Organic-Inorganic Reactions during Progressive Burial: Key to Porosity and Permeability Enhancement and Preservation [and Discussion]

R. C. Surdam, Laura J. Crossey, G. Eglinton, B. Durand, J. D. Pigott, R. Raiswell and R. A. Berner

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Organic–inorganic reactions during progressive burial: key to porosity and permeability enhancement and preservation

By R. C. Surdam and Laura J. Crossey
Department of Geology and Geophysics, University of Wyoming, Laramie, Wyoming 82071, *U.S.A.*

[Plate 1]

The development of porosity and permeability enhancement and preservation or both in many sandstones is a function of aluminosilicate or carbonate mineral stability. The dissolution of aluminosilicate minerals and subsequent porosity and permeability enhancement is a problem of aluminium mobility. Our experimental data demonstrate that it is possible to increase the mobility of aluminium significantly and to transport it as an organic complex in organic acid solutions. These organic acids, primarily carboxylic and phenolic acids, also have the ability to dissolve carbonate grains and cements.

W. W. Carothers & Y. K. Kharaka (*Geochim. cosmochim. Acta* **44**, 323–332 (1980)) have shown that concentrations of carboxylic acid anions range up to $5000/10^6$ (by mass) over a temperature range of 80–100 °C in some oil-field formation waters. Our experiments show that acetic acid solutions at the same concentration and over the same temperature range can increase the solubility of aluminium by one order of magnitude, whereas oxalic acid solutions increase the solubility by three orders of magnitude. Phenols such as hydroquinone and catechol are almost as effective as oxalate. The textural relations observed in the experiments are identical to those in sandstones containing porosity enhancement as a result of aluminosilicate dissolution.

A natural consequence of the burial of sedimentary prisms is the maturation of organic material. Nuclear magnetic resonance (n.m.r.) studies have shown that carbonyl and phenol groups are removed from the kerogen molecule before the generation of hydrocarbons. Thermal degradation or the action of mineral oxidants, or both (the reduction of Fe^{3+} released from clay diagenesis and the reduction of polysulphides are two examples) may be the mechanisms by which the peripheral groups containing the phenols and carboxylic acids are released from the kerogen molecule. The experiments suggest that the enhancement of porosity in a sandstone as the result of aluminosilicate or carbonate dissolution is the natural consequence of the interaction of organic and inorganic reactions during progressive diagenesis. Because of the time and temperature dependence of these reactions, the actual reaction sequences will be sensitive to the thermal and stratigraphic history of the source reservoir sediments.

INTRODUCTION

Other workers have examined separately the inorganic (Boles & Franks 1979) and organic (Curtis 1978) relations between shales and sandstones. However, little attention has been given to the organic–inorganic reactive interaction between shales and associated sandstones. This paper evaluates the potential for reactions between organic and inorganic phases in a sedimentary prism undergoing progressive burial. In particular, we focus on the temperature interval between 80 and 200 °C, which is considered here to include both the boundary between diagenesis and catagenesis of the organic constituents in the source rocks and the zone of porosity enhancement in the sandstones (though many workers define 50 °C as the catagenesis–diagenesis boundary). This paper examines the reaction processes linking source and reservoir rocks, in particular those having the potential for transfer and redistribution of material in the subsurface. Finally, we offer a conceptual model for the reaction pathways of a sand–shale package in an aqueous environment undergoing progressive diagenesis.

Structure of kerogen

The structure of kerogen is a key element in the evaluation of potential organic–inorganic reactions during the progressive burial of sediments. Other workers have described the processes characterizing the early diagenesis (0–300 m burial) of organic material (this symposium). Similarly, much is known about the maturation of kerogen to hydrocarbons (see, for example, Tissot & Welte 1978; Hunt 1979; this symposium). In contrast, little is known about the processes characterizing the reactive history of kerogen between early diagenesis (i.e. within 300 m of the surface) and the entrance to the liquid hydrocarbon window. To fill this gap, it is imperative to have in mind a general structural image of kerogen. A detailed structural determination of kerogen is not available; however, a simple general model of kerogen will suffice for the purposes of this paper.

It should be noted that the composition of kerogen varies greatly and so significant variations in the structure of kerogen are to be expected. Typically, kerogens are classified on the basis of H:C and O:C atomic ratios and into three and sometimes four types according to these ratios (see figure 1 and also Durand (this symposium); Tissot & Welte 1978; Hunt 1979). As previously noted, each of the three significant types of kerogen differ chemically and probably structurally, but for our purposes the details of these differences are not as important as the gross structure of kerogen. Several types of data yield insights into the general structure of kerogen.

Oxidative degradation

Much of what is known about kerogen structure has come from a variety of chemical techniques (Vitorovic 1980). One of the most informative methods has been the carbon-balance permanganate oxidative-degradation technique. In this technique the kerogen is subjected to stepwise oxidation at a constant temperature in an aqueous solution; at each oxidation step the products are analysed. In brief, the kerogen is progressively degraded and the kerogen structure is interpreted by reconstructing the reaction products. Table 1 presents the type and amount of each product obtained from several kerogen types. Large variations in the amount of oxidation products are observed, but the type of products remain relatively constant. The variations are presumably related to differences in the kerogen structures and compositions.

Table 1. Oxidation results

formation	oxalate[a]/10^6	acetate[a]/10^6	propionate[a]/10^6	formate[a]/10^6
Green River	191	43	393	173
Monterey	144	34	283	254
Woodford	203	29	276	369
Australian brown coal	12000	1850	1640	1176

[a] Fluid:solid ratio is equal to 100:1.

Note in table 2 that up to 60% of the oxidation products are in the form of carboxylic acids (both mono- and difunctional forms).

One model of the kerogen molecule that emerges from these studies is that of a kerogen core surrounded by unsaturated fatty acid, unbranched monocarboxylic acid, isoprenoid hydrocarbon, aliphatic hydrocarbon and dicarboxylic acid (Vitorovic 1980). In brief, mono- and difunctional carboxylic acids are bonded peripherally to the core of the molecule. Because these short chains are attached by only one bond, they are likely to be broken in early stages of thermal cracking.

Table 2. Organic acid production with the use of oxidation techniques

formation	difunctional carboxylic acid	monofunctional carboxylic acid	carboxylic acid
	percentage of organic carbon as:		
Green River	7	33	40
Monterey	8	47	55
Woodford	11	47	58
Australian brown coal	41	23	64

Oxidative degradation of kerogen involves pervasive oxidation in which no hydrocarbons are produced; in the natural system oxidative potential will be limited by the availability of mineral oxidants. As a result of oxidation some chemical changes may be induced in the peripheral functional groups during the experiment. The amount of chemical alteration is difficult to evaluate, but the fact that oxygen-containing functional groups (such as carboxylic acids) occupy many of the peripheral positions in the kerogen structure is supported by van Krevelen diagrams showing the compositional evolutionary paths of kerogen during maturation (figure 1).

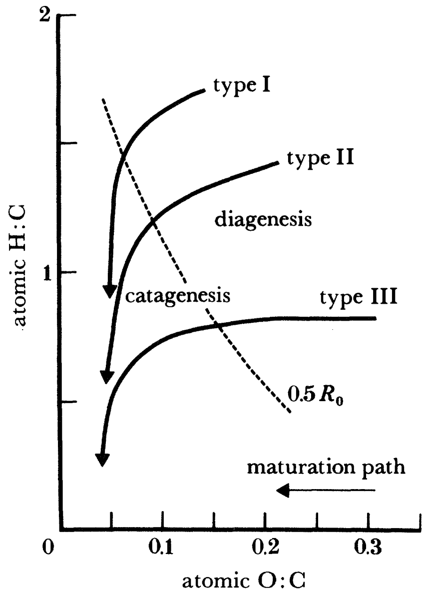

Figure 1. Van Krevelen diagram showing typical reaction pathways for type I, II and III kerogens during diagenesis and catagenesis.

Van Krevelen diagrams

The behaviour of various kerogen types during diagenesis and before catagenesis indicates that oxygen-containing functional groups are among the first to be cleaved from the kerogen core (figure 1). This is true regardless of kerogen type; initially the O:C ratio changes much more dramatically than the H:C ratio. Thus, the maturation path of natural kerogens supports the conclusions from oxidation experiments that the peripheral groups are mainly oxygen-containing functional groups (such as carboxylic acid). The detailed description of the chemical species and amounts of available organic acid groups awaits further documentation.

Thermal degradation

Thermal degradation experiments also support the general model of cleaving carboxylic acid groups during diagenesis of kerogen (Surdam *et al.* 1984). However, few aqueous pyrolysis experiments have been reported. Fortunately this type of work is now being done (Lewan, this symposium). In those aqueous pyrolysis experiments that have been reported both monofunctional and difunctional carboxylic acids have been reported as low-temperature reaction products (Surdam *et al.* 1984).

Nuclear magnetic resonance

The technique of solid nuclear magnetic resonance provides a new way to evaluate the structure of kerogen (Miknis 1982). This technique yields structural information for kerogen by direct analysis (see figure 2). Although the technique is now just being used in the evaluation of carbon bonding it has already resulted in important insights (Miknis 1982). For example, figure 2 shows that kerogen contains not only the expected aliphatic and aromatic functional groups, but also significant amounts of phenolic and carbonylic functional groups. These latter two functional groups have the potential to produce a variety of carboxylic acids and phenols as they are cleaved from the kerogen core. Figure 3 shows the progressive changes in composition and structure during burial of kerogen of a similar type from close to the surface into the liquid hydrocarbon window. Obviously the carbonyls and phenols are cleaved from the kerogen before it enters the liquid hydrocarbon window (figure 3). Thus, there is the potential

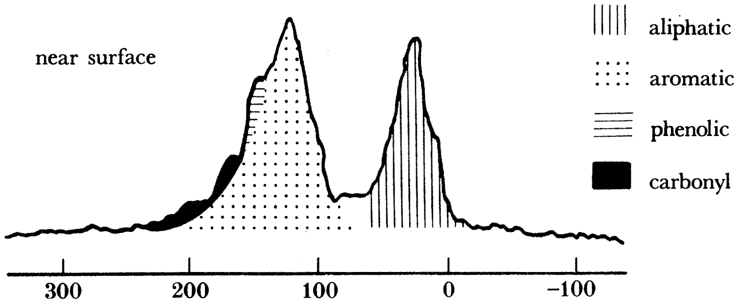

FIGURE 2. Schematic n.m.r. trace from immature type III kerogen showing aliphatic, aromatic, phenolic and carbonylic fractions. (64 % carbon; aliphatic fraction 0.37).

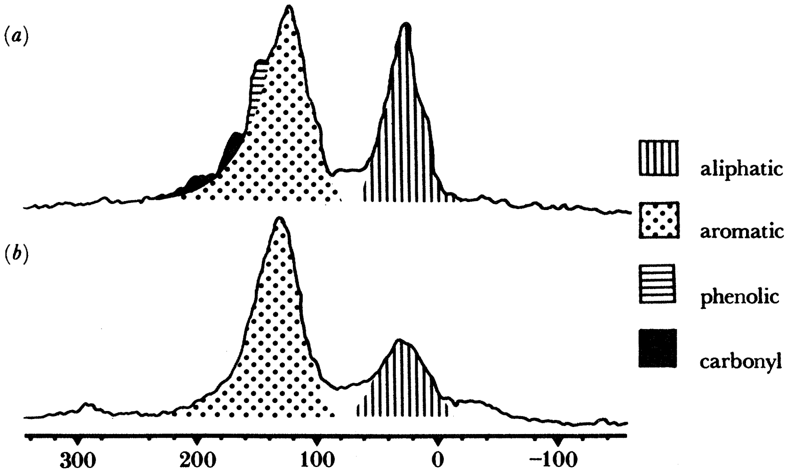

FIGURE 3. Diagram showing the successive changes in kerogen with depth from one lithologic unit sampled at both shallow and deep intervals. (*a*) Near surface; 64% carbon, aliphatic fraction 0.37. (*b*) Depth of 2756 m; 65% carbon, aliphatic fraction 0.22.

to generate significant amounts of organic solvents just before the generation of liquid hydrocarbons from kerogen.

In summary, all the evidence that is available supports the working hypothesis that oxygen-bearing functional groups such as carbonyls and phenols must be cleaved from the kerogen core before liquid hydrocarbons are generated. In addition, these data suggest that potential organic solvents (both carboxylic acids and phenols can be highly soluble in water) may be produced in significant volume.

OIL-FIELD BRINES

Carothers & Kharaka (1978), working primarily with oil-field waters from the San Joaquin Valley of California and the Texas Gulf Coast, showed that over the temperature range 80–200 °C there can be up to $5000/10^6$ carboxylic acids present in oil-field waters. In addition, for 95 formation waters studied from relatively young (Eocene–Miocene) oil and gas fields, it was shown that the carboxylic acid anions generally contribute 50–100 % of the measured alkalinity over the 80–140 °C temperature range. The carboxylic acid anion dominance with respect to alkalinity is particularly pronounced in the 80–120 °C temperature range (figure 4). Figure 5 summarizes the work of Carothers & Kharaka (1978, 1980) in oil-field water chemistry. They suggest that water-soluble carboxylic acids are generated as a result of thermocatalytic degradation of kerogen in the source rock. Furthermore, in the temperature range 120–200 °C the carboxylic acids are destroyed as a result of thermal decarboxylation (see figure 5).

Surdam *et al.* (1984) studied 13 oil-field waters coming mainly from Cretaceous fields in the Rocky Mountains and found monofunctional and difunctional carboxylic acids. Acetic acid (monofunctional) was present in concentrations up to $10000/10^6$. Thus the earlier suggestion that copious quantities of organic solvents may be generated by kerogen during diagenesis is validated. Difunctional carboxylic acids (i.e. maleic and malonic acids) were present in 11 of the 13 waters studied. The difunctional carboxylic acids are present in concentrations up to

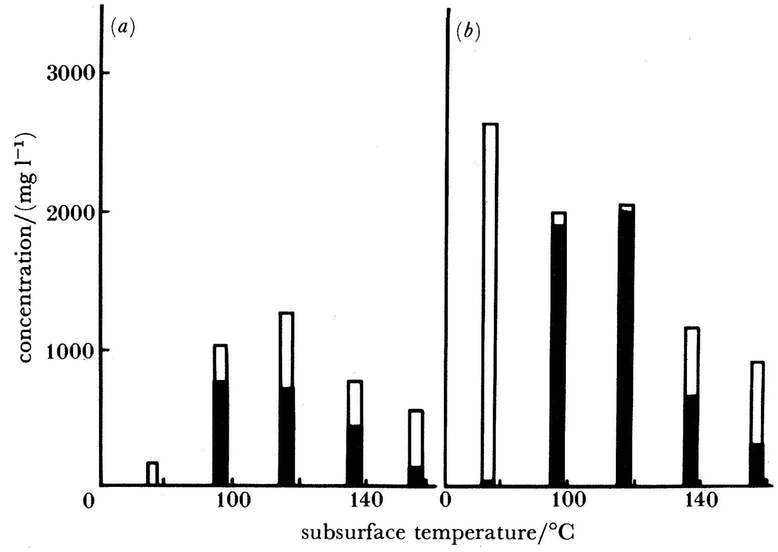

FIGURE 4. Histograms of alkalinity (concentration versus temperature) for the oil-field waters studied by Carothers & Kharaka (1978); (*a*) Texas, (*b*) California. Note that alkalinity is dominated by carboxylic anions over the temperature interval 80–140 °C. Samples with temperatures greater than 80 °C were averaged over 20 K intervals. Modified from Carothers & Kharaka (1978), ■, carboxylic acids; □, HCO_3^-.

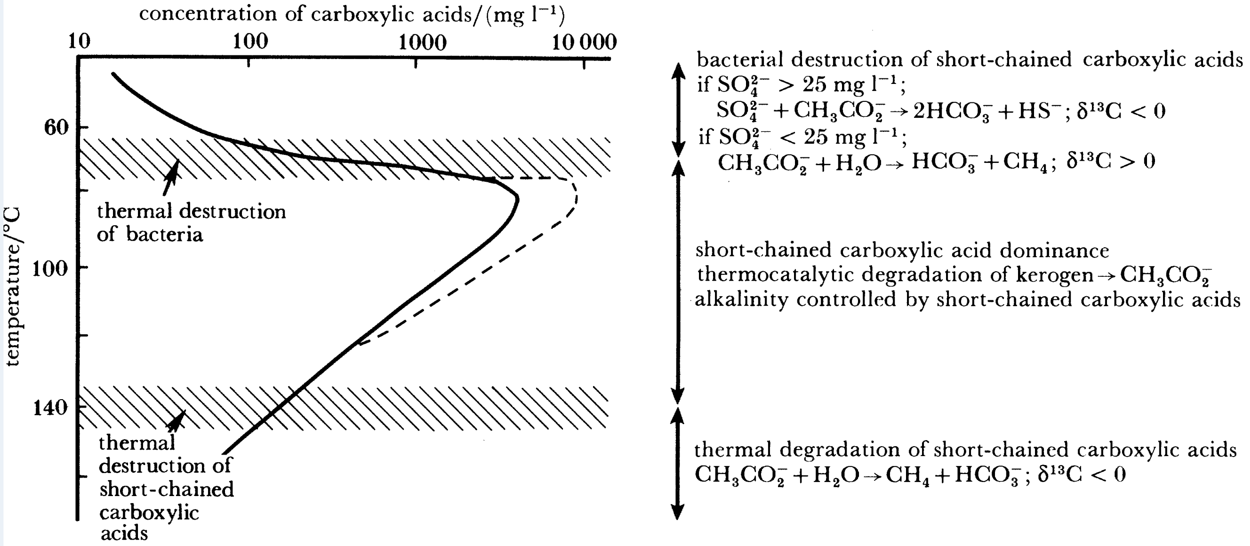

FIGURE 5. Schematic diagram summarizing the available oil-field water chemistry versus subsurface temperature data (Carothers & Kharaka 1978; Surdam *et al.* 1984). Note the upper and lower temperature limits of the short-chained carboxylic acid maximum. Lower stability of these carboxylic acids is determined by bacterial degradation and upper stability is controlled by decarboxylation. Also shown on the diagram are the $\delta^{13}C$ data for oil-field waters, simplified from Carothers & Kharaka (1980).

$25/10^6$ (Surdam *et al.* 1984). As these waters have undergone extensive diagenetic reaction in the course of migration, the presence of highly reactive difunctional carboxylic acids may be more important than their concentrations.

In brief, the work on oil-field waters suggests that large volumes of water-soluble carboxylic acids (mainly monofunctional acids such as acetic acid) are generated during thermocatalytic degradation of kerogen over the 80–120 °C temperature range. In fact, over this range the carboxylic acids typically dominate the alkalinity in oil-field waters for which data is available (table 3). Difunctional carboxylic acids have been reported at levels up to $25/10^6$ in waters that have undergone significant chemical evolution before sampling. Lastly, oil-field brine chemistry is compatible with the earlier discussions of kerogen structure and composition.

Table 3. North Coles Levee water analysis (Stevens)

sample identification	25–31	18–30	14–31	12–31
laboratory pH	6.75	7.00	6.94	7.05
$Ca^{2+}/10^6$	830	889	899	624
$Mg^{2+}/10^6$	35.6	33.6	17.4	33.6
$Na^{+}/10^6$	8724	10100	9253	7559
$K^{+}/10^6$	258	233	169	245
Ca^{2+}/meq l^{-1}	41.42	44.36	44.36	31.14
Mg^{2+}/meq l^{-1}	2.93	2.76	1.43	2.76
Na^{+}/meq l^{-1}	379.47	439.32	402.48	328.80
K^{+}/meq l^{-1}	6.60	5.96	4.32	6.27
$Cl^{-}/10^6$	11056	13871	12639	10528
$F^{-}/10^6$	306	324	352	317
$PO_4^{2-}/10^6$	8	23	31	23
$Br^{-}/10^6$	129	134	120	102
$SO_4^{2-}/10^6$	5	25	35	29
Cl^{-}/meq l^{-1}	311.85	391.25	356.50	296.96
F^{-}/meq l^{-1}	16.11	17.05	18.53	16.68
PO_4^{2-}/meq l^{-1}	0.17	0.48	0.65	0.48
Br^{-}/meq l^{-1}	1.61	1.68	1.50	1.28
SO_4^{2-}/meq l^{-1}	0.10	0.52	0.73	0.60
titratable alkalinity/meq l^{-1}	79.00	74.00	80.00	54.50
balance	21.57	7.42	−5.32	−1.54
total meq l^{-1}	839.26	977.39	910.50	739.47
percentage excess	5	2	−1	0
total CO_2 at 25 °C/(mmol l^{-1})	4.21	4.90	3.40	5.35
HCO_3^-/(mmol l^{-1})	3.01	4.00	2.70	4.46
HCO_3^-/(meq l^{-1})	3.01	4.00	2.70	4.46
H_2CO_3/(mmol^{-1})	1.20	0.90	0.70	0.89
lg p_{CO_2}/atm	−1.45	−1.58	−1.69	−1.58
t.d.s.[a]/(mg l^{-1})	21352	25633	23505	19461
HCO_3 (total alkalinity, percentage)	3.81	5.41	3.38	8.18
organic acids				
acetate/10^6	3700	3750	3730	2670
propionate/10^6	980	862	896	600

[a] Total dissolved solids.

Coal gasification condensates

Little is known about the phenolic composition of oil-field waters; this is largely because of analytical difficulties. However, in some oil-field waters there is a significant disparity between total dissolved carbon and carboxylic acids. Judging from the work of Mason (1984) on coal gasification condensates this disparity may be explained by the presence of phenols. Mason (1984), studying liquid effluents resulting from condensation at the Hanna Basin coal gasification project, reported total dissolved carbon values of $8000/10^6$. Most (85–90 %) of this was in the form of phenols. Carboxylic acids, primarily acetic acid, made up most of the remaining dissolved organic carbon. Thus, there is the potential for the generation of large volumes of phenols during diagenesis of certain types of kerogen if any analogy exists between large-scale coal gasification experiments and natural maturation reactions. Preliminary analysis indicates that in waters produced from the Stevens sandstone in the North Coles Levee field (San Joaquin Valley of California), phenols constitute 5–10% of the dissolved organic carbon. At present we are making a concerted effort to determine the phenol content of selected oil-field waters. Both the n.m.r. work discussed earlier and coal gasification data suggest that for some types of kerogen the potential exists for generation of large quantities of phenols before liquid hydrocarbon generation.

CLAY DIAGENESIS

As discussed earlier, oxidation reactions can result in the generation of difunctional carboxylic acids (tables 1 and 2). The potential for oxidation reactions in fine-grained rocks was described by Curtis (1978), Hoffman & Hower (1979) and Eslinger *et al.* (1979). They stressed not only the potential of amorphous iron as a mineral oxidant, but also clay reactions. In addition, sulphur in polysulphides such as pyrite may act as a mineral oxidant (Wilson Orr, personal communication 1983). The mineral oxidant that will be discussed in this paper is ferric iron in clay minerals. Boles & Franks (1979) have suggested the following reaction for the mixed-layer clay to illite reaction:

$$3.93\ \mathrm{K^+} + 1.57\ \text{smectite} \rightarrow \text{illite} + 1.57\ \mathrm{Na^+} + 3.14\ \mathrm{Ca^{2+}} + 4.28\ \mathrm{Mg^{2+}} + 4.78\ \mathrm{Fe^{3+}} + 24.66\ \mathrm{Si^{4+}} + 57\ \mathrm{O^{2-}} + 11.4\ \mathrm{OH^-} + 15.7\ \mathrm{H_2O}.$$

The reduction of the ferric iron either as it is released during clay diagenesis or within the clay structure itself must be balanced by an oxidation reaction. The most reasonable choice for the reducing agent is organic material (such as kerogen). Figures 6 and 7 show the variation of iron and potassium with depth for fine-grained sediment from the Tertiary Gulf Coast. These data (Hower *et al.* 1976) suggest that approximately 60% of the iron in the clay minerals is released over the stratigraphic interval when the mixed-layer clay minerals become ordered (28% expandibility in figure 6). The released iron is in a reduced state (i.e. $\mathrm{Fe^{2+}}$), because the diagenetic minerals spatially and temporally related to the clay ordering (structural) are chlorite and ferroan carbonates (Boles & Franks 1979). Thus, any ferric iron released during clay diagenesis is immediately reduced to ferrous iron and probably balanced by oxidation reactions in the organic material. Eslinger *et al.* (1979) have suggested that the ferric iron in clay minerals may be reduced within the clay structure. This is an intriguing idea, especially with regard to earlier work by Johns & Shimoyama (1972) and Almon (1974).

Johns & Shimoyama (1972) demonstrated that the presence of clay minerals (particularly mixed-layer clay) can be a catalyst to liquid hydrocarbon cracking reactions. Almon (1974), trying to delineate the process responsible for the catalytic effect of clay minerals on hydrocarbon-generating reactions, suggested that the process is an electron transfer reaction yielding two free radicals (i.e. alkane and carboxyl group radicals). In more detail, Almon (1974) demonstrated that catalysis of the reaction could be viewed in terms of electron acceptor sites within the clay mineral structure. These acceptor sites are either octahedrally coordinated aluminium at the edges of crystals or $\mathrm{Fe^{3+}}$ within the clay lattice. The proposed mechanism involved electron transfer from the kerogen to the clay acceptor sites (i.e. $\mathrm{Fe^{3+}}$) to produce two

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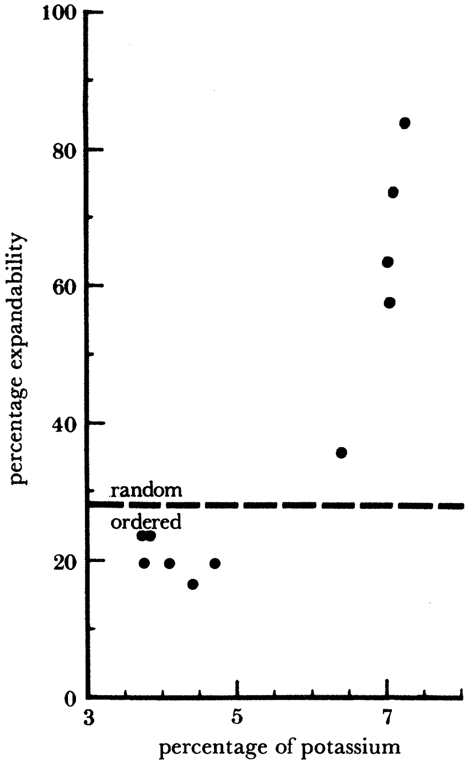

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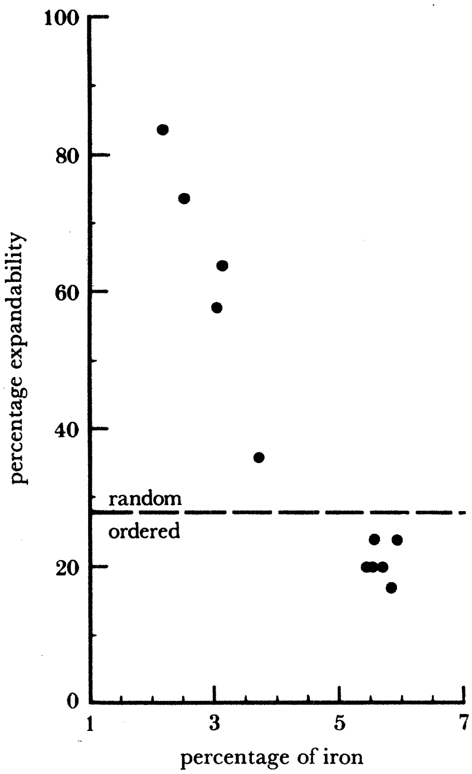

FIGURE 6. Diagram showing the variation in total iron in the mixed-layer clays with the precentage of expandability in the Gulf Coast Tertiary (less than 0.1 μm fraction). Data from Hower *et al.* (1976). Note the apparent decrease in iron content of the clays over the stratigraphic interval from 80–20 % expandability. The clays change from random to ordered structures at approximately 28 % expandability.

FIGURE 7. As figure 6, but showing the variation in potassium with the percentage of expandability.

free-radical groups. Almon (1974) suggested that one of the radicals may be a carboxyl group. Moreover, he demonstrated that kinetically this reaction mechanism could occur to a significant extent over reasonable geological time.

By using Mössbauer techniques, Eslinger *et al.* (1979) showed that the reduction of Fe^{3+} to Fe^{2+} with increasing depth may occur within the mixed-layer clay lattice. If this is true and Almon's reaction mechanism is operable and in fact accelerated with burial, it explains why Fe^{2+} is expelled during the structural ordering of the clays. Fe^{2+} would not be compatible with the octahedral site. Thus the iron released during structural ordering (figure 6) of the mixed-layer clays and the concomitant formation of chlorite and ferrous carbonates, seen in many diagenetic sequences, can be explained by an oxidation–reduction reaction involving the interaction of clay diagenesis and kerogen maturation.

The coincidence in time, temperature and space of mixed-layer smectite–illite ordering reactions in shales (100–110 °C) and the peak concentrations of organic acids (80–120 °C) in oil-field waters suggests a possible mechanism for the generation of difunctional organic solvents. The reduction of mineral oxidants and simultaneous oxidation of kerogen may be an effective process for enhancing the release of peripheral organic acid groups (phenolic, carboxylic, etc.) during thermal degradation.

The cleaving of peripheral groups from the kerogen core by an oxidation–reduction

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mechanism in a natural system will affect the diagenesis of associated sandstones. Crossey *et al.* (1984) have shown that in the Gulf Coast, the reduction of Fe^{3+} in mixed-layer clays contained in Tertiary shales and the concomitant oxidation of kerogen could account for all the observed framework grain dissolution observed in adjacent sandstones (2–4 % porosity). The mass-balance calculation used Gulf Coast shale mineralogic data, average values for total organic carbon (0.5 % by mass), type III kerogen, 50 % mixed-layer clay content in the shales, and sand:shale ratios of 1:10 and 1:20. It was assumed that 60 % of the ferric iron contained in the smectite–illite clays oxidizes carbon in kerogen to a difunctional carboxylic acid. By using the solubility of andesine in oxalic acid (Surdam *et al.* 1984) the amount of potential framework grain dissolution was calculated (see figures 8, 9 and table 4).

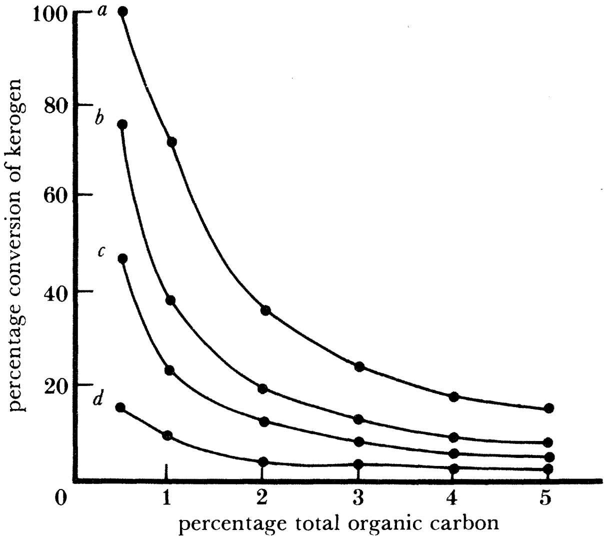

FIGURE 8. Results of the calculations for reduction of Fe^{3+} from clays and oxidation of organics to acetate and CO_2 for three types of kerogen. The percentage of kerogen converted is shown as the ordinate, whereas the total organic carbon of kerogen is plotted as the abscissa. Gulf Coast shales typically have 0.5 % total organic carbon and it was assumed that they consist of 50 % mixed-layer clay. From Crossey *et al.* (1984). (*a*) Type III → acetate; (*b*) type II → acetate; (*c*) type I → acetate; (*d*) type III → CO_2.

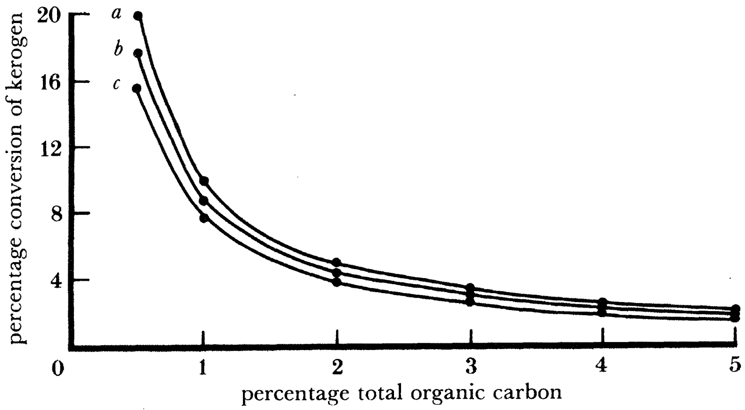

FIGURE 9. As figure 8, but showing the percentage conversion when oxalate is the oxidation product. (*a*) Type III → oxalate; (*b*) type II → oxalate; (*c*) type I → oxalate.

Table 4. Potential enhanced porosity resulting from plagioclase framework grain dissolution in the Gulf Coast

kerogen type	shale:sand	volume percentage change due to andesine dissolution
III	10:1	2.6
III	20:1	5.2

Not only does the ordering of the mixed-layer clays offer the potential for oxidation–reduction reactions, but it also results in a significant increase in fluid flux (see figure 10). If transfer or redistribution of material is to occur, some type of fluid flux is necessary to transport the water-soluble organic acids and their dissolved or chelated load.

In summary, during the diagenesis of the organic-rich, fine-grained source rocks there is the potential to evolve copious quantities of water-soluble organic acids (figure 5). In the next two sections we will discuss the interaction of these organic acids with the carbonate minerals and with the aluminosilicate minerals.

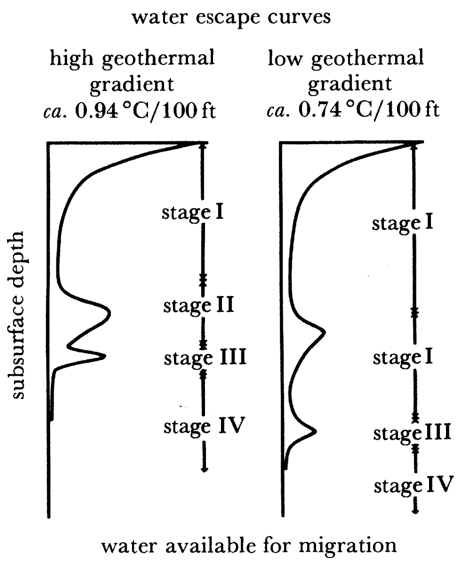

Figure 10. Schematic diagram showing the potential fluid flux associated with clay diagenesis (decrease in expandability and in ordering). Two thermal gradients are shown. (From Perry 1972.) (1 ft = 0.3048 m.)

Organic acids and carbonate stability

Conventionally the stability of carbonate minerals during progressive burial is evaluated in terms of pH and the aqueous species Ca^{2+}, H_2CO_3, HCO_3^- and CO_3^{2-}. Typically, alkalinity is attributed solely to the aqueous carbonate species with no allowance for the presence of organic acid anions. Thus, a standard explanation of carbonate stability in the subsurface is usually based on the well known fact that with increasing p_{CO_2} the solubility of calcite increases (Holland & Borcsik 1976). Hence the destabilization of carbonate grains and cements is attributed to an elevated p_{CO_2} as a result of decarboxylation reactions. This is an important process, particularly at temperatures greater than 120–140 °C when the organic acids react to form CO_2, CH_4 and H_2O.

However, in the temperature range 80–120 °C the presence of organic acid anions must not be overlooked. We have already summarized the work of Carothers & Kharka (1978), who reported that in this range organic acids, i.e. acetate, dominate the alkalinity (see figures 4, 5). For example, table 3 shows analyses of oil-field water from the North Coles Levee oil field in which over 95% of the alkalinity can be attributed to organic acid anions.

The effect of organic acids on the carbonate system must be taken into consideration because at the concentrations present in oil-field waters they will dominate alkalinity. For example, the acetate buffer is 100 times more effective than any of the carbonate species. In the light of our present knowledge of the properties of oil-field waters, it is reasonable to suggest that over the range 80–120 °C the pH of the waters will be controlled by carboxylic acid anions. Moreover, acetate is typically the most abundant anion (see table 3 of Carothers & Kharaka 1978) and the maximum buffering capacity of acetate is at a pH value of 5.4.

If the carbonate system is buffered externally by acetate, then as p_{CO_2} increases the solubility of calcite decreases. Figure 11 demonstrates this relation. For example, if the pH is externally buffered at a pH of 6, the solution composition is confined to a diagonal line (pH = 6) and will move to the lower right as p_{CO_2} increases (i.e. decreased carbonate solubility). The value of p_{CO_2} increases from left to right along the abscissa, as does $\Sigma\,CO_3^{2-}$ (figure 12).

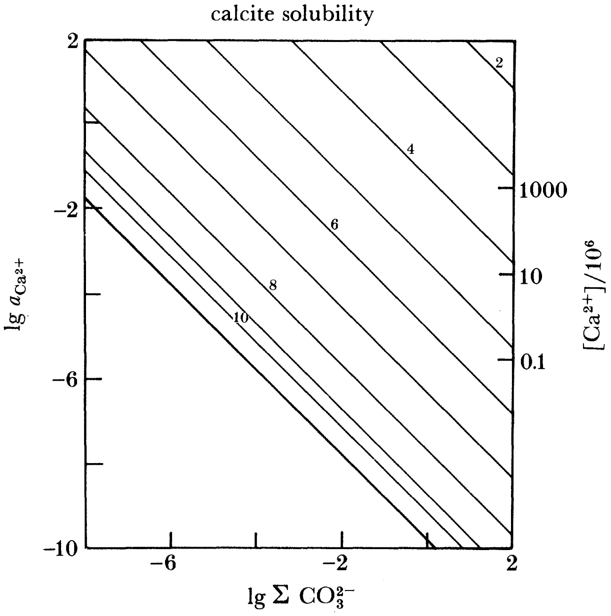

FIGURE 11. Calculated equilibrium surface for calcite at 100 °C projected onto the $\lg a_{Ca^{2+}} - \lg \Sigma\, CO_3^{2-}$ plane. Solid lines represent contours of constant pH (numbered values). Note that if the system is externally buffered (restricted to a constant pH value and $\Sigma\, CO_3^{2-} (= H_2CO_3 + HCO_3^- + CO_3^{2-})$ is increased by increasing p_{CO_2} (see figure 12), the calcite solubility is decreased. Values were calculated from data in Helgeson (1969). From Surdam *et al.* (1984).

In contrast, if the carboxylic acid anions are low in concentration relative to the carbonate species, then the alkalinity will be dominated by the carbonate system. In this case, if the initial pH is greater than 5 and p_{CO_2} increases, the waters will move toward a lower pH (figure 12) and the carbonate mineral will become more soluble (figure 11). Thus, depending on the p_{CO_2}

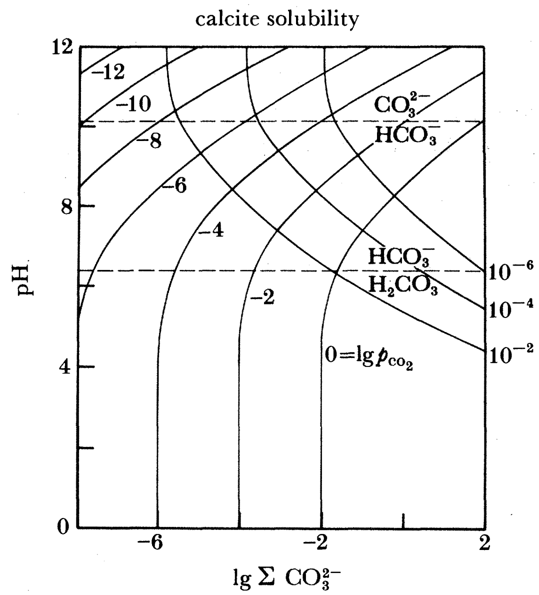

FIGURE 12. Calculated equilibrium surface for calcite at 100 °C projected onto the pH–lg $\Sigma\, CO_3^{2-}$ plane. Solid lines represent f_{CO_2} isopleths and contours of constant Ca^{2+} activity (see labels). Light broken lines separate the pH regions where different carbonate species (H_2CO_3, HCO_3^- and CO_3^{2-}) are dominant. Note the relation between $\Sigma\, CO_3^{2-}$ and p_{CO_2}. From Surdam *et al.* 1984.

and the detailed imbalance between the carbonate and carboxylic systems in the temperature range 80–120 °C, carbonates will be either less soluble (with the potential for carbonate precipitation and porosity destruction) or they will be more soluble (with the potential for carbonate dissolution and porosity enhancement). Thus, depending on the details of the organic–inorganic interaction, the primary porosity may be either enhanced or damaged by carbonate dissolution or precipitation.

At temperatures greater than 120 °C the carboxylic acids begin to decarboxylate thermally ($CH_3COOH \rightarrow CH_4 + CO_2$ or $CH_3CO_2^- + H_2O \rightarrow CH_4 + HCO_3^-$). As this proceeds the alkalinity will become dominated by the carbonate system in the interval 120–160 °C. Implicit in the decarboxylation process is the elevation of p_{CO_2}; there is good observational evidence to support the premise that elevated p_{CO_2} will be associated with organic acid decarboxylation in the subsurface (see, for example, Franks & Forester 1984). By using a Gulf Coast example they show that as depth increases there is a significant increase in the CO_2 content of produced gases. Progressive thermal decarboxylation of organic acids presents another opportunity for either preservation of remnant porosity (at least, it will not be destroyed by carbonate precipitation) or the enhancement of the remnant porosity (by carbonate dissolution). Of course, the simultaneous formation of other silicate phases such as chlorite and quartz overgrowths may offset any porosity gains achieved by carbonate reactions.

ORGANIC ACIDS AND ALUMINOSILICATE MINERALS

At 100 °C in an aqueous environment the solubility of many aluminosilicate minerals can be elevated by the presence of carboxylic acids (Surdam *et al.* 1984). Under these conditions the problem of aluminosilicate dissolution can be viewed in terms of aluminium mobility (see tables 4, 5; figure 13, plate 1; and Surdam *et al.* 1984). Monofunctional carboxylic acids typically elevate the solubility of aluminium by an order of magnitude or more (figure 14).

The data plotted in figure 14 and shown in tables 5 and 6 were experimentally derived by placing the appropriate aluminosilicate in aqueous solutions containing organic acids (either oxalate or acetate) for two weeks at 100 °C. For a detailed description of the analytical procedures, experiments and results shown in figure 14 and tables 5 and 6 see Surdam *et al.* (1984).

As can be seen in figure 13 the destabilization or alteration of plagioclase is not sufficient

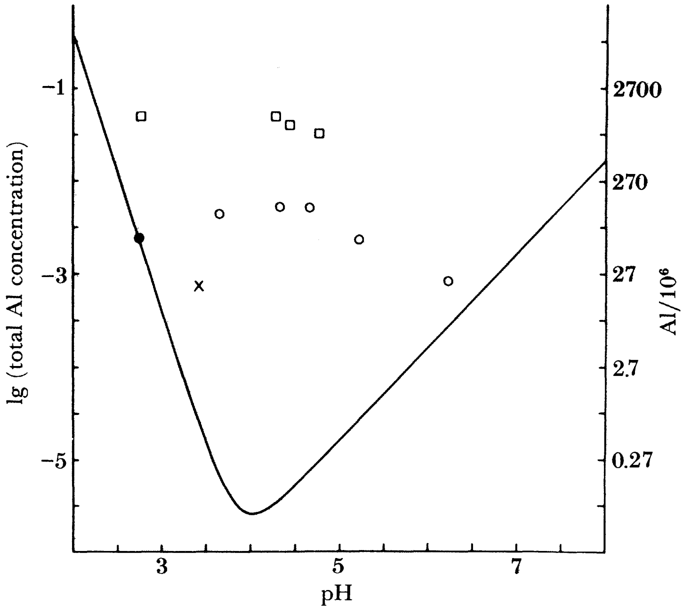

FIGURE 14. Gibbsite solubility curve at 100 °C. Circles, squares and crosses represent Al data from experiments described in Surdam *et al.* (1984). □, 10000/10^6 oxalate; ○, 1000/10^6 oxalate; ●, no oxalate; ×, 10000/10^6 acetate. It should be noted that the values reported by Surdam *et al.* (1984) are not equilibrium values; not only were the experiments run for only two weeks, but in nearly all the runs an aluminosilicate gel phase formed during cooling and before analysis of the end products. From Surdam *et al.* (1984).

TABLE 5. OXALIC ACID DISSOLUTION EXPERIMENT (TWO WEEKS AT 100 °C)

	initial solution concentration	Al/10^6	SiO$_2$/10^6	Ox^{2-}/10^6†	final pH
andesine	distilled H$_2$O	< 1	67	n.d.‡	7.70
andesine	10/10^6 Ox^{2-}	3.2	55	8	6.65
andesine	100/10^6 Ox^{2-}	3.9	143	26	5.95
andesine	1000/10^6 Ox^{2-}	130	421	600	4.30
andesine	10000/10^6 Ox^{2-}	1300	413	7600	2.50
albite	1000/10^6 Ox^{2-}	75	349	570	3.60
albite	10000/10^6 Ox^{2-}	790	506	7140	1.70
labradorite	1000/10^6 Ox^{2-}	125	376	880	4.65
labradorite	10000/10^6 Ox^{2-}	1400	374	7900	2.70
anorthite	1000/10^6 Ox^{2-}	80	376	490	4.25
microcline	10000/10^6 Ox^{2-}	150	540	4890	1.75
laumontite	1000/10^6 Ox^{2-}	137	596	690	3.50
clinoptilolite	1000/10^6 Ox^{2-}	137	441	970	4.50
blank	10000/10^6 Ox^{2-}	< 1	< 1	8200	1.50

† Ox^{2-} = oxalate anion. ‡ n.d. = not detected.

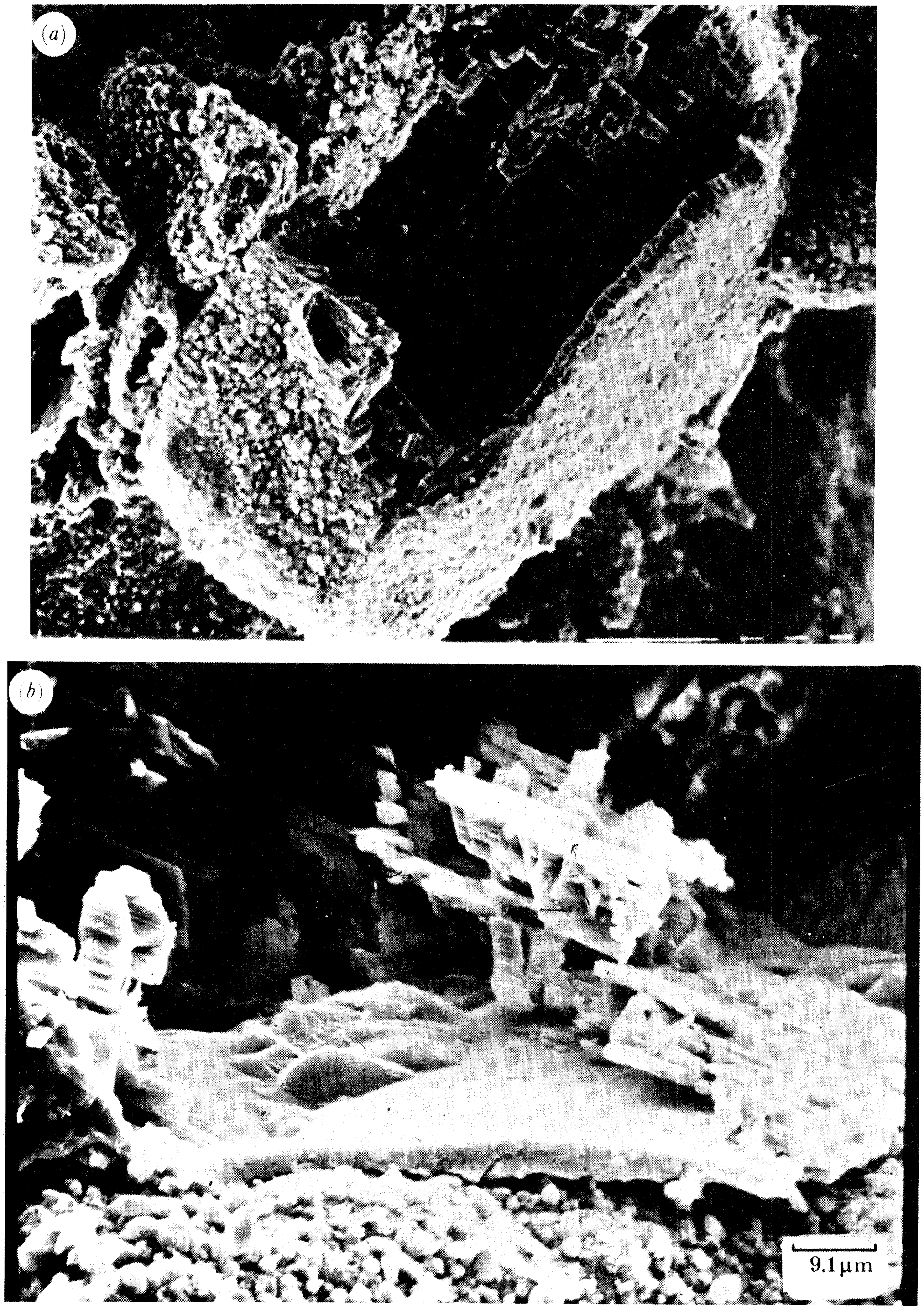

FIGURE 13. Plagioclase framework grains in various stages of dissolution. Note that in each case the plagioclase is dissolving, not just altering. (*a*) Eocene volcanogenic sandstone, Lysite Mountain, Wyoming. (*b*) Vicksburg Formation, Gulf Coast.

Table 6. Buffered oxalic dissolution experiment (andesine, two weeks at 100 °C)

	initial solution concentration	Al/10^6	$SiO_2/10^6$	$Ox^{2-}/10^6$† (final)	initial pH	final pH
andesine	1000/10^6 Ox^{2-}	112	479	690	3.15	3.65
andesine	1000/10^6 Ox^{2-}	80	382	580	4.00	4.20
andesine	1000/10^6 Ox^{2-}	72	275	640	5.00	5.15
andesine	1000/10^6 Ox^{2-}	25	104	860	6.05	6.15
andesine	HCl	67	348	0	2.00	2.00

† Solutions buffered with 10000/10^6 Ac^-(NaAC+HAC).

to explain the observed textures: the plagioclase must be destabilized and the aluminium mobilized. If the aluminium is not mobilized the plagioclase would alter *in situ* to kaolinite or other secondary mineral phases. The carboxylic acids, particularly the difunctional forms, are good chelating (complexing) agents for the aluminium. If the framework grain is destabilized in the presence of carboxylic acid the aluminium will be complexed and available for transport. Figure 15 shows a schematic diagram of the complexation of aluminium by oxalic acid.

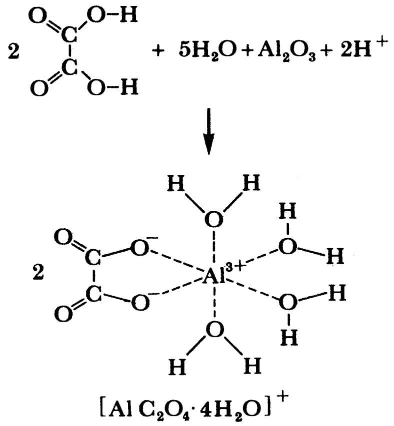

Figure 15. Schematic diagram showing complexation of Al^{3+} by oxalic acid. Note pH dependence of complex. From Surdam *et al.* (1984).

It should be noted that although we have emphasized carboxylic acids in our discussions, they are by no means the only available complexing agents. Phenols are another set of available organic acids that may be derived from kerogen and can be outstanding chelating agents for metals. Figure 16 shows the results of some experimental work completed on the solubility of andesine in the presence of various phenols. The experiments were run at 100 °C for two weeks and the concentration of the phenolic or carboxylic anion was 1000/10^6 in solutions buffered by sodium acetate–acetic acid. The phenols hydroquinone and catechol are as effective as oxalate in complexing aluminium and can thus elevate the solubility of aluminium by two orders of magnitude at concentration levels of 1000/10^6 (figure 16). Thus it appears that the complexing activity of both carboxylic and phenolic acids can elevate the solubility of aluminium to the levels necessary to explain the textures observed in figure 13. In brief, the carboxylic and phenolic acids provide an ideal mechanism to mobilize significant quantities of material in the subsurface during diagenesis.

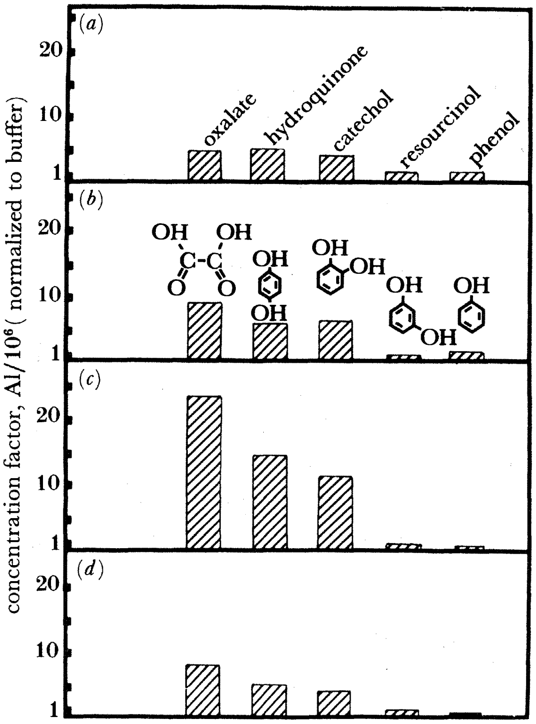

FIGURE 16. Solubility of aluminium in andesine dissolution experiments. Aqueous phases contained 1000/10^6 phenols or carboxylic acids. The pH in the aqueous phase was buffered by a sodium acetate–acetic acid buffer; (*a*) pH = 3, (*b*) pH = 4, (*c*) pH = 5, (*d*) pH = 6. Runs were made at 100 °C for two weeks. Aluminium values were normalized to the acetate buffer.

In addition to the dissolution of framework grains, they have the ability to dissolve carbonate and aluminosilicate minerals out of pores and pore throats, thereby enhancing or preserving porosity and permeability just before hydrocarbon generation. Porosity and permeability preservation and enhancement becomes a natural consequence of the interaction between progressive kerogen maturation and diagenesis of inorganic cements and framework grains.

MASS TRANSFER

What is the ultimate destination of the mobilized material? If the dissolution of framework grains or cements is to improve significantly the reservoir characteristics of a sandstone, the transported material must be moved beyond the system of interest. In cases where the porosity enhancement is the result of aluminosilicate dissolution most of the transported material probably forms kaolinite. The late kaolinite characterizing many sandstone reservoirs is probably the result of the mass transfer of material arising from the dissolution of aluminosilicate minerals. In a few cases, we have observed late-forming kaolinite impregnated with hydrocarbons. The kaolinite forms when the aluminium complexes destabilize. The destabilization of the complex is probably a result of variations in the pH of the interstitial fluids. Significant variations in pH could result from compositional (mineralogical) variations within the reservoir sandstone (i.e. mixing of fluids) or variations in the mineralogy of the fluid conduit. The components for the diagenetic kaolinite occurring in pores and pore throats in many sandstones had to be transported (even if only a short distance) to the site of deposition by some kind of complex. Aluminium solubility values in the absence of complexing are so low that unreasonably large numbers of pore volumes of interstitial fluids are required for the transport of the aluminium.

Dissolved carbonate material may be transported further and thus it is more difficult to speculate on its ultimate destination. Most of the dissolved carbonate is probably precipitated higher in the stratigraphic section; however, so little pertinent data exist that it is impossible to speculate further.

Conceptual model for porosity and permeability preservation and enhancement

By integrating the time, temperature and spatial relations among the generation of carboxylic and phenolic acids, the availability of mineral oxidants, and the maturation of hydrocarbons, it is possible to construct a conceptual model of the progressive diagenesis of clastic rocks. Considering the interaction of four diagenetic parameters (aluminosilicate minerals, carbonate minerals, organic acids (carboxylic and phenolic) and CO_2) several diagenetic pathways are possible during a typical burial history. A general schematic flow diagram of possible reaction paths through the 80–120 °C temperature zone is presented in figure 17. In the range 120–200 °C (the exact temperature is dependent on the thermal stability of the organic acids) another reaction pathway becomes available for the carbonate mineral system (figure 18). The pathways shown in figure 18 are based on elevated p_{CO_2} and substantial

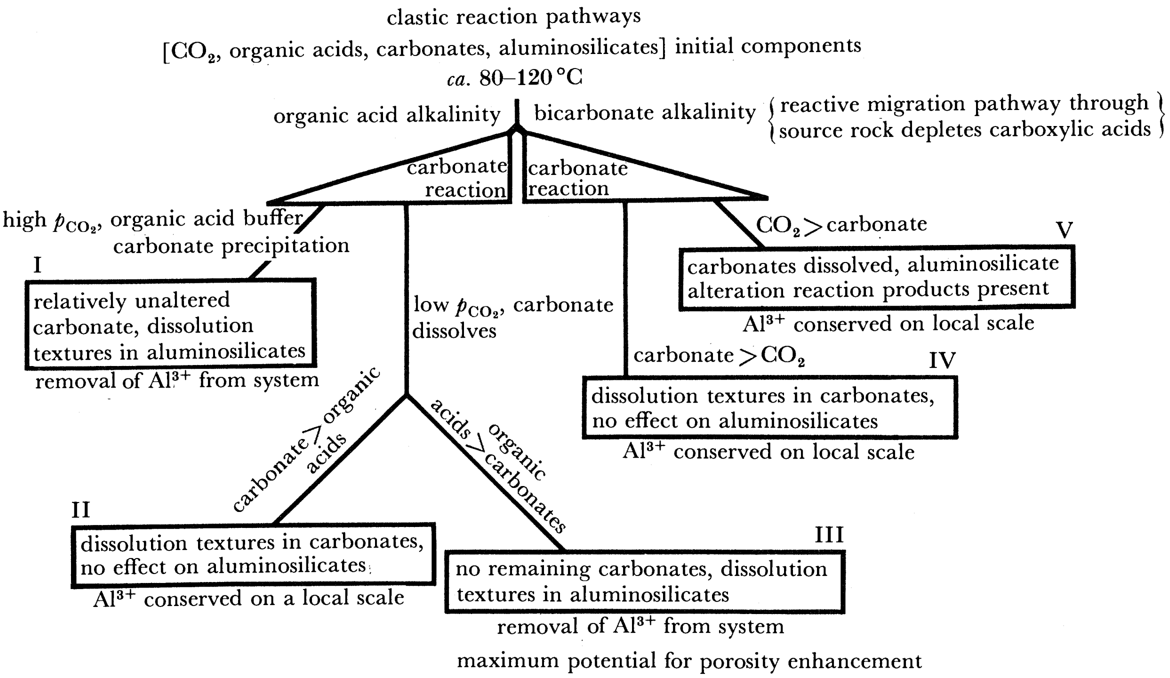

Figure 17. Flow diagram combining aspects of organic and inorganic diagenesis. The initial components are organic acids (carboxylic and phenolic acids), CO_2, carbonate minerals and aluminosilicate minerals. The system is designed to represent simplified sandstone reservoir conditions over the temperature interval of 80–120 °C. Modified from Surdam *et al.* (1984).

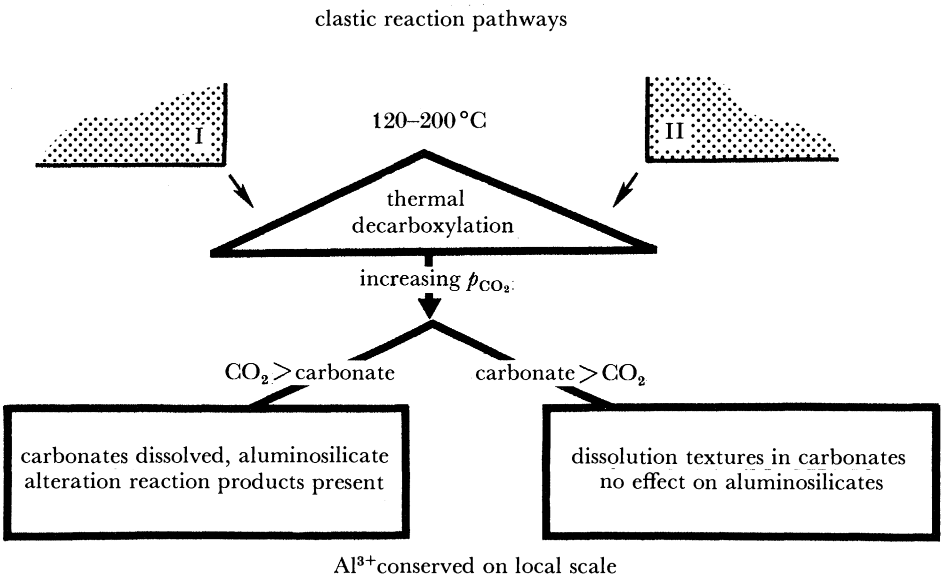

Figure 18. Flow diagram combining aspects of organic and inorganic diagenesis. The initial components are CO_2 (elevated as a result of the thermal decarboxylation of organic acids) and carbonate and aluminosilicate minerals. The system is designed to represent simplified sandstone reservoir conditions over the temperature interval 120–200 °C.

decreases in organic acid concentrations; they assume that the alkalinity is dominated by the carbonate system. It should be noted that the pathways in the range 120–200 °C may be complicated by the simultaneous formation of other diagenetic phases such as chlorite and quartz. See, for example, Larese *et al.* (1984). Lastly, it should be noted that whereas the initial precipitous increase in concentration of organic acids takes place over a ±10 K interval around 80 °C, the boundaries between the diagrams shown in figures 17 and 18 are gradational. There is likely to be much more uncertainty about the transition temperature between organic acid-dominated and carbonate-dominated alkalinity with progressive burial. The transition temperature will be controlled by thermal stability of the organic acid mixture of the interstitial fluids and must be evaluated on a site-specific basis.

Complicating factors

The diagrams presented in figures 17 and 18 may be complicated if other components are added to the system (such as H_2S). In addition, carbonate diagenesis has been grossly simplified by representing it by calcite alone. Despite these notable omissions, the models presented in figures 17 and 18 are offered as general working conceptual guides to be refined with time.

To be reactive in the adjacent sandstones the organic acids generated in the source rocks must be released from the fine-grained rocks without undergoing significant modification by reaction. It is evident that hydrocarbons and aqueous phases do not migrate through 'impermeable' shale in the same way as through more porous sandstones. Carboxylic and phenolic acids of interest are water soluble, and their transport will be influenced by water-releasing reactions in the source rocks (i.e. mixed-layer clay diagenesis) and other dehydration reactions (i.e. opal c.t. to quartz). The migration of the aqueous solutions out of the fine-grained rocks along microfractures rather than tortuously around individual grains will tend to reduce the volume of rock contacted by the solution, and reduce the potential for reaction by the fluids. Also, the fluids will be transported more rapidly as they may be confined to a migration system of relatively small volume compared with that of the adjacent sandstone. Nonetheless, the reactivity of the solvent-bearing fluids may be reduced depending on (i) the geometry of the migration pathway, (ii) the transport velocity, (iii) the mineralogy of the source rock and (iv) the overall distance of transport.

Other important factors that must be considered when using the model are; (i) the relative proportions of organic acids and carbonate species (i.e. acetate or carbonate buffer), (ii) the kerogen composition and quantity, (iii) the early cementation history in the temperature interval 20–80 °C and (iv) the availability of mineral oxidants.

Optimum conditions for preservation or enhancement of porosity–permeability

The position of the organic acid maximum in figure 5 is significant, particularly when viewed in the context of hydrocarbon generation (see especially Surdam *et al.* 1984). The maximum occurs just before liquid hydrocarbon generation and generally overlaps a wide range of diagenetic phenomenon. Some of the diagenetic events generally initiated in or associated with the 80–120 °C temperature interval are smectite–illite ordering, albitization, kaolinite formation, carbonate formation or dissolution, plagioclase dissolution, chlorite formation and overpressuring (for more details see Boles & Franks 1979). Organic acids may be affected by any of these other diagenetic factors. Therefore, to maximize the effectiveness of the organic acids in preserving or enhancing porosity the generation of these solvents must be spatially compressed as close as possible to the generation of liquid hydrocarbons. Ideally, it would be best to have the organic acids sweep through the sandstone just ahead of hydrocarbon migration. If too much time is available between the organic acid maximum and the zone of intense hydrocarbon generation, other diagenetic mineral phases (such as quartz and chlorite) will precipitate in the pores and pore throats, thus eliminating any gains made by the organic acids.

An optimum diagenetic scenario for the preservation and enhancement of porosity and permeability in sandstone will probably contain the following characteristics.

(i) Organic-rich source rocks adjacent to potential reservoir rocks (short migration routes).

(ii) Rapid evolution from organic solvent generation to hydrocarbon maturation (thermal perturbations such as crustal attenuation; or, on a smaller scale, overpressuring).

(iii) Adequate fluid flux (clay diagenesis or other dehydration reactions are necessary); this process may be assisted by convection (Wood & Hewett 1984).

(iv) Available conduits in potential reservoir rocks (fractures, unconformities, and remnant porosity and permeability).

The basic premise to the working hypothesis presented in this paper is that the geochemistry of the progressive burial of sediments can only be correctly evaluated if the interactions of organic and inorganic constituents are delineated. Some of the present uncertainty about progressive diagenesis of sedimentary prisms can be eliminated by examining the rock system with respect to porosity and permeability in terms of organic acids (carboxylic and phenolic), carbonate minerals, aluminosilicate minerals and CO_2.

Bob Siebert of Conoco has continually assisted us, both in terms of ideas and inspiration. Discussions with J. R. Boles (U.C.S.B.), T. Dunn and M. Lewan (Amoco), R. Lahann and D. Curry (Conoco), H. Dahl (Texaco) and S. Dixon (Mobil) have been helpful. In addition, there have been many discussions with other individuals, too numerous to personally acknowledge, that raised questions or sparked ideas. Without the 'in-house' support of S. Boese, E. S. Hagen, R. Kablanow, H. Heasler, K. Fischer, D. McGowan and Y. Peigui the work would have been more difficult, if not impossible. Conoco, Amoco, Mobil and Texaco have financially supported various aspects of this work; we are thankful for this support. B. Siebert and T. Dunn provided photomicrographs.

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Discussion

G. Eglinton (*Organic Geochemistry Unit, School of Chemistry, University of Bristol*). Professor Surdam's suggestion involves a reaction between type III kerogen and ferric iron in the minerals at temperatures of about 80 °C to produce carboxylic acids. Do other kerogen types react in the same way and is there any evidence that low molecular mass carboxylic acids are produced by this mechanism in the natural environment?

R. C. Surdam. We have not yet succeeded in producing a reaction between ferric iron and kerogen. One of the difficulties is that ferric oxalate is insoluble. The work of Eslinger (1979) on Mössbauer spectroscopy suggests that the iron may be reduced within the clay mineral. The insolubility of the oxalate then does not inhibit the reaction, nor is it necessary to extract the iron from the clay. The calculated yield of difunctional carboxylic acid by iron oxidation does not depend strongly on the kerogen type. The yield of acids such as acetic acid, however, does depend on the kerogen type when the oxidation is produced by ferric iron. We have not found the difunctional carboxylic acids in oil-field waters in the concentrations we require. We do find abundant kaolinite in the subsurface, indicating that aluminium was mobile at some point. We have, however, been unable to find aluminium in solution. One of the indications that our proposals are correct is the recent discovery of a nodule of calcium oxalate by Britoil at a depth of 2.5 km beneath the North Sea.

B. Durand (*Institut Français du Pétrole, Rueil Malmaison, France*). Has Professor Surdam any information on whether oils can be altered by this kind of mineral oxidation?

R. C. Surdam. No, I have no information.

J. D. Pigott (*School of Geology and Geophysics, University of Oklahoma, U.S.A.*). Professor Surdam states that he has failed to find any significant concentration of aluminium in formation waters, yet silica and aluminium are presumably both released during the dissolution of feldspar. What happens to the aluminium and silica?

R. C. Surdam. The complexes between the acids and aluminium exist only over particular ranges of temperature, and the temperature history of the formation waters is unknown. It is also possible that the aluminium was precipitated by a change in pH. The abundance of kaolinite strongly suggests that the aluminium was mobile at some time. There are also a number of sandstones in which the feldspar has been replaced by kaolinite *in situ*. The solubility of silica is less affected by the presence of carboxylic acids, and is therefore harder to transport than is the aluminium.

R. Raiswell (*Department of Earth Sciences, Leeds University*). The reactions Professor Surdam has discussed are also relevant to porosity destruction. How close to saturation are the oil-field waters with respect to calcium fatty acid salts? Berner (1968) did some experiments to discover the effect of oxalates and other acids on calcite nucleation and discovered that they blocked the nucleation very effectively. Is there any evidence for such effects in the material Professor Surdam has examined?

Reference

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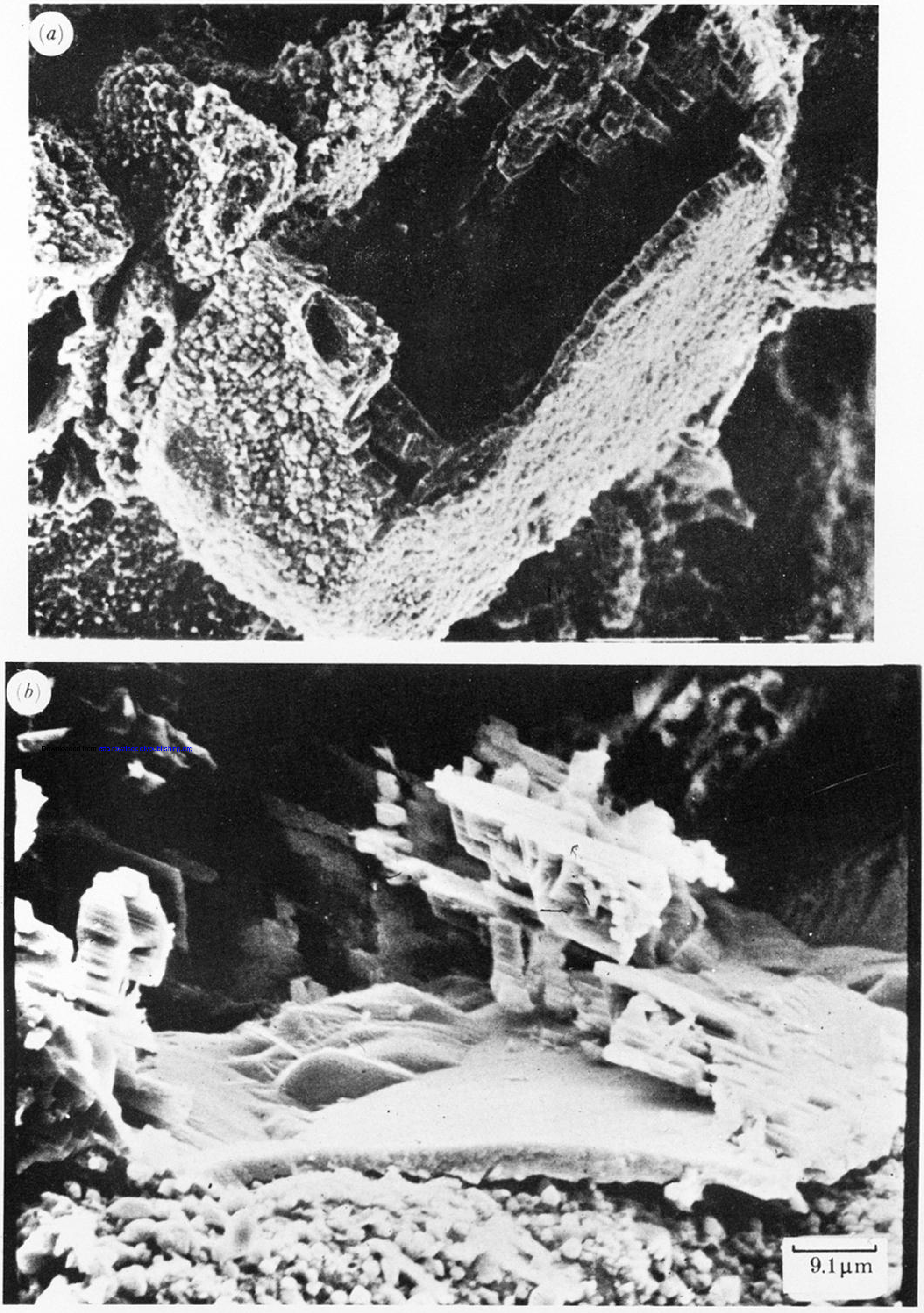
R. A. Berner (*Department of Geology and Geophysics, Yale University, U.S.A.*). At room temperature all the calcium fatty acid salts are thermodynamically unstable with respect to hydrocarbons and calcite. I would not therefore expect to find these salts at higher temperatures.



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