibria in the system CO_2 - H_2O (solid lines) and for the system CO_2 - H_2O - NaCl for 2 mol% NaCl (dashed lines; data from TAKENOUCHI and KENNEDY, 1964, 1965) and (b) CH_4 in the liquid phase at vapor-liquid equilibria for the system CH_4 - H_2O (data from LARSEN and PRAUSNITZ, 1984). Hydrostatic, P_H , and lithostatic, P_L , pressures for 30°C km^{-1} .

amounts than CO_2 (1 wt% as compared to 22 wt% for CO_2) but which has much lower solubilities (0.25 mol% as compared to 2 mol% for CO_2) would also be accumulated in these solutions.

Fluid velocities that would result in CO_2 enrichment and possible saturation of pore fluids would have to be opposite in direction and similar in magnitude to the downward velocity, or subsidence rate, of the sediments. Vertical fluid velocities in geopressured sediments fit this criteria. As shown above, they can be upward and slightly larger, but similar in magnitude, to the sediment subsidence rates. In contrast, flow in nongeopressured sediments can be either downward or upward with likely flow rates on the order of meters per year, two orders of magnitude greater than sediment subsidence rates, and thus likely too fast to result in significant CO_2 accumulation.

As geopressured fluids are enriched in these gases, additional temperature and pressure decreases during continued upward fluid flow act to bring the fluids closer to CO_2 and CH_4 saturation, or even to exceed saturation and thus release these gases because of decreased gas solubilities. 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 CO_2 solubility in pure H_2O and a 16% decrease in CH_4 solubility in pure H_2O . Furthermore, as these CO_2 - and CH_4 -rich pore fluids are discharged out of the geopressured sediments the drop in pressure from lithostatic to hydrostatic results in a large drop in CO_2 and CH_4 solubilities. At 100°C the drop in fluid pressure from lithostatic, at 750 bar, to hydrostatic, at 200 bar, decreases CO_2 solubility by 33% and CH_4 solubility by 50%, both in pure H_2O . Local drops in fluid pressure may also occur as a result of sediment fracturing and similarly could result in gas saturation and possibly localized vapor separation.

It is therefore expected that geopressured pore fluids within kerogen-rich sediments near or above the 100°C isotherm could become enriched and potentially saturated with respect to CO_2 and CH_4 . 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 CO_2 - and CH_4 -rich vapor. In nongeopressured or kerogen-poor sediments, CO_2 enrichment of pore fluids is less likely, unless there is another CO_2 source, because the higher fluid velocities in nongeopressured sediments will result in the dispersal of the gases released during kerogen thermal decomposition.

FLUID-MINERAL EQUILIBRIA

Equilibrium relationships among authigenic minerals expected in kerogen-rich geopressured sediments, as compared to those expected in nongeopressured or kerogen-poor sediments, 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 re-

ported by HELGESON et al. (1978, with updates through 1984) with the aid of the program SUPCRT (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 et al. (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 CO_2 and CH_4 in solution decreases the $a_{\text{H}_2\text{O}}$ from unity. Methods for correcting for the effects of CO_2 impurities in equilibrium calculations are outlined by WALTHER and HELGESON (1980) and BOWERS et al. (1984). The effects of CO_2 impurities on the fugacity of H_2O were calculated for higher temperature solutions, 400°C, for which fugacity coefficients for the system CO_2 - H_2O were available (BOWERS et al., 1984). These higher temperature calculations permit an estimation of the magnitude of possible errors that result from using the $a_{\text{H}_2\text{O}}$ as unity. The fugacity of H_2O was found to shift less than 1% for fluids having CO_2 contents up to 6 mol%. Thus, using an $a_{\text{H}_2\text{O}}$ of unity to represent equilibrium in solution with up to 6 mol% CO_2 results in only small shifts in equilibrium calculations for reactions in which the reaction coefficient for water is small. Based on these calculated uncertainties, the effect of gas impurities on the fugacity of H_2O , and therefore the $a_{\text{H}_2\text{O}}$, is not considered for the systems of interest in this study.

Salts can also alter the activity of water. The dominant ions in aqueous fluids in sandstones from the geopressured Gulf Coast are generally sodium and chloride, although some areas have fluids with calcium concentrations greater than sodium (MORTON and LAND, 1987). Concentrations of NaCl generally increase with increased depth, ranging from less than 1 mol% at shallow depths to 6 mol% at 3 km (SCHMIDT, 1973; MORTON and LAND, 1987). In some cases sodium chloride concentrations decrease in the upper portions of the geopressured section, to less than 1.2 mol% (SCHMIDT, 1973; MORTON and LAND, 1987). In shales the NaCl concentration stays below 2.5 mol% at all depths (SCHMIDT, 1973; OSMASTON, 1975). At the high concentrations of 6 mol% NaCl, the $a_{\text{H}_2\text{O}}$ is reduced by as much as 5%, while for concentrations on the order of 1.2 mol%, the effects on the $a_{\text{H}_2\text{O}}$ is not significant (HELGESON et al., 1969). The effect of a decrease in $a_{\text{H}_2\text{O}}$ on the prediction of mineral stabilities is most important for reactions in which the reaction coefficient for H_2O is greater than one. For the reactions important in the CO_2 -rich solutions for the system considered in this study, the coefficient for H_2O is generally unity. Therefore, the simpli-

fication of $a_{\text{H}_2\text{O}}$ equals unity does not result in large shifts in the equilibrium surfaces calculated.

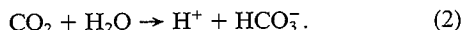
Gas fugacities, f_i , are calculated using the Henry's law relation

$$f_i = H_i X_i, \quad (1)$$

where H_i is the Henry's law constant and X_i is the mole fraction of the gas in solution. Henry's law constants for CO_2 as a function of temperature and NaCl content of the solution are taken from ELLIS and GOLDING (1963), and for CH_4 as a function of temperature are taken from NAUMOV et al. (1974) and CRAMER (1982). The mole fractions of CO_2 and CH_4 at saturation are taken from Fig. 1.

CO_2

When CO_2 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 et al., 1963). In near-neutral solutions, between 100 and 150°C, HCO_3^- and H_2CO_3^* are the dominant carbonate complexes in solution (BARNES, 1979). Dissolving CO_2 into a solution in which a dominant carbonate complex is HCO_3^- releases hydrogen ions as described by the reaction



With adequate CO_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 (SIEBERT et al., 1984; FRANKS and FORESTER, 1984). Because of the high carbonate content of this CO_2 -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 (SCHMIDT and McDONALD, 1979; SIEBERT et al., 1984; FRANKS and FORESTER, 1984). When the source of CO_2 is depleted, the continued hydrolysis of feldspars can increase the solution pH to near neutral. The results of this process and the authigenic minerals deposited as a result of it are discussed in a later section.

The loss of CO_2 from near-neutral pore fluids as a result of vapor separation may result in a shift in aqueous complexing opposite to that caused by the addition of CO_2 to solution [Eqn. (2)]. Calculations of the effects of separation of a CO_2 -rich vapor from near-neutral solutions indicate 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 geopressed fluids if these fluids are initially near carbonate-mineral equilibrium.

Thus authigenic carbonate minerals could deposit in geopressed sediments in response to local pressure decreases and subsequent vapor separation during upward fluid flow. This deposition is most likely in the upper portions of the geopressed section where pressure gradients between geopressed and nongeopressed sediments are largest, and along fractures in which the rapid pressure drop is most likely to result in vapor separation. Sealing of fractures with carbonate minerals would contribute to the perpetuation of a crack-healing process (WALDER and NUR, 1984) in geopressed sediments, thereby maintaining elevated fluid pressures.

$\text{SiO}_2\text{-H}_2\text{O}$

Quartz and amorphous silica define the extremes in solubility in the system $\text{SiO}_2\text{-H}_2\text{O}$, with quartz being the least soluble and amorphous silica the most soluble (Fig. 2). Solubilities of both quartz and amorphous silica decrease as temperature and pressure decrease. Quartz precipitation may be slow at temperatures less than 150°C (RIMSTIDT and BARNES, 1980), and, therefore, reaction kinetics, rather than solubility, could control quartz deposition in the upper portions of the geopressed section. The calculation below, however, indicates that fluid velocities on the order of a millimeter per year or less, as predicted for compaction driven flow, are slow enough to allow quartz to equilibrate in response to the resulting temperature and pressure changes.

The differential rate equation for the system $\text{SiO}_2\text{-H}_2\text{O}$, integrated with respect to time as derived by RIMSTIDT and BARNES (1980), is

$$t_1 - t_0 = -\frac{1}{(k^+)(\frac{A}{M})} \ln \left(\frac{k^+ - k^- (a_{\text{SiO}_2(\text{aq})})_1}{k^+ - k^- (a_{\text{SiO}_2(\text{aq})})_0} \right) \quad (3)$$

where k^+ is the dissolution rate constant for quartz,

$$k^+ = 1.174 - 2.028 \times 10^{-3} T - \frac{4158}{T}, \quad (4)$$

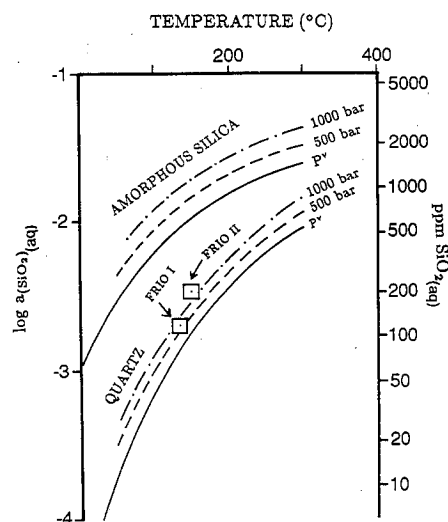


FIG. 2. Quartz and amorphous silica solubility as a function of the temperature at P_v , the vapor pressure of pure H_2O , (solid), 500 bars (dashed), and 1000 bars (dot-dashed).

k^- is the precipitation rate constant for quartz,

$$k^- = -0.707 - \frac{2598}{T}, \quad (5)$$

and A/M is the ratio of the area of the mineral surface to the mass of solution. The derivation of Eqn. (3) assumes a near-neutral solution. This criteria is met by the system of interest, with the pH of ground waters in sandstones being generally within 1 pH unit from neutral (WHITE et al., 1963). Fluids from volcanoclastic sandstones can be much more basic, on the order of 2 units above neutral.

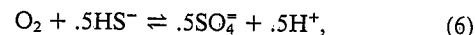
Other assumptions in the derivation of Eqn. (3) include that the solution is dilute, that there is a constant total mass in the system during the reaction, and that the total fluid pressure is below 500 bar. These conditions are probably not met by the system of interest. To account for the uncertainties in predicting the rate of quartz precipitation as a result of these inconsistencies, a "worst case" situation is applied so as to predict a maximum probable time necessary for quartz precipitation by (1) using a minimum probable ratio of the area of the mineral surface to the mass of solution, $A/M = 4.3 \text{ m}^2 \text{ kg}^{-1}$, representing a sediment composed of 4 mm spheres with a porosity of 0.26, while the actual A/M ratio would be higher for geopressed sediments which are more likely composed of assorted sizes of nonspherical grains and have porosities of less than 0.26; (2) calculating quartz precipitation at 50°C , a temperature at which the precipitation rates will be slower than the higher temperatures of the systems of interest; and (3) assuming the starting solution to be in equilibrium with amorphous silica, 0.0032 molal SiO_2 , a higher amount of silica than is probably present in supersaturated pore fluids.

Under these "worst case" conditions it would take less than 32 years to deposit the approximately 0.0028 molal of SiO_2 necessary to bring the solution to equilibrium with quartz. When compared to fluid velocities on the order of a mm a^{-1} , the time necessary for deposition of this amount of quartz is relatively short and occurs while the fluid flows less than about 32 mm. The flow of geopressed fluids is therefore slow enough to give the fluid sufficient time to maintain equilibrium with quartz through quartz precipitation.

Transport of quartz-saturated pore fluid to shallower depths as expected in geopressed sediments, therefore, results in quartz deposition in response to temperature and pressure decreases, maintaining equilibrium in solution (Fig. 2). The largest mass of authigenic quartz would be expected to deposit in the upper portions and along the margins of the geopressed zone where the velocity, and, therefore, the cumulative flow of silica-rich fluids from below, is the greatest. In addition, silica deposition would also be favored at the top of the geopressed zone where fluid pressures drop from near lithostatic to hydrostatic. This is consistent with the calculations of quartz precipitation as a result of compactive displacement of pore fluids by WALDER and NUR (1984). Their work suggests that quartz deposition heals crack, and thereby contributes to the maintenance of elevated fluid pressures during burial.

Oxidation-reduction

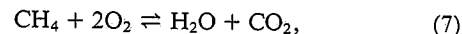
The *in situ* redox state of subsurface fluids is often predicted through equilibrium relationships between iron- and sulfur-bearing minerals and aqueous species. This permits the redox state of a ground water, as defined by the $\log a_{\text{SO}_4^{2-}} \cdot a_{\text{H}^+}^2$ and $\log a_{\text{HS}^-} \cdot a_{\text{H}^+}$ by the reaction



to be estimated from possible buffering reactions between pyrite, a common authigenic mineral, and hematite, magnetite, and pyrrhotite (Fig. 3). The presence of each of these mineral pairs represents a line on Fig. 3 which defines redox 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.

In contrast, in kerogen-rich geopressed sediments, carbon-bearing gases and organic molecules, added to solution as a consequence of kerogen maturation, may result in a redox state that is controlled by relationships between carbon species rather than that of sulfur and iron. This is because pore fluids in these sediments can have CO_2 , CH_4 , and organic carbon compounds, such as carboxylic acids (CAROTHERS and KHARAKA, 1978), present in concentrations that are several orders of magnitude greater than concentrations of sulfur and iron species. Equilibrium between CO_2 and CH_4 , and carboxylic acids, therefore, are used to predict an f_{O_2} for pore fluids under these carbon rich conditions.

Equilibrium between CO_2 and CH_4 ,



with the assumption that $f_{\text{CO}_2} = f_{\text{CH}_4}$, gives a $\log f_{\text{O}_2}$ of -56 at 100°C and 590 bars (lithostatic pressure) and -49 at 150°C and 980 bars (lithostatic pressure). Large shifts in the values of f_{CO_2} and f_{CH_4} used in predicting f_{O_2} from gas equilibria result in relatively small changes in the f_{O_2} predicted. For example a shift from $2f_{\text{CO}_2} = f_{\text{CH}_4}$ to $f_{\text{CO}_2} = 2f_{\text{CH}_4}$ results in a small shift in the predicted f_{O_2} from -56.0 to -55.7 at 100°C and 590 bars. Furthermore, the fugacities of these gases under

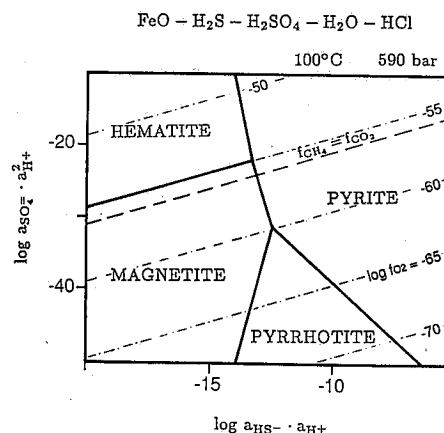
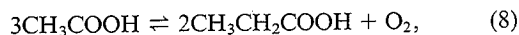


FIG. 3. Chemical equilibrium diagram for the system $\text{FeO-H}_2\text{S-H}_2\text{SO}_4\text{-H}_2\text{O-HCl}$ At 100°C and 590 bar with $\log a_{\text{Fe}^{2+}}/a_{\text{H}^+}^2$ conserved. $\log f_{\text{O}_2}$ dash-dot lines and $f_{\text{CO}_2} = f_{\text{CH}_4}$ dashed line.

saturated conditions are nearly equal with a $\log f_{\text{CO}_2} = 2.06$ and $\log f_{\text{CH}_4} = 2.10$ at 100°C and 590 bars. Thus given the possible range in actual fugacities in these fluids an assumption of equal gas fugacities to predict the f_{O_2} is probably reasonable.

Equilibria between acetic and propionic acids,

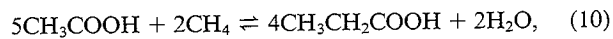


in sedimentary pore waters yield a $\log f_{\text{O}_2}$ ranging from approximately -56.2 to -57.2 at 100°C and 300 bars (SHOCK, 1988, 1989). This range in f_{O_2} predicted from carboxylic acid equilibria is in good agreement with the f_{O_2} of -56 at 100°C predicted by the assumption of CO_2 and CH_4 equilibria. The different pressures considered in calculations by these two methods of predicting f_{O_2} , 300 versus 590 bars, result in small shifts, less than a tenth of a log unit, in the predicted oxygen fugacities. For the higher temperature of 150°C, data to calculate f_{O_2} from carboxylic acid equilibria were not available to compare with the f_{O_2} calculated by the assumption of CO_2 and CH_4 equilibria with $f_{\text{CO}_2} = f_{\text{CH}_4}$.

It is possible, however, that CO_2 and CH_4 are not in equilibrium and that the near agreement between these two methods of predicting f_{O_2} discussed above is fortuitous. Assuming acetic acid and propionic acid equilibria, SHOCK (1989) calculated the f_{CO_2} ,



and f_{CH_4} ,



for sedimentary pore fluid analyses reported by CAROTHERS and KHARAKA (1978). The calculated $\log f_{\text{CO}_2}$ range from 1.6 to 2.7, and $\log f_{\text{CH}_4}$ range from 3.5 to 4.5. SHOCK (1989) concludes that these $\log f_{\text{CO}_2}$ values are reasonable, but that the calculated values of $\log f_{\text{CH}_4}$ are too large to be possible. From these data Shock infers that CO_2 is stable with respect to the organic acids, while CH_4 is metastable, and thus CH_4 is also metastable with respect to CO_2 .

Instead, these data suggest that both CO_2 and CH_4 may be metastable with respect to organic acids. Fifty percent of the samples studied by SHOCK (1989) have values of $\log f_{\text{CO}_2}$ in excess of the maximum possible $\log f_{\text{CO}_2}$ at CO_2 saturation (1.96) at the pressure and temperature of SHOCK's (1989) calculations. Some of the f_{CO_2} values calculated by SHOCK (1989) even exceed the total fluid pressure of the system, 300 bars ($\log 300 \text{ bars} = 2.47$), used in the calculations. These considerations suggest that CO_2 may also be metastable with respect to organic acids, leaving open the possibility that CO_2 and CH_4 are equilibrated. Therefore, it is assumed adequate in this study to apply gas equilibria to predict the f_{O_2} of the solution at 150°C for which carboxylic acid data were not available for comparison.

Thus, for the fluid-mineral equilibrium calculations presented in the following section the oxidation state of the solution in kerogen-rich geopressed sediments is assumed limited by CO_2 and CH_4 equilibrium under the condition that $f_{\text{CO}_2} = f_{\text{CH}_4}$. In nongeopressed or kerogen-poor sediments, f_{O_2} is assumed buffered by equilibrium between pyrite, a common authigenic mineral, and other iron and sulfide

minerals, hematite, magnetite, and pyrrhotite. Although there are uncertainties in the values of f_{O_2} calculated by these methods, shifts in the predicted values of f_{O_2} of up to a log unit result in only small shifts in the resulting equilibrium boundaries on the diagrams presented in the next section, and no changes in the relative mineralogic relationships predicted.

Silicate-carbonate-sulfate system

Equilibrium relationships between minerals in this system are examined through the use of activity diagrams constructed for the two subsystems $\text{CaO-FeO-MgO-Al}_2\text{O}_3\text{-CO}_2\text{-H}_2\text{S-H}_2\text{SO}_4\text{-SiO}_2\text{-H}_2\text{O-HCl}$ and $\text{CaO-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2\text{-H}_2\text{O-HCl}$. Through the use of these diagrams and the chemical constraints placed on the kerogen-rich geopressed system, versus those placed on the nongeopressed or kerogen-poor system, it is possible to place limits on the hydrogen ion activity ratios for Ca^{++} , Mg^{++} , Fe^{++} , and CO_3^{--} , in addition to those constraints already placed on the $\log a_{\text{SO}_4^{--}} \cdot a_{\text{H}^{++}}^2$ and $\log a_{\text{HS}^-} \cdot a_{\text{H}^{++}}$ by redox considerations and on SiO_2 by the assumption of quartz saturation. The ratios for Na^+ or K^+ would not be constrained for the system studied. However, the sodium-chloride nature of sedimentary basin fluids permits some estimate as to the relative values of these parameters.

CaO-FeO-MgO-Al₂O₃-CO₂-H₂S-H₂SO₄-SiO₂-H₂O-HCl.

To facilitate the study of this complex geologic system, equilibrium activity diagrams (GARRELS and CHRIST, 1965; HELGESON, 1969, 1970a; HELGESON et al., 1969; BOWERS et al., 1984) constructed with more than one balancing ion (JOHNSON and NORTON, 1985) are used (e.g., Fig. 4). These diagrams are constructed by writing the hydrolysis reactions for all minerals in the multicomponent system of interest. 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 (e.g., Table 1).

Equilibrium relationships among minerals in this subsystem are 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 (Fig. 5) 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 $\log a_{\text{Al}^{3+}}/a_{\text{H}^{++}}^3$ (Table 1). The a_{SiO_2} is determined by the assumption of quartz equilibrium. To consider mineral stability relationships in kerogen-rich geopressed sediments the $\log a_{\text{SO}_4^{--}} \cdot a_{\text{H}^{++}}^2$ and $\log a_{\text{HS}^-} \cdot a_{\text{H}^{++}}$ are set by equilibrium between the gases CO_2 and CH_4 (Fig. 5a), while in nongeopressed or kerogen-poor sediments the $\log a_{\text{SO}_4^{--}} \cdot a_{\text{H}^{++}}^2$ and $a_{\text{HS}^-} \cdot a_{\text{H}^{++}}$ are set by equilibrium between pyrite and hematite or magnetite (Fig. 5b), as discussed above.

These diagrams allow prediction of equilibrium-mineral assemblages by the relationships between adjacent and overlapping stability fields. All the minerals in the SUPCRT data base, which includes many possible authigenic minerals for this system, are considered in preparation of these activity diagrams. Ankerite, a common sandstone cement, is not considered in this study because thermochemical data for ankerite at elevated temperatures were not available. The

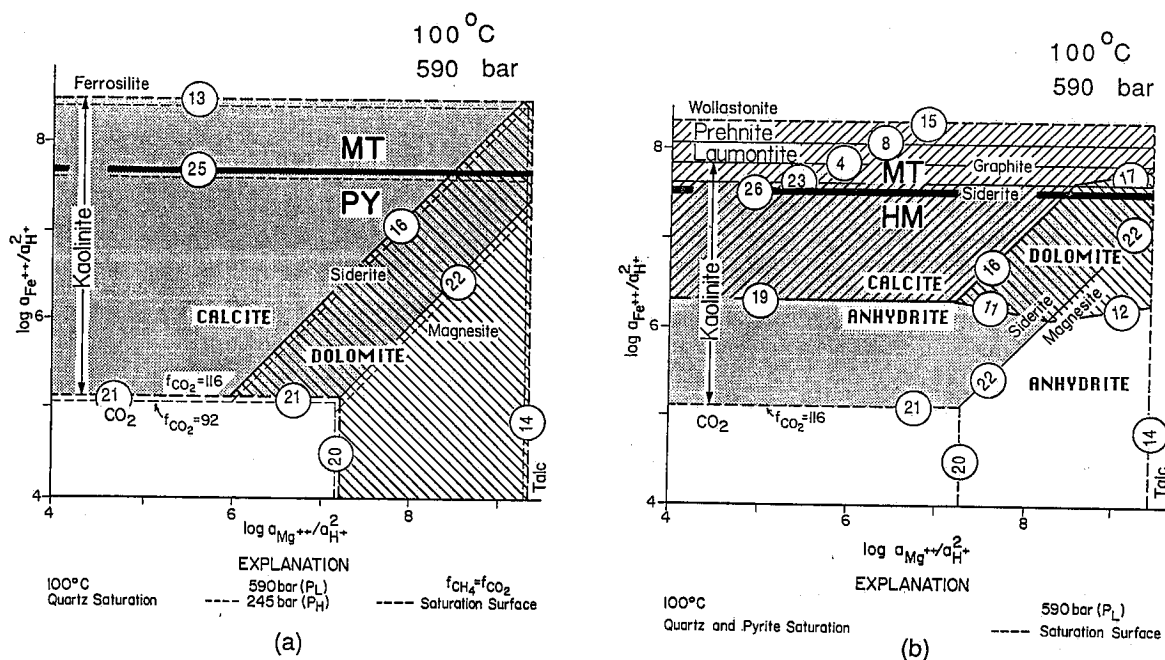


FIG. 4. Annotated chemical equilibrium diagrams in the system $CaO-FeO-MgO-Al_2O_3-CO_2-H_2S-H_2SO_4-SiO_2-H_2O-HCl$. Circled numbers correspond to the equation numbers in Table 1. (a) Kerogen-rich geopressed conditions at 100°C, lithostatic (solid lines) and hydrostatic (fine dashed lines) pressures, and $\log a_{SO_4^{2-}} \cdot a_{H^+}^2 / \log a_{HS^-} \cdot a_{H^+}$ set by the condition that $f_{CH_4} = f_{CO_2}$, and (b) nongeopressed or kerogen-poor conditions at 100°C, lithostatic pressure, and pyrite equilibrium such that pyrite-hematite or pyrite-magnetite equilibria determine the $\log a_{SO_4^{2-}} \cdot a_{H^+}^2$ and $\log \times a_{HS^-} \cdot a_{H^+}$, which vary across the figure. MT = magnetite, PY = pyrite, HM = hematite, the $\log a_{SiO_2}$ is equal to quartz saturation, and $\log a_{CO_3^{2-}} \cdot a_{H^+}^2$, $\log a_{Ca^{++}}/a_{H^+}^2$, and $\log a_{Al^{3+}}/a_{H^+}^3$ are conserved. Bold dashed lines are saturation surfaces at lithostatic pressure.

presence of minerals on these diagrams does not necessarily mean that the mineral will precipitate under the conditions considered. In addition, the presence of a stability field or saturation surface for a mineral that is never authigenic in the system of interest is necessary on the figures to place constraints on possible fluid compositions.

These diagrams were constructed for 100 and 150°C fluids in sediments having a thermal gradient of 30°C km⁻¹. Fluids at 100°C, therefore, occur at 2.5 km in the upper portion of the geopressed zone in Gulf Coast sediments, and fluids at 150°C occur at 4.2 km, well within the geopressed zone. The pressure selected for each diagram is the lithostatic pressure at the above depths, 590 bars at 2.5 km and 980 bars at 4.2 km. Fluid-pressure changes from hydrostatic to lithostatic shift the location of the equilibrium surfaces on these diagrams only slightly, as represented by the fine dashed lines on Fig. 5a. The relative locations of mineral stability surfaces change little as a result of temperature increases from 100 to 150°C for both systems, although many of the surfaces shift to lower values of $\log a_{Fe^{++}}/a_{H^+}^2$ and $\log a_{Mg^{++}}/a_{H^+}^2$ with increased temperature.

Stability relations for the kerogen-rich geopressed system (Fig. 5a) are divided into two fields, pyrite at lower $\log a_{Fe^{++}}/a_{H^+}^2$ and magnetite at higher $\log a_{Fe^{++}}/a_{H^+}^2$. As $\log a_{Fe^{++}}/a_{H^+}^2$ increases, the values of $\log a_{SO_4^{2-}} \cdot a_{H^+}^2$ and $\log a_{HS^-} \cdot a_{H^+}$ decrease in the pyrite stability field (Fig. 6a), while the ratio of $\log a_{SO_4^{2-}} \cdot a_{H^+}^2 / \log a_{HS^-} \cdot a_{H^+}$, and thus the oxidation potential of the solution, remains constant. In the

magnetite field both $\log a_{SO_4^{2-}} \cdot a_{H^+}^2$ and $\log a_{HS^-} \cdot a_{H^+}$ remain constant at -23.8 and -13.0, respectively. The $\log a_{CO_3^{2-}} \cdot a_{H^+}^2$ decreases radially across Fig. 5a from a high of -17.7 at CO_2 saturation, to a low of -20.3 at ferrosilite saturation (Fig. 6b). The position of $\log a_{CO_3^{2-}} \cdot a_{H^+}^2$ contours are shifted by the position of the siderite-magnesite stability surface. The $\log a_{Ca^{++}}/a_{H^+}^2$ 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. The kaolinite stability field fills the region between the CO_2 saturation surface and the ferrosilite and talc saturation surfaces.

Stability relations for the kerogen-poor or nongeopressed sediments are represented on the diagrams in Fig. 5b. The oxidation potential on these diagrams decreases from the bottom of the hematite field to the top of the magnetite field. In the oxidized solution the stability field for calcite and dolomite is limited by anhydrite equilibrium. In the reduced solution the stability field of siderite is limited by graphite equilibrium and the stability field for kaolinite is limited by laumontite and prehnite. The upper limit on $\log a_{Fe^{++}}/a_{H^+}^2$ is set by wollastonite saturation, rather than by ferrosilite saturation as in Fig. 5a.

In using these diagrams to predict possible authigenic mineralogies there are several limitations imposed by the limited system that these diagrams represent. Since sodium and potassium are not included in the system these diagrams

Table 1: Mineral reactions for activity diagrams.

1. $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{SiO}_2 + \text{CaCO}_3 + 3\text{H}_2\text{O} + \text{Fe}^{++} \rightleftharpoons 2\text{H}^+ + \text{FeCO}_3 + \text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$
2. $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{SiO}_2 + \text{CaMg}(\text{CO}_3)_2 + 3\text{H}_2\text{O} + 2\text{Fe}^{++} \rightleftharpoons \text{Mg}^{++} + 2\text{H}^+ + 2\text{FeCO}_3 + \text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$
3. $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{SiO}_2 + \text{CaMg}(\text{CO}_3)_2 + 3\text{H}_2\text{O} + \text{Mg}^{++} \rightleftharpoons 2\text{H}^+ + 2\text{MgCO}_3 + \text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$
4. $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{SiO}_2 + \text{CaCO}_3 + 6\text{Fe}^{++} + 8\text{H}_2\text{O} \rightleftharpoons 12\text{H}^+ + 2\text{Fe}_3\text{O}_4 + \text{C} + \text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$
5. $\text{Ca}_2\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 + \text{FeCO}_3 + \text{SiO}_2 + 2\text{H}^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}^{++} + \text{CaCO}_3 + \text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$
6. $\text{Ca}_2\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 + 2\text{FeCO}_3 + \text{SiO}_2 + 2\text{H}^+ + 2\text{H}_2\text{O} + \text{Mg}^{++} \rightleftharpoons 2\text{Fe}^{++} + \text{CaMg}(\text{CO}_3)_2 + \text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$
7. $\text{Ca}_2\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 + 2\text{MgCO}_3 + \text{SiO}_2 + 2\text{H}^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{Mg}^{++} + \text{CaMg}(\text{CO}_3)_2 + \text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$
8. $\text{Ca}_2\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 + \text{C} + 2\text{Fe}_3\text{O}_4 + 12\text{H}^+ + \text{SiO}_2 \rightleftharpoons 6\text{Fe}^{++} + 3\text{H}_2\text{O} + \text{CaCO}_3 + \text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$
9. $2\text{CaMg}(\text{CO}_3)_2 + \text{FeS}_2 + 1.75\text{SO}_4^{++} + 3\text{Fe}^{++} + \text{H}_2\text{O} \rightleftharpoons 0.25\text{H}^+ + 2\text{Mg}^{++} + 1.75\text{HS}^- + 4\text{FeCO}_3 + 2\text{CaSO}_4$
10. $2\text{CaMg}(\text{CO}_3)_2 + \text{FeS}_2 + 1.75\text{SO}_4^{++} + 2\text{Mg}^{++} + \text{H}_2\text{O} \rightleftharpoons 0.25\text{H}^+ + \text{Fe}^{++} + 1.75\text{HS}^- + 4\text{MgCO}_3 + 2\text{CaSO}_4$
11. $2\text{CaMg}(\text{CO}_3)_2 + \text{FeS}_2 + 7\text{Fe}_2\text{O}_3 + 26\text{H}^+ \rightleftharpoons 11\text{Fe}^{++} + 2\text{Mg}^{++} + 13\text{H}_2\text{O} + 2\text{CaSO}_4 + 4\text{FeCO}_3$
12. $2\text{CaMg}(\text{CO}_3)_2 + \text{FeS}_2 + 7\text{Fe}_2\text{O}_3 + 26\text{H}^+ + 2\text{Mg}^{++} \rightleftharpoons 15\text{Fe}^{++} + 13\text{H}_2\text{O} + 2\text{CaSO}_4 + 4\text{MgCO}_3$
13. $\text{FeSiO}_3 + 2\text{H}^+ \rightleftharpoons \text{Fe}^{++} + \text{SiO}_2 + \text{H}_2\text{O}$
14. $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 6\text{H}^+ \rightleftharpoons 3\text{Mg}^{++} + 4\text{SiO}_2 + 4\text{H}_2\text{O}$
15. $\text{CaSiO}_3 + \text{C} + 2\text{Fe}_3\text{O}_4 + 12\text{H}^+ \rightleftharpoons 6\text{Fe}^{++} + 6\text{H}_2\text{O} + \text{SiO}_2 + \text{CaCO}_3$
16. $\text{CaCO}_3 + \text{FeCO}_3 + \text{Mg}^{++} \rightleftharpoons \text{Fe}^{++} + \text{CaMg}(\text{CO}_3)_2$
17. $\text{CaCO}_3 + \text{C} + 2\text{Fe}_3\text{O}_4 + \text{Mg}^{++} + 10\text{H}^+ \rightleftharpoons 6\text{Fe}^{++} + 5\text{H}_2\text{O} + \text{CaMg}(\text{CO}_3)_2$
18. $2\text{CaCO}_3 + \text{FeS}_2 + 1.75\text{SO}_4^{++} + \text{Fe}^{++} + \text{H}_2\text{O} \rightleftharpoons 0.25\text{H}^+ + 1.75\text{HS}^- + 2\text{FeCO}_3 + 2\text{CaSO}_4$
19. $2\text{CaCO}_3 + \text{FeS}_2 + 7\text{Fe}_2\text{O}_3 + 26\text{H}^+ \rightleftharpoons 13\text{Fe}^{++} + 13\text{H}_2\text{O} + 2\text{FeCO}_3 + 2\text{CaSO}_4$
20. $\text{MgCO}_3 + 2\text{H}^+ \rightleftharpoons \text{Mg}^{++} + \text{H}_2\text{O} + \text{CO}_2(\text{gas})$
21. $\text{FeCO}_3 + 2\text{H}^+ \rightleftharpoons \text{Fe}^{++} + \text{H}_2\text{O} + \text{CO}_2(\text{gas})$
22. $\text{FeCO}_3 + \text{Mg}^{++} \rightleftharpoons \text{Fe}^{++} + \text{MgCO}_3$
23. $\text{FeCO}_3 + 6\text{H}_2\text{O} + 5\text{Fe}^{++} \rightleftharpoons 10\text{H}^+ + 2\text{Fe}_3\text{O}_4 + \text{C}$
24. $\text{Fe}_3\text{O}_4 + 5\text{H}^+ \rightleftharpoons 3\text{Fe}^{++} + 3\text{H}_2\text{O} + 0.5\text{O}_2$
25. $\text{Fe}_3\text{O}_4 + 2\text{FeS} + 8\text{H}^+ \rightleftharpoons 4\text{Fe}^{++} + 4\text{H}_2\text{O} + \text{FeS}_2$
26. $\text{Fe}_2\text{O}_3 + \text{Fe}^{++} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}_3\text{O}_4 + 2\text{H}^+$

do not provide information on the deposition of minerals that contain sodium or potassium, such as the possible authigenic minerals K-feldspar, muscovite, and albite. In contrast, because these diagrams are constructed for a system that includes calcium, iron, and magnesium, the presence of kaolinite is in lieu of the calcium aluminum silicate minerals, such as laumontite, and the magnesium aluminum silicate minerals, such as chlorite (clinoclhor-14A, in the SUPCRT data base). Thus the kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, field may also represent a Na-K aluminum silicate, while precluding equilibrium with a Ca-Mg-Fe aluminum silicate.

Ankerite, a Ca-Mg-Fe carbonate and common sandstone cement, is not considered on these diagrams because of the lack of thermochemical data, but if it were considered it may replace a portion of the calcite-siderite-magnesite-dolomite stability fields. Thus in the discussion, reference is generally made to equilibrium with a carbonate mineral, rather than to the specific carbonate mineral or suite of carbonate minerals that could be in equilibrium. Lastly the coexistence of mineral phases on these diagrams only indicates that they may occur together in equilibrium; however, it does not in-

dicate that these minerals are all in equilibrium or would all precipitate from a solution together. Changes in fluid composition, temperature, or pressure could result in a shift in equilibrium such that one or more of the minerals may precipitate from the solution.

Equilibrium conditions present in fluids from kerogen-rich geopressed sediments would be represented by the region near the CO_2 saturation surface on Fig. 5a, where a Ca-Fe-Mg-poor aluminum silicate mineral, such as kaolinite, a carbonate, pyrite, and quartz are in equilibrium. In contrast in nongeopressed or kerogen-poor sediments under CO_2 poor and reduced conditions, as represented by the top portion of the diagrams in Fig. 5b, equilibrium with the Ca-aluminum silicate, laumontite, is possible along with calcite-graphite-magnetite-pyrite-quartz. This reduced and CO_2 -poor condition might occur either in the absence or presence of CH_4 , such that it may represent fluids that have gained CH_4 from kerogen decomposition but at temperatures other than the range over which CO_2 enrichment would occur.

In nongeopressed or kerogen-rich sediments under CO_2 -rich and oxidized conditions, as represented by the bottom

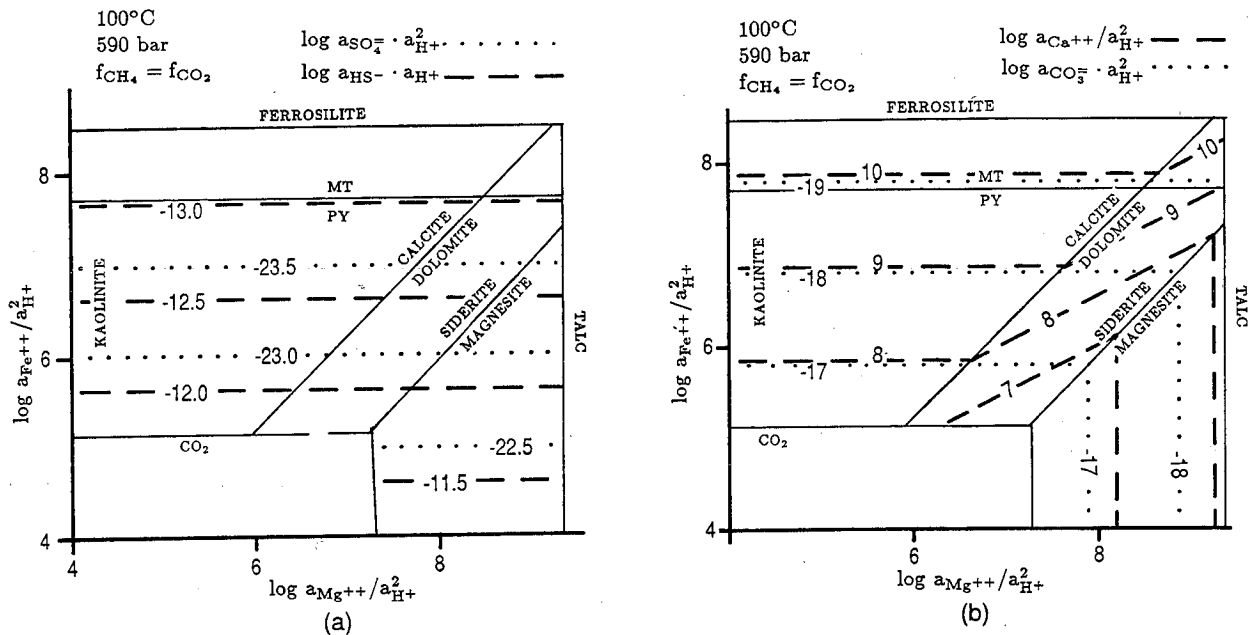


FIG. 6. Contours of (a) $\log a_{\text{SO}_4^{2-}} \cdot a_{\text{H}^+}^2$ (dot-dashed) and $\log a_{\text{HS}^-} \cdot a_{\text{H}^+}$ (dotted), and (b) $\log a_{\text{CO}_3^{2-}} \cdot a_{\text{H}^+}^2$ (dot-dashed) and $\log a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$ (dotted) at 100°C and 590 bar. Mineral stability surfaces for the kerogen-rich geopressed system (solid) are from Fig. 5a.

$\text{CaO-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2\text{-H}_2\text{O-HCl}$. This system, which includes sodium, permits further evaluation of the composition of the authigenic aluminum silicates under the conditions studied. Equilibrium relationships among minerals at lithostatic pressures 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 Fig. 7. The paragonite field on these diagrams represents the sodium end member, $\text{NaAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$, of solid solution for illite-

sericite clays (AAGAARD and HELGESON, 1983). Muscovite represents the potassium end member in this solid solution. The actual composition of the illite-sericite clays would determine the activity of the end member component and thereby the size of the "paragonite" stability field.

From the relationships on these diagrams (Fig. 7) it is apparent that kaolinite is more stable than laumontite, paragonite(illite), or albite in a more acid solution. In addition,

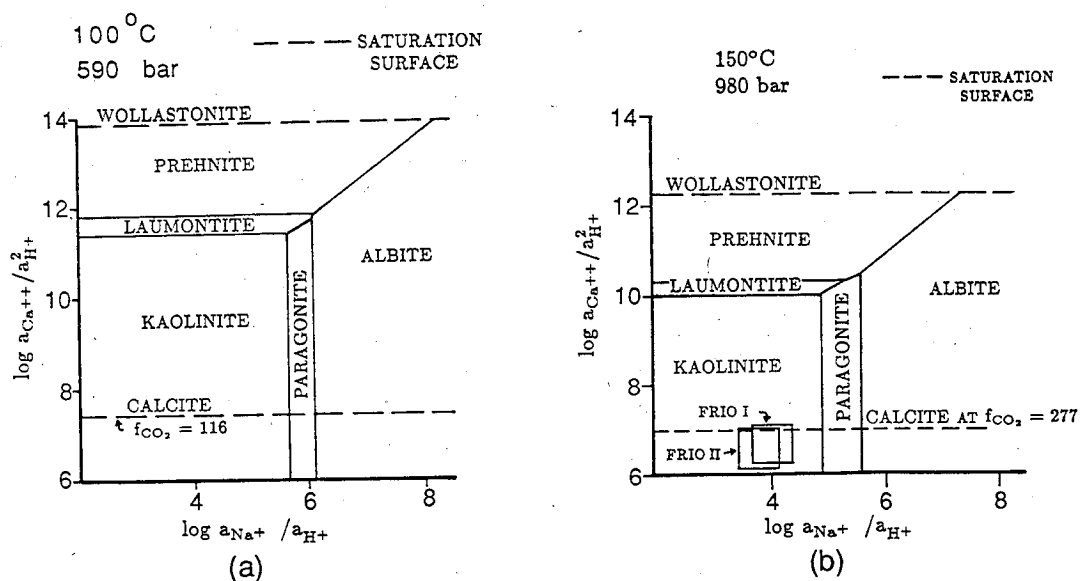


FIG. 7. Chemical equilibrium diagrams in the system $\text{CaO-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2\text{-H}_2\text{O-HCl}$ at 590 bar and 100°C and 590 bar and 150°C. Calcite saturation surface is for f_{CO_2} at CO_2 saturation. In construction of this figure $\log a_{\text{Al}^{3+}}/a_{\text{H}^+}^3$ is conserved and $\log a_{\text{SiO}_2}$ is set at quartz saturation. Dashed lines are saturation surfaces.

laumontite stability increases in a solution rich in Ca^{++} , and paragonite(illite) 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 it lowers the stability field of both paragonite(illite) and albite by 1 log unit of $\log a_{\text{Na}^{+}}/a_{\text{H}^{+}}$. A shift from lithostatic to hydrostatic pressure shifts the equilibrium surfaces on Fig. 7 less than two tenths of a log unit.

The calcite saturation surface is also drawn on Fig. 7. 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 Fig. 7 indicate that calcite equilibrium limits the $\log a_{\text{Ca}^{++}}/a_{\text{H}^{+}}^2$ well below laumontite equilibrium in a solution either saturated with CO_2 , or near CO_2 saturation. Furthermore, these equilibrium relationships indicate that kaolinite-calcite could deposit from an acidic, high f_{CO_2} pore fluid and that paragonite(illite)-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 geopressured sediments provide the mechanisms for feldspar dissolution and kaolinite-carbonate deposition followed by illite-carbonate and albite-carbonate deposition. The majority of CO_2 released during kerogen maturation is generated at approximately 100°C, with the highest temperature of release at approximately 135°C (HUNT, 1979). CO_2 dissolves in the geopressured pore fluids, resulting in a shift in aqueous carbonate complexing, which releases hydrogen ions and acidifies the pore fluid [Eqn. (2)]. Reaction of a pore fluid with a large $a_{\text{H}^{+}}$ (acid), and small $a_{\text{K}^{+}}$, $a_{\text{Na}^{+}}$ and $a_{\text{Ca}^{++}}$, with the sediments may cause dissolution 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 et al., 1984; FRANKS and FORESTER, 1984).

Detrital and authigenic carbonate minerals are not in all cases dissolved by this pore fluid with a large $a_{\text{H}^{+}}$ (acid) and small $a_{\text{Ca}^{++}}$ because its high a_{CO_3} maintains the solution near or in equilibrium with carbonate minerals. This mechanism is suggested by SIEBERT et al. (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 with continued burial of the sediments, continued feldspar dissolution decreases the $a_{\text{H}^{+}}$. This decrease in $a_{\text{H}^{+}}$, along with the continued increase in $a_{\text{K}^{+}}$, $a_{\text{Na}^{+}}$, and $a_{\text{Ca}^{++}}$ from feldspar dissolution, shifts the fluid equilibrium from kaolinite, through the narrow paragonite(illite) stability field, and ultimately on to albite equilibrium as the sediments are buried.

Reaction path calculations (HELGESON et al., 1969) completed by HELGESON (1970b) and SVERJENSKY (1984) predict similar effects for the reaction of acid 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 increased $a_{\text{Na}^{+}}$, $a_{\text{K}^{+}}$, and a_{SiO_2} , and a decreased $a_{\text{H}^{+}}$. The relative change in the $a_{\text{H}^{+}}$ is much greater than the change in the cation concentrations. The decrease in the $a_{\text{H}^{+}}$, therefore, results in large increases in the $\log a_{\text{Na}^{+}}/a_{\text{H}^{+}}$, $\log a_{\text{K}^{+}}/a_{\text{H}^{+}}$, and $\log a_{\text{Ca}^{++}}/a_{\text{H}^{+}}^2$ of the solution. SVERJENSKY's (1984) reaction path calculation indicates 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 final equilibration with albite.

Predicted authigenic mineral assemblages

There are three distinct environments of alteration in kerogen-rich geopressured sediments. (1) Quartz deposition should occur as a result of the upward flow of fluids and temperature and pressure decreases. The largest proportion of quartz deposition should occur at the top and margins of the geopressured sediments where the flux of compaction-driven flow is greatest, and should decrease with increased depth as fluid velocities decrease. This quartz deposition occurs independently of the kerogen content of the fluid and therefore represents geopressured conditions with or without the presence of kerogen. (2) Carbonate minerals could deposit above the zone of CO_2 release from kerogen decomposition as a result of the upward flow of fluids either saturated or nearly 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 occur in the zone of CO_2 generation. CO_2 dissolves in pore fluids, producing an acid solution that reacts with the sandstone. With continued burial after CO_2 generation by kerogen, degradation ceases; continued dissolution of feldspars by these acid solutions can increase the solution pH. The solution subsequently equilibrates with K-feldspar, and continued dissolution of primary Ca-Na plagioclase shifts the solution equilibrium toward illite and ultimately albite, resulting in illite-carbonate and albite-carbonate deposition.

In contrast, alteration minerals that should not deposit from pore fluid in kerogen-rich geopressured sediments include laumontite and anhydrite (Fig. 5a). Despite the continued addition of calcium to solution during feldspar dissolution, the high f_{CO_2} of the solution causes calcite equilibrium to limit the $\log a_{\text{Ca}^{++}}/a_{\text{H}^{+}}^2$ to below that necessary for laumontite equilibrium and precipitation (Fig. 7). Because of high CH_4 in these fluids, they remain too reduced to permit anhydrite precipitation. These minerals, however, could deposit from pore fluids within kerogen-poor geopressured sediments (Fig. 5b). They could also deposit from pore fluids within kerogen-rich nongeopressured sediments in which CO_2 and CH_4 from kerogen maturation do not accumulate in the pore fluids.

FRIO FORMATION

The above predictions are typical of observed relationships in the Frio Formation of the Texas Gulf Coast. The Frio Formation was chosen for comparison because it is geopressured (BEBOUT et al., 1978), contains approximately 0.5% kerogen (GALLOWAY et al., 1982), and its 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 et al., 1984). Rock fragments in the Frio sandstones are predominantly volcanic and compose from 10 to 50% of the rock. Alteration in the Frio sandstone, as described by LOUCKS et al. (1984), FRANKS and FORESTER (1984), LAND (1984), KAISER (1984), LAND et al. (1987), and MILLIKEN (1989), is dominated by the deposition of quartz, calcite, kaolinite, and albite.

Quartz

Authigenic quartz in the Frio sandstone rarely occurs above 2.5 km (MILLIKEN et al., 1981; LAND, 1984). Below 2.5 km, authigenic quartz in the Frio Formation averages 2.5 vol% of the rock (LAND, 1984). An increase in the degree of quartz cementation corresponds approximately with the top of the present-day geopressured zone in the Frio and to a lesser extent with the top of the geopressured zone in the Wilcox formation, which lies stratigraphically below the Frio (LAND and FISHER, 1987).

The $\delta^{18}\text{O}$ of quartz cement from the Frio Formation averages $+31\text{‰} \pm 1.5\text{‰}$ at all depths analyzed (LAND, 1984). LAND (1984) suggests that, since pore water more positive than a $\delta^{18}\text{O}$ of $+8\text{‰}$ is unknown and unlikely to predominate in Tertiary Gulf Coast sediments, precipitation of quartz with this isotopic signature must have occurred at a temperature below 100°C . In addition, the rarity of quartz overgrowths at depths less than 2.5 km makes precipitation from descending meteoric ground water unlikely (LAND, 1984). LAND (1984) concludes that the data from the Frio Formation is consistent with the precipitation of authigenic quartz at approximately 60°C from ascending water having a $\delta^{18}\text{O}$ of about $+4$ to $+5\text{‰}$. This estimated range in $\delta^{18}\text{O}$ for geopressured pore fluids is reasonable compared to the $\delta^{18}\text{O}$ measured in the Frio fluid sampled from the Pleasant Bayou well of $+4.9$ and $+5.4\text{‰}$ (Table 2).

These data, however, do not preclude the deposition of some quartz at higher temperatures and thus greater depths within the geopressured 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.

Thus the petrographic and isotopic data on quartz precipitation support the prediction that quartz will deposit from geopressured fluids moving upward to regions of lower temperature and pressure. These data are also consistent with the prediction that the largest mass of authigenic quartz will precipitate in the upper portions of the geopressured system

Table 2: Analyses of liquid samples from Pleasant Bayou No. 2 well.

	I*	II*		I*	II*
Depth (m)	4462	4740	SiO ₂	120	200
Temperature ($^\circ\text{C}$)	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	38,000	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 Kharaka et al. (1980). 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.

where fluid fluxes and pressure gradients (from lithostatic to hydrostatic) are the largest.

Calcite

Carbonate cement in the Frio Formation is predominantly calcite with less than 10% dolomite and composes an average of 5.3% of the rock (LAND, 1984). The $\delta^{18}\text{O}$ and trace-element composition of the carbonate cements are uniform with depth which suggests 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 (LAND, 1984). In a review of calcite emplacement in Cenozoic sandstones (which include the Frio and Wilcox), LAND et al. (1987) find (1) that calcite was generally emplaced relatively early during burial and prior to the migration of liquid hydrocarbons, (2) that most carbonate cements are subsurface phases rather than surficial soil or shallow ground-water phases, and (3) that, although very shallow sandstones may lack carbonate cements, there seems to be no relationship between the degree of carbonate cementation and the position (past or present) of the top of geopressing in any unit. LINDQUIST (1977) found petrographic evidence that calcite cementation in all cases preceded the development of secondary porosity. In contrast, LOUCKS et al. (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.

Thus, with carbonate cement being sparser in shallower sediments, and with its emplacement preceding both the development of secondary porosity and the migration of liquid

petroleum, it is possible that carbonate cement deposits from CO₂-rich fluids above the zone of CO₂ release during kerogen maturation. In addition, the description of carbonate deposition occurring during and after the development of secondary porosity by LOUCKS et al. (1984) would support the deposition of carbonate minerals as a consequence of calcite saturation of the CO₂-rich fluids during feldspar dissolution and secondary porosity development.

Carbon isotopic values for carbonate cements from both the Frio and underlying Wilcox formations have values between -2 and -6‰ for samples below approximately 3.5 km, and between -3 and -14‰ for samples above approximately 3.5 km (LAND and FISHER, 1987). Temperatures at 3.5 km would be approximately 135°C, the upper range on the temperature of CO₂ release from kerogen. The wider range in carbon isotopes for carbonates deposited above the zone of CO₂ release suggests a wider range in the carbon isotopic composition of fluids contributing to the deposition of these carbonate cements. LAND and FISHER (1987) suggest that ¹³C-depleted methane (-46‰) released from kerogen (-26‰) could result in isotopically lighter pore fluids and thereby in the wider range in carbon isotopes found in these shallower cements. Carbon gas separation from these pore fluids might also result in a wider range in carbon isotopes. Thus these isotope data, in addition to the petrographic data, are consistent with carbonate cements being deposited from the gas-rich fluids above the zone of CO₂ release.

Silicates

A zone of secondary porosity has developed in the Frio sandstone at approximately 3.4 km (LOUCKS et al., 1984). This secondary porosity is caused by dissolution of primary K-feldspar, Na-Ca feldspar, volcanic rock fragments and, in some locations, calcite. The association of this zone of secondary porosity development with hydrocarbon maturation and the production of CO₂ has been well established (e.g., SIEBERT et al., 1984; FRANKS and FORESTER, 1984). Kaolinite deposition, albitization, and smectite/illite transition have all been associated with the development of this zone.

MILLIKEN et al. (1981) describe the alteration in this zone of secondary porosity from core collected from a single "hydrocarbon field" in Brazoria County, Texas. They found that there are three diagenetic zones. The shallowest zone, which occurs above the zone of secondary porosity, includes quartz and carbonate precipitation. Deposition in this zone is consistent with that described in the sections above. The central zone includes the zone of secondary porosity development. Within this zone kaolinite precipitation occurs mainly in the upper portion where leaching, and thus secondary porosity development, was the most intense. Smectite/illite transition and albitization reach maximums deeper in this zone where leaching is less intense. Carbonate precipitation continues throughout this central zone. In the third and lowermost diagenetic zone secondary porosity development is diminished, and the smectite/illite transition and albitization are nearly complete, while carbonate precipitation continues.

This localized study by MILLIKEN et al. (1981) is of particular interest because the field studied is known to be geopressured, in contrast to the more regional studies that include

the entire Gulf Coast and thus portions of the Frio that are not geopressured. Regional studies of alteration in the Frio Formation (e.g., LAND, 1984; LOUCKS et al., 1984; LAND and FISHER, 1987; LAND et al., 1987; MILLIKEN, 1989), however, generally describe alteration similar to that described by MILLIKEN et al. (1981).

In these more regional studies, carbonate cement associated with kaolinite in the zone of secondary porosity was found to be composed of iron-rich dolomite and ankerite, in addition to calcite (LOUCKS et al., 1984). Isotopic data suggest that kaolinite in the Frio was deposited at temperatures between approximately 100 to 140°C (LAND, 1984). Throughout the Frio, albitization was found to generally precede to completion at a depth slightly greater than the depth at which K-feldspar removal appears completely (LAND et al., 1987). Comparison of alteration in the Frio sandstone with that in the geopressured Wilcox indicates that this relationship between albitization and feldspar removal is similar in both units, but occur approximately 500 m deeper in the Frio (LAND and FISHER, 1987). The isotopic compositions of Frio and Wilcox authigenic albite are similar suggesting that both formations approached similar conditions of temperature and δ¹⁸O water at the time of albitization (LAND, 1984).

These observed alteration assemblages compare well with the predictions of this study that (1) kaolinite-carbonate will deposit in the zone of maximum secondary porosity development and CO₂ release, and (2) illite-carbonate and albite-carbonate will deposit in deeper zones of decreasing secondary porosity and limited CO₂ release. The presence of either calcite or Fe or Mg-rich carbonates in these zones is also consistent with the relationships on Fig. 5a. Pyrite or quartz are not described as precipitates in this zone, but are stable in the region of concern on Fig. 5a, while quartz is stable on Fig. 7. This is not a problem, as they are only used to limit fluid composition. As stated above, the presence of their overlapping fields does not necessarily indicate that they will precipitate.

Also as predicted, minerals such as laumontite and anhydrite are not present in significant amounts in the geopressured Frio or Wilcox. MILLIKEN (1989) indicates that some authigenic K-feldspar and laumontite occur in the Frio but that they are not volumetrically significant. The minor presence of these phases is not inconsistent with the thermochemical prediction since the Frio does not develop geopressing in all areas of the Gulf Coast. K-feldspar precipitation is not predicted or excluded by the above analysis because potassium was not considered in the systems studied. Geopressured fluids commonly contain two orders of magnitude more sodium than potassium (e.g., MORTON and LAND, 1987). The preference for deposition of Na-feldspar over K-feldspar thus may be a result of the high concentrations of sodium relative to potassium.

Fluid composition

Numerous chemical analyses are available for fluids from the Frio Formation (cf. MORTON and LAND, 1987). However, only two of these analyses, reported by KHARAKA et al. (1980), include the compositions of both the gas and liquid fractions and calculations of the subsurface pH. These two analyses

(Tables 2 and 3) are used in this study to calculate subsurface fluid-mineral equilibria for present day fluids for comparison with the predictions made above. These samples are collected from 4462 m at 138°C and from 4740 m at 150°C within the Frio sandstone from the Pleasant Bayou No. 2 well, Brazoria County, Texas. The subsurface collection pressures of 787 bar at 4450 m, and 843 bar at 4740 m, approach lithostatic pressures. 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 by Kharaka et al. (1980) for both these fluid samples. There are many potential errors in making these calculations and in collecting and analyzing for the gases lost from solution. Thus the calculated pH is at best within a few tenths of the actual subsurface pH. KHARAKA et al. (1980) also calculate that these subsurface fluids are saturated with respect to CH₄, but they did not address CO₂ saturation or solubility.

The 138 and 150°C subsurface temperatures of these fluids place them stratigraphically below the zone of CO₂ release. The depths in which those samples were collected, 4.46 and 4.74 km, are also below the depth of 4.27 km in which LAND and MILLIKEN (1981) find that few K-feldspars are preserved and all intermediate plagioclase has been albitized or dissolved in core from the Pleasant Bayou well. Thus these fluids are collected from below zone three of MILLIKEN et al. (1981).

Despite these fluids being collected from below the depths of interest in this study, two properties of these fluids support the above predictions: (1) the log a_{SiO_2} in these Frio fluid samples plotted on Fig. 2 shows both samples to be very near equilibrium with quartz at the subsurface temperatures and pressures, and (2) the shallower sample, which at 138°C is closer to the zone of CO₂ release, contains twice as much CO₂ as the deeper sample, which at 150°C is buried well below the zone of CO₂ release (Table 3).

These fluids plot in the kaolinite stability field on Fig. 7 suggesting that, below the zone of albitization and secondary porosity development, fluid equilibrium is shifted away from albite. The concentration of aluminum in these fluid samples is not provided by KHARAKA et al. (1980). Therefore, it is not possible to determine which if any aluminum silicate

minerals these fluids are in equilibrium with. Thus the placement of these fluid samples in the kaolinite saturation surface on Fig. 7 does not necessarily indicate that kaolinite is in equilibrium with the fluid or would be precipitated as an authigenic phase. As neither kaolinite or albite are described as authigenic phases at the depth of these fluids samples, their equilibration cannot be inferred.

CONCLUSIONS

Chemical and hydrologic conditions present within kerogen-rich geopressed sediments during diagenesis may differ significantly from those present within nongeopressed or kerogen-poor sediments. In geopressed sediments compaction-driven flow dominates such that fluids are transported upward to regions of lower temperature and pressure. Compaction-driven flow also results in relatively low flow rates (on the order of a millimeter per year or less) with the greatest flux of fluid in the upper portions and margins of the geopressed sediments. In contrast, flow in nongeopressed sediments is generally gravity driven and can be faster (on the order of meters per year) than flow in geopressed sediments.

Kerogen present within geopressed sediments decomposes, releasing CO₂ and lesser CH₄ between approximately 100 and 135°C, temperatures generally present in the upper portions of the geopressed zone. The opposing rates of sediment subsidence and upward fluid flow in geopressed sediments permit fluids to become greatly enriched in CO₂ and CH₄, possibly to the point of saturation. 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 nongeopressed sediments the generally higher fluid velocities can act to flush the gases from the sediments rather than concentrating them. In kerogen-poor geopressed sediments, pore fluids may lack a source of CO₂ and CH₄ and, therefore, may not become enriched in these gases.

The importance of this gas enrichment to the prediction of alteration-mineral assemblages is a product of the relatively low solubility of CO₂, and to a lesser extent that of CH₄, at the temperatures and pressures commonly present in the upper portions of the geopressed section. Because of these low solubilities, saturation limits of these gases can be used to place limits on the subsurface fluid composition and alteration-mineral assemblages.

The chemical and hydrologic conditions present during diagenesis of kerogen-rich geopressed sediments could produce alteration-mineral assemblages having both distinctive mineralogies and depositional patterns. Authigenic quartz deposition should occur at the top of the geopressed zone and decrease rapidly in occurrence with increased depth as a result of the decreased flux of upward fluid flow with increased depth. Carbonate minerals should deposit above the zone of CO₂ generation, in part from the upward flux of CO₂-saturated fluids and the subsequent decreases in fluid temperature and pressure and CO₂ solubility. Feldspar dissolution and kaolinite-carbonate deposition would occur within and above the zone of maximum CO₂ generation, while illite-carbonate and albite-carbonate precipitation would occur

Table 3: Analyses of gas samples from Pleasant Bayou No. 2 well.

	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 Kharaka et al. (1980). Units mole % unless otherwise noted.

b) Units m³gas/m³water.

c) nd = analysis not available.

within and below the zone of CO₂ generation. These predictions are in part borne out by observation of 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 geopressed sediments or nongeopressed sediments. The minerals laumontite and anhydrite could deposit from pore fluids in these sediments but should not deposit from fluid in kerogen-rich geopressed sediments.

The diagenetic history of mature sedimentary basins is complex with the sediments undergoing diverse chemical conditions. The predicted mineralogic relationships presented in this text, therefore, should prove useful in reconstructing geologic conditions in older basins and ultimately in assisting in the prediction of petroleum formation, migration, and entrapment.

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