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Organic Acids in Geological Processes

With 151 Figures

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Chapter 1 Introduction to the Role of Organic Acids in Geological Processes

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Summary

This chapter is intended to provide sufficient information to allow one to read the following chapters in any order they prefer. The objective and need for this book are presented in the introductory section. Nomenclature for organic acids is presented on an elementary level for nongeochemists. A historical account is then given on the role of organic acids in geological processes, which is followed by a brief synopsis of each chapter. The final section explores the needs for future research in terms of natural system studies and laboratory experimental studies.

1 Introduction

Organic acids have had a rich and diverse presence in the earth sciences and particularly in geochemistry. Fatty and amino acids extracted from meteorites have provoked controversies regarding the origin of life and concerns on terrestrial contamination (Hayes 1967; Cronin et al. 1988). Fatty acids have been used to interpret the precursory organisms responsible for organic matter deposited in modern sediments and the level of thermal diagenesis experienced by organic matter buried in sedimentary rocks (Parker 1969). These organic acids also have been considered a source of natural gas (Carothers and Kharaka 1978) and petroleum (Shimoyama and Johns 1971). In addition, certain types of carboxylic acids in petroleum have been advocated as indicators of migration distance (Jaffé et al. 1988). Amino acids have been used to age date fossil remains (Lee et al. 1976) and marine sediments (Kvenvolden et al. 1973). Considerable effort has been placed on understanding the structural complexity of high-molecular-weight

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polymeric acids peculiar to some formation waters (Barden et al. 1984) and humic acids in soils (Stevenson 1982).

Several comprehensive books have been published on the geochemical aspects of organic acids. Lochte and Littmann (1955) wrote *The Petroleum Acids and Bases*, which presents analytical methods and the identities of organic acids and bases found in petroleum. Hare et al. (1980) edited the book entitled *Biogeochemistry of Amino Acids*. This compilation of papers emphasized natural occurrence, analytical methods for study, experimental results on racemization, and age-dating applications of amino acids. The book entitled *Organic Geochemistry of Natural Waters* by Thurman (1985) gives a thorough account of the types and abundances of organic acids in natural surface and near-surface waters. Aiken et al. (1985) have edited a book entitled *Humic Substances in Soil, Sediment, and Water*, in which natural occurrences and chemistry of humic and fulvic acids are discussed in detail.

Whereas all of these mentioned books provide pertinent information on natural occurrences, analyses and isolations, or structural characterizations of organic acids, there remains a need for a book concerning the influence of organic acids on geological *processes*. Organic acids have been invoked as influential participants in soil formation, surface weathering, subsurface porosity generation, and ore formation. Although controversy surrounds the alleged role of organic acids in some of these geological processes, a collection of data and interpretations may provide insights and research directions for future resolution of these controversies. This book is an attempt to bring together current knowledge on the role of organic acids in geological processes. No overall consensus is sought in this book, and the following chapters are authored by dedicated researchers representing a diversity of interests, approaches, and hypotheses concerning organic acids.

2 Organic Acid Nomenclature

Organic acids are molecules consisting of a carbon-to-carbon bonded framework containing at least one functional group capable of relinquishing a proton. The functional group most commonly responsible for acidity in naturally occurring organic acids is the carboxylic group (—COOH). This functional group typically relinquishes a proton in water between pH values of 3 and 10 depending on the overall chemical character of the organic acid. Natural surface and subsurface waters have pH values within this range. As a result, these dissolved organic molecules may occur in significant concentrations as both a protonated acid and a deprotonated anion. An acid anion is named by omitting the word acid and replacing the *-ic* suffix of the acid name with an *-ate* suffix (e.g., acetic acid/acetate). This nomenclature is essential when describing unique properties or reactivities of an anion relative to its acid. However, it may be inferred in the absence of discussion on water chemistry and speciation that the use of an acid name alone collectively refers to both the acid and its anion irrespective of their relative concentrations. More specific nomenclature for organic acids is determined by the composition and structure of the molecule hosting the carboxylic group.

Aliphatic framework molecules most common in organic acids include alkanes (saturated hydrocarbons) and alkenes (unsaturated hydrocarbons). These saturated and unsaturated aliphatic carboxylic acids may be acyclic (straight or branched chains) or alicyclic (aliphatic rings). Acyclic aliphatic monocarboxylic acids are also referred to as fatty acids (Table 1). The first five saturated acids (formic to valeric) of this type are sometimes referred to as short-chain, low-molecular-weight, or volatile fatty acids. Although a nomenclature for these acids has been established by the International Union of Pure and Applied Chemistry (IUPAC), the convention of using the trivial names for the first five saturated acids has remained. Similarly, trivial names are used for the aliphatic dicarboxylic acids (Table 2) that are saturated with two to four carbon atoms (C_2–C_4) and unsaturated with four carbon atoms (C_4). Alicyclic carboxylic acids contain one or more saturated or partially unsaturated rings. These acids most commonly occur

Table 1. Examples of trivial names and IUPAC names for acyclic (i.e., straight or branched chains) aliphatic monocarboxylic acids (i.e., fatty acids). Preferred names are italicized

Degree of saturation	Trivial name	IUPAC name[a]	Chemical formula[b]
Saturated	*Formic*	Methanoic	$HCOOH$
	Acetic	Ethanoic	CH_3COOH
	Propionic	Propanoic	CH_3CH_2COOH
	Butyric	Butanoic	$CH_3(CH_2)_2COOH$
	Valeric	Pentanoic	$CH_3(CH_2)_3COOH$
	Isovaleric	*3-Methylbutanoic*	$CH_3[CH_3]CHCH_2COOH$
	Caproic	*Hexanoic*	$CH_3(CH_2)_4COOH$
	Isocaproic	*4-Methylpentanoic*	$CH_3[CH_3]CH(CH_2)_2COOH$
	Enanthic	*Heptanoic*	$CH_3(CH_2)_5COOH$
	Caprylic	*Octanoic*	$CH_3(CH_2)_6COOH$
	Capric	*Decanoic*	$CH_3(CH_2)_8COOH$
	Lauric	*Dodeaanoic*	$CH_3(CH_2)_{10}COOH$
Unsaturated	Acrylic	*Propenoic*	$CH_2{:}CHCOOH$
	Cratonic	*2-Butenoic*	$CH_3CH{:}CHCOOH$
	Allylacetic	*4-Pentenoic*	$CH_2{:}CH(CH_2)_2COOH$
	Hydrosorbic	*3-Hexenoic*	$CH_3CH_2CH{:}CHCH_2COOH$
	Dehydracetic	*4-Hexenoic*	$CH_3CH{:}CH(CH_2)_2COOH$
	Oleic	*cis-9-Octadecenoic*	$CH_3(CH_2)_7CH{:}CH(CH_2)_7COOH$
	Vaccenic	*trans-11-Octadecenoic*	$CH_3(CH_2)_5CH{:}CH(CH_2)_9COOH$
Polyunsaturated	Sorbic	*2,4-Hexadienoic*	$CH_3CH{:}CHCH{:}CHCOOH$
	Linoleic	*cis,cis-19,12-Octadecadienoic*	$CH_3(CH_2)_3(CH{:}CH)_3(CH_2)_7COOH$
	Linolenic	*cis,cis,cis-9,12,15-Octadecadiernoic*	$CH_3(CH_2CH{:}CH)_3(CH_2)_7COOH$

[a] International Union of Pure and Applied Chemistry.

[b] [ ], branched group and :, double bond.

Table 2. Examples of trivial names and IUPAC names for acyclic (i.e., straight or branched chains) aliphatic dicarboxylic acids. Preferred names are italicized

Degree of saturation	Trivial name	IUPAC name[a]	Chemical formula
Saturated	*Oxalic*	Ethanedioic	$HOOCCOOH$
	Malonic	Propanedioic	$HOOCCH_2COOH$
	Succinic	Butanedioic	$HOOC(CH_2)_2COOH$
	Glutaric	*Pentanedioic*	$HOOC(CH_2)_3COOH$
	Adipic	*Hexanedioic*	$HOOC(CH_2)_4COOH$
	Pimelic	*Heptanedioic*	$HOOC(CH_2)_5COOH$
	Suberic	*Octanedioic*	$HOOC(CH_2)_6COOH$
Unsaturated	*Maleic*	*cis*-Butenedioic	$HOOCCH{:}CHCOOH$
	Fumaric	*trans*-Butenedioic	$HOOCCH{:}CHCOOH$

[a] See Table 1 footnotes.

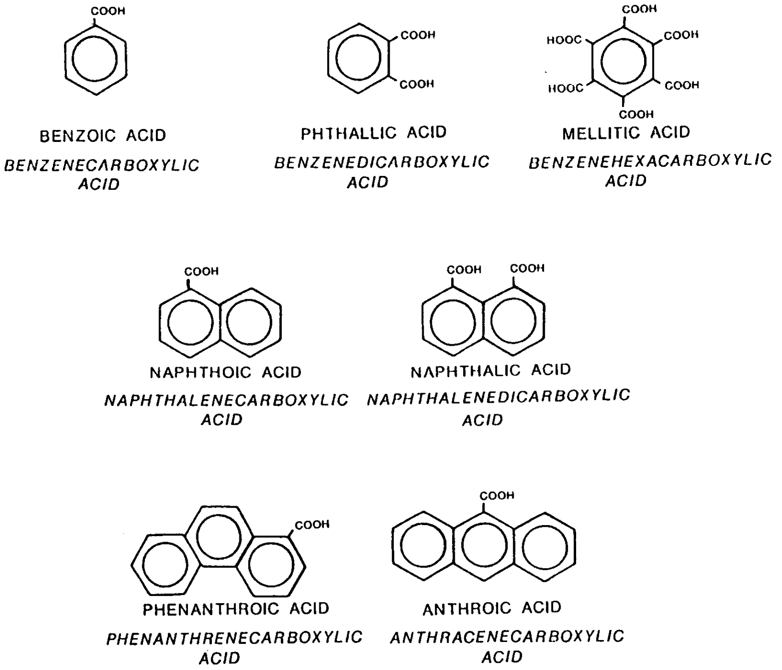
in petroleum rather than formation waters, and they are sometimes referred to as naphthenic acids (Lochte and Littmann 1955). Alicyclic carboxylic acids containing only one aliphatic ring typically subscribe to the IUPAC nomenclature (e.g., cyclohexane carboxylic acid), and those containing two or more aliphatic rings subscribe to the trivial nomenclature (e.g., oleanolic acid).

Aromatic carboxylic acids contain one or more conjugated six-carbon rings (i.e., benzene) with one or more carboxylic groups. The acids containing one benzene ring typically are referred to by their trivial names, but acids with two or more fused benzene rings are referred to by their IUPAC or trivial names. Examples of aromatic carboxylic acids and their nomenclatures are shown in Fig. 1a. Hydroxyl ($-OH$) and methoxyl ($-OCH_3$) functional groups may be directly bound to the benzene rings of these carboxylic acids (Fig. 1b). It becomes apparent from the examples of these highly functionalized acids in Fig. 1b that the nomenclature becomes more ungovernable as the number and types of functional groups increase. As a result, most high-molecular-weight and highly functionalized organic acids that are relevant to geological processes are referred to by their trivial names. Extreme examples of this convention are the humic and fulvic acids, which are operational names based on acid insolubility and solubility of nonvolatile, high-molecular-weight (500 to 5000 amu), highly functionalized, organic acids with a structural framework of aliphatic and aromatic components.

3 History of Organic Acids in Geological Processes

According to Zinger and Kravchik (1972), the first published data on organic acids in oil-field waters were by Potylitsin in 1882. The first English language author on the subject appears to have been Rogers (1917). A hiatus in the

(a) AROMATIC CARBOXYLIC ACIDS



(b) HYDROXY/METHOXY AROMATIC CARBOXYLIC ACIDS

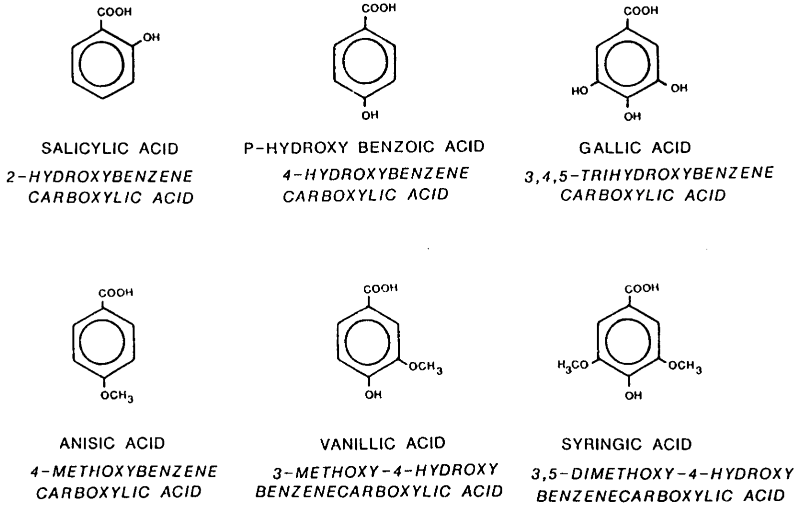


Fig. 1. Examples of **a** aromatic carboxylic acids and **b** hydroxyl/methoxy aromatic carboxylic acids. Trivial names are given in regular type and IUPAC names are *italicized*

study of naturally occurring organic acids followed until it was recognized in the 1940s that organic acids in formation waters caused significant corrosion to oil-field equipment and production pipes (Menaul 1944; Greco and Griffin 1946). This corrosion was particularly apparent in gas-condensate wells producing from depths in excess of 1.5 km at temperatures greater than 70 °C (Lowe 1953). The negative economic impact of this corrosion on production costs prompted the Natural Gasoline Association of America to establish the Corrosion Committee to collect and administer industrial contributions for funding research concerning this corrosion problem. Results of studies funded by this initiative were collectively published under the editorship of Prange et al. (1953). Papers in the book that provided particularly relevant data and observations on the corrosive role of organic acids are by Shock (1953), Chesney (1953), and Prange (1953). As an example, Fig. 2 shows the combined influence of CO_2 partial pressure and concentrations of

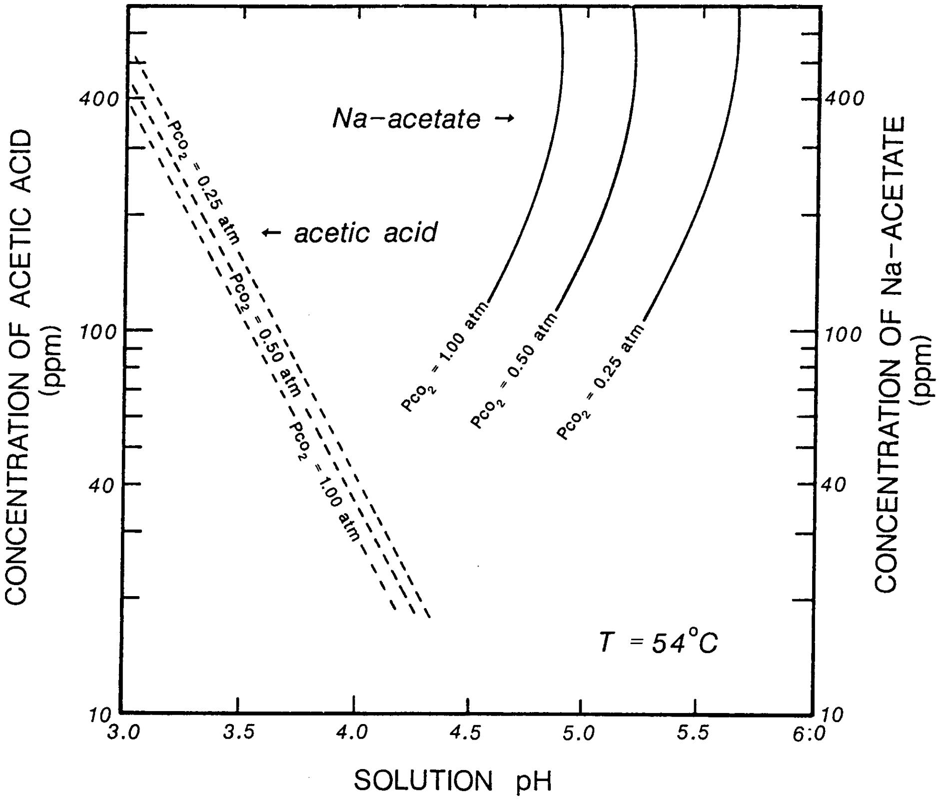


Fig. 2. Diagram of experimental data showing the influence of CO_2 partial pressure and concentrations of acetic acid (*dashed lines*) and sodium acetate (*solid lines*) on the pH of a water at 54 °C. (After Shock 1953)

acetic acid and sodium acetate on the pH of water at 54 °C in laboratory experiments summarized by Shock (1953). Later studies by Russian investigators also attributed corrosion of production field pipes to organic acids (Obuchova and Kutovaya 1968).

Within the geochemistry community, early efforts were directed toward documentation of organic acid occurrences or their proximity indicators to petroleum accumulations (e.g., Collins et al. 1961; Gullikson et al. 1961; Bykova and Nikitina 1964; Shvets and Seletskiy 1968; Shvets 1970; Bykova et al. 1971; Zinger and Kravchik 1972; Kudryakov 1974; Kartsev 1976). Willey et al. (1975) were probably the first to use modern analytical techniques to quantify organic acids. They showed that the measured alkalinity values of waters from Kettleman North Dome oil field, California, were dominated (75 to 100%) by organic acids. Failure to consider this contribution by organic acids to alkalinity results in overestimating carbonate concentrations. Equilibrium calculations based on this overestimate result in exaggerated saturation states for carbonate minerals. Matusevich and Shvets (1973) and Carothers and Kharaka (1978) demonstrated a correlation between organic acids in formation waters from oil fields and temperature. At temperatures below about 80 °C, the acids are assumed to be consumed by bacteria, whereas at temperatures exceeding 140 °C, the acids undergo decarboxylation. Organic acids are most abundant around 90 °C (Fisher 1987). Carothers and Kharaka (1978) believe organic acids are assumed to undergo decarboxylation while in reservoir rocks to form methane. Other papers of significance in the study of organic acids in oil-field waters include Hatton and Hanor (1984), Hanor and Workman (1986), Kharaka et al. (1986), Means and Hubbard (1987), Barth (1987), Fisher (1987), MacGowan and Surdam (1988), and Fisher and Boles (1990).

Surdam and his students (1984) were the first to recognize that organic acids have the potential to dissolve minerals, including aluminous silicates, to create secondary porosity in the subsurface. Until this time, secondary porosity was believed to originate primarily through the action of carbon dioxide (Schmidt and McDonald 1979). Lundegard et al. (1984) and Bjørlykke (1984) showed that the volume of available carbon dioxide from decarboxylation of organic matter was inadequate to explain the volume of secondary porosity believed to exist in sandstones of the Frio Formation in the Gulf Coast, USA. Surdam knew, from Huang and Keller's 1970 work, that organic acids dissolve minerals in soils and suggested that organic acids derived from kerogen in source rocks had the capability to dissolve carbonate and silicate minerals in subsurface sandstones. Organic acids are known to complex metals, which is of significance to diagenesis and the origin of hydrothermal ore deposits. Surdam, in later work (MacGowan and Surdam 1988; Surdam et al. 1989), stressed the importance of dicarboxylic acids in creating secondary porosity in sandstones. Surdam et al. (1984, 1989), MacGowan and Surdam (1988, 1990) and MacGowan et al. (1990) have reported on the relationship of organic and inorganic reactions during diagenesis of sandstones. They advocate the importance of organic acids in creating secondary porosity in sandstones. This view has been challenged by Giles and his coworkers (Giles and Marshall 1986; Giles and de Boer 1989, 1990).

Because of the interest in organic acids and their significance to secondary porosity, a variety of laboratory studies have been conducted. Organic matter has been heated to generate organic acids (e.g., Kawamura and Ishiwatari 1985; Kawamura et al. 1986; Eglinton et al. 1987; Kawamura and Kaplan 1987; Lundegard and Senftle 1987; Barth et al. 1988). Crossey (1991) experimentally investigated the thermal degradation of organic acids. Laboratory studies of the effect of organic acids on the dissolution of aluminosilicates were made by Surdam et al. (1984), Mast and Drever (1987), Bevan and Savage (1989), Hajash et al. (1989), and Stoessell and Pittman (1990). The experiments of Stoessell and Pittman (1990) did not produce as much dissolution of feldspar as the other studies. Fein (1991a) experimentally evaluated acetate complexing and incorporated the results in thermodynamic models, which indicated that the presence of acetate in formation waters cannot significantly increase porosity in sandstones through mineral dissolution. A companion study by Fein (1991b) indicated that Al-oxalate complexing is more important than Al-acetate complexing.

Harrison and Thyne (1992) used geochemical modeling (EQ3/6) to evaluate the effects of organic acids. They concluded that organic acid anions are ineffective at neutral to alkaline pH in modifying aluminosilicate minerals, but may be effective over a wide range of pH in dissolving carbonate minerals. Lundegard and Land (1989) also used geochemical modeling to investigate the effectiveness of acetate anions in buffering the pH of natural waters. They concluded that for the Gulf Coast Basin, an increase in partial pressure of carbon dioxide would have promoted calcite dissolution despite the buffering effects of the acetate. Lundegard and Kharaka (1990) reached the same conclusion.

The kinetics of the decarboxylation reaction for acetic acid anions have been studied by Kharaka et al. (1983) and Palmer and Drummond (1986). Apparently, the decarboxylation reactions are slow under diagenetic conditions. Shock (1988) has investigated the stability of organic acids in sedimentary basins on the basis of thermodynamic metastability.

There has been considerable interest in the role of organic acid anions in weathering and groundwater. Antweiler and Drever (1983) presented evidence that organic acid complexes increase the mobility of aluminum and iron in the weathering of volcanic ash. The dissolution of quartz by organic acids in groundwaters (Bennett and Siegel 1987; Bennett 1991) and of quartz and aluminosilicates in peat bogs (Bennett et al. 1991) has been documented. Laboratory dissolution of quartz in dilute aqueous solutions of organic acids at 25 °C suggests that organic acids in organic-rich soils and weathering zones are capable of complexing silica at neutral pH (Bennett et al. 1988). The analytical work of Marley et al. (1989) using laser Raman and

Fourier transform infrared spectroscopies appears to support the observation that organic dicarboxylic acids can lead to enhanced solubility of quartz.

During the 1980s, there was considerable research activity on the hydrothermal transport of metals by organic acid complexes. Papers of interest include Giordano and Barnes (1981), Giordano (1985, 1989), Drummond and Palmer (1986), Hennet et al. (1988), and Yang et al. (1989).

4 Brief Synopsis of Chapters

Chapter 2, by MacGowan and Surdam, covers the procedures and problems related to the collection of formation waters and analysis of organic acid anions. Early studies documented only monocarboxylic acid anions in oil-field waters. MacGowan and Surdam (1988) showed later that dicarboxylic acid anions can also be abundant (up to 2540 ppm malonate) in oil-field waters. Other laboratories have not confirmed these high values for carboxylic acid anions. This may be due to sampling or analytical procedural problems. Ion chromatography exclusion currently is the most popular analytical technique for analysis of carboxylic acid anions in sedimentary formation waters. MacGowan and Surdam show that this technique is difficult to apply and requires patience and time. It is almost an art form and requires multiple runs. In addition, the resampling of wells through time may yield inconsistent values of organic acids. For example, MacGowan and Surdam (Chap. 2, Table 1) sampled one well four times and obtained acetate concentrations ranging from 56 to 2435 ppm. This variation is to be expected according to MacGowan and Surdam because when a sample is taken from the separator the mixture of oil and water varies, which can lead to varying results.

Chapter 3, by Lundegard and Kharaka, provides an overview of the distribution and nature of organic acids in the subsurface. At temperatures less than 40 and greater than 180 °C, concentrations of organic acid anions are less than a few hundred mg/l. At intermediate temperatures, there is a crude relationship between temperature and the maximum observed concentrations. Factors that contribute to the variation in quantity of organic acids are attributed to the richness and type of organic matter in the source rocks and the thermal history of the source rocks. Post-generation factors that affect organic acids in formation waters include variability of dilution, biodegradation, and effects of natural catalysis on decarboxylation. It is useful to consider the potential geochemical effects that the maximum organic acid concentrations have on the geochemical system. However, it is more important to consider the effect of "normal" concentrations because available data suggest that organic acid concentrations >3000 mg/l are rare. New data on the generation of organic acids from reservoired oil under thermal stress are also presented and discussed.

Chapter 4, by Lewan and Fisher, examines the role petroleum source rocks play in supplying organic acids to formation waters during their thermal maturation in the subsurface of subsiding sedimentary basins. The vastness and dynamics of sedimentary basins and the lack of data on subsurface waters associated with petroleum source rocks necessitate the use of laboratory pyrolysis experiments to gain insights on this potential source of organic acids. The authors discuss important experimental conditions that should be considered in laboratory simulations of organic matter maturation. Experimental data published in the literature are summarized and compared, along with new data from their laboratory not previously published. Bonding of organic acids in sedimentary organic matter appears to be noncovalent in character. Maximum conversion of sedimentary organic matter to short-chain carboxylic acids appears to be 2.5 wt%. Half of these organic acids may be lost during early diagenesis as a result of diffusion. The authors' calculations suggest that the sluggishness of this process prevents significant and timely quantities of organic acids from generating secondary porosity on a basinwide scale. Another implication presented in this chapter is that currently observed organic acids in formation waters associated with petroleum accumulations may have originally been carried as dissolved species in the petroleum and released into the associated formation waters as the migrating petroleum reequilibrates with cooler, lower salinity, or lower gas pressure conditions of a reservoir.

Chapter 5, by Pittman and Hathon, reviews published material-balance considerations for calculating whether sufficient acids can be generated from kerogen in shales to account for secondary porosity generally believed to be present in sandstones. This chapter also presents what is believed to be the first published material-balance calculations based on actual data on source rocks and sandstones for a given area (deep part of the Denver Basin), rather than using estimates or hypothetical considerations. Source rock geochemistry provided information on the volume and type of organic matter for each source rock. Point-count analysis for porous sandstones throughout the stratigraphic column yielded data on the amount and type of secondary porosity. Geophysical logs were used to determine the thickness of source rock and sandstone units for calculating volumes. The modeling is based on hydrous pyrolysis of thermally immature source rocks to establish the conversion efficiency of kerogen oxygen to mono- and dicarboxylic acids. Under optimum conditions for organic acid activity, the authors calculate that 1.72% secondary porosity could form in the sandstones of the basin from CO_2 and carboxylic acids; whereas, by point-count analysis, using a conservative approach to identifying secondary porosity, there is at least 2.49% secondary porosity in sandstones in the basin.

Chapter 6, by Drever and Vance, provides a useful overview of the distribution and significance of organic acids in soils. Low-molecular-mass acids (e.g., acetic, oxalic, formic) exist in dynamic balance within soils. They are rapidly produced and consumed by microorganisms. Concentrations of organic acids are generally highest in the organic layer at the top of the soil profile and decrease with depth. Organic acids affect the mineralogy of soils by complexing and transporting Fe and Al. There is considerable controversy regarding whether organic acids at natural concentrations significantly accelerate the rate of dissolution of primary silicate minerals. It is not likely that organic acids are important in the weathering of granitic rocks, but they may be important in the weathering of more mafic rocks. Organic acid concentrations may be significantly higher in microenvironments surrounding rootlets or fungal hyphae than in bulk soil solutions.

***Chapter** 7*, by Bennett and Casey, covers the chemistry and mechanisms of the dissolution of silicate minerals by organic acids. Organic acids chelate silica and aluminum via ligand-exchange complexation mechanisms. Silica is complexed at near-neutral pH values, whereas aluminum is most effectively chelated at acidic pH values. The chemistry of solution complexation can be applied to silicate surfaces where ligand-promoted dissolution is commonly faster than dissolution in nonorganic systems. Steep chemical gradients and high concentrations of organic acids exist in the vicinity of microbial colonies, which suggest that microbial activity may be important in some weathering processes. Bennett and Casey present examples from peat bogs, underclays, and petroleum-contaminated groundwaters.

In ***Chapter 8***, Hajash reviews experimental data on dissolution of feldspar. These data vary because of the initial solids, fluids, experimental systems, and procedures used by different investigators. Hajash concludes that most data indicate that carboxylic acids enhance the solubility of feldspar, especially at moderately acidic (pH 4 to 5) conditions. Dicarboxylic acids in some subsurface brines suggests the acids have been stabilized by complexation with metal ions. The kinetics for decarboxylation of mono- and dicarboxylic acids are more effective than monocarboxylic acids. Generally, the aluminum content of the reacted solutions varies inversely with pH and directly with the organic acid concentration. The effectiveness of organic acids in dissolution and buffering processes is a function of their type and concentration, pH, temperature, reaction kinetics, and flow rate. Mobility of aluminum during diagenesis may also be influenced by the presence of carbonate or mafic minerals and the activity of CO_2 or other dissolved components in formation waters.

***Chapter** 9*, by Bell and Palmer, reviews experimental studies concerned with the decomposition of organic acids and their anions. In the absence of an effective catalytic surface, acetic acid may be expected to survive indefinitely. However, there are many potential catalysts. Laboratory determined activation energies for the decarboxylation of acetic acid varies from 34 to $170\,\mathrm{kJ\,mol^{-1}}$ for stainless steel and titanium oxide, respectively. Reaction rates for the decarboxylation of dicarboxylic acids are extremely fast and uncomplexed acids are not likely to survive geologically significant lengths of time. However, the observed occurrence of dicarboxylic acids in some subsurface brines suggests the acids have been stabilized by complexation with metal ions. The kinetics for decarboxylation of mono- and dicarboxylic acids are first-order with respect to total carboxylate concentration, and their rate constants are greater in the acid form than in the anionic form. Rate constants at intermediate pH values follow a linear relation between the acid and anion forms for dicarboxylic acids and are greater than the acid form for monocarboxylic acids.

Chapter 10, by Shock, considers the application of thermodynamic calculations to geochemical processes involving organic acids. This chapter starts with a discussion of how to calculate standard state thermodynamic properties of aqueous organic acids. Thermodynamic calculations are then applied to decarboxylation reactions involving organic acids and to redox reactions between organic acids, CO_2, and hydrocarbons. The decrease in concentration of carboxylic acids with increasing temperature from 80 to 200 °C, as first published by Carothers and Kharaka (1978), does not exist when all currently available data are plotted. Shock believes there is no basis for drawing an upper temperature limit on this plot as Surdam et al. (1984) have done. High concentrations of acetic acid in oil-field brines are preserved in a metastable state with respect to the decarboxylation reaction and hydrogen fugacity is controlled by the presence of petroleum. The decarboxylation reaction of acetic acid in sedimentary basins is inhibited and cannot be in stable equilibrium with both CO_2 and CH_4. The potential for metastable equilibrium between acetic acid and CO_2 is large under geologically realistic conditions, but the potential for metastable equilibrium involving acetic acid and CH_4 is severely limited.

Chapter 11, by Giordano, is an overview of organic acid complexing in the genesis of ore deposits. Models for Mississippi Valley-type ore solutions and ore fluid for red-bed-related, base-metal deposits are evaluated in this chapter. These models are limited by availability of thermodynamic data, but their chief deficiency is lack of well-constrained geochemical parameters for the ore-forming systems. These models suggest that metal-organic complexes may be important in transporting lead, zinc, and other metals in ore fluids for these two major types of deposits. The significance of aliphatic-carboxylate complexes in transporting ore metals is inversely related to the activities of hydrogen sulfide, bisulfide, and chloride. Transport of metals and reduced sulfur in the same ore fluid may occur in the form of organosulfur complexes.

Chapter 12, by Harrison and Thyne, provides an overview of geochemical modeling for rock-water interactions in the presence of organic acids. Geochemical modeling is useful because it provides insight into the role of organic acids and their anions in subsurface formation waters by defining boundary conditions under which such interactions may be significant. These authors conclude that aluminum acetate complexes are of minor importance; whereas aluminum oxalate dominates the species distribution of Al under acidic conditions. They believe that organic acids contribute to the overall patterns of fluid-rock interaction, but appear unlikely to dominate such reactions except in restricted geochemical environments where their concentrations are in excess of typical values. Probable environments meeting this requirement include wetlands, gasoline-contaminated groundwaters, and sandstones adjacent to organic-rich shales.

Chapter 13, by Surdam and Yin, provides an overview of the relationship for organic-inorganic diagenesis and provides a detailed case history. They suggest that a sequential set of carbonate reactions characterizes many clastic source/reservoir rock systems during progressive burial. With increasing thermal exposure during burial, the sequence is: (1) formation of carbonate cements that preserve intergranular pore volume; (2) dissolution of early carbonate cements, which may enhance porosity and result in positive porosity anomalies; (3) formation of late carbonate cements, which may retard compaction; and (4) if tempertures are high enough and if quartz cementation is inhibited, dissolution of late carbonate cements, again enhancing porosity. Coupling the above sequence of carbonate reactions with parallel organic reactions, including generation and decarboxylation of organic acids, Surdam and Yin construct a predictive, process-oriented model. This model consists of three operations: (1) reaction pathway diagnostics; (2) kinetic modeling of organic reactions; and (3) simulation of the rock/water interactions in either time or temperature space. They believe the integration of the above three operations allows prediction of zones of carbonate dissolution in source/reservoir rock systems.

Chapter 14, by Giles, de Boer, and Marshall, evaluates the hypothesis that organic acids create significant secondary porosity in sandstones and enhance aluminum mobility in the subsurface. They believe the hypothesis fails because: (1) evidence does not support a sudden increase in secondary porosity pore volume over the temperature range where carboxylic acids are most abundant; (2) experimental data on the dissolution of feldspars by organic acids show little evidence to support enhanced dissolution or increased aluminum mobility except at unrealistically low pH values; (3) complexing of aluminum by organic acids is unlikely in natural formation waters because of the competition of other ions for the organic acid ligands; (4) acids generated in a shale source rock would quickly be neutralized either in the source rock (unless it was exceptionally rich in organic matter) or along migration pathways; and (5) mass-balance calculations suggest that source rocks would have to be unreasonably abundant to generate enough carboxylic acids to account for even a few percent of secondary porosity.

5 Future Research

Although the following chapters present current observations and views on the role of organic acids in geological processes, additional research is needed to elevate the current evolving hypotheses into working scientific concepts. The future research needed to reach this goal is discussed under two headings: (1) natural system studies and (2) laboratory experimental studies. Both types of studies are included in this book and their interdependence is unquestionable. Natural system studies provide the critical observations in natural settings that define the boundary conditions within which geological processes operate. Usually, the vastness and dynamics of the natural system result in limited and static data with wide knowledge gaps that allow for multiple interpretations. These knowledge gaps in natural system studies may be bridged in part by laboratory experimental studies. The success of bridging these knowledge gaps by laboratory experiments depends on designing experiments that best simulate the natural system.

5.1 Natural System Studies

1. There is general agreement that dicarboxylic acids have a more significant effect on dissolution of silicate minerals than monocarboxylic acids, but their presence and abundance in natural formation waters remain uncertain. A collaborative study involving different laboratories is needed to resolve this uncertainty. Each laboratory would analyze aliquots of formation waters collected from a series of wells representing different subsurface conditions and water chemistries. The analytical results would be reviewed by the participating laboratories with the objectives of resolving analytical problems and establishing accepted procedures and standards. This type of study could also be expanded to include analyses of monocarboxylic acids and more complex higher-molecular-weight organic acids.

2. Experimental data clearly demonstrate that organic acids can have a significant influence on mineral dissolution reactions when pH values are less than 5 (Fig. 2). The uncertainty here is whether natural waters, particularly subsurface formation waters, typically attain these low pH values. Drilling engineers in the late 1940s and early 1950s faced a similar uncertainty in explaining the high rate of corrosion to drill pipes in some condensate wells. Initially, they did not consider the corrosion process to be related to organic acids because of the high pH values (≥6) of the produced waters as measured in the laboratory. Subsequent studies showed that the pH values measured in laboratories under atmospheric conditions were not representative, and that pH values measured under subsurface conditions were low enough (<5) to invoke organic acids as important participants in the corrosion process (Shock 1953). Procedures and apparatus for measuring the pH of formation waters at wellhead pressures (Carlson 1949) and flow rates (Collins 1964) have been shown to provide pH values more representative of the subsurface waters. Downhole drill-stem testing equipment is currently available for sampling subsurface formation waters. Currently, these downhole tools may be equipped with optical sensors for in situ viewing of fluid phase behavior or resistivity probes for in situ estimates on water salinities

(Badry et al. 1993), but no tools are currently equipped with electrodes for in situ measurements of pH. pH electrodes that operate at high temperatures (e.g., 200–300 °C) are currently being developed (Bourcier et al. 1987), and research into their use during subsurface drill-stem tests of formation waters may provide the best results in determining this important variable.

3. The existing data base on the subsurface occurrence of organic acids consists almost exclusively of formation waters associated with petroleum accumulations. Between the years 1970 and 1990, more than 200000 exploration wells were drilled in the United States and only 13% of these wells encountered petroleum (Energy Information Administration 1991). Future research in natural system studies should make a concerted effort to expand the current data base with analyses of formation waters not associated with petroleum accumulation. Comparisons of organic acid types and abundances in formation waters associated and not associated with petroleum accumulations may provide new data relevant to the origin and emplacement of organic acids. In addition, a concerted effort to collect subsurface waters associated with humic coals and organic-rich shales at different levels of thermal maturity would provide critical data to our understanding of the origin of organic acids.

4. There appears to be general agreement that organic acids can accumulate in high enough concentrations to influence processes in soil and groundwater microenvironments or in subsurface rocks immediately adjacent to organic-rich rocks. Future research is needed to determine whether variations in the physical, chemical, and biological controls on these localized occurrences can influence neighboring processes that are more regionally operative. Natural system studies of this type will require more detailed sampling and consideration of microbial activity.

5. Although organic acids have been shown to be capable of enhancing metal transport in ore fluids at 75 to 150 °C, their occurrence in ore fluids remains to be established. Future research directed at identifying and quantifying organic acids in fluid inclusions of ore minerals or gangue is needed. This type of data would provide the geochemical constraints necessary to test and develop models for ore-forming systems. A method for analyzing short-chain organic acids in fluid inclusions has been developed (Hofstra and Emsbo 1992). This technique also could be profitably applied to fluid inclusions in mineral cements of petroleum-bearing strata.

5.2 Laboratory Experimental Studies

1. The hypothesis that organic acids in formation waters are derived from coexisting petroleum as a result of reequilibration of the two immiscible phases under reservoir conditions needs further study. Although partition coefficients for organic acids in water and pure hydrocarbons are available at 25 °C and 1 atm (Leo et al. 1971), partition coefficients for organic acids in

water and petroleum are not available under reservoir conditions. The laboratory experimental study by Knaepen et al. (1990) has shown that the partition coefficients for ethyl acetate in water and petroleum can be significantly different with increasing water salinity, dissolved gas content, and temperature. Future research using a similar experimental approach to determine partition coefficients for organic acids under reservoir conditions is needed. Other variables worth considering include the composition of petroleum and the factors that influence the time required for partition coefficients to reach equilibrium.

2. Laboratory experiments have demonstrated that mono- and dicarboxylic acids, in low salinity solutions with pH values lower than 5, enhance solubility and increase dissolution rates of feldspars and clay minerals at temperatures between 70 and 100 °C. Future laboratory experiments should be conducted with brines of various salinities and compositions, dissolved CO_2 at different partial pressures, and different mineral assemblages representative of subsurface conditions. These experiments will more closely simulate the natural system and provide data on the effects of cation competition for complexing sites, salinity on silica solubility, enhanced acidity due to dissolved CO_2, and mineral interactions on overall dissolution rates.

3. Experimental studies concerned with the stability of mono- and dicarboxylic organic acids have focused on decarboxylation as the primary reaction responsible for their destruction. These studies have typically evaluated kinetics of the assumed decarboxylation reaction by monitoring changes in the organic acid concentrations. It is essential that future experimentation identify and monitor the resulting products, as well as the loss of reactant. This approach will better define the destructive reactions, and assist in evaluating the significance of organic acid destruction through oxidation and condensation reactions. The importance of catalytic surfaces in the destruction of monocarboxylic organic acids suggests that future experiments be conducted in the presence of mineral surfaces common in the natural system (e.g., quartz, clay minerals, and feldspars). Other potentially significant variables worth considering in future experiments are differences in stability between different metal-organic complexes and between organic acids dissolved in water and those dissolved in petroleum.

4. From a petrographic perspective, the recognition of secondary porosity in sandstones is based on textural evidence visible in thin sections using criteria presented by Schmidt and McDonald (1979). There is no problem recognizing secondary porosity in thin sections when the porosity is intragranular or moldic. However, a problem arises when one attempts to determine how much, if any, intergranular porosity is secondary in origin due to dissolution of cement (e.g., carbonates). Textural evidence gained from the scanning electron microscope is helpful in some situations (Burley and Kantorowicz 1986; Larese and Pittman 1987), but there is currently no known way to quantify the amount of secondary porosity. As a result, petrologists subjectively interpret the textural evidence as indicative of sparse

or abundant intergranular secondary porosity depending on their experience, training, or bias. It is also possible that secondary porosity has been overestimated due to the presence of artifact porosity, which mimics secondary porosity (Pittman 1992).

A replacement texture imprint commonly is visible under the scanning electron microscope on sand grain surfaces and/or on preexisting cements after exposure by leaching of carbonate cement from sandstone in the laboratory. Larese and Pittman (1988 unpubl. data) observed replacement textures in every rock that they studied using this technique, which commonly requires the use of high magnification; however, it is unknown if a replacement imprint is visible in every pore. If so, then this technique could be used to quantify the amount of secondary intergranular porosity in naturally porous sandstone. Certainly, some method is needed for quantifying the amount of secondary intergranular porosity.

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