Geoscience Canada

Diagenesis #11. Early diagenetic pore water/sediment interaction: Modern offshore basins

Reinhard Hesse

Volume 13, numéro 3, september 1986

URI : https://id.erudit.org/iderudit/geocan13_3art03

Aller au sommaire du numéro

Éditeur(s)

The Geological Association of Canada

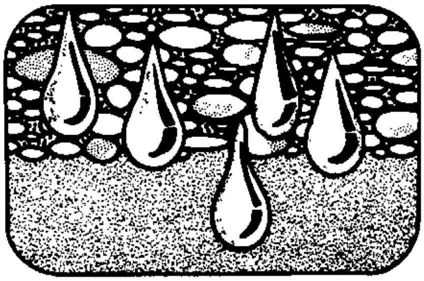
ISSN

0315-0941 (imprimé)
1911-4850 (numérique)

Découvrir la revue

Citer cet article

Hesse, R. (1986). Diagenesis #11. Early diagenetic pore water/sediment interaction: Modern offshore basins. *Geoscience Canada*, *13*(3), 165–196.



Diagenesis #11. Early diagenetic pore water/ sediment interaction: Modern offshore basins

Reinhard Hesse
Department of Geological Sciences
McGill University
Montreal, Quebec H3A 2A7

Introduction

Rock-water interaction, which receives so much attention by geothermal engineers, igneous and metamorphic petrologists, is of tantamount interest to sedimentary petrologists studying diagenesis. Water is the principal transport medium in diagenesis acting as the carrier of dissolved substances from sites of dissolution to sites of precipitation in the sediment column and facilitating chemical exchange between sedimentary basins and the hydrosphere. Where water is absent because mineral cements or non-aqueous fluids such as liquid or gaseous hydrocarbons fill the pores, diagenetic reactions are inhibited or slowed down drastically. For most diagenetic reactions the presence of water in the sediment pores is thus a prerequisite. Pore-water analyses are, therefore, of great significance in the study of diagenesis, particularly early diagenesis for which water is as volumetrically important as the solid phases. Pore waters are much more sensitive to changes in diagenetic environments than solids and therefore are the preferred diagnostic objects for the study of early diagenesis. There are three aspects of diagenesis to which pore-water studies contribute most:

(1) The detection of diagenetic reactions actively occurring in the sediment at the time of sampling (drilling) by tracing the products of these reactions released to, or the reactants consumed from, the pore water through observed concentration changes in vertical or lateral profiles.

(2) Distinction between the principal modes of solute transport, i.e. between advection (convection) and diffusion, and determination of their flux rates.

(3) Assessment of mineral-solution equilibria. As it is a widely held view that diagenetic processes in actively subsiding sedimentary basins do not lead to thermodynamic equilibrium between the potential reaction partners, pore-water chemistry can provide clues to this question by providing the data necessary for calculation of the saturation state with respect to the minerals of interest. Such calculations have been carried out for common authigenic minerals in ancient basins on land (Merino, 1975; Nesbitt, 1980, 1985) and in a few cases also for modern offshore basins.

The general plan for this review is to follow the early diagenetic pore-water evolution in modern offshore basins tracing the changes that occur with increasing burial from the sources to the sinks of the dissolved species. The three principal processes causing these changes are reactions, diffusion and advection whose combination produces eight different types of pore-water profiles. These will be discussed in order of increasing complexity. Relatively simple, more or less straight-line pore-water profiles are encountered in low sedimentation-rate environments of the pelagic realm and can be understood in terms of diffusive and convective transport of solutes. These are discussed first together with some mineralization reactions that are characteristic for the early diagenetic history of these environments. The more complex profiles observed in organic-matter rich, high sedimentation-rate basins of the continental margins (with their reaction-dominated trends) follow. In these basins, extensive mineralization reactions serve as sinks for the dissolved substances. They are treated in a separate section. Ion exchange reactions and adsorption are additional sinks that may help to understand the behaviour of some ionic species in these basins. The definition of the boundaries for "the stage of early diagenesis" is deferred to the end of the article, because it is based on the deliberations of this review.

Terminology

The diagenetic evolution of pore water starts with "connate water" which is the water trapped between the sediment particles during deposition. Initially this connate water may considerably exceed the volume of the solids. Freshly deposited clayey-silty sediments may contain as much as 90% (by volume) water, and sands up to 40% or 50%. However, with burial to depths of only a few metres the water content is very rapidly reduced in volume.

There has been considerable confusion in the literature concerning the term "connate water". Due to reactions with the solids, pore waters usually undergo significant compositional changes in the subsurface. Buried interstitial waters commonly are strikingly different in composition and total amount of dissolved species from their connate-water precursors in marine or terrestrial environments. The term connate water, in the sense advocated by Case (1955), however, should be used only for pore waters still displaying the compositional and isotopic signatures inherited from their parental source in the ocean or lake water bodies. Generally this applies only to the shallowest levels of burial, often not more than a few centimetres or millimetres below the sediment/water interface over which distance the pore water is still in diffusional contact with the overlying water body. Only in exceptional situations, such as certain types of pelagic sediments, may this zone of diffusional or convectional exchange extend downward a few hundred metres in the subsurface. The definition of "connate water" by Kharaka *et al.* (1985) as "water that was deposited with sediments or other rocks in the basin and which has been out of contact with the atmosphere since its deposition" is similar to White's (1965) definition. This definition appears too broad, because it does not take into account compositional changes that may take place immediately after deposition and which may become so profound as to obscure the origin and source of the water. To call such pore waters "connate" would not be in line with the very meaning of the word and intent of the early authors (e.g. Case, 1955) who introduced the term.

Changes in pore-water chemistry at depth are often coupled with increasing concentrations of dissolved solids. Maximum salinities are encountered in the deep parts of sedimentary basins, particulary in the vicinity of salt domes or deeply buried evaporites where values of 200-300 $g \cdot L^{-1}$ of dissolved solids are not exceptional (an up to eight-fold increase compared to normal seawater salinity). Salinities as high as 60‰ have been reported, but these occur in ore fluids of porphyry copper deposits (Roedder, 1977) not related to burial diagenesis.

Highly saline waters are called *brines*. According to Carpenter (1978), brines have salinities in excess of 10‰, which would limit application of the term to a relatively small sample of all deep subsurface waters. Following Kharaka *et al.* (1985a), salinities above seawater salinity of 3.5‰ are sufficient for a pore water (or any other hypersaline body of water) to qualify as a brine. In the petroleum industry it is common practice to call pore waters encountered in oil-bearing sedimentary formations "*formation waters*", a term which strictly applies to the "water present in the rocks immediately before drilling", whereas the general term "*interstitial water* " is applicable to all types of pore waters from all depths and different kinds of sedimentary basins: modern offshore basins on the continental margins and ocean floors, modern lakes or river basins and ancient basins on land, irrespective of age or sampling procedure. Waters with salinities lower than those of brines, i.e. between 3.5 and 1‰, are simply called "*saline waters*", those with salinities between 1.0 and 0.1‰ "*brackish*", and those with still lower concentrations of dissolved salts, "*fresh waters*". Another important term is "*meteoric water* " originally defined as "water that was recently involved in atmospheric circulation" (White, 1957,

p. 1661). This is "water derived from rain, snow, water courses, and other bodies of surface water that percolates in rocks and displaces their interstitial water" (Kharaka and Carothers, 1982). The time of the last contact with the atmosphere has been dropped intentionally from the definition by these authors, because water with the characteristics of meteoric waters may be very old. A modifier such as "Miocene" or "Pleistocene meteoric water" may be used, however, to denote its age, i.e. the time of its removal from contact with the atmosphere if known.

Sources of Pore-Water Data

Information concerning the chemical evolution of pore waters during burial diagenesis in modern offshore basins comes from three principal sources:

(1) studies of piston and gravity cores;
(2) the interstitial water-sampling program and related sediment studies of the Deep Sea Drilling Project (DSDP) and its successor program, the Ocean Drilling Program (ODP); and,
(3) offshore oil and gas wells.

The first is restricted to the upper 10 to 20 m of the sediment column in modern subaqueous environments, which is the maximum depth of penetration by conventional coring devices such as piston and gravity corers. Since the classical study by Emery and Rittenberg (1952) on California Borderland basin sediments, this type of analysis has been applied to surface sediments all over the world's oceans and of many lakes. It covers the very earliest stages of diagenesis for which Berner (1980) provides an excellent theoretical treatment and review.

In the past two decades, a second important source of information has been the Deep Sea Drilling Project. Although perhaps not as widely noticed as some other of its spectacular results, the interstitial water program has been one of the outstanding successes of this project. It provided a consistent data body of thousands of pore-water analyses covering the depth range from a few metres to about 1500 m subsurface. As an outcome of this program and the piston core studies mentioned before, we now have a fairly good understanding of the variations in pore-water chemistry that occur in the upper 1000 or 1500 m of the sediment column in different open-ocean as well as deep-water continental margin environments. Between 1968 and 1983 more than 1000 bore holes were drilled by the DSDP at 624 drill sites and for more than half of these pore-water data are available. Results have been summarized during various phases of the project (Manheim and Sayles, 1974; Sayles and Manheim, 1975; Gieskes, 1975, 1981, 1983) and this article includes an update of those earlier reviews.

Innumerable holes drilled for oil and gas or other resources in sedimentary basins on the continental shelves and slopes, from which formation waters have been sampled, provide the third source of information. There is not much overlap with the results of the DSDP, which concentrated on the ocean basins and deeper portions of the continental margins and stayed away from potential hydrocarbon provinces on the upper margins and shelves on which offshore oil drilling has focussed. Penetration reached in exploration wells for oil and gas generally exceeds that of the drill holes of the DSDP and, therefore, pore-water compositions from deeper, more advanced levels of diagenesis may be obtained, which are the subject of a forthcoming-article.

Extraction of the pore water from unconsolidated to moderately consolidated sediments by squeezing with stainless steel squeezers (Manheim and Sayles, 1974) may lead to systematic errors due to temperature increases between the ocean floor and the laboratory. Increases of 1 to 50% in chloride and dissolved silica, for a temperature difference of 20°C (Bischoff *et al.*, 1970; Fanning and Pilson, 1971) have been observed. For potassium, enrichments of up to 13% have been found, whereas magnesium and calcium can show depletions of up to 2.5 and 5%, respectively. These shifts can be avoided by standardized extraction procedures under regulated temperatures, including centrifugation for less consolidated samples.

Diagenetic Regimes of Pore-Fluid Evolution in Modern Offshore Basins

Diagenetic environments of subsurface pore-water evolution in modern offshore basins can be divided into two main regimes:

I. Low to intermediate sedimentation-rate basins (or environments) mostly associated with oxic and suboxic diagenesis and convection- and diffusion-controlled pore-water profiles, and

II. High sedimentation-rate basins characterized by anoxic diagenesis and reaction-controlled pore-water profiles. Despite the great variation in the chemical composition of pore-water analyses from offshore basins all over the world, this broad classification in terms of two main environments or regimes does justice to most of the data and will help not to miss the wood for trees. Situations not covered by this simple two-end-member scheme are included in a third category:

III. Special environments.

The reason for the dominant effect of sedimentation rate on pore-water chemistry, particularly during early diagenesis in marine basins, is its close positive correlation with organic matter content of the sediments and its tendency to counteract the role of diffusion. Organic matter is the most unstable and most reactive sediment constituent. It is metabolized rapidly by bacteria during early diagenesis and the metabolites including the basic nutrients carbon, nitrogen, phosphorus, sulphur, and hydrogen are released to the pore water. These become involved in the first diagenetic mineralization reactions and trigger other reactions. Organic matter concentration, therefore, determines the early diagenetic reactivity of the sediment, that is, rates and types of reactions.

The correlation between sedimentation rate (expressed in g-cm^{-2} per 1000 years (10^3 a)) and organic carbon accumulation rate (expressed in the same units) has been shown to be linear on a logarithmic scale (Figure 1) for open marine pelagic and hemipelagic environments (Heath *et al.*, 1977; Müller and Suess, 1979). This is basically the result of increased preservation of organic matter in more rapidly deposited sediments. The faster the sediment is buried, the more rapidly its organic matter is removed from contact with oxidizing bottom and pore waters, in which bacteria are most efficient in decomposing organic matter. Rapid sedimentation, therefore, is a prerequisite for organic matter to survive the first steps of deposition and burial and to become available for subsequent diagenetic reactions. Variations in primary production rate in the surface waters appear to be of secondary importance only, as demonstrated by those authors. Positive correlation between sedimentation rate and organic carbon content of the sediments is not universal, however, and does not apply for stagnant or semi-stagnant basins with oxygen-deficient bottom waters. The same applies to areas with extremely high sedimentation rates. In stagnant or euxinic basins, bottom waters act as a trap for organic matter protecting it from oxidation. Such basins are rare, however, in modern oceans. Excessive input of terrigenous materials has a diluting effect, thus also producing a negative correlation between sedimentation rate and organic carbon content (Gautier *et al.*, 1984; Johnson Ibach, 1982).

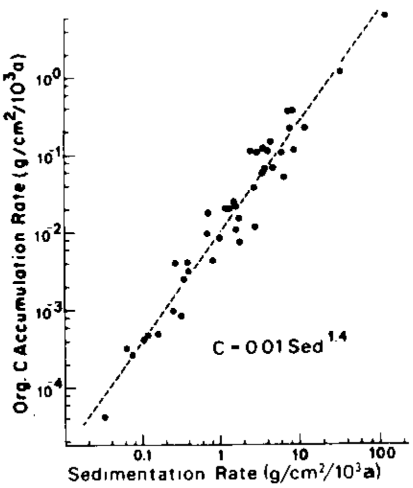


Figure 1 *Organic carbon accumulation rate as a function of sedimentation rate. (From Heath* et al.*, 1977).*

The effect of sedimentation rate on the diagenetic evolution of pore waters is twofold. Apart from the effects caused by coupling with organic matter concentration, sedimentation rate also controls pore-water evolution through its effects on diffusion rates. Where sedimentation rates exceed diffusion rates, diffusive transport cannot keep pace with burial. Chemical concentration changes produced by diagenetic reactions will be preserved much better during burial and for much longer periods of time. An analogous relationship exists between sedimentation rate and advection rate.

The linkage of sedimentation rate to the three principal diagenetic processes that control pore-water chemistry, i.e. (1) chemical reactions in the sediment/pore-water system triggered by organic matter decomposition, (2) transport of solutes by diffusion, and (3) transport by advection (convection), explains the overriding effect of this single parameter on early diagenetic pore-water evolution. Where sedimentation rates are low, the reactivity of the sediment during early diagenesis is low due to reduced organic matter concentrations, and diffusion (or advection) may efficiently dissipate existing concentration gradients. The result are simple, often straight-line vertical concentration profiles. Where sedimentation rates are high, the chemical reactivity of the sediment is high due to generally increased organic matter preservation. Consequently, early diagenetic reactions are intense. The efficiency of diffusion (and advection) in dissipating gradients established by the reactions, however, is low. Complex pore-water profiles result.

Table 1 **Major types of interstitial water profiles**

I Low to intermediate sedimentation rate basins
1. Convection controlled profiles - no chemical gradients (Figure 5, DSDP site 495)
2. Diffusion controlled profiles with linear correlation between changes in Ca and Mg concentration (Figure 6)
3. Reaction controlled profiles in suboxic environments (Figures 3, 5, site 495)

II High sedimentation-rate basins
4. Reaction controlled profiles in anoxic environments with no chloride gradients (Figure 5, upper part of DSDP site 570)
5. Profiles with fresh water influx (Figure 13)
6. Gas-hydrate affected profiles with downward decreasing chlorinity and increasing $\delta^{18}O$ values (Figures 5, 16)

III Special environments
7. Evaporite-dissolution affected profiles (Figure 17)
8. Hydrothermal activity and intrusion of igneous dikes and sills (Figure 18)

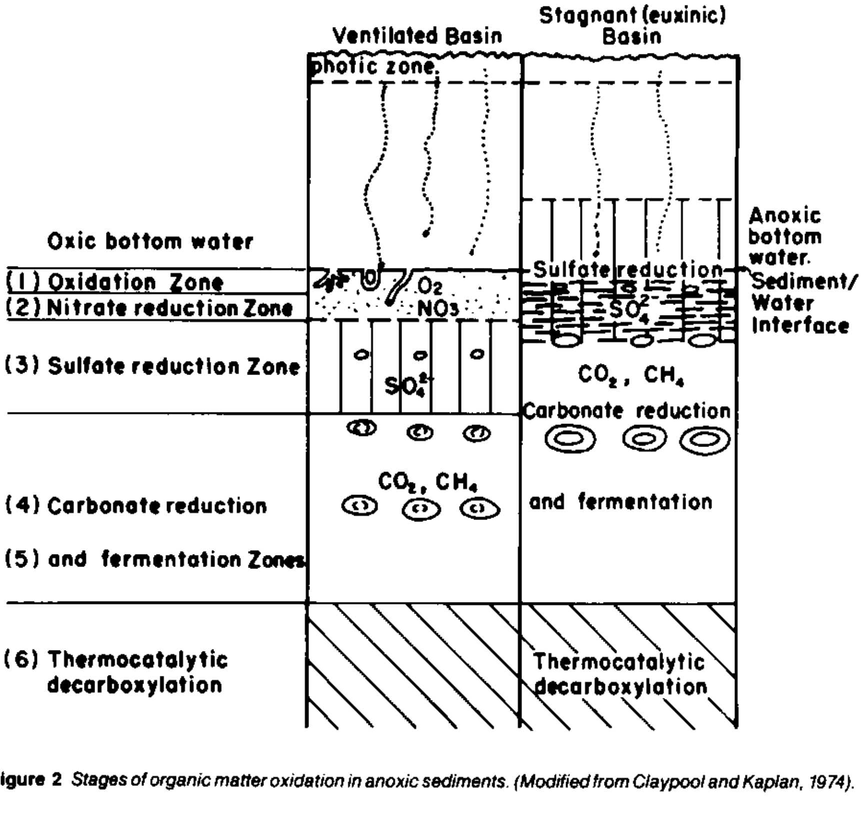


Figure 2 *Stages of organic matter oxidation in anoxic sediments. (Modified from Claypool and Kaplan, 1974).*

Interaction of the three general processes, i.e. reactions, diffusion, and advection, in the two or three main types of environments of pore-water evolution gives rise to the eight different types of vertical pore-water profiles (Table 1) mentioned in the introduction. This list of eight is not meant to be exhaustive and is merely intended to provide guidance in recognizing general trends among the highly variable pore-water compositions encountered in the subsurface. It will serve as a frame of reference in the following discussion of the two or three end-member environments of pore-water evolution. Before addressing these environments, two of the general processes, i.e. (1) early diagenetic organic matter oxidation as the key mechanism in early diagenetic reactions and (2) diffusion will be discussed in more detail in the next two sections. The role of the third mechanism, (3) advection, will be dealt with in connection with the relevant types of pore-water profiles (i.e. types 1 and 8).

Other geologic factors besides sedimentation rate such as the composition of the starting fluids, i.e. the connate waters (sea water *vs.* fresh water) or the tectonic stage of basin evolution that would be equally important in a global survey, may be considered secondary for the purpose of this review article which is concerned solely with modern marine basins. For these the effects of diastrophism (uplift and deformation) and meteoric water influx are not the rule although they may cause significant modification in certain basins or parts thereof.

Early Diagenetic Organic-Matter Oxidation

Organic matter represents highly reduced carbon compounds which are among the strongest reductants in freshly deposited sediments. The organic matter dispersed in the sediment provides an energy source for sediment-dwelling organisms, foremost bacteria, to maintain their metabolism through oxidation reactions. Bacterially mediated oxidation of organic matter becomes the first and most efficient mechanism to alter the chemical composition of pore waters during early diagenesis. The well-established organic matter oxidation reactions start immediately after deposition. According to the source of the oxidant (electron acceptor), six different zones or stages have been distinguished in the oxidative break-down of organic matter during burial (Claypool and Kaplan, 1974; Curtis, 1978). These are (Figure 2):

(1) the oxidation zone,
(2) the nitrate reduction zone,
(3) the sulphate reduction zone,
(4) the carbonate reduction zone,
(5) the fermentation zone, and,
(6) the thermocatalytic decarboxylation zone,
which represent a burial-depth zonation. The first five zones require the presence of bacteria. At the lower boundary of zone (5), bacterial activity ceases and thermocatalytic reactions take over. This is a natural lower boundary for the zone of early diagenesis.

(1) In the oxidation zone, freely dissolved oxygen is available from sea water trapped in the sediment or supplied by diffusion from the overlying bottom water. The pore water of the oxidation zone may, therefore, be called "connate" in the strictest sense of the word. Bacteria are not the only oxygen-consuming organisms active in this zone, which is the habitat of a diverse group of endobenthonic micro- and macro-organisms. Aerobic bacteria are the most efficient users of oxygen in this zone, however. The amount of dead animal or plant matter left undestroyed in the sediment after passage through the oxidation zone is a function of the residence time in this zone. In oxidizing organic matter and breaking it down into smaller molecules the bacteria gain energy for their metabolism. Because of their small size, in the micron range, they possess a large surface-area/mass ratio which favours the exchange of dissolved substances with the pore water through the cell walls. Microbial degradation of organic molecules leads to a loss of functional groups, particularly hydrocarbon chains and carboxyl-groups and the smaller molecules are partly converted to carbon dioxide according to an overall reaction which may be written as

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

where the bulk composition of organic matter has been simplified to CH_2O.

The efficient use of oxygen by aerobic respirators may lead to temporary or local oxygen depletion, particularly in regions of rapid sedimentation where replenishment from the overlying bottom water by diffusion may not keep pace with consumption. Obligatory aerobic organisms will then cease to exist, but facultative aerobes which can switch from an aerobic to an anaerobic mode of respiration may still be present.

The oxidation zone is easily recognized by its brownish-yellowish sediment color, where it is present. In organic matter-rich sediments, it may be only a few centimetres or millimetres thick — in contrast to the carbon-free brown abyssal clay discussed below. In stagnant or euxinic basins the oxidation zone is absent.

(2) The nitrate reduction zone commences where the concentration of dissolved oxygen drops below about 0.5 mL $O_2 \cdot (L\ H_2O)^{-1}$ (Devol, 1978), which corresponds to the oxygen level at which most benthonic macro-organisms disappear from the sediment (Rhoads and Morse, 1971). Dysaerobic bacteria, which live at dissolved oxygen levels between 1.0 and 0.1 mL $O_2 \cdot (L\ H_2O)^{-1}$, are characteristic for this environment, which may be called suboxic. The term "suboxic diagenesis" thus refers to the nitrate reduction zone. Concentration of nitrate tends to increase from the ambient bottom water value of 0.03-0.04 mM (mM = millimoles$\cdot L^{-1}$) to a maximum in the oxidation zone where ammonia released from organic matter decomposition is oxidized (Froelich *et al.*, 1979). From this maximum, nitrate decreases downward to zero at the base of the nitrate reduction zone. The lower boundary of the nitrate reduction zone is characterized by the change from positive to negative electrochemical potentials and the appearance of anaerobic bacteria. When the electrochemical potential is lowered sufficiently, oxides and hydroxides of manganese, which at higher oxidation potentials have a very low solubility, will be reduced and go into solution as shown schematically in Figure 3 (Froelich *et al.*, 1979) thus serving as an important source of oxidant in addition to nitrate of the pore water. The exact Eh-level at which manganese reduction occurs depends on the different oxides and hydroxides involved having different Gibbs free energies (Table 2). Iron reduction will occur after manganese reduction at somewhat greater depth, often overlapping with the sulphate reduction zone when the redox potential has been lowered further. Both manganese and iron reduction are hydrogen-ion consuming reactions, as the equations in Table 2 show, increasing the pH which may be a prerequisite for the precipitation of early diagenetic carbonates in concretions (see later section).

(3) Suboxic conditions of the nitrate reduction zone are followed by the truly anoxic conditions in the underlying sulphate reduction zone. Although the sulphate-reducing bacterium *Desulfovibrio desulfuricans* is the dominant bacterial species, as only few species can tolerate the toxic effects of the hydrogen sulphide produced in this zone, it is not the only one. The sulphate reducers oxidize relatively small organic molecules such as lactic acid and four-carbon dicarboxylic acids. These are produced by fermenting bacteria whose symbiosis with the sulphate-reducing bacteria is required by the process. A simplified equation for this rather complex process is

$$2CH_2O + (SO_4)^{2-} \rightarrow S^{2-} + 2H^+ + 2(HCO_3)^-.$$

As soluble ferrous iron usually becomes available through reduction of ferric oxyhydroxides and oxides in the sulphate reduction zone and the lower part of the nitrate reduction zone of terrigenous sediments, dissolved sulphide concentrations remain relatively low (less than 5 mM), because of the instantaneous precipitation of metastable iron-monosulphides which later transform to pyrite. In iron-poor marine carbonate muds the process will take a different course of events.

Sulphate reduction is diagnostic for the pore waters of marine sediments as compared to freshwater sediments, which are often low in sulphate and lack the sulphate reduction step in the early diagenetic evolution of their pore waters. In marine sediments the sulphate reduction zone is considerably thicker than the nitrate reduction zone because dissolved sulphate is about three orders of magnitude more abundant (27 mM) in oceanic bottom waters than nitrate. However, in organic-matter rich sediments the combined thickness of the nitrate and sulphate reduction zones is often less than a few metres and in certain regions may be as small as 10 or 20 cm (Reeburgh, 1983).

(4) In each of the three oxidation steps discussed so far one of the main products of bacterial organic matter decomposition has been carbonic acid and its dissociated species bicarbonate HCO_3^- or carbonate CO_3^{2-}. Below the sulphate reduction zone the carbonate itself becomes one of the main oxidants for further bacterial oxidation of organic matter. In the carbonate reduction zone bacterial carbonate reduction leads — for the first time in the burial history of organic-matter rich sediments — to the production of methane.

The process appears to require a reducing intermediate (e.g. hydrogen) also derived from bacterial organic matter degradation (Berner, 1980). For example, the oxidation of ethanol will yield acetic acid and hydrogen according to the reaction

$$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 2H_2.$$

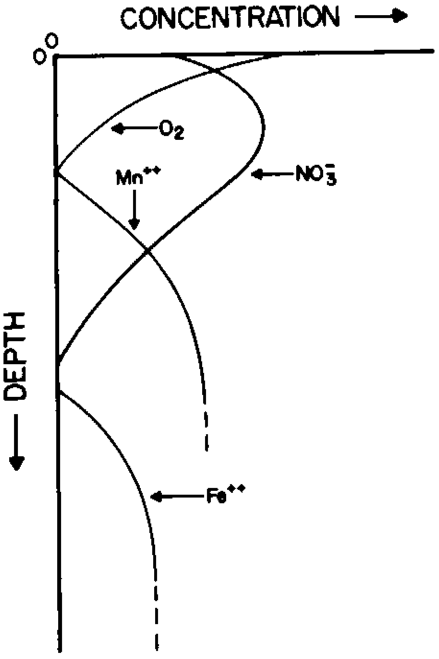


Figure 3 *Schematic diagram for the depth distribution of dissolved O_2, NO_3^-, Mn^{2+} and Fe^{2+} in suboxic environments (pore-water profile type 3). (From Berner, 1980, after Froelich* et al., *1979).*

The hydrogen may be used by true methanogenic bacteria such as *Methanobacterium thermoautotrophicum* to reduce CO_2 produced in this and the previous zones (according to a reaction of the general type $CH_2O + H_2O \rightarrow CO_2 + 4H$ which is enzyme catalyzed and produces atomic H) by the redox reaction

$$8H + CO_2 \rightarrow CH_4 + 2H_2O.$$

The process of methane formation thus appears as a disproportionation of organic matter into carbon dioxide and methane (Goldhaber and Kaplan, 1974) and it is not clear at present whether a direct transformation of organic compounds into methane by bacteria is possible. Although methanogenic bacteria exist over a wide temperature range (0 - 75°C, Zeikus and Wolfe, 1972), the optimum for individual species spans only a few degrees. For example, the thermophylic *M. thermoautotrophicum* has its optimal temperature range between 65 and 70°C.

Methane production and sulphate reduction are not mutually exclusive processes (Claypool and Kvenvolden, 1983), but they seem to be fairly well separated, because CH_4 levels in the sulphate reduction zone are low and significant CH_4 production seems to start only after the disappearance of more than 80%, if not complete depletion of the dissolved sulphate (Sansone and Martens, 1981). A possible reason is that methane producing bacteria may not be able to tolerate the levels of H_2S or HS^- existing in the sulphate reduction zone, although this seems questionable in view of the fact that methane bacteria have been found in the presence of unreacted HS^- below the sulphate reduction zone. Alternative explanations are (i) that free hydrogen may not be available for CO_2 reduction in the presence of sulphate reducing bacteria or (ii) that the methane which may be produced in the sulphate reduction zone is immediately oxidized to CO_2. This latter process would also inhibit the appearance of CH_4 in the sulphate reduction zone due to upward diffusion.

(5) The fifth oxidation mechanism is bacterial fermentation where the oxygen contained in organic compounds is transferred to oxidize organic matter, simultaneously yielding CO_2 and CH_4. From what has been said above it is not clear whether this step is a separate step or whether in fact bacterial carbonate reduction always requires fermentation processes as symbiotic reactions.

(6) Bacterial activity decreases decisively at temperatures above 75°C and only few populations still exist at higher temperatures. Organic matter oxidation, however,

Table 2 Stages of organic matter oxidation (modified from Froelich *et al.*, 1979)

C : N : P = 106 : 16 : 1 = Redfield ratio for primary organic matter.
The organic matter involved in reactions (1) to (4) does not necessarily have this ratio.

	ΔG°' of metabolic processes coupled with oxidation reactions (in kcal·(mol)$^{-1}$ glucose)
(1) Oxidation by freely dissolved O_2 (aerobic respiration)	
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\,O_2 \rightarrow$ $106\,CO_2 + 16\,HNO_3 + 122\,H_2O$	-763
Manganese reduction	
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 236\,MnO_2 + 472\,H^+ \rightarrow$ $236\,Mn^{2+} + 106\,CO_2 + 8\,N_2 + H_3PO_4 + 366\,H_2O$	-748 (birnessite) -698 (pyrolusite)
(2) Nitrate reduction	
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 99.4\,HNO_3 \rightarrow$ $106\,CO_2 + 55.2\,N_2 + H_3PO_4 + 177.2\,H_2O$	-724
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 84.4\,HNO_3 \rightarrow$ $106\,CO_2 + 42.4\,N_2 + 16\,NH_3 + H_3PO_4 + 148.4\,H_2O$	-658
Iron reduction	
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 212\,Fe_2O_3$ (or 424 FeOOH) $+ 848\,H^+ \rightarrow$ $424\,Fe^{2+} + 106\,CO_2 + 16\,NH_3 + 530\,H_2O$ (or 742 H_2O)	-337 (hematite) -318 (limonitic goethite)
(3) Sulphate reduction	
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\,(SO_4)^{2-} \rightarrow$ $106\,CO_2 + 16\,NH_3 + 53\,S^{2-} + H_3PO_4 + 106\,H_2O$	-91
(4) Carbonate reduction	
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 53\,CO_2 + 53\,CH_4 + 16\,NH_3 + H_3PO_4$	-84

continues to proceed at temperatures above 75°C, but under abiogenic conditions. Once the activation energy has been reached, the reactions will occur spontaneously. These thermocatalytic reations include the decarboxylation of organic acids according to the general formula R-COOH → RH + CO_2 where the organic acid group COOH is converted to CO_2 and R- is the organic radical. This process occurs at more elevated temperatures (above 75°C) and deeper burial levels and is probably very important in generating aggressive acidic pore waters at depths which may be responsible for the dissolution of carbonates and feldspars and the generation of secondary porosity. These are additional arguments for choosing the boundary between zones (5) and (6) as the

Table 3 Diffusion in Sediments

Fick's First Law

$$(1)\quad J_i = -D_i\frac{\partial C_i}{\partial z}$$

J_i = flux of species i

D_i = diffusion coefficient$[cm^2\ s^{-1}]$

$\frac{\partial C_i}{\partial z}$ = vertical concentration gradient

Fick's Second Law

$$(2)\quad \frac{\partial C_i}{\partial t} = -\frac{\partial J_i}{\partial z} = \frac{\partial(D_i\frac{\partial C_i}{\partial z})}{\partial z} = D_i\frac{\partial^2 C_i}{\partial z^2}$$

Fick's Second Law in polar co-ordinates

$$(3)\quad \frac{\partial C_i}{\partial t} = -\frac{\partial J_i}{\partial r} = \frac{1}{r^2}\,\frac{\partial(r^2 D_i\frac{\partial C_i}{\partial r})}{\partial r}$$

Fick's First Law for charged species i

$$(4)\quad J_i = v_i(RT\frac{\partial C_i}{\partial z} + Z_iC_i\mathfrak{F}\frac{\partial E}{\partial z})$$

$$= -v_iRT(\frac{\partial C_i}{\partial z} - \frac{Z_iC_i\mathfrak{F}\Sigma_jZ_jv_j\frac{\partial C_j}{\partial z}}{\mathfrak{F}\Sigma_jZ_j^2v_jC_j})$$

$$(5)\quad \text{or } D_i = -v_iRT(1 - \frac{Z_iC_i\mathfrak{F}\Sigma_jZ_jv_j\frac{\partial C_i}{\partial z}\,\frac{\partial C_j}{\partial z}}{\mathfrak{F}\Sigma_jZ_j^2v_jC_j})$$

v_i = mobility of i-th ion at infinite dilution

$\frac{\partial E}{\partial z}$ = gradient of electrical potential E

Z_i = charge of the i-th species

$\mathfrak{F}$ = Faraday constant

Sediment diffusion coefficient D_s

$$(6)\quad D_s = \frac{D}{\theta^2}$$

$\theta = \frac{\partial l}{\partial z} \geq 1$ tortuosity

∂l = actual path length of ion in solution

$\theta = \phi F$, where ϕ is porosity

F is formation factor

Diffusion flux in sediments J_s

$$J_s = -\phi D_s\frac{\partial C}{\partial z}$$

$$(7)\quad \frac{\partial C}{\partial t} = -\frac{1}{\phi}\,\frac{\partial J_s}{\partial z} = -\frac{1}{\phi}\,\frac{\partial(\phi D_s\frac{\partial C}{\partial z})}{\partial z}$$

$F = \frac{R}{R_o}$, where R is electrical resistivity of sediment

R_o is resistivity of pore water

$F = \phi^{-n}$, for n = 2: $D_s = \phi^2 D$

Mean diffusion path length

$$(8)\quad Z_m = (D_st)^{0.5}$$

General diagenetic equation

$$(9)\quad \phi\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial z}(\phi D_s\frac{\partial C_i}{\partial z}) - \phi\frac{\partial(vC_i)}{\partial z} + \Sigma_kR_k$$

v = velocity of advective flow

R_k = k-th reaction

boundary between early (or shallow) and intermediate diagenesis as discussed more fully in the final section of this article.

The sequential order in which zones (1) to (6) follow one another, most of them apparently without significant overlap, is related to the difference in the Gibbs free energy associated with each of the oxidation reactions listed in Table 2 (based on glucose as organic substrate). Utilization of dissolved oxygen as an oxidant is evidently the most energy efficient process. For each later step in the sequence the energy yield is less suggesting that specific bacterial populations associated with the various reactions in the subsurface follow each other in the order of decreasing energy efficiency of their metabolic reactions.

Details of the biochemical reactions involved in bacterial metabolism are still poorly understood. Probably all of them include enzymatic reactions. It is known, for example, that methanogens can only use acetic acid or acetate and shorter hydrocarbon molecules for conversion into methane (Mechalas, 1974). Because acetic acid levels in the pore waters of marine sediments are relatively low, other strains of bacteria must be present to produce the intermediate substances which are then being used in the methane generating process. Similarly, sulphate-reducing bacteria use relatively short-chained organic acids which must be provided by symbiotic bacteria breaking down larger organic molecules. Thus different interacting bacterial populations must be present at any one time in the sulphate reduction and methane producing zones which are involved in a series of simultaneous and partially symbiotic reactions. With the conventional spectrum of pore-water analyses we only see the end products of these chain reactions.

Diffusion as a Diagenetic Transport Mechanism

Diffusion operates to dissipate concentration differences. Thus the driving forces for diffusion are chemical potential gradients and gradients of the electrical potential caused by charged species. The flux J_i of a dissolved chemical species i due to molecular diffusion is directly proportional to the concentration gradient $\frac{\partial C_i}{\partial z}$. The factor of proportionality is the diffusion coefficient D_i. If we restrict ourselves to vertical concentration gradients, which are dominant during early diagenesis, then the flux J_i is given by the one-dimensional form of Fick's first law of diffusion (equation (1), Table 3). If electrical potential gradients are taken into account, a more complex version of Fick's law results (equation (4), Table 3).

Variations in concentration with time $\frac{\partial C_i}{\partial z}$ which may result, e.g. from variation in the input rate of soluble substances during sedimentation, will cause vertical gradients of fluxes $\frac{\partial C_i}{\partial z}$ which are obtained from Fick's second law. In the form given (equation (2), Table 3) it is based on the assumption of a constant diffusion coefficient D_i which, however, is not applicable for many dissolved species in natural sediments undergoing compaction. For the common occurrence of concretion growth during diagenesis, which is a diffusion-controlled process, flux gradients are perpendicular to a sphere or ellipsoid, for which Fick's law is more conveniently expressed in spherical co-ordinates (equation (3), Table 3).

Reservoirs that are in diffusive communication are connected by concentration profiles of the dissolved species which bridge the concentration difference and are straight lines, if the diffusion coefficients are constant, or curved ones, if the diffusion coefficients vary with time or depth of burial. Curved profiles, on the other hand, may also result from transport by advection or reactions within the sediment. In the general diagenetic equation (equation (9), Table 3) the total flux of a dissolved species J_i or its gradient $\frac{\partial C_i}{\partial z}$ is the sum of three terms, the diffusive flux, the advective flux and the flux resulting from ongoing reactions. To distinguish between the various contributions each situation has to be analysed individually.

A depth dependency of the diffusion coefficient is to be expected from its relation to porosity via tortuosity. Tortuosity θ is a measure of the distortion of the diffusion pathway of solute species due to the presence of solid particles. Tortuosity is a function of porosity and the formation factor **F**, which is the resistivity ratio $\mathbf{R/R_o}$ of a natural sediment (**R**) and its pore water ($\mathbf{R_o}$) (see Table 3). The bulk (or sediment) diffusion coefficient $\mathbf{D_s}$, therefore, depends strongly on porosity and, for that matter, on depth. For more compacted sediments considerably smaller coefficients result. Apart from its effect on the sediment diffusion coefficient $\mathbf{D_s}$, porosity ϕ has to be included in all of the equations (1) to (4) as a separate factor, because under diagenetic conditions diffusion occurs only in the pore water. This leads to equations of the form given in equation 7 (Table 3).

Table 4 Diffusion coefficients and mean diffusion path length

	D_s	Z_m (in m)
Na^+	7.4	154.2
Ca^{2+}	4.4	117.8
Cl^-	10.2	179.0
$(SO_4)^{2-}$	5.0	125.8

where,

D_s is the bulk sediment diffusion coefficient (10^{-6} cm^2·s^{-1}).
(Data from Li and Gregory (1974) for brown abyssal clay with a porosity of 71% at T = 20-25°C, quoted in Berner, 1980).
Z_m is the mean diffusion path length calculated for t (time) = 1 Ma.

Over what distances can diffusion affect transport of dissolved species in actively subsiding sedimentary sequences? It is possible to calculate the mean diffusion path length $\mathbf{Z_m}$ (Gieskes, 1975), which is the distance over which diffusion will dissipate concentration anomalies for a given period of time (equation (8), Table 3). For a period of one million years diffusion path lengths for young, unconsolidated sediments are characteristically between 100 and 200 m (Table 4), which exceed the thickness of most pelagic sediments accumulated in a million years. It is, therefore, entirely feasible that in pelagic sediments the sediment-water interface and the igneous rocks (layer 2) of the oceanic crust are still in diffusive communication, even after deposition of several hundred metres of sediment. This will always be the case, if the diffusive communication length **Z**, which is the diffusion coefficient $\mathbf{D_s}$ divided by sedimentation rate ω (Gieskes, 1975), exceeds sediment thickness.

I. Low to Intermediate Sedimentation-rate Basins (pore-water profile types 1 to 3)

These have sedimentation rates of less than about 50 m·Ma^{-1} characteristic for eupelagic or true pelagic sediments. They represent the most slowly deposited sediments on earth including the brown abyssal clay, the prototype of a pelagic sediment, with sedimentation rates of less than 5 m·Ma^{-1}. Biogenic pelagic sediments are deposited somewhat faster, at rates ranging from less than 10 m·Ma^{-1} up to 100 m·Ma^{-1} for most modern siliceous and calcareous oozes (e.g. Scholle *et al.*, 1983, p. 640).

Pore-water profiles for pelagic sediment sites of the DSDP display three principally different trends: those with no pronounced gradients at all (type 1); others with vertical gradients but linear correlation between major ions, especially calcium and magnesium (type 2); and a third group with gradients but no linear correlation between the major ions (type 3). The first group of sites occurs close to mid-ocean ridges and has a limited sediment thickness, generally less than 200 m, the second group at greater distances from the ridges and under a thicker sediment cover (Figure 4), the third group in more reactive pelagic sediments. The first group is convection-controlled, the second diffusion-controlled and displays oxic to suboxic diagenesis. The third group is characterized by suboxic (to anoxic) diagenesis and is reaction-dominated but formerly may have been convection-dominated.

Convective pore-water circulation on the flanks of mid-ocean ridges (type 1 pore-water profiles). The first type of behaviour, i.e. profiles with no gradients for most ions, is illustrated by DSDP site 495 (Figure 5). McDuff (1981) has argued that the straight vertical profiles of sea water composition are probably caused by convection of sea water through the sediment column. This is in line with geothermal studies (Anderson *et al.*, 1977, 1979) which suggest that heat loss on the flanks of mid-ocean ridges is by convective rather than conductive transport and that the heat-transporting fluids must percolate through the sediments (layer 1) of the oceanic crust. Postulated convective flow cells have a diameter (or wavelength) of 5 to 10 km and several of them may occur side-by-side on the ridge flanks thus extending from the ridge crest outward to basement ages of up to 80 Ma. The cell structure requires that regions of discharge from the crust alternate with regions of recharge, but it is not clear how the former manifest themselves in the pore-water chemistry. Active hydrothermal systems that have been drilled at various sites by the DSDP are characterized by ongoing reactions in the sediments or intrusions of igneous dykes and sills producing complicated pore-water profiles that are far from straight lines (pore-water profile type 8). Discharge associated with simple, convection-controlled vertical profiles may have been encountered in one area at 20°S on the East Pacific Rise (Bender *et al.*, 1986), but only the uppermost 2 m of the sediment were sampled. For discharge areas, which are probably much narrower and more focussed than the broad recharge areas, non-linear profiles would be expected with greater depth of penetration.

Once the sediment cover on the oceanic crust exceeds a certain thickness, it becomes a seal for convection due to porosity reduction. When convection is no longer operative, diffusion sets in to bridge the concentration differences between sea water at the top and hydrothermally altered fluids at the base of the sedimentary section, thus smoothing out concentration gradients. In discharge areas, porosity-reducing processes, such as

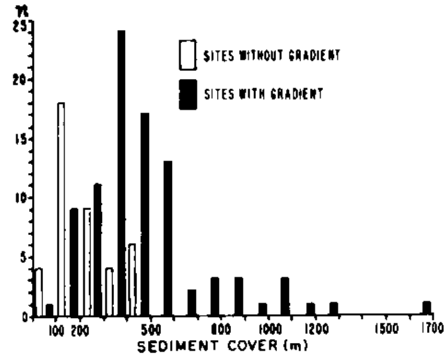


Figure 4 *Frequency distribution of drill sites with and without concentration gradients for major pore water cations in pelagic (and hemipelagic) sediments as a function of sediment thickness on basaltic crust (based on DSDP legs 1-85, data for legs 1-53 compiled by McDuff, 1981). n - number of drill sites.*

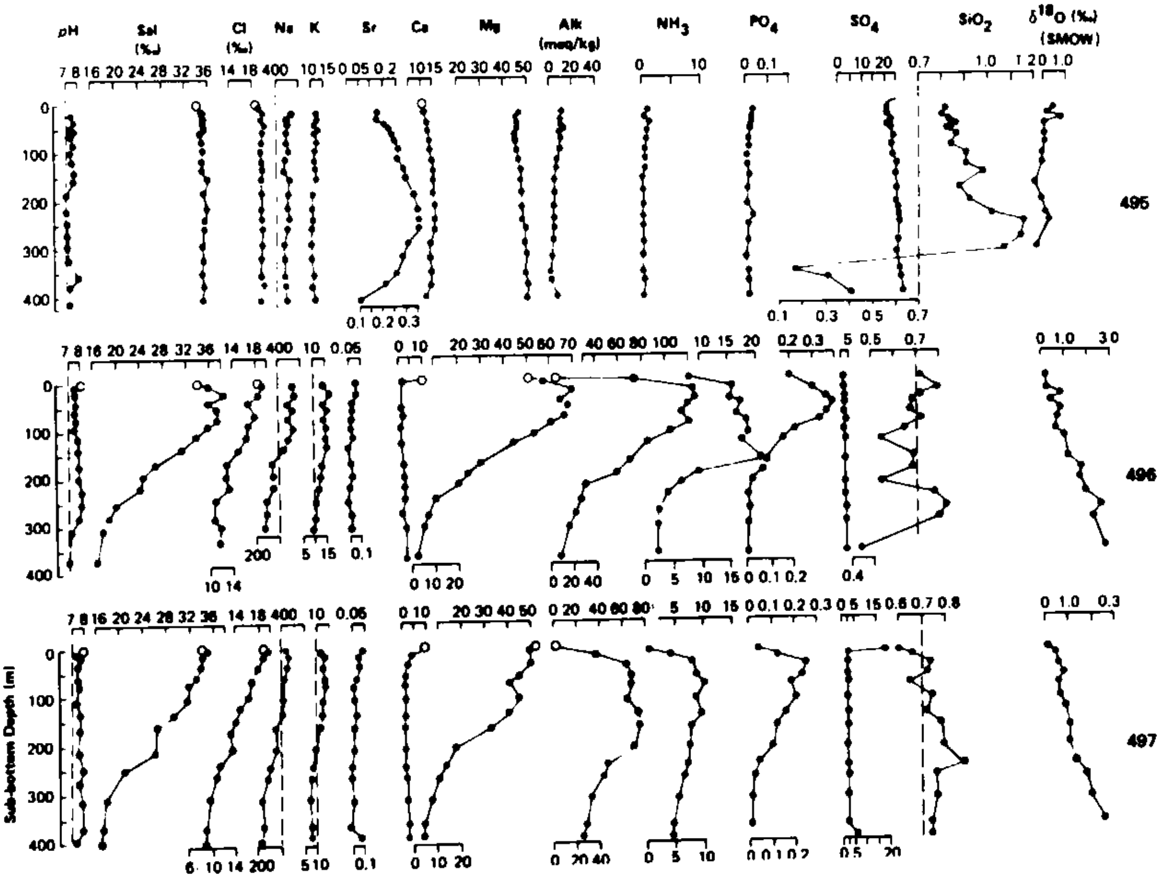
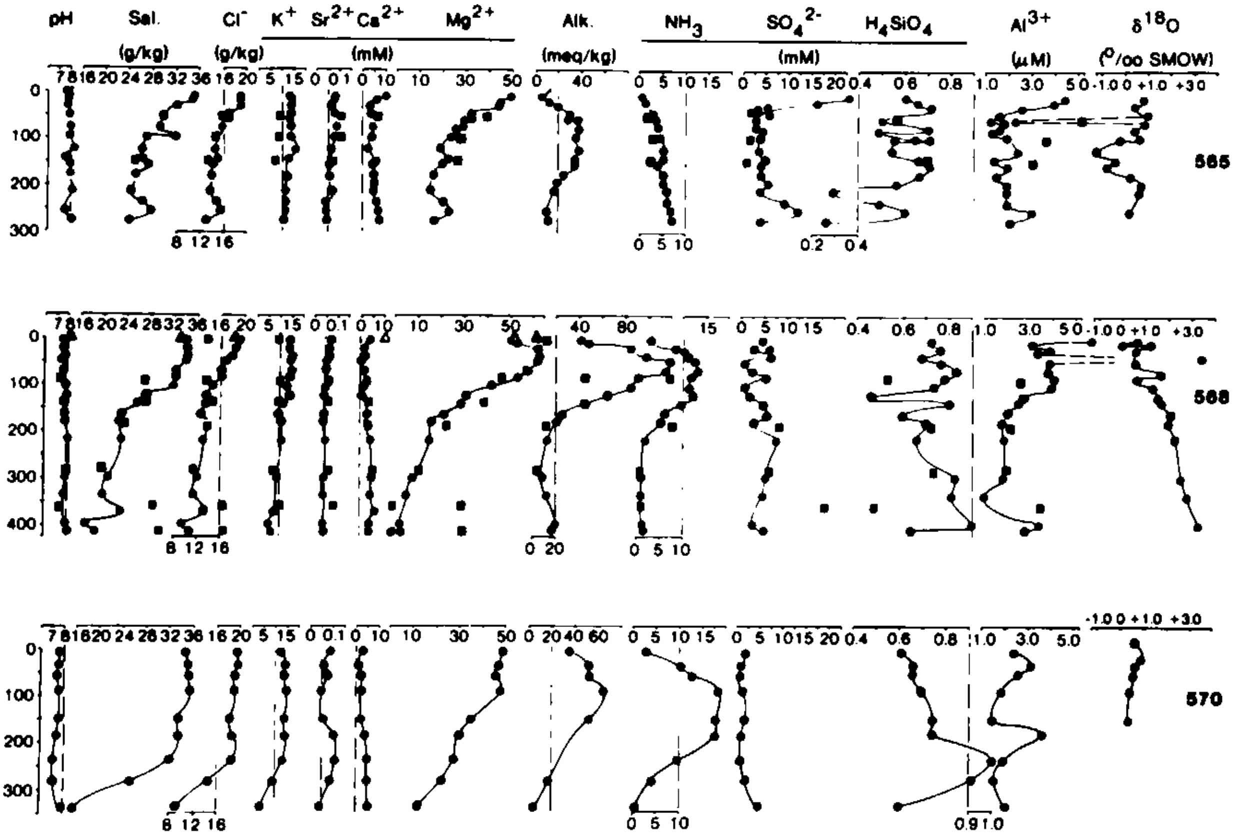
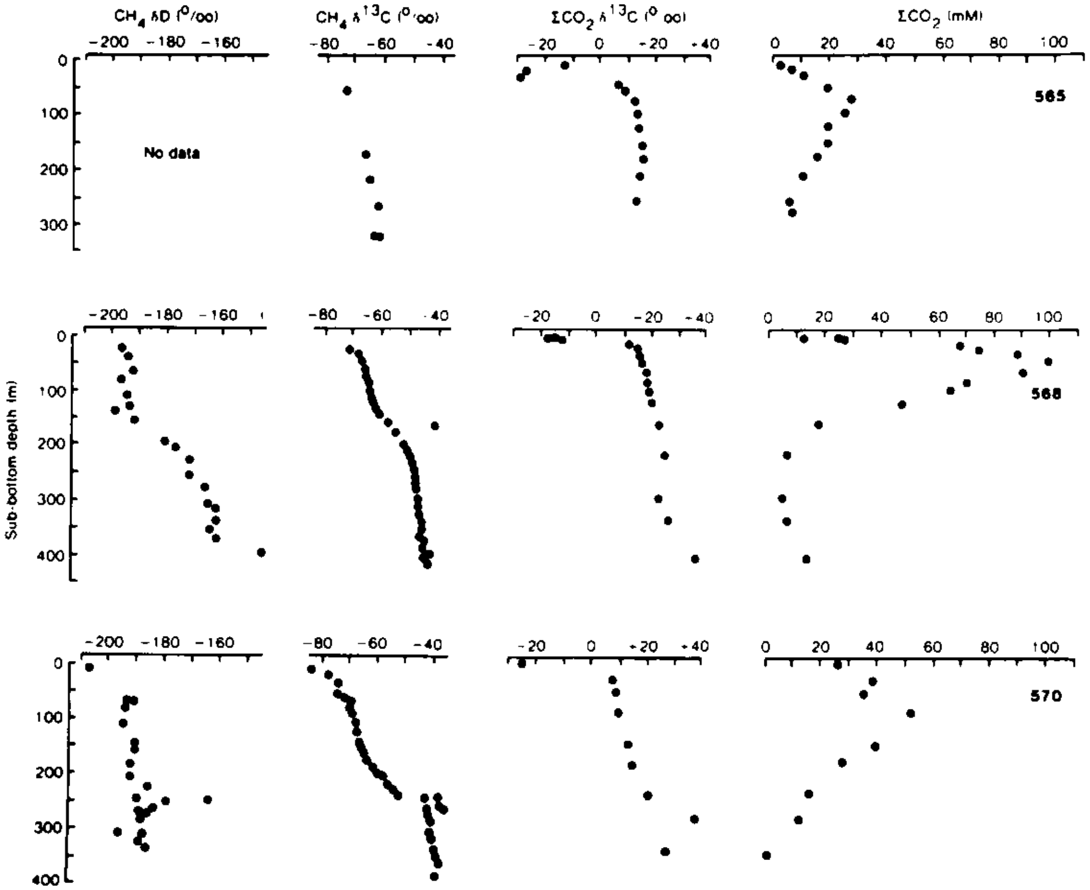


Figure 5 *(Above and opposite page). Pore-water chemistry and isotopic composition of DSDP drill sites 495 (pore-water profile, mixed type 1 & 2 & 3), 496 (type 6), 497 (type 6), 565 (type 6), 568 (type 6), and 570 (mixed type 4 & 6). Sites 495, 496, 497 (leg 67)(Harrison* et al.,*1982), Sites 565, 568, 570 (leg 84)(Hesse* et al.*, 1985; carbon-isotope ratios from Claypool* et al.*, 1985) on Middle America trench slope and oceanic crust of the Cocos plate (site 495) off Guatemala. Sites 565 (continental slope off Nicoya Peninsula, Costa Rica) and 568: squares identify* in situ *water samples.*


pH
Sal. (g/kg)
Cl⁻ (g/kg)
K⁺
Sr²⁺
Ca²⁺
Mg²⁺
(mM)
Alk. (meq/kg)
NH₃
SO₄²⁻
H₄SiO₄
(mM)
Al³⁺ (μM)
δ¹⁸O (‰ SMOW)
565
568
570
0
100
200
300
400
8 12 16
0 5 10
0.2 0.4
0 20
0.9 1.0
-1.0 0 +1.0 +3.0


CH₄ δD (‰)
CH₄ δ¹³C (‰)
ΣCO₂ δ¹³C (‰)
ΣCO₂ (mM)
-200 -180 -160
-80 -60 -40
-20 0 +20 +40
0 20 40 60 80 100
No data
565
568
570
Sub-bottom depth (m)
0
100
200
300
400

recrystallization and cementation, may be accelerated due to elevated temperatures sealing off convection early, i.e. even under a relatively thin sediment cover. Thus discharge-related straight-line profiles would not be expected.

Site 495 on the Cocos plate off Guatemala is located about 20 km oceanward from the Middle America Trench and bottomed in basalt of Early Miocene oceanic crust. At this site convection may have ceased not too long ago, but the previous convection-controlled profiles are still preserved due to a lack or sluggishness of reactions in layers 1 and 2. Its straight-line pore-water profiles with near seawater concentrations for most ions (Harrison *et al.*, 1982) are the more remarkable, because major lithological changes occur in the sediment column penetrated by the drill — from Pleistocene to Upper Miocene olive-grey hemipelagic mud (upper 170 m) through Middle Miocene brown abyssal clay (10 m) to Middle to Lower Miocene white, pale brownish and greenish calcareous ooze and chalk (120 m) and pale brown to purplish manganiferous chalk and limestone (30 m) overlying the basalt. As Figure 5 shows, none of the major ions seems to be affected in its vertical trend by any of the lithological boundaries (at 170 m, 180 m, 399 m and 428 m depth), although these are relatively sharp.

The only exceptions are silica and strontium and, in part, calcium, which display appreciable variations although these are also not related to any of the major compositional boundaries between the lithologic units. (These variations are exaggerated in Figure 5 due to the different scales used for Sr^{2+} and SiO_2 compared to most other ions.) SiO_2, Sr^{2+} and Ca^{2+} are species involved in active diagenetic reactions taking place in the sediment column at the time of drilling. Strontium is released by carbonate recrystallization. Its maximum near 250 m sub-bottom depth occurs approximately at the level where the transition from calcareous ooze to chalk is observed in the cores.

Silica concentration profiles are known to be highly variable with depth and dependent on lithology; site 495 is an excellent example. Increases in dissolved silica in the upper few 100 m of biogenic pelagic sediments are related to the dissolution of opal-A of the tests of siliceous organisms, mostly diatoms and radiolaria, while marked decreases in silica which occur at greater depths are related to the reprecipitation as opal-CT. In site 495, the marked decrease in dissolved silica near 325 m sub-bottom coincides with the first porcellanite nodules observed in this hole, confirming the relationship with opal-CT precipitation. The diagenesis of siliceous oozes and associated mechanisms of chert formation will not be discussed further at this point, as these are subjects of a separate review article.

Thus the two dissolved species of site 495 which display pronounced maxima in their concentration profiles, Sr^{2+} and SiO_2, are clearly involved in ongoing reactions. The convective flow system appears to have ceased to operate not too long ago at this site because it failed to obliterate the effects of these reactions, and the reaction products liberated are redistributed by diffusion (as in the case of Sr^{2+}) or consumed by the precipitation of solid phases (as in the case of SiO_2). Site 495 thus, in fact, is a mixed site showing the effects of former convection, of diffusion and of ongoing reactions. Its sediment thickness exceeds 400 m, which is higher than for most convection-controlled sites (Figure 4), but this is not surprising in view of the mixed nature of this site.

Diffusion-controlled pore-water trends (type 2 pore-water profiles). The brown abyssal clay is a good example for diffusion-controlled pore-water profiles. It is virtually free of organic carbon. Any organic matter that may be deposited is removed by oxidation in the oxidation zone. A few tenths of a percent or less of highly refractory organic matter may remain, according to analyses of many drill holes in the Pacific (Initial Reports of the DSDP). In the absence of reactive organic carbon, which is the main reducing agent in marine sediments, iron and manganese remain in their oxidized, higher valence states in the sediment which therefore retains its brown colour during burial. During later stages of burial the sediment may gradually change to red when the brown iron hydroxides are converted to hematite. Although freely dissolved oxygen may disappear completely from these pore waters at deeper burial levels, they do not normally become reducing enough to change the Fe^{3+} to Fe^{2+} and thus leave the red colour unchanged.

Various other types of pelagic sediments besides the brown abyssal clay display diffusion-controlled pore-water profiles. These are characterized by linear correlation between the concentration changes for calcium and magnesium as well as for oxygen isotope ratios. This phenomenon, particularly the inverse relationship between calcium and magnesium (Figure 6) had attracted considerable interest in the past and led to different hypotheses. Sayles and Manheim (1975) thought that the diagenetic formation of high-magnesium calcite was responsible for the ΔCa-ΔMg correlation, a conclusion which, if substantiated, would have been in conflict with the common experience of carbonate petrologists that high-Mg calcite transforms diagenetically to low-Mg calcite, but not *vice versa*. Because the starting material in deep-sea sediments is low-magnesium calcite, a stable phase would have been replaced by a less stable phase during progressive diagenesis, in violation of Ostwald's rule. Donnelly and Merrill (1977) related the magnesium decrease with depth to silica diagenesis. Lerman (1975, 1977) and Lerman and Lietzke (1977) considered the effects of diffusion but neglected to include variable diffusion coefficients which forced them to invoke reactions in the sediment to explain the gradients. In their re-evaluation of the problem, McDuff and Gieskes (1976) and McDuff (1978, 1981) included depth-variable diffusion coefficients, with the result that they were able to argue successfully that these profiles with coupled changes for Ca and Mg are essentially diffusion-controlled. Considerable variations in the numerical value of the diffusion coefficients result from changes in porosity, temperature and tortuosity with depth and these can be measured directly (porosity, drill hole temperature) or indirectly (tortuosity) using electrical resistivity determinations. By setting the velocity of advective flow v and the contribution from reactions **R** in equation (9) of Table 3 equal to zero, that is, assuming that the two elements Ca and Mg behave conservatively and do not experience losses to, or additions from, the sediment column, McDuff and Gieskes (1976) were able to match calculated profiles with the measured ones. Thus, only a diffusive flux seems to be important. Successful modelling suggests that such an interpretation is acceptable; it does not prove that it is the only possible one. What are the reactions in the basalt of the oceanic crust that lead to the release of Ca and the consumption of Mg underlying the linear correlation between the changes (ΔCa-ΔMg) of these two elements? These are generally hydrolysis reactions of the alumino-silicates of the primary basaltic rocks. They produce cations, hydroxyl ions and silicic acid as soluble species. Mg^{2+} produced in these reactions is taken up entirely by the basalt in secondary minerals such as brucite or saponite. The hydroxyl ions produced are largely removed from solution by precipitation with excess Mg^{2+}, i.e. the Mg^{2+} supplied by diffusion. In this way basalt alteration provides a sink for Mg^{2+} and also a source for Ca^{2+}. According to McDuff (1981), Mg^{2+} uptake may exceed Ca^{2+} release at low hydrolysis rates. Because the reactions affecting the basaltic rocks may also occur in the lower parts of the sediment column, if these are rich in volcanic material, dissolved Mg^{2+} may be reduced to zero above the sediment/basalt boundary. In this case, the continued increase in Ca^{2+} downward, and the hydroxyl production associated with it,Jare compensated by a flux of Na^{+} supplied from sea water by diffusion into the oceanic crust, which is reflected in a distinct depth gradient for Na^{+}.

The strongest argument in favour of diffusion-controlled gradients for Ca^{2+} and Mg^{2+} that are linearly correlated is their correlation with changes in oxygen isotope ratios (Figure 7). Often these display a distinct downward decrease of $\delta^{18}O$ resulting in moderately negative values at a few 100 m subsurface depth. As pointed out by Lawrence *et al.* (1975) and Gieskes and Lawrence (1981), the only quantitatively important fractionation

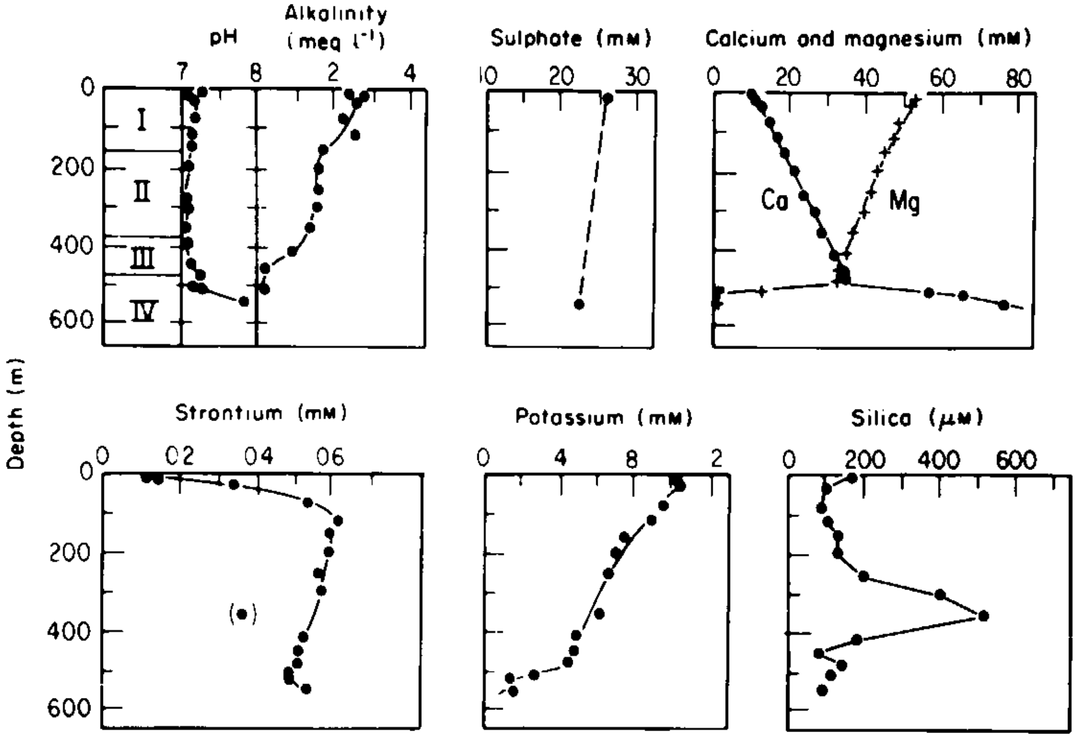


Figure 6 *DSDP site 528 on the Walvis Ridge, South Atlantic, with linear correlation between downward Ca^{2+} increase and Mg^{2+} decrease (pore-water profile, type 2). Dissolved Mg^{2+} drops rapidly to zero below the first basalt, at the same level Ca^{2+} increases rapidly. Dissolved Sr^{2+} shows typical trend for pelagic carbonates with a maximum around 100 m, resulting from carbonate dissolution. Lithology: I: calcareous ooze, II: nanno-fossil ooze and chalk, III: chalk with interbedded turbidites, IV: interbedded sedimentary rocks and basalt. (From Gieskes, 1983).*

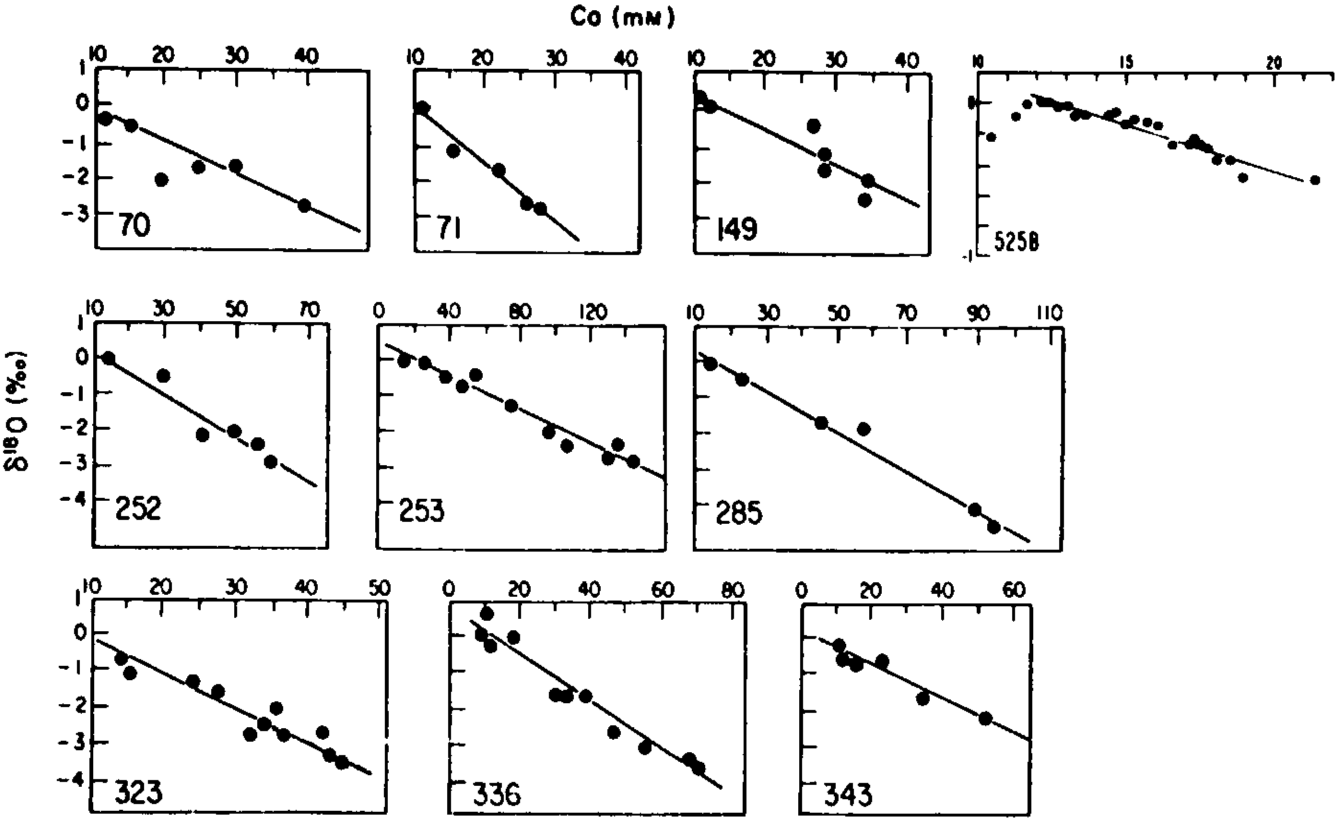


Figure 7 *Negative correlation between dissolved Ca concentration and $\delta^{18}O$ of DSDP pore-water profiles. (From Gieskes, 1983; data from Lawrence and Gieskes, 1981).*

mechanism in pelagic sediments that could bring about a preferential removal of heavy oxygen from the pore water is the formation of phyllosilicates in alteration reactions of basaltic minerals and glasses, either in the igneous part (layer 2) of the crust or in volcaniclastic sediments (layer 1).

It has been suggested, however, that slight downward decreases in the oxygen isotope ratio observed in pore waters of Miocene pelagic carbonates in the South Atlantic (hole 525B, leg 74 of the DSDP on the eastern flank of Walvis Ridge) represent a fossil sea water trend reflecting the withdrawal of isotopically light water from the ocean and storage in continental ice caps (Bath and Shackleton, 1984). An ice cap started to form on Antarctica in mid-Miocene time. Hydrogen isotope ratios of these pore waters also decrease downward at at rate of about eight times the $\delta^{18}O$-decrease (Figure 8a) corresponding to the isotope fractionation effect associated with evaporation of sea water. The absolute values of the $\delta^{18}O$ shift are small, however, amounting to not more than 0.5‰ over 250 m depth (Figure 8b). In their detailed study Bath and Shackleton compared the pore-water data with the $\delta^{18}O$ values for benthonic foraminifera from the same hole (Shackleton *et al.*, 1984) which display a downward decrease of 1.4‰ $\delta^{18}O$ over the same depth interval. The narrower range for the pore water is attributed to diffusive dissipation. This raises the difficulty that the diffusion coefficient required to match the observed profile has a value of only 10^{-7} cm²·s⁻¹, whereas diffusion coefficients commonly found for the types of sediments in question are in the range of 10^{-5} to 10^{-6}. With these higher coefficients the gradient would have been smoothed out at least 30% more. A large reservoir of paleo-oceanwater with low δD and $\delta^{18}O$ values might exist, however, in the basalt of layer 2 of the ocean crust and might allow higher gradients in sediments of layer 1 to persist, as suggested by Lawrence and Gieskes (1981), if transport in layer 2 is still by advection and in layer 1 by diffusion. The $\delta^{18}O$ values show a linear correlation Rith Ca (Figure 7, interstitial water data for Ca in site 525B from Gieskes *et al.*, 1984) and, alternatively, could be related to alteration reactions in the volcanic basement, whose products are distributed upward by diffusion. However, this does not explain the hydrogen data, because no hydrogen-isotopic fractionation is expected for this process. All known hydrogen-bearing low-temperature silicates are depleted in deuterium relative to sea water or interstitial waters (Savin, 1980). δD values of interstitial waters are, therefore, more reliable indicators for the isotopic composition of the original connate water than $\delta^{18}O$ values.

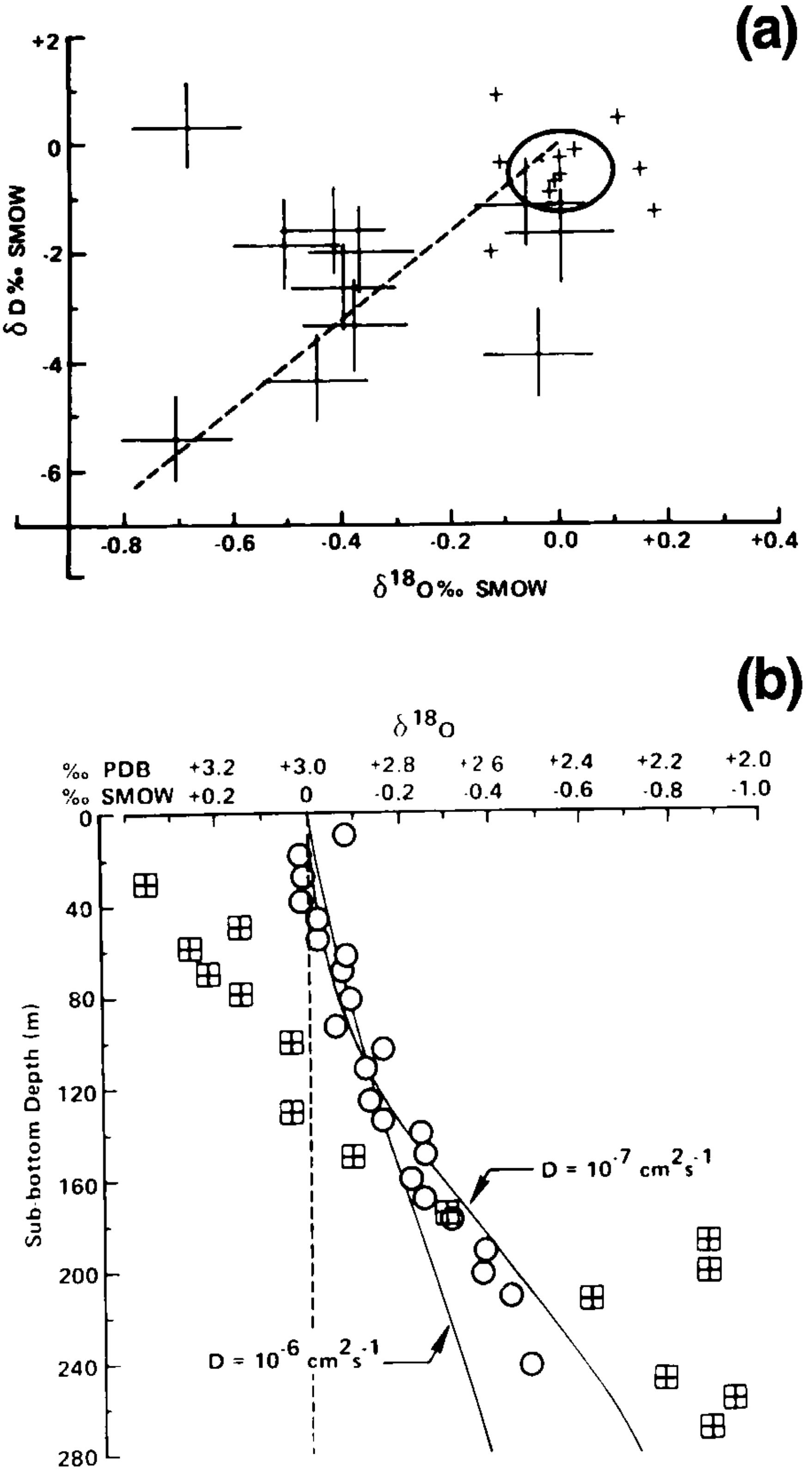


Figure 8 *(a) Oxygen and hydrogen isotope data for DSDP hole 525B from Bath and Shackleton (1984). The error bars are derived from the topmost 12 samples (small crosses), which all plot close to 0 on both coordinates. An error ellipse (1 standard deviation) has been drawn around the mean of these values and the diameters of this ellipse have been used for the error bars of the remaining samples assuming that the variability among the top samples is a reliable estimate of the analytical uncertainty. The dashed line has a slope of 8, indicating that the isotopic trend reflects evaporation of sea water.* **(b)** *3-point running average data (open circles) for pore water $\delta^{18}O$ values and (squares) for benthonic foraminifera from the same hole. The less steep gradient for the pore-water data is attributed to diffusive dissipation. The two solid curves are calculated diffusion-controlled trends resulting from an assumed isotopic composition of mid-Miocene (14 Ma) ocean water of -0.9‰ $\delta^{18}O$ and two different values for the average sediment diffusion coefficient.*

Reaction-controlled pore-water profiles in suboxic (to anoxic) pelagic to hemipelagic environments (type 3 pore-water profiles). These have somewhat higher organic matter contents than the previous group (type 2) but still low enough values so that diagenesis remains oxic to suboxic (Figure 3). In other words, the oxidant demand is such that the free oxygen reservoir will be depleted but not the nitrate reservoir. Many of the DSDP drill sites grouped as type 2 or type 1 sites may in fact be mixed sites and belong to group 3, because the upper few metres of the sediment column, which are often left unsampled, may show the effects of suboxic diagenesis. Deeper down in the holes, however, these effects may have been obliterated by diffusion. Piston-core studies with closely spaced samples in the upper few metres of the sediment are the appropriate approach to this environment. Müller and Mangini (1980) estimate that sedimentation rates of less than 40 m·Ma^{-1} are required for suboxic diagenesis. For higher rates, increased organic matter content will eventually exhaust the nitrate reservoir and establish anoxic conditions of the sulphate reduction zone.

"Mixed" site 495 apparently belongs to this latter category. A close look at Figure 5 reveals that some of the dissolved species, especially ammonia, phosphate and alkalinity show slight enrichments whereas sulphate shows a slight decrease near the top of the sediment column. This reveals that the typical organic-matter decomposition-reactions discussed before do in fact occur at present in this site, albeit apparently rather sluggishly. This is what is expected, because the hemipelagic muds in the upper 100 m of the column still contain between 1 and 2% organic carbon (Figure 9). They will have undergone at least the first two stages, but also part of the third stage of bacterial organic matter oxidation, although not much of this can be seen because most of the existing gradients were probably dissipated initially by convective flow and later by diffusion.

In certain regions alternating zones occur of oxic and suboxic diagenesis on the one hand and anoxic diagenesis on the other, which show up in vertical profiles, e.g., as alternating brown and green layers and corresponding variations in pore-water chemistry. They are caused by temporal fluctuations in organic matter supply, which, for example, may be associated with the influx of rapidly deposited, organic-matter rich, terrigenous muddy turbidites into an environment of pelagic sedimentation (Colley *et al.*, 1984). If the turbidites are rich enough in organic matter, their chemical signature may not be obliterated by diffusion although an oxidation front may move down (or up) from the overlying (or underlying) pelagic sediment and turn the upper (lower) part of the green or grey turbidite brown (Wilson *et al.*, 1985).

Recrystallization of biogenic pelagic carbonates. Biogenic pelagic carbonates provide another example of diffusion- and reaction-controlled pore-water profiles in low to intermediate sedimentation-rate areas, which unveil the role of solid sediment constituents other than organic matter in early

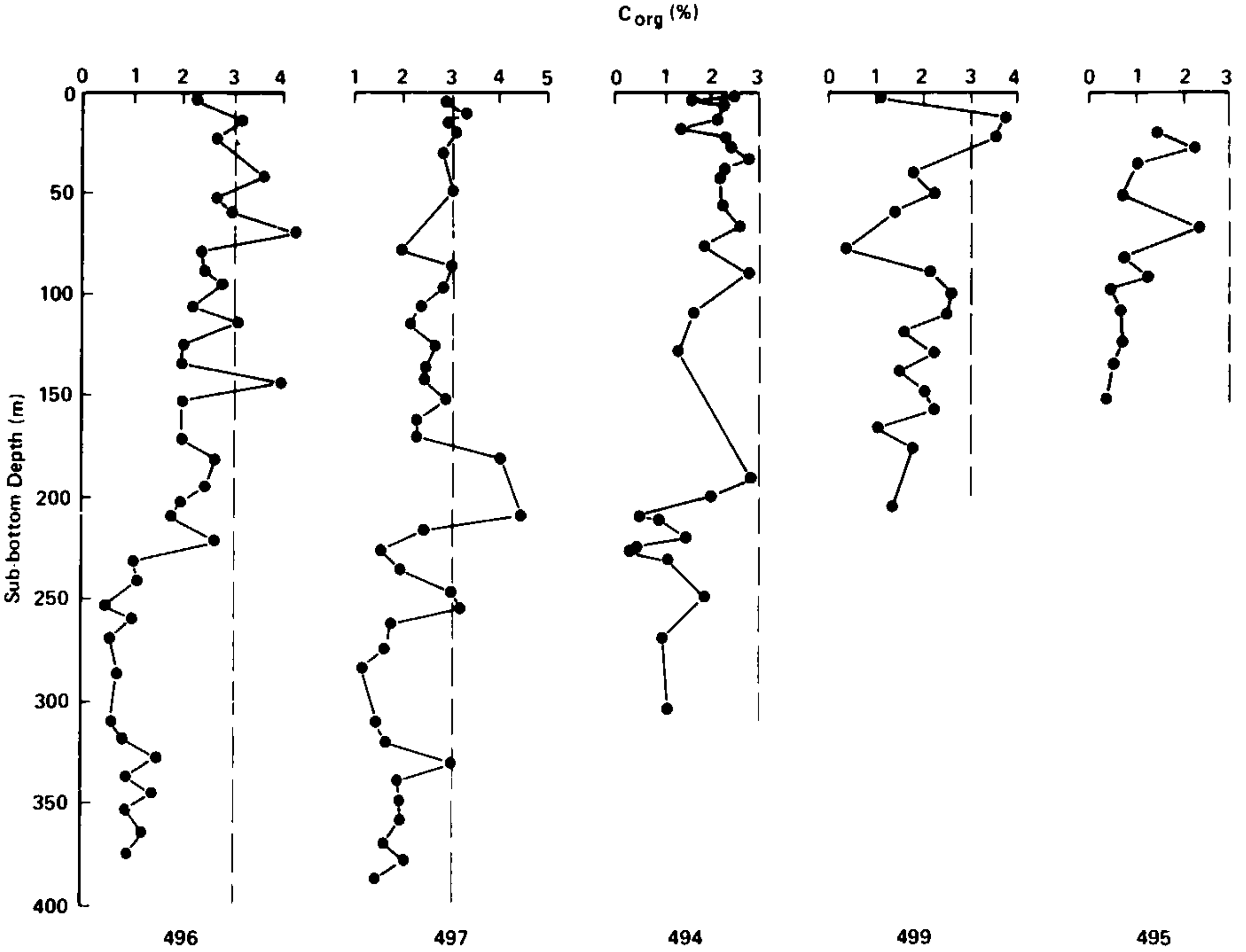


Figure 9 *Organic carbon distribution in DSDP drill sites on the middle (496, 497) and lower slope (494) of the Middle America Trench, in the trench (499) and on the adjacent oceanic crust of the Cocos plate (495) off Guatemala. (From Harrison* et al.*, 1982).*

diagenesis. It may be surprising that the recrystallization of pelagic carbonates which is reflected by a distinct Sr^{2+} anomaly at a 100 to a few 100 m subsurface depth (Figure 10a) does not seem to have a significant effect on Ca^{2+} concentration gradients. Recrystallization of deep-sea pelagic carbonates in the subsurface occurs because the small and delicate tests of foraminifera and coccoliths, which are the only major carbonate constituents of pelagic sediments, have a large reactive surface area easily subjected to pressure solution. Their Sr content is three to five times higher than that of the inorganic calcite reprecipitated from solution (Baker *et al.*, 1982; Elderfield *et al.*, 1982). Thus a distinct Sr signal is observed, whereas the calcium (and magnesium) concentration is not much affected, particularly not in low sedimentation-rate sites with low alkalinity levels. In these sites about the same amount of calcite that goes into solution appears to be immediately reprecipitated, often as overgrowths on single-crystal skeletal elements of the Coccolithophorida, especially discoasters (Figure 11). In site 495, a small Ca^{2+} maximum is associated with the Sr^{2+} maximum (Figure 5), possibly indicating that in the absence of a diffusion supported Ca-flux from the basaltic basement a signal stemming from the recrystallization reaction may still be preserved.

The maximum of dissolved Sr^{2+} near the calcareous ooze/chalk boundary appears to be associated with a maximum in the recrystallization rate. From this maximum, dissolved Sr^{2+} is transported by diffusion both upward toward the sediment/water interface and downward toward a sink deeper in the sediment column or the basaltic oceanic crust. The ooze/chalk boundary may be viewed as a diagenetic front which moves upward through the sediment column as burial proceeds (Gieskes *et al.*, 1986). Below the boundary, in the chalk, recrystallization is slowed down considerably. According to Stout (1985) the dissolved Sr^{2+} profiles with the gradual downward increase toward the maximum can be successfully modelled assuming diffusive transport and a constant production rate of Sr^{2+} for the reaction term in the general diagenetic equation (equation 9 in Table 3). As shown by Baker *et al.* (1982) this would still allow for variable recrystallization rates, because the inorganically precipitated calcite consumes much less Sr^{2+} than is released by the dissolving biogenic calcite. The lower sink toward which dissolved Sr^{2+} diffuses downward, is provided by volcanogenic sediment deeper in the column or basaltic basement which behave similar to mid-ocean ridge basalt during low-temperature alteration. The rate of carbonate recrystallization in pelagic sediments depends also on sedimentation rate (Gieskes and Johnston, 1984), which controls the production of CO_3^{2-} or HCO_3^- in the sediment, as discussed in the section on "early diagenetic organic matter oxidation". The Sr^{2+} maximum occurs thus at greatly variable subsurface depths. Direct evidence for the diffusive transport of Sr^{2+} in pelagic carbonates is provided by strontium isotope ratios. Sr-isotope curves for the pore waters of pelagic carbonates break down into two parts (Figure 10b). In the upper part above the Sr-maximum $^{87}Sr/^{86}Sr$ ratios are generally lower than the contemporaneous seawater curve of Burke *et al.* (1982) and Palmer and Elderfield (1985). Below the maximum they tend to be higher than or equal to paleo-seawater ratios for coeval sediments. This requires both upward and downward diffusion of dissolved Sr^{2+} from the site of maximum recrystallization (i.e. the dissolved Sr-maximum), where the isotopic composition is closest to that of contemporaneous sea water. Because sea water has become increasingly heavier in strontium isotopes during the last 100 Ma toward the present, the Sr-maximum is a source of relatively light Sr isotopes for the section above it and of relatively heavy isotopes for the section below it.

DSDP site 289 on the Ontong-Java Plateau in the Southwest Pacific differs from other carbonate sites in that the Sr-isotopic composition of the pore water below the ooze/chalk boundary is very close to the paleo-seawater curve (Figure 10b). In this site maximum dissolved Sr-concentrations are reached at about 400 m sub-bottom and below this depth no significant decrease is

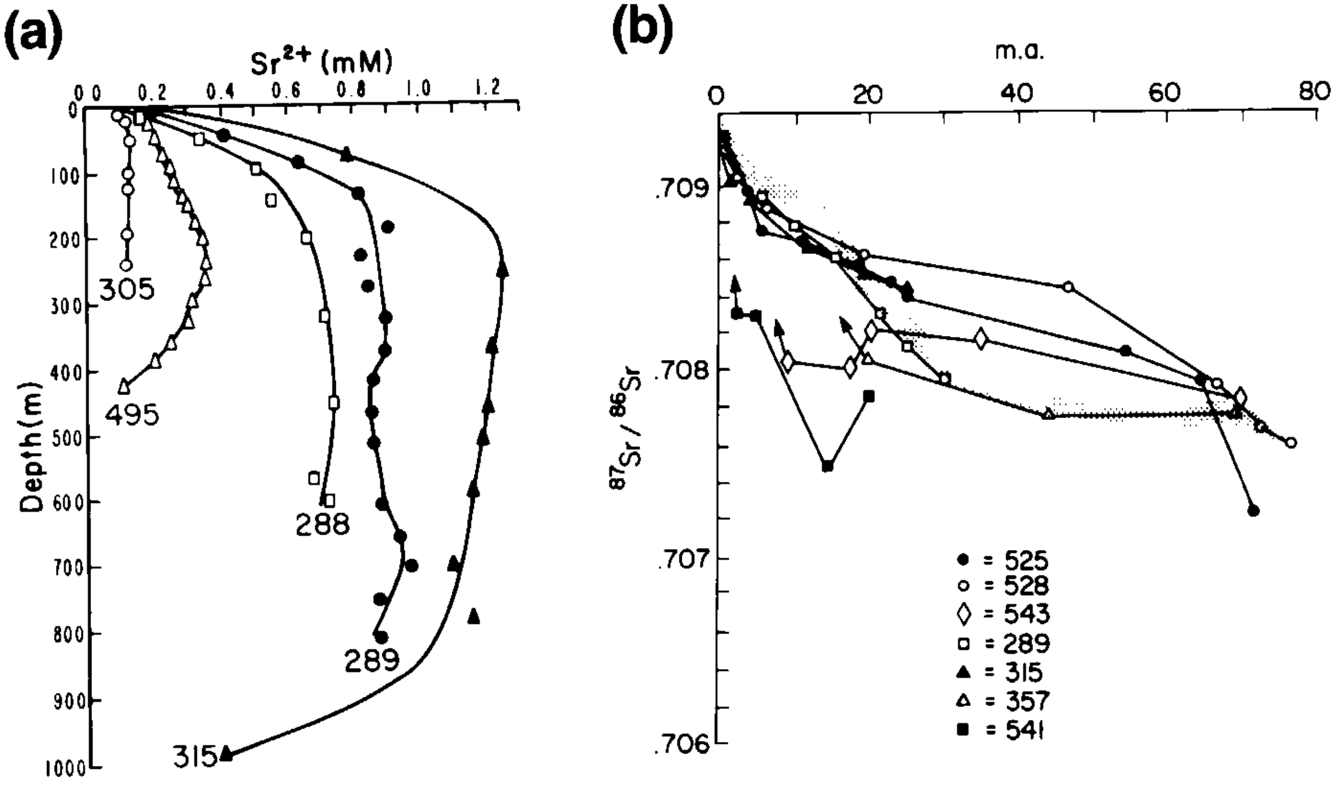


Figure 10 *(a) Typical dissolved Sr^{2+} concentration profiles in pelagic sediments, Pacific drill sites, DSDP. (Modified from Baker* et al., *1982). (b) Sr-isotope ratios vs. sediment age in pore waters from various DSDP drill sites and Sr-isotope curve of sea water (stippled) for the last 80 Ma. (From Gieskes* et al., *1986).*

observed (Figure 10a) suggesting that the downward diffusive flux in this thick chalk-limestone section is very small or nil — in line with the isotopic data which also suggest that in the chalk section of this hole isotopic equilibrium exists between the pore waters and their host sediments.

In carbonate-poor sediments of sites 541 and 543 near the toe of the Lesser Antilles island-arc slope, Sr-isotopic ratios of the pore waters in the upper part of the holes fall much below the paleo-seawater curve (Figure 10b). The dissolved $^{87}Sr/^{86}Sr$ ratios are too low to be due to upward diffusion, particularly as insufficient carbonate is available for recrystallization. Here, alteration of volcanic sediment particles with low Sr-isotope ratios (of about 0.704) must be invoked as the dominant source of the anomaly (Gieskes *et al.*, 1986). Alteration of volcanogenic sediment as a source of a light Sr-isotope signal is often accompanied by magnesium losses from the pore water in excess to those attributable to diffusive fluxes.

Other early diagenetic mineralization reactions in pelagic sediments. Zeolites provide additional, well-documented examples of early diagenetic mineralization in slowly deposited pelagic sediments, particularly volcanogenic pelagic sediments (Kastner and Stonecipher, 1978). The crystallization of zeolites from volcanogenic material proceeds through the formation of palagonite, a yellow-brownish alteration product of volcanic glass, which appears to be a common precursor of zeolites. The downward decrease of K^+ in the pore waters of many pelagic drill sites may be related to the formation of the main potassium-bearing zeolite, phillipsite $(K,Ca)Al_3Si_5O_{16} \cdot 6H_2O$. Other common zeolites formed during early diagenesis in pelagic sediments such as clinoptilolite and analcite leave a less characteristic imprint on pore-water composition. As Kastner and Stonecipher (1978) have shown, phillipsite is most abundant in the youngest sediments at shallowest subsurface levels and decreases in abundance with age and burial depth, whereas clinoptilolite shows the opposite behavior. The transformation of zeolites into K-feldspar with progressive burial has been documented repeatedly and is another sink for K^+, as are adsorption and ion exchange with clays.

Widespread neoformation of clay minerals does not seem to occur in pelagic environments at shallow burial levels (Kastner, 1981). "Reversed weathering" (MacKenzie and Garrels, 1966), which would have involved clay mineral reconstitution in the oceans through the uptake of silica and cations by amorphous aluminosilicates, has not been found to occur on a large scale. Small amounts of very fine-grained smectite may form, however, in early diagenetic environments (Chamley and Millot, 1972; Johnson, 1976; Moberly *et al.*, 1968; Hein *et al.*, 1979a) and the $\delta^{18}O$ and Mg^{2+} decreases mentioned earlier most likely involve newly formed clay minerals besides zeolites. Decreases of dissolved aluminium at shallow subsurface depths may also require the formation of small amounts of authigenic clay minerals (Stoffyn-Egli, 1982) and this mechanism may also operate at deeper levels in the subsurface (e.g. high-sedimentation rate DSDP sites 565 and 568, Hesse *et al.*, 1985; Figure 5). The formation of Al-rich di-octahedral chlorites was suggested by Mackin and Aller (1984) for shelf sediments of the East China Sea where other aluminium removal mechanisms such as complexation with dissolved organic matter or adsorption on amorphous silica surfaces are less likely to occur, whereas in the above DSDP sites these and the formation of smectite (Helm, 1985) might be sufficient to account for the dissolved aluminium decrease.

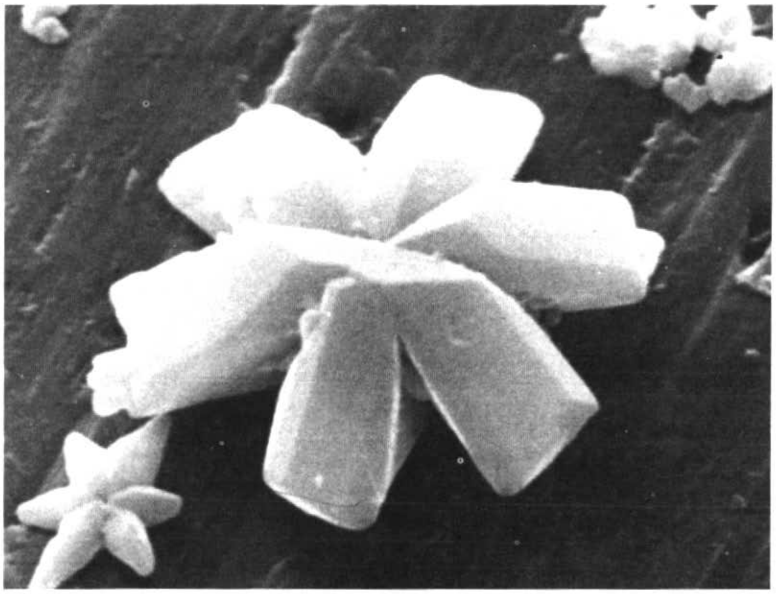


Figure 11 *Calcite overgrowth with well-developed crystal faces on discoaster. DSDP site 199, Caroline Abyssal Plain, 6090 m water depth, Early Pliocene carbonate turbidite, 59 m sub-bottom depth.*

These examples show that in a given drill site usually several mechanisms contribute to the make-up of the pore-water chemistry. In low sedimentation-rate environments such as the pelagic realm, convection- and diffusion-dominated pore-water profiles prevail, but reactions may significantly modify vertical trends as shown for Sr^{2+}, K^+ and SiO_2. Thus every drill hole and every element has to be investigated specifically. In the following section, reaction-dominated pore-water trends will be analysed which are characteristic for high sedimentation-rate environments. Some of these can also be found, however, in low-rate environments as examples of the foregoing discussion have shown.

II. High Sedimentation-rate Basins

These are characteristic of the continental margins, where sedimentation rates up to 500 $m \cdot Ma^{-1}$ and more, i.e. rates two orders of magnitude higher than for the brown abyssal clay, are no exception. High sedimentation rates at the continental margins result from the increased input of terrigenous material which tends to be rich in terrestrial organic matter. Rapid burial enhances preservation of this organic material. An additional source is *marine* organic matter which is supplied at increased rates in areas of high biogenic surface productivity associated with regions of upwelling of nutrient-rich deeper waters. Because zones of upwelling are concentrated around the margins of the continents, continental slope and outer shelf sediments may contain significant proportions of marine organic matter which is highly reactive and has a high potential for liquid hydrocarbon generation.

In high sedimentation-rate basins, the role of diffusion in smoothing out concentration anomalies is suppressed, because sedimentation rates exceed diffusion rates. In addition, anomalies produced by ongoing reactions will be much more pronounced than in low-rate basins because of the elevated concentration of reactive organic matter. Initial organic carbon contents of these sediments often exceed 2 or 3% (Figure 9).

Pore-water trends in continental margin environments: major element and isotope chemistry in anoxic sediments (type 4 pore-water profiles). The sequence of organic matter oxidation reactions discussed in a previous section is best reflected in the vertical trends of pore-water chemistry in rapidly deposited sediments of the continental margins. These sediments pass very rapidly through the oxidation and nitrate reduction zones during burial and essentially experience anoxic diagenesis. The main chemical species released to the pore water from the microbial breakdown of organic matter and the concomitant reduction of oxidants are the nutrients ΣCO_2 (including the species CO_2, H_2CO_3, HCO_3^- and CO_3^{2-}), phosphate, ammonia and sulphide. The main oxidants consumed in the process are $O_2(aq)$, NO_3^- and SO_4^{2-} and also CO_3^{2-}. CO_2 production occurs at all stages from (1) to (6), consumption from stage (4) downward. A distinction between the CO_2 released and the CO_2 consumed at different stages is possible due to the strong isotopic fractionation effects associated with some of the reactions, particularly methane generation beginning in stage (4). In order to understand fully the chemical trends, reactions other than organic-matter decomposition have also to be considered. These include ion-exchange reactions, adsorption, and the precipitation of (early) diagenetic mineral phases. These, and reactions coupled with phase changes (i.e. gas-hydrate formation), which introduce further fractionation effects and diversification of the chemical trends, will be discussed in the following sections.

Drill holes of the DSDP in the East Pacific off Guatemala will again be used as examples, because they are representative for high-sedimentation rate continental margin environments and display some trends but also some special features with unusual clarity. The landward slope of the Middle America trench off Guatemala was drilled during two legs of the DSDP (legs 67 and 84) in two parallel transects close to each other thus providing a unique opportunity to check the reproducibility of the results of interstitial water analyses in nearby drill holes. A third transect of holes was drilled in the same general area on the slope off Mexico (DSDP leg 66).

Drill sites 496, 497 and 568 which are located on the mid-slope in water depths between 2000 and 2400 m are characterized by extreme maxima for carbonate alkalinity, ammonia and dissolved phosphate in the upper parts between 50 and 200 m sub-bottom (Figure 5). These maxima occur in the carbonate reduction and fermentation zones, i.e. below the sulphate reduction zone which is about 5 m thick in this region as sulphate is absent in samples taken below that depth. Carbonate alkalinity exceeds a record 120 milliequivalents (meq)·kg^{-1} between 23 and 45 m sub-bottom in hole 496 — the highest value ever reported from deep-water sediments. PO_4^{3-} reaches a maximum of 0.4 mM and NH_4^+ of 21 mM in the same hole. In comparison with the alkalinity maximum at 35 m sub-bottom depth, the other two maxima are displaced downward to 56 and 175 m, respectively.

The fact that the carbonate alkalinity maximum occurs *within* the carbonate reduction zone (and not at its upper boundary) shows that carbonate (or bicarbonate) production continues in this zone due to various fermentation reactions, initially at a faster rate than

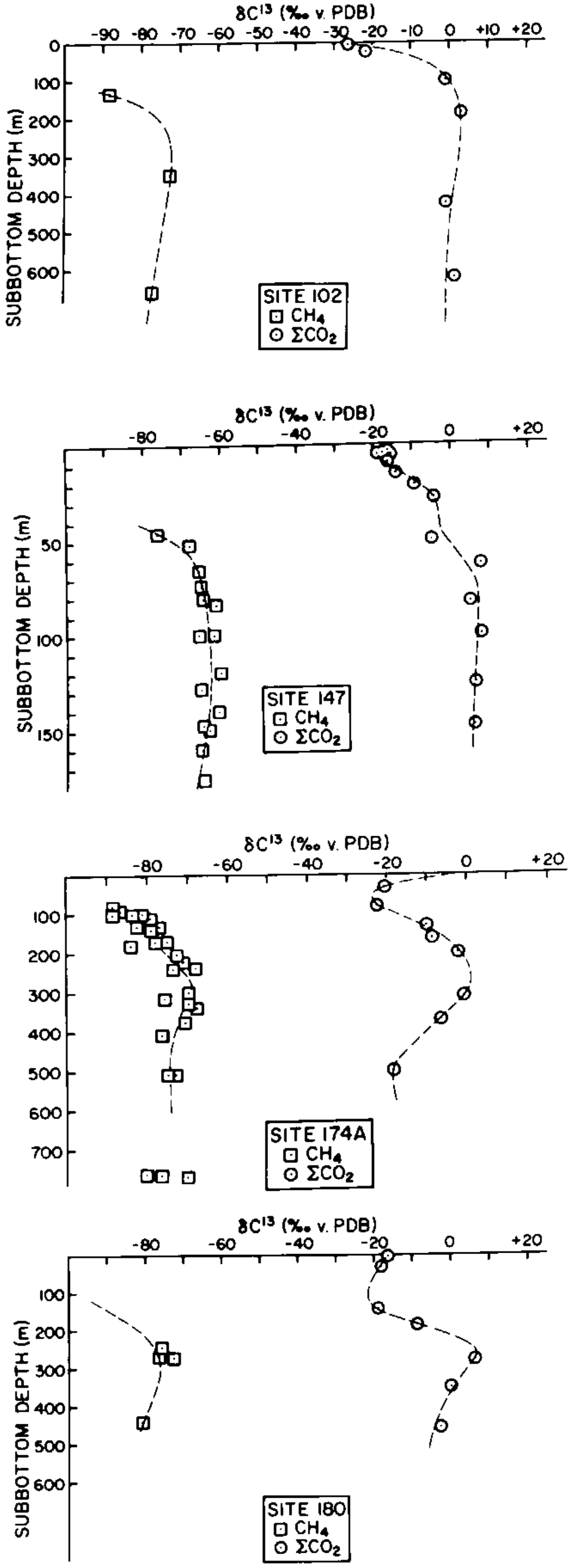


Figure 12 *$\delta^{13}C$ depth trends in CH_4 and CO_2 in four DSDP drill sites (102: Blake-Bahama Outer Ridge; 147: Cariaco Trench; 174A: Astoria Fan; 180: Aleutian trench floor). (From Claypool and Kaplan, 1974).*

consumption. Eventually, however, consumption by methane generation (and precipitation of carbonate concretions, as discussed later) become dominant.

Direct insight into the interplay of the various processes may be gained from carbon-isotope analyses. During the first three steps of organic-matter decomposition (i.e. in the oxidation, nitrate reduction and sulphate reduction zones) negligible isotopic fractionation occurs. The CO_2 (or HCO_3^-, CO_3^{2-}) released has about the same isotopic composition as the parent organic material, i.e. a $\delta^{13}C$ of about -25‰ (relative to the PDB standard) for marine organic matter. The pore water becoming enriched with CO_2 from this source in the upper three zones will gradually approach a $\delta^{13}C$ value of -20 to -25‰ (Figure 12, especially site 174A). In the carbonate reduction and fermentation zones, however, the disproportionation of organic matter into CH_4 and CO_2 is accompanied by a strong isotope fractionation effect. The CH_4 generated has a C-isotopic composition which is about 70% lighter than the carbon of the parent material and may thus attain $\delta^{13}C$-values as negative as -90 or -100‰. This is a kinetic effect (Rosenfeld and Silverman, 1959) by which the CO_2 with light carbon is preferentially reduced to CH_4. The residual CO_2 consequently becomes enriched in $\delta^{13}C$ reaching positive δ-values (Figure 12) as high as + 15 to + 25‰ (e.g. Curtis *et al.*, 1972). As the dissolved carbonate becomes progressively heavier, so does the methane produced from it at deeper levels. Through this feed-back mechanism (a Rayleigh-distillation process) the $\delta^{13}C$-curves for both methane and dissolved carbonate show parallel trends (about 70 δ-units apart) with depth. These are often characterized by a slight decrease in $\delta^{13}C$ at greater depths due to the release of relatively light carbon by the continuing breakdown of organic matter in fermentation reactions. The parallelism of the carbon-isotope curves for methane and CO_2 is convincing evidence that carbonate reduction is actually involved in biogenic methane generation. More recently (Claypool *et al.*, 1985) $\delta^{13}C$ values as high as +36 to +38‰ have been measured for CO_2 coexisting with methane as heavy as -41‰ in deeper parts of DSDP holes 568 and 570 (Figure 5). Methane of biogenic origin is usually lighter than -55‰, and $\delta^{13}C$-values heavier than -45‰ are characteristic for thermogenic gas (Schoell, 1983). However, there is no evidence for upward migration of thermocatalytic methane on the Guatemalan trench slope and the cause for the extreme enrichment in heavy carbon of both CH_4 and CO_2 is not clear. The magnitude of the fractionation effect ($\delta^{13}C_{CO_2} - \delta^{13}C_{CO_2}$ = 77‰) is still about the same as that usually observed with bacterial methane production.

In, or immediately below, the sulphate reduction zone $\delta^{13}C$ values for CO_2 more negative than -28‰ have been observed locally, e.g. in DSDP hole 533 on the Blake Bahama Outer Ridge (-31.4‰0, Claypool and Threlkeld, 1983), which require a source more depleted in heavy carbon than average organic matter. This could be due to the predominance of isotopically lighter terrestrial organic matter (Sackett and Thompson, 1963) or the anaerobic oxidation of methane diffusing upward into the sulphate reduction zone. In ancient rocks, a record of these processes may be preserved in carbonate concretions which incorporate carbonate of given isotopic composition from the pore water (with a small liquid to solid fractionation) in their concentric growth shells (see below).

Before following further the fate of the products of organic matter decomposition in mineralization processes, the behaviour of some other major elements will be dealt with. Of the two main dissolved constituents of sea water, chloride and sodium, the former does not participate in reactions, because of its large ionic radius which prevents it from incorporation into the crystal lattices of common authigenic or hydrothermal mineral phases. As a non-reactive species, chloride often does not display vertical concentration gradients, at least not at shallow burial depths. If, on the other hand, chloride gradients are observed, one of the following processes may be inferred: (a) dilution by mixing with meteoric waters or fresh water from other sources, (b) salinity increase due to halite dissolution or loss of water in hydration reactions, e.g. in basalt of the oceanic crust, or (c) slight changes in seawater chlorinity during glacial-interglacial cycles.

Profiles with meteoric water influx (type 5 pore-water profiles). The influx of meteoric waters in subsurface aquifers at considerable depth and distance from shore was demonstrated in some test drill holes for the Deep Sea Drilling Project on the continental shelf off Florida (Manheim, 1967). In permeable Eocene to Cretaceous limestones fresh water was encountered up to 120 km from shore (Figure 13). Fresh water buried during Pleistocene low sea-level stands has been reported from the Black (Manheim and Chan, 1974; Manheim and Schug, 1978) and Baltic Seas (Suess, 1976), when these inland seas became lakes.

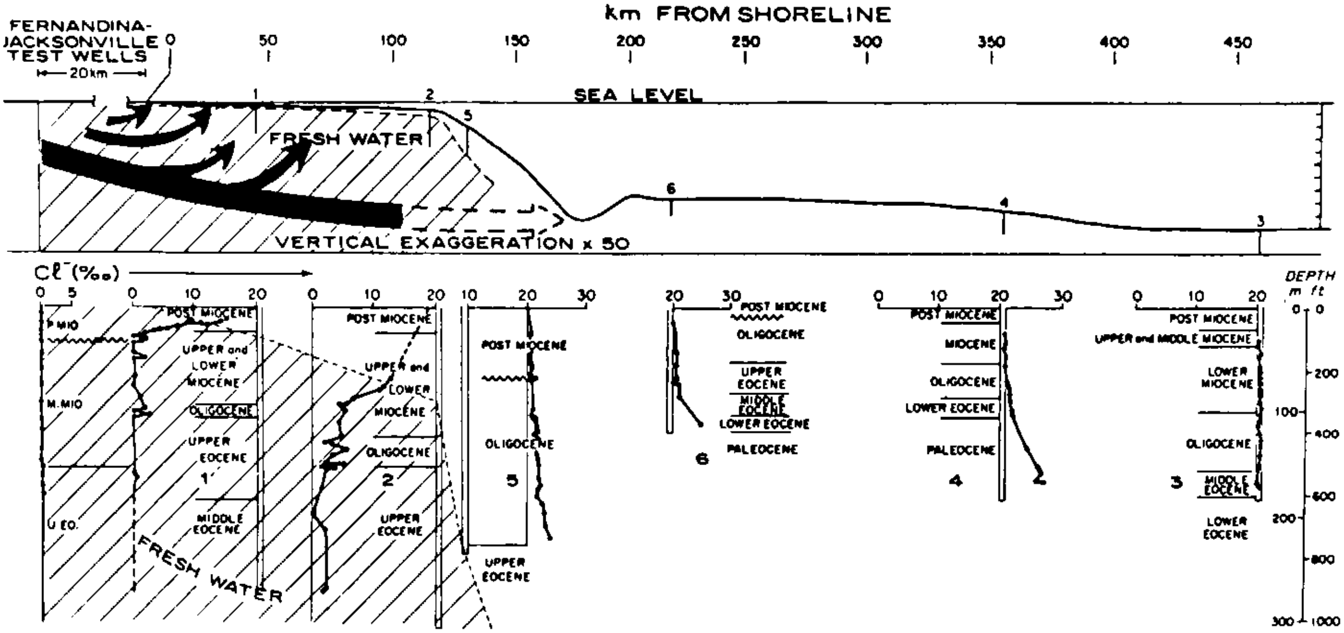


Figure 13 *Fresh and brackish water in drill holes on the Florida continental shelf indicating subsurface discharge within carbonate aquifers up to 120 km from the coast (pore-water profile, type 5). (From Manheim and Sayles, 1974).*

The effects of gas hydrates on pore-water chemistry: Salt and isotope fractionation (type 6 pore-water profiles). An interesting freshwater source of a different nature is the occurrence of gas hydrates which will also leave a distinct isotopic imprint on the pore water. A significant downward chlorinity decrease coupled with a $\delta^{18}O$ increase (up to 3.3‰) has been observed in gas-hydrate bearing sections of DSDP drill holes (Harrison *et al.*, 1982; Jenden and Gieskes, 1983; Gieskes *et al.*, 1985; Hesse *et al.*, 1985) and interpreted as release of fresh water from the thawing of hydrates, either at the base of hydrate zones or in the sampling process (Hesse and Harrison, 1981). Gas hydrates are ice-like substances which form in organic-matter rich sediments with strong bacterial methane production. The crystal structure of gas hydrates (clathrates) is similar to that of zeolites containing large cavities (cages) in which gas molecules, such as CH_4, CO_2, H_2S, N_2 but also higher hydrocarbons up to the size of iso-butane, may be accommodated. These gas molecules are not chemically bound in the structure, but are held in the cages by van der Waals forces and hydrogen bonds, which make the structure more stable than that of normal ice. The formation of gas hydrates from water and methane involves a negative molar volume change. Prerequisites for the formation and stability of methane hydrates are high gas concentrations, elevated pressures and relatively low temperatures. These conditions exist in terrigenous continental slope and rise environments, particularly in the lower latitudes where the supply of terrestrial organic matter to the oceans is prolific. In water depths between 500 and 5000 m, hydrostatic pressures are sufficient for gas hydrates to be stable up to + 10 to + 30°C (Figure 14). Gas-hydrate zones can thus attain a thickness of up to 1 km (or more), depending on the availability of methane-generating organic matter in outer, deeper continental margin environments. Because the ground is frozen or partially frozen in hydrate zones, they appear as relatively transparent zones on seismic profiles, often bound at the bottom by a strong seismic reflector, the so-called "bottom simulating reflector" (BSR)(Figure 15) which is named for its tendency to occur at a constant distance below the ocean-bottom reflecting the pressure dependence of hydrate stability. The BSR is caused by the presence of free gas at the base of the hydrate zone, where the hydrates thaw and release quantities of gas well in excess of methane solubility in the pore water. An amplitude reversal associated with the seismic signal from the BSR attests to the presence of free gas, which is sealed in by the gas-tight cap of hydrate-impregnated sediments above.

Like normal ice, gas hydrates do not incorporate dissolved salts but concentrate heavy isotopes of oxygen and hydrogen in their

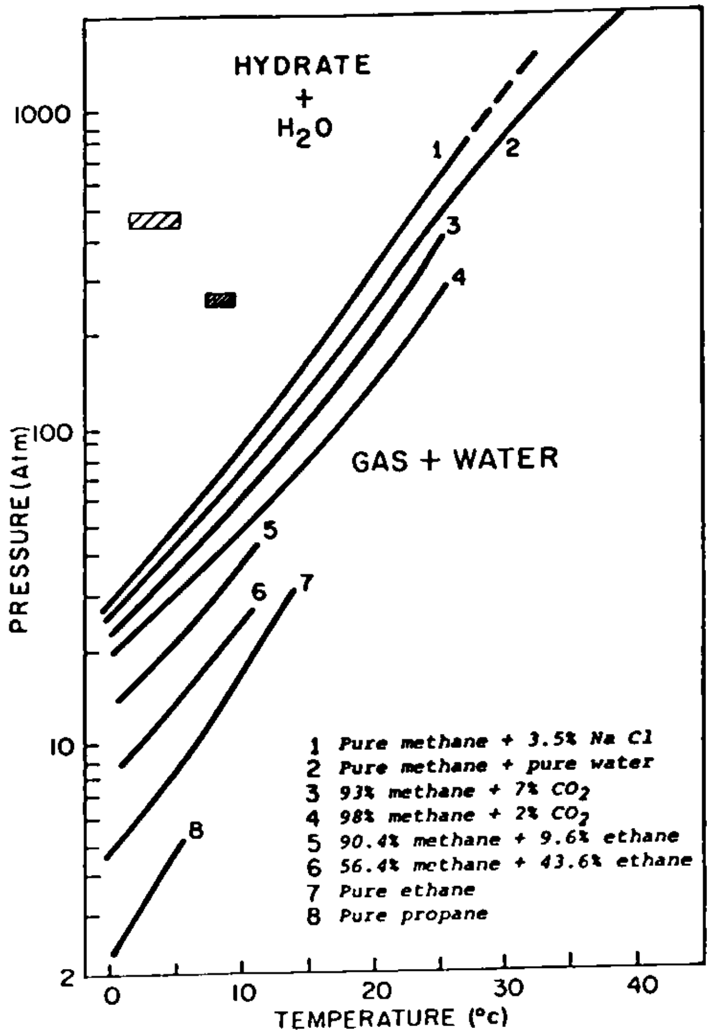


Figure 14 *Stability field of hydrates with various gas compositions. (From Hesse and Harrison, 1981, after Tucholke* et al., *1977). Boxes indicate estimated P-T conditions for DSDP sites 497 (closely spaced diagonal lines) and 498A*

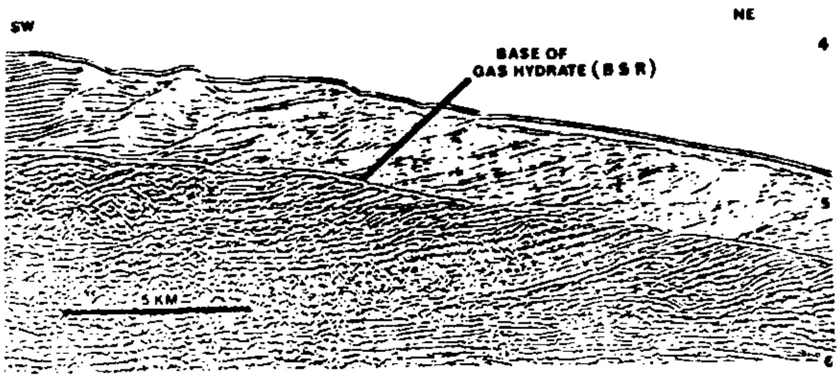


Figure 15 *Multichannel seismic reflection profile of gas hydrate zone with bottom simulating reflector (BSR) on Blake-Bahama Outer Ridge. (From Shipley* et al., *1979). Vertical scale: Two-way seismic travel time in seconds.*

structure thus causing salt and isotope fractionation. As a consequence the remaining pore fluid not involved in hydrate formation will be enriched in dissolved salts and light isotopes. During burial and compaction when partial separation of the pore fluids and the solid sediment constituents takes place, — the solids being buried, the liquids moving up relative to the solids, — gas hydrates carry down fresh water in solid, ice-like form to greater burial depth. When the hydrates thaw at the base of the hydrate zone or in the sampling process, they release this fresh water, which is also isotopically heavy. Mixing with the remaining pore water, which due to compaction is much reduced in volume compared to the uncompacted sediment near the sea floor where the hydrates first form, produces the observed trends of down-hole chlorinity decrease and $\delta^{18}O$ increase (Figure 5, sites 496, 497, 565, 568, 570).

Positive $\delta^{18}O$ values are a reliable indicator for gas hydrates as fresh water source, because fresh water from a meteoric source would produce negative $\delta^{18}O$ values. However, positive $\delta^{18}O$ values are not invariably associated with a chlorinity decrease related to hydrate decomposition, as shown by the pore water profile for site 565 drilled in 3 km water depth on the continental slope off Costa Rica (Figure 5). Here, a more or less continuous downward chlorinity decrease is accompanied by a zone of negative $\delta^{18}O$ values at sub-bottom depths between 95 and 170 m (with a minimum δ-value of -1.26‰, Hesse *et al.*, 1985). Note that the elevated chlorinity values between 235 and 255 m are probably due to contamination by sea water, because Mg^{2+} and SO_4^{2-} are also anomalously high. If the negative $\delta^{18}O$ values were the result of meteoric water influx, one would not expect the chlorinity to be lowered significantly, because pore waters in aquifers at 3.5 km subsurface depth tend to have chlorinities considerably higher than fresh water. Alternatively, if the lowered chlorinity in those isotopically light zones is due to hydrate decomposition as suggested by Hesse *et al.* (1985), a different isotopic fractionation mechanism producing isotopically light water has to be superimposed on the hydrate fractionation mechanism. This would be the alteration of volcanic glass to zeolites and smectites discussed before.

Hesse and co-workers (1985) discussed the chlorinity vs. depth trends for sites 496 and 568 and concluded that, if the low-chloride waters in these sites were produced by downward diffusion of Cl^- toward (or upward advection of fresh water from) a pool of low-chlorinity water below the hydrate zone, a trend indicated by the dash-dot line in Figure 16 would be expected reflecting downward decreasing diffusion coefficients. The trends actually observed suggest that diffusion and advection in these high sedimentation-rate sites are insignificant and that the gradual chloride profiles result from a rather uniform distribution of hydrates with gradually increasing concentrations downward. In other drill sites, e.g. site 570 on the Guatemalan trench slope, sites 490 to 492 on the Mexican trench slope (Gieskes *et al.*, 1985) or site 533 on the Blake-Bahama Outer Ridge (Jenden and Gieskes, 1983) chlorinities fluctuate and minima probably coincide with local concentrations of gas-hydrates in preferred horizons.

These considerations militate against the possibility of upward migration by diffusion or advection to the hydrate zone of isotopically heavier waters that form at great depths in sedimentary basins due to isotopic exchange reactions between the pore fluids and solids at more elevated temperatures (Clayton *et al.*, 1966; L. Land, pers. comm., 1985). It is tempting to invoke advection of deeper waters in view of the anomalously high levels of compaction and dewatering that have been reported from modern subduction zone complexes beneath trench slopes (Carson, 1977; Carson *et al.*, 1974). Theoretically, dewatering may be a diffuse, trench-slope wide process or a process of concentrated flow along structurally controlled pathways. In the pore-water profiles studied so far there is no indication whatsoever for a diffuse, uniform process. If active dewatering occurs with absolute upward motion of the pore fluids (rather than only relative upward motion with respect to the subsiding sediments), it would have to be along focussed, localized pathways as reported from some active margins (see section on authigenic carbonates). If the isotopically heavy pore waters recovered from hydrate zones were derived by advection or diffusion of heavier fluids from below, rather than by hydrate fractionation, why then do we not see the same isotopic signal in hydrate-free environments of a similar tectonic setting? More importantly, why then do the hydrogen isotopes show the same trends as the oxygen isotopes in hydrate zones (e.g. in site 533 of the DSDP, Jenden and Gieskes, 1983), whereas in deep formation waters they do not, i.e. the deuterium enrichment characteristically lags behind the enrichment in $\delta^{18}O$? This again is evidence that advection or diffusion of deeper pore waters in modern active margin environments does not occur on a broad scale as a uniform advection or diffusion front.

Attempts at sampling the pore fluids from hydrate zones *in situ* and retrieving the expected high-salinity (high chlorinity) and isotopically light waters that have been rejected from the crystal lattices of hydrates have not yet been successful. *In situ* water samples taken during leg 84 of the DSDP at sites 565 and 568 showed agreement with the analyses of pore waters squeezed onboard the drill ship except for the deepest samples in hole 568 which, however, were probably contaminated by sea water (Hesse *et al.*, 1985; see Figures 5, 16). The explanation for this unexpected finding is that hydrate decomposition presumably took place in the sediment before the completion of sampling, because of the pressure drop that propagates from the sampler into the surrounding sediment which, after all, is a prerequisite for water flow

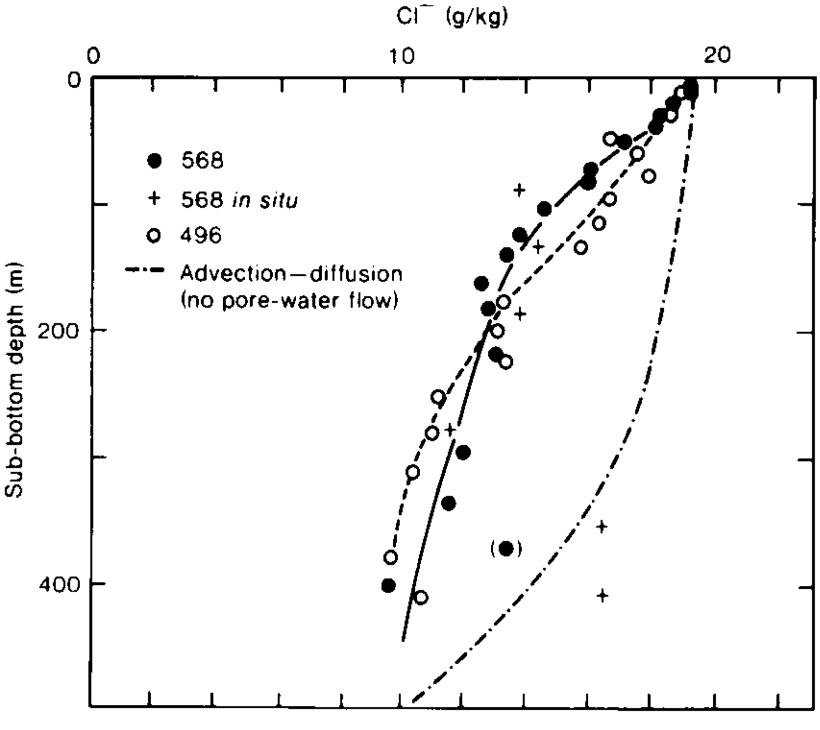


Figure 16 *Chlorinity versus depth profiles for DSDP sites 496 and 568. (From Hesse* et al., *1985).*

into the sampling device. A modified sampling procedure with high-pressure gas displacement of pore fluids might shed light on this unsolved problem in the future.

Gas-hydrate zones provide an opportunity to evaluate the amount of organic carbon converted into methane during early diagenesis, because most of the methane generated is probably still trapped and little has escaped to the ocean floor, in contrast to regions without gas hydrate development and their sealing effects. From the assumptions listed in Table 5 a figure of about 1.0 weight% of carbon is calculated that is lost to the hydrate zone, or 25 to 30% of the organic carbon initially embedded in the sediment. This is somewhat less than the loss of organic carbon seen in holes 496 and 497, where the downward decrease between the sea floor and 400 m sub-bottom is about 3%, or 1.5% C_{org} averaged over the entire column (Figure 9). Thus, most of this decrease can be explained by bacterial organic matter decomposition and little is due to depositional factors. These calculations also show that, in sediments with initial C_{org} concentrations above 3 or 4%, there is more than enough organic matter available for the formation of gas hydrates.

The figure of at least 50% dilution of the pore water by fresh water released from hydrate decomposition at the base of a 400 m thick gas hydrate zone (or during sampling from within this zone) offers an interesting possibility to evaluate the efficiency of the isotopic fractionation mechanism. Experimental determinations have confirmed that the isotopic fractionation factor for a clathrate-water system (α = 1.027, Davidson *et al.*, 1983) is close to that of the ice-water system (α = 1.03, O'Neil, 1968). With this fractionation factor $\delta^{18}O$ values at the base of a hydrate zone, where at least 50% of the pore water is derived from hydrate melting, should be about 1.4‰, compared to values of up to 3.3‰ actually observed. Because advection or diffusion of isotopically heavy waters from greater depths in the active margin environments considered here is not very likely as discussed earlier, a multiple fractionation mechanism has been invoked (Hesse *et al.*, 1985), by which the base of the hydrate zone migrates vertically up and down with time, e.g. as a result of heat-flow variations. Heavy water released by melting hydrates could again be used when the hydrate base moves downward to form new, heavier hydrates.

Besides hydrate decomposition there are other dehydration reactions causing fresh water release manifesting itself as salinity and chlorinity decrease at depth, particularly in zones of abnormally high fluid pressure. Because these are generally associated with more advanced stages of diagenesis (middle diagenesis) at greater burial depth, they will not be discussed and we shall turn our attention to other processes operating at shallow burial levels during early diagenesis.

Table 5 **Amount of organic carbon converted to methane which is trapped in gas-hydrate zones**

Assumptions	
Thickness of gas-hydrate zone	400 m
Average porosity over this thickness	50%
Total water content of 400 m thick sediment column	20 L H_2O $(cm)^{-1}$
Chlorinity reduction from top to bottom of hydrate zone (e.g. from 19% to 9.5% in sites 496 and 497)	50%
Dilution of pore water by fresh water released	
from hydrates at base of hydrate zone	50%
at top of hydrate zone	0%
Average dilution over 400 m thick sediment column	25%
Average bulk density of 400 m thick sediment column	1.5 g $(cm)^{-3}$
Calculations	
Total fresh water released from hydrates over 400m	5 L
Number of moles H_2O released	277
Number of moles CH_4 corresponding to 277 moles H_2O in methane hydrate of composition $CH_4 \cdot 6H_2O$	45
Weight of carbon corresponding to 45 moles CH_4	540 g
Total weight of 400-m-thick-column·$(cm)^{-2}$	60,000 g
Percent of organic carbon converted to methane still contained in hydrate zone	0.9

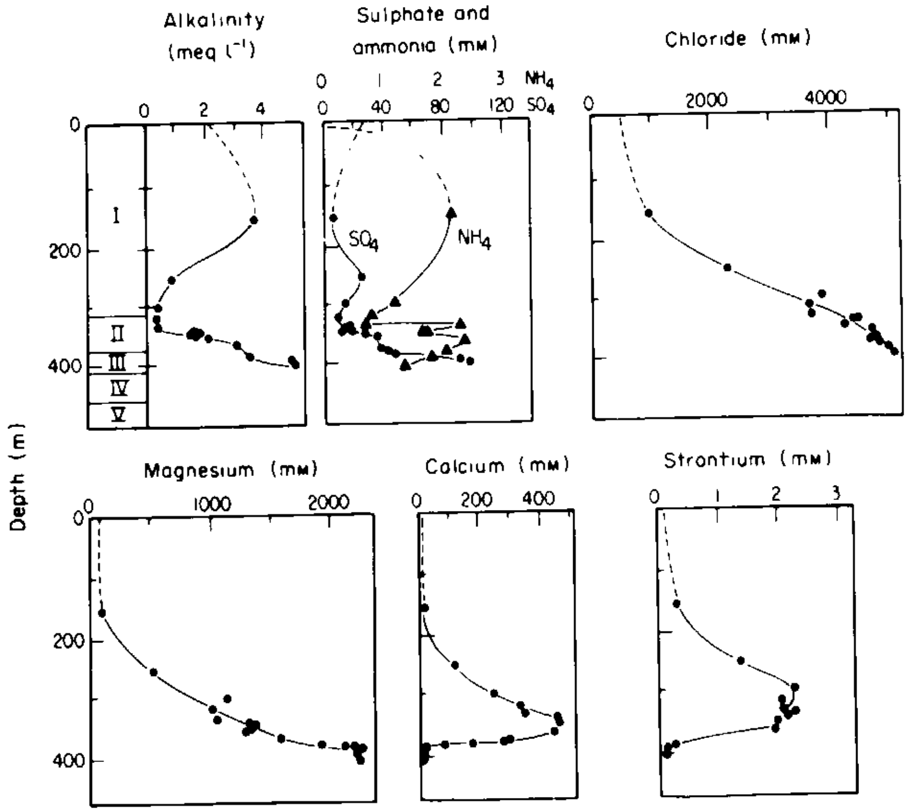


Figure 17 *Interstitial water profiles for DSDP site 374 in the Balearic Basin of the western Mediterranean Sea indicating dissolution of evaporite minerals at 380 m sub-bottom depth (pore-water profile, type 7). (From Gieskes, 1983, after McDuff* et al., *1978). Lithology: **I**: marls; **II**: nannofossil ooze; **III**: dolomitic marls; **IV**: gypsum, anhydrite; **V**: halite.*

Evaporite dissolution at depth (type 7 pore-water profiles). Halite dissolution in the vicinity of salt-domes and evaporite layers is the main, although not the only source for high salinity NaCl and (Ca, Na_2)Cl_2 brines. These typically occur at great depths in sedimentary basins penetrated by deeper wells. However, relatively shallow increases in chlorinity have been encountered at a number of drill sites of the DSDP in regions known to be underlain by evaporites, e.g. the Mediterranean Sea (McDuff *et al.*, 1978; Sayles *et al.*, 1972), Red Sea (Manheim *et al.*, 1974), Gulf of Mexico (Manheim *et al.*, 1969), and Atlantic continental margin provinces off the Guyanas (Waterman *et al.*, 1972), Namibia (Sotelo and Gieskes, 1978) and Morocco (Couture *et al.*, 1978; Gieskes *et al.*, 1980). In some of these the increase in chloride concentration is not accompanied by a corresponding sodium increase, e.g. at site 374 in the Balearic Basin of the Mediterranean Sea (McDuff *et al.*, 1978) indicating dissolution of other complex chlorides (Figure 17). At this site, the rare magnesium-rich mineral lueneburgite ($Mg_3(PO_4)_2B_2O(OH)_4 \cdot 6H_2O$) was also found (Müller and Fabricius, 1978).

Another mechanism that has been invoked for the origin of high chlorinity brines at great depths in sedimentary basins in which evaporites are absent is membrane filtration by shales (e.g. Graf, 1982). As the discussion on membrane filtration has focussed on the deeper parts of sedimentary basins, the somewhat controversial issue (e.g. Manheim and Horn, 1968; Dickey, 1969) will not be taken up here.

Hydrothermal activity and intrusion of igneous dykes and sills (type 8 pore-water profiles). Hydrothermally influenced drill sites mentioned earlier in conjunction with convection-controlled pore-water profiles may also show downward increases in chlorinity as a result of water removal in hydration reactions (Figure 18). For example, site 477 in the Guaymas Basin, Gulf of California, is located on a high heat-flow anomaly associated with a local spreading axis, for which a geothermal gradient of 88°C·(100 m)$^{-1}$ was estimated for the sediment column leading to temperatures of 200°C at the bottom of the hole at 300 m sub-bottom depth. Distinct downward increases in Li^+, K^+, and Rb^+ in the pore waters of this site are attributed to hydrothermal alteration of the sediments, which become depleted in alkali metals as these are released to the pore water (Gieskes *et al.*, 1982b). The observed Ca^{2+} increase and Mg^{2+} decrease are similar to diffusion controlled sites, although sedimentation rates are very high (greater than 2000 m·Ma^{-1}). These changes probably result from the release of Ca^{2+} and uptake of Mg^{2+} by the hydrothermally altered volcanics of the basaltic crust and the volcaniclastic sediment particles. The Sr^{2+} maximum at 140 m sub-bottom depth may indicate removal of Sr^{2+} deeper in the hole by basalt-sea water interaction at low rock/water ratios, as observed elsewhere (Menzies and Seyfried, 1979), and this may also be responsible for the downward decreasing $^{87}Sr/^{86}Sr$ ratios.

The basaltic sill at 58 to 105.5 m sub-bottom was apparently cool at the time of drilling. Its age of probably more than 20,000 years indicates that the thickness of the sediment cover at the time of the intrusion was probably less than 25 m at this high sedimentation-rate site. The sill has a distinct effect on the dissolved Mg^{2+} and ammonia concentrations, which are lowered, and the dissolved sulphate concentration which is raised in the pore waters of the sediment immediately above and below.

Early Diagenetic Mineralization Reactions in High Sedimentation-rate Basins

Processes and chemical reactions of pore-water evolution discussed so far have centered on organic matter decomposition reactions and the anions and neutral species produced. In order to account more fully for the observed vertical trends, consumption of the dissolved metabolites by precipitation of authigenic minerals will be discussed next, which will also direct attention to some of the dissolved cations. The first mineralization reactions occurring in freshly deposited sediments include the formation of iron sulphides, rarely manganese sulphide, and various carbonates which form the main authigenic constituents of concretions. They are a familiar feature of organic matter-rich sediments and have been studied both in modern anoxic environments and their ancient equivalents, i.e. black shales, although the number of studies directed at the solid authigenic phases, particularly from modern offshore basins, is remarkably limited compared to the wealth of pore-water data available. In part this reflects the difficulties of detecting some

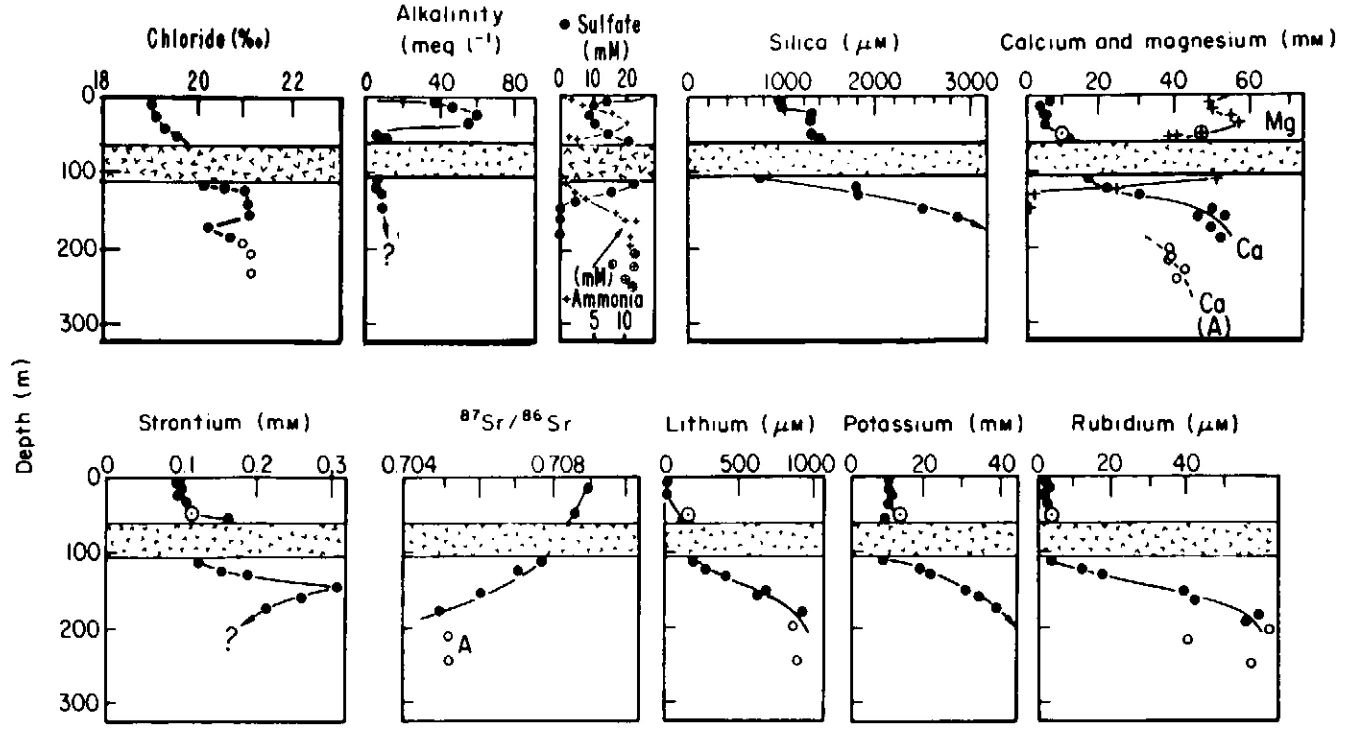


Figure 18 *Hydrothermally influenced pore-water profiles of DSDP site 477, Guaymas Basin, Gulf of California (pore-water profile, type 8; Gieskes, 1983, after Gieskes* et al., *1982b). Open circles: site 477A.*

of the authigenic solid phases. Pyrite and carbonates are noticeable exceptions. Other examples of early diagenetic precipitates include the zeolites and certain clay minerals such as smectites, which are characteristic for volcanogenic and slowly deposited pelagic sediments discussed in a previous section.

Early diagenetic sulphide precipitation. In the presence of soluble ferrous iron the sulphide produced in the sulphate reduction zone will immediately precipitate as metastable iron monosulphides such as mackinawite ($FeS_{0.90}$ to $FeS_{0.96}$ with up to 10% Fe substituted for by Ni^{2+} and Co^{2+}), greigite (Fe_3S_4, a cubic mineral probably with the structure of an inverse spinel) and amorphous FeS. These intermediate phases are kinetically favoured at higher supersaturation over the direct precipitation of pyrite, which has a much lower solubility product (2.4×10^{-28} as compared to 2.8×10^{-18} for mackinawite; Berner, 1967; Goldhaber and Kaplan, 1974). Pyrite originating by transformation from these precursor phases displays a characteristic framboidal (raspberry-like) structure composed of tiny euhedral crystals of uniform size. This particular structure does not require the involvement of spherical microorganisms, organic globules, a gel stage or gaseous vacuoles, because it has been produced inorganically in experiments by reacting iron monosulphides with elemental sulphur to pyrite (Berner, 1969; Farrand, 1970).

Euhedral pyrite, which often overgrows the early framboidal pyrite, appears to form somewhat later and at lower saturation levels. The process may also be pH-controlled, because at low pH the solutions may be undersaturated with respect to mackinawite but supersaturated with respect to pyrite and precipitate pyrite, whereas at higher pH (above 6.5) they may be supersaturated with respect to both minerals and favour precipitation of the more soluble phase mackinawite (Goldhaber and Kaplan, 1974).

These relationships are corroborated by the distribution of sulphur isotopes in pyrite-bearing carbonate concretions. A large isotopic fractionation effect is related to bacterial sulphate reduction. The sulphide produced is about 50% lighter than seawater sulphate (Goldhaber and Kaplan, 1980) which at present has a $\delta^{34}S$ value of + 20‰ relative to the CDT (Canyon Diablo Troilite) standard. Open-system conditions as in stagnant basins where sulphate reduction starts above the sediment/water interface, should supply light sulphide with $\delta^{34}S$ values in the range of -20‰ to -30‰ to the sediment. Closed-system conditions, as during rapid sulphate reduction in organic-matter rich sediments on the other hand, should involve a Raleigh distillation process leading to increasingly heavier sulphides as the light sulphur is preferentially withdrawn in the early stages. The average isotopic composition, however, would be equal to seawater sulphate. The sulphur-isotopic composition of early diagenetic pyrite may then provide information on the environment, in which anoxic, organic-matter rich sediments were deposited. As Gautier (1985) found in Cretaceous shales from the Western Interior Seaway, samples with high organic matter concentrations (4 - 10%) display a narrow range of very light isotopic sulphur compositions in pyrite ($\delta^{34}S$ = -35‰ to -25‰) indicating open-system sulphate reduction, in large part probably in the water column above the sediment under stagnant conditions. Samples with less than 3% organic carbon, on the other hand, show a wide range of $\delta^{34}S$ values (from -35‰ to + 18‰) suggesting closed-system conditions or a rapid change from initially open to closed system conditions probably under oxidizing bottom waters. A similar grouping of sulphur isotopic analyses into two main environments was reported by Schwarcz and Burnie (1973).

In Lower Jurassic carbonate concretions from Yorkshire, England, Raiswell (1982) found the lightest $\delta^{34}S$ values (-23‰ to -26‰, Figure 19) associated with dispersed framboidal pyrite occurring both in the host sediment and in the concretions. In this case, the framboidal pyrite is interpreted as a phase that formed prior to concretion growth under open-system conditions, not above the sediment/water interface but close to it in the sediment (Figure 20). Under these conditions isotopically light sulphur may be replenished from seawater sulphate and the alkalinity generated in the process of sulphate reduction may still be lost to the ocean bottom by diffusion, which would explain the delay of carbonate precipitation. Molecular diffusion and bioturbational irrigation are also required to explain the excess of solid sulphide found in some organic-matter rich sediments over the sulphide concentration that could be derived from the sulphate initially present in the pore water plus the sulphur contained in the organic matter (Goldhaber and Kaplan, 1980). Monosulphidic precursors of the framboids are favoured by high supersaturation associated with the initial stages of bacterial sulphate reduction, when reactive organic matter concentration is highest resulting in maximum reduction rates. In non-euxinic terrigenous sediments, iron availability from highly reactive ferric hydroxides is generally not a rate-limiting factor for sulphide precipitation at this stage (Berner, 1984; Raiswell and Berner, 1985). Euhedral pyrite, which in part nucleated on the framboidal pyrite, becomes progressively heavier from the center ($\delta^{34}S$ = -24‰ to -14.5‰) toward the concretion margins ($\delta^{34}S$ = -5.5‰ to -2.5‰) reflecting the establishment of closed-system conditions. Because no new light sulphate is supplied from sea water by diffusion, preferred utilization of light sulphur early in the reduction process makes the remaining sulphate reservoir progressively heavier. Isotopically heavy, large euhedral pyrite crystals which line the rims of these concretions show displacive and sectorial growth forming hopper-shapes and sometimes cone-in-cone structure (Carstens, 1986).

The rare occurrence of authigenic manganese sulphide (alabandite) in modern anoxic sediments of the Baltic Sea (Baron and Debyser, 1957; Suess, 1979) has been ascribed to high dissolved Mn^{2+} concentrations that are typical for anoxic bottom water in local depressions of this restricted basin. Thus alabandite precipitates rather than the usual iron sulphides.

Authigenic carbonates: Calcite and siderite (Figure 20). A prerequisite for authigenic carbonate precipitation in organic matter-rich sediments is a relatively high pH which is buffered by reactions other than those of the carbonate system. If pH is controlled by the carbonate system, increased P_{CO_2} due to organic matter oxidation will raise the bicarbonate rather than carbonate activity and lower pH. This appears to be the case in oxic environments, in contrast to anoxic environments. pH buffering by hydrogen sulphide and other weak acids in the sulphate reduction zone as well as hydrogen ion uptake by the reduction of manganese oxides and hydroxides in the nitrate reduction zone (and iron

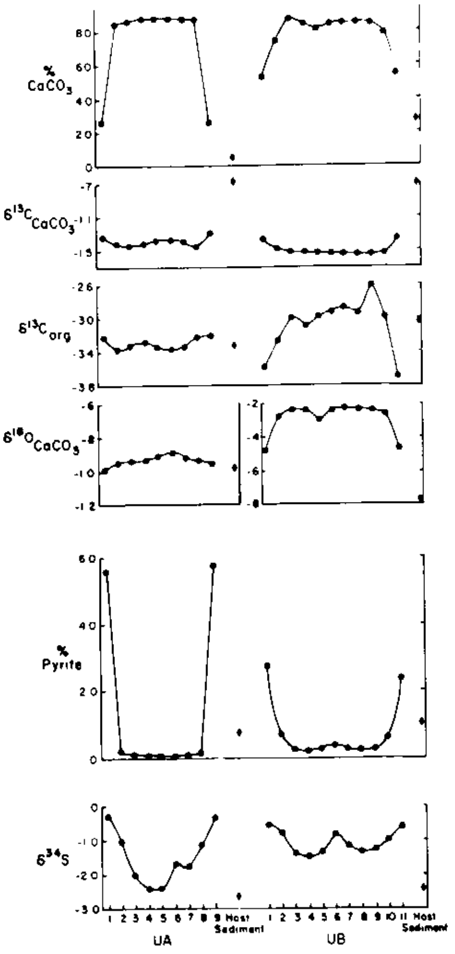


Figure 19 *Centre-to-rim mineralogical and isotopic variations in Liassic (Lower Jurassic) carbonate concretions from northern England. (From Coleman and Raiswell, 1981). Centre of concretion.* ***UA*** *at sample 5;* ***UB*** *at sample 6.*

oxides and hydroxides in the sulphate reduction zone) will raise the pH sufficiently to cause supersaturation with respect to carbonates (Suess, 1979). This involves reactions of the type

$$Me_2O_3 + 3H_2O + 2e^- \rightarrow 2Me^{2+} + 6OH^-, \text{and}$$

$$4MeOOH + H_2O + CH_2O \rightarrow 4Me^{2+} + CO_2 + 8OH^-$$

where, Me^{2+} represents Mn^{2+} or Fe^{2+} ions. In the carbonate reduction and fermentation zones, it is probably the hydrogen consumption in the bacterial formation of methane in the presence of metal ions according to a reaction

$$Me^{2+} + 2HCO_3^- + 8H^+ + 8e^- \rightarrow CH_4 + MeCO_3 + 3H_2O$$

which increases the pH such that supersaturation with respect to carbonates and precipitation result. (The pH measured in DSDP water samples squeezed onboard the ship or in other deep subsurface samples is generally different from the *in situ* value due to losses of dissolved gases (CO_2, H_2S) and changes in temperature and pressure affecting the stability of hydrogen-bearing aqueous species (Kharaka *et al.*, 1980). With the computer program SOLMNEQ II (Kharaka *et al.*, 1985b) the necessary corrections for *in situ* conditions can be calculated).

Under these circumstances calcite, dolomite, siderite, rhodochrosite and more complex iron-manganese carbonates may form in organic-matter oxidation zones (2) to (5). Fe-carbonates cannot form in the sulphate reduction zone in the presence of dissolved sulphide which competes for the dissolved iron. Likewise, experiments by Baker and Kastner (1981) suggest that dolomite formation is inhibited in the presence of substantial dissolved sulphate. Authigenic calcite, on the other hand, is among the earliest diagenetic minerals and may start to precipitate in the sulphate reduction zone together with or shortly after the first mono-sulphides.

The most conspicuous result of early diagenetic carbonate precipitation is the formation of concretions. However, authigenic carbonates may also occur as dispersed crystals in the sediment, form overgrowths on detrital cores, or coalesce to produce laterally extensive beds. In deep-water black-shale sequences of the Cambro-Ordovician Cap-des-Rosiers Formation in Quebec, diagenetic envelopes have been observed by the author on calcilutitic turbidites and around starved ripples of clastic carbonate. These are similar to the "basal micritic limestone" below Devonian carbonate turbidites from the Rhenish Schiefergebirge described by Eder (1970). Later diagenetic fabrics also include replacements, particularly by dolomite crystals.

In concretions or laterally extensive diagenetic beds, the carbonates characteristically are pore-filling cements whose decreasing concentration from centre (up to 85 or 90% by volume) to rim (as little as 25%) reflect the porosity at the time of precipitation. For porosities estimated in this way the term "minus-cement porosity" is used in the literature. High minus-cement porosities in the range of 70 to 90% in the inner shells of many concretions attest to the common early diagenetic initiation of concretion growth. It is important that normally the growth of carbonate concretions is not displacive. Particles of the host sediment are not pushed aside by the growing carbonate crystals, in contrast to gypsum or anhydrite nodules precipitated from hypersaline brines. Grain-size of the carbonates is usually micritic. An exception are spherulitic carbonate concretions and slowly growing cone-in-cone cements which cause some mechanical displacement of the host sediment. In this case the carbonate content may not be used for porosity estimates. The same warning applies to concretions showing signs of recrystallization. Cementation in the early stages of concretion growth, on the other hand, is often not complete as shown by septarian concretions. Their cracks, which characteristically are widest in the centre and become narrower toward the concretion margins, indicate post-cementation compaction. They are shrinkage cracks showing that cementation initially left some pore space unfilled. Near the termination of concretion growth, cementation and compaction in the outer shells reach about the same degree as in the surrounding host sediments thus forming a solid carapace around the concretion, which allowed the centre to respond to further dewatering by shrinkage. However, the total volume of septaria in concretions is generally small (less than 3%, Gautier, 1985) and so is the pore volume initially not filled by cement.

Supporting evidence for the early diagenetic initiation of growth of common carbonate concretions comes from numerous observations besides carbonate concentration, including the undisturbed nature of original bedding features, the degree of preservation

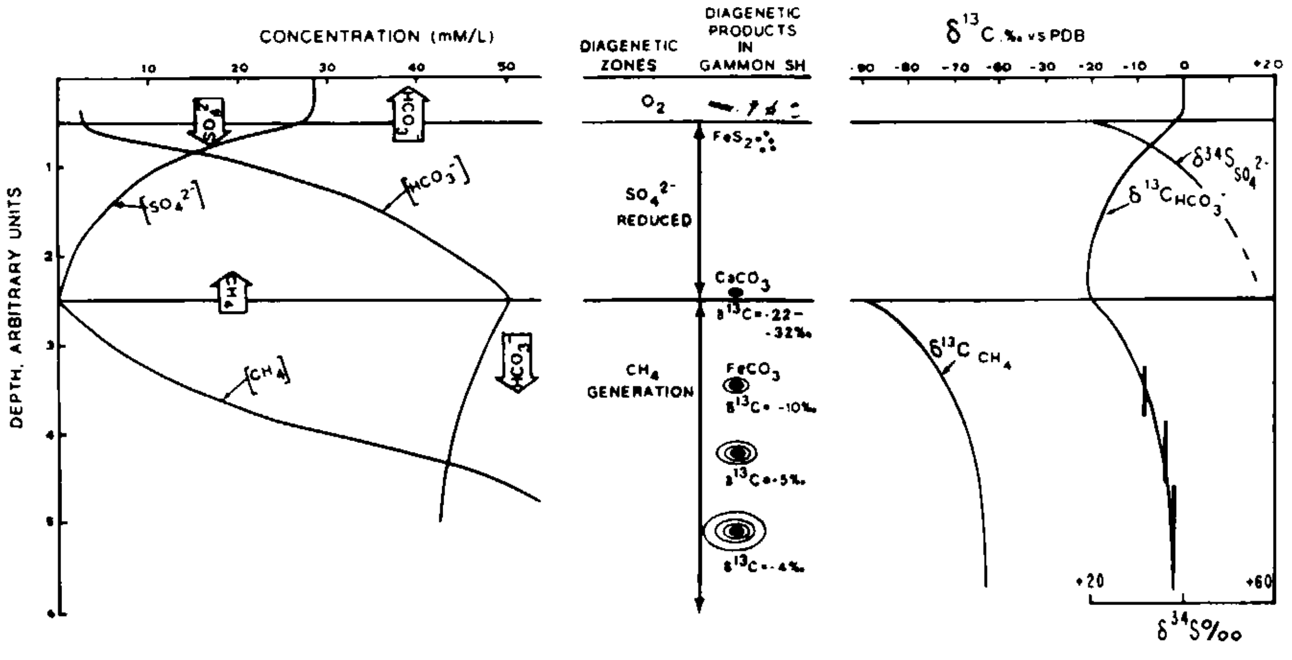


Figure 20 *Relationship between early diagenetic mineralization reactions in carbonate concretions and depth trend of dissolved chemical species and carbon isotopes in pore waters from which concretions precipitated. (From Gautier and Claypool, 1984). Note that the alkalinity maximum often does not coincide with the base of the sulphate zone, but occurs deeper in the methane generating zone (cf. Fig. 5).*

of the original shape of fecal pellets and fossils, clay fabric analyses but most notably isotopic analyses.

Oertel and Curtis (1972) have shown that in the centre of some Carboniferous carbonate concretions from England clay particle orientation is essentially random as it would be expected for a flocculated clay suspension with 80 or 90% water content in which carbonate precipitation occurred. Toward the concretion margins a distinct trend emerges of preferred orientation of the basal planes of clay particles parallel to bedding. Preferred orientation is best developed in the host sediment. This reflects the increasing effect of burial compaction with time as the concretion continues to grow.

Chemical and isotopic compositions of many carbonate concretions in black shale sequences reveal centre-to-rim variations that can be explained in terms of the organic-matter oxidation processes and related pore-water trends discussed before (Curtis *et al.*, 1972; Irwin *et al.*, 1977). In the case of a concretion starting to form in the sulphate reduction zone and continuing to grow in the carbonate reduction and fermentation zones, an early calcitic nucleus will be surrounded by a sideritic rim. Examples of this kind have been described by Gautier and Claypool (1984) and Gautier (1985) from the Upper Cretaceous Gammon Shale of the northern Great Plains of the United States. In these concretions a calcitic core with a $\delta^{13}C$ value of about -22‰ and a carbonate concentration of 85% iron-free calcite is mantled by an isotopically heavier ($\delta^{13}C$ increasing outward from -10‰ to -4‰) sideritic rim with 70 to 80% carbonate. Oxygen isotopes are similar to those of calcite precipitated from modern sea water at temperatures above 15°C, i.e. $\delta^{18}O$ values are between -2‰ and -3‰ and get progressively lighter outward in the siderite rim (to about -7‰). Because the calcite is associated with abundant framboidal pyrite, there can be little doubt that the iron-free calcite formed in the sulphate reduction zone. More specifically, it probably formed in the lower part of the sulphate reduction zone, because the $\delta^{13}C$ of -22‰ shows the maximum effect of organic-matter oxidation and the carbonate crystals in contact with the pyrite framboids radiate outward from the latter indicating that these formed first. Uptake of iron in the carbonate phase during siderite precipitation, on the other hand, shows that the concretion continued to grow in the methane generation zones (4) and (5) where dissolved iron becomes available and the carbonate becomes isotopically distinctly heavier because of the withdrawal of light carbon in methane. In the sulphate reduction zone ferrous iron concentrations in the presence of dissolved sulphide (at concentrations typically on the order of $10^{-3.5}$ moles·L^{-1}) are 10^{-16} moles L^{-1} (for pH = 7.5 and Eh = -0.245 mV), far too low for iron-carbonates to form. Siderite formation requires dissolved Fe^{2+} concentrations of at least 10^{-7} moles·L^{-1} (Curtis, 1967).

Numerous examples have now been documented showing that concretions may start to grow close to the sediment/water interface. In the case of the Gammon Shale, concretion growth was presumably complete a few tens of metres below the sea floor, perhaps as little as 10 m (Gautier, 1985). In other examples there is evidence that siderite formation may have occurred at considerably greater burial depth, e.g. 800 to 1200 m subbottom on the East Coast continental rise off the United States (DSDP leg 93, Botz and von Rad, 1986).

Interpretation of O-, C- and S-isotopic results from the same concretion sometimes seems to lead to conflicting conclusions as in the case of a Lower Jurassic concretion described by Coleman and Raiswell (1981). $\delta^{18}O$ values as low as -9‰ to -10‰ require burial temperatures of 60°C or depths of 1 to 2 km, which are incompatible with a shallow burial origin suggested by carbon and sulphur isotopes and other evidence. Alternative isotopic fractionation mechanisms, such as alteration of volcanic glass to clay, would shift the oxygen isotopic composition of the water, from which the carbonate precipitated, in the right direction, toward negative δ-values. However, it is difficult to accomplish the magnitude of the shift required (-6‰ to -7‰) in the short depth interval available. If the shift is not caused by meteoric water influx in the subsurface, as suggested for late diagenetic calcite filling septarian cracks in concretions of the Jurassic Oxford Clay in England (Hudson, 1978), then additional mechanisms are required for which fractionation by carbonate precipitation itself (Irwin *et al.*, 1977), but also gas-hydrate formation are possibilities.

Authigenic dolomite ("deep-sea dolomite"). Dolomite and high-magnesium calcite are other common authigenic carbonates in anoxic sediments besides calcite and siderite. The burial diagenetic origin of dolomite in deep water, organic matter-rich terrigenous muds and biogenic siliceous oozes, i.e. of the so-called "deep-sea dolomites" is now an accepted fact since a number of studies were performed on DSDP material (i.e. leg 63, Pisciotto and Mahoney, 1981; leg 64, Kelts and McKenzie, 1982; leg 66, Wada *et al.*, 1981; leg 76, Matsumoto, 1983). Identical occurrences of bedded or nodular dolomite are exposed on land, e.g. in the Ordovician Cloridorme Formation in Quebec (Islam, 1981) or the Miocene Monterey Formation of California, for which an early diagenetic origin was already recognized by Bramlette (1946). Diatoms may be well preserved in the concretions as opal-A when the surrounding siliceous sediments have reached the opal-CT or quartz stage. These dolomites display a wide range in $\delta^{13}C$ values from -30‰ to +30‰ which has been interpreted as evidence for their formation in the sulphate reduction, carbonate reduction and fermentation zones (Arthur *et al.*, 1983, Gautier, 1985, Hennessy and Knauth, 1985). Baker and Burns (1985), for example invoke dolomite precipitation in the sulphate reduction zone and supply of magnesium by diffusion from overlying sea water in the case of dolomite-rich deep-sea sediments (containing more than 2 wt.% dolomite). Dolomite formation in sulphate-bearing environments is controversial, however (see above), and is not required to explain light carbon-isotopic compositions. As the findings of Ritger *et al.* (in press) and earlier results of Russell *et al.* (1967) from the Oregon and Washington continental slope show, dolomite, high-magnesium calcite and aragonite with extremely light carbon ($\delta^{13}C$ ranging from -32‰ to -66‰) form as concretions, crusts and chimneys on the sea floor where they have been sampled by piston cores and from submersibles. They are apparently related to active sediment dewatering in the accretionary prism above the subduction zone of the Oregon-Washington margin leading to upward methane migration concentrated along localized, structurally controlled pathways. The bicarbonate derived from oxidation of the methane to CO_2 raises alkalinity leading to carbonate precipitation.

Dolomite concretions and beds of the Monterey Formation have received special attention (Garrison *et al.*, 1984), because of the interest in the Monterey as the main source for hydrocarbons in California. A detailed isotopic study by Kushnir and Kastner (1984) showed that nodular dolomite concretions span a wide range in $\delta^{13}C$ values indicating growth over a considerable burial depth interval and contrasting remarkably with bedded dolomite with a very narrow range in isotopic values.

In drill sites of the DSDP with authigenic carbonates, Ca and Mg depth profiles are clearly reaction-controlled as shown by sites 496, 497, 565 and 568 to 570 (Figure 5). Ca decreases from the seawater value are rapid and concentrations remain low over most of the depths penetrated with only slight increases at the deepest levels. This contrasts markedly with diffusion-controlled sites and their pronounced downward Ca-increases. Mg, after increasing initially, is reduced considerably more rapidly than in diffusion-controlled sites. The initial increase is probably related to ion exchange reactions with clays, which, however, may also contribute to the later decrease, in cases where this is not accounted for by carbonate precipitation. In these sites, carbonate consumption by precipitation of solid carbonates is also required in order to model successfully the ΣCO_2 and $\delta^{13}C$ (of CO_2 and of CH_4) depth profiles (Claypool *et al.*, 1985). Mg-depletion without attendant carbonate alkalinity reduction in anoxic sediments of the Santa Barbara Basin has been attributed to uptake by clay minerals with high cation-exchange capacity

(Sholkovitz, 1973). The cation-exchange capacity is increased when iron-oxide coatings are removed from clay minerals in reducing environments (Carroll, 1958).

Complex authigenic carbonates. The occurrence of complex authigenic carbonates rich in Mn and Fe, which show transitions to end-member rhodochrosite and siderite, has only been described from a few DSDP drill sites (e.g. Hein *et al.*, 1979b; Okada, 1980; Wada *et al.*, 1981). The isotopic composition of similar concretions in Cretaceous black shales of the Western Alps ($\delta^{13}C$ varying between -11‰ and -6‰, $\delta^{18}O$ between -9.6‰ and -4.4‰; Tassé and Hesse, 1984) suggests the formation at somewhat greater burial depths in the methane generation zone. This requires mobilization of manganese at those depths, which is in line with secondary maxima in Mn-depth profiles between a 100 and 200 m sub-bottom at various DSDP drill sites discussed by Gieskes (1981). Because these show a close correlation with maxima in the dissolved silica profiles, Gieskes (1981) suggested Mn-release from opal-A dissolution as a by-product of silica diagenesis.

Ion exchange reactions and adsorption. None of the processes discussed so far for rapidly deposited, organic-matter rich sediments explains the depths profiles for dissolved ammonia and phosphate. As the reader may recall from a previous section, dissolved ammonia often has a maximum below the alkalinity maximum (Figure 5), while the phosphate maximum occurs in an intermediate position. Build-up of both ammonia and phosphate concentrations to their maxima in the methane generation zones underlines the importance of continuing fermentation processes (e.g. deamination of proteins).

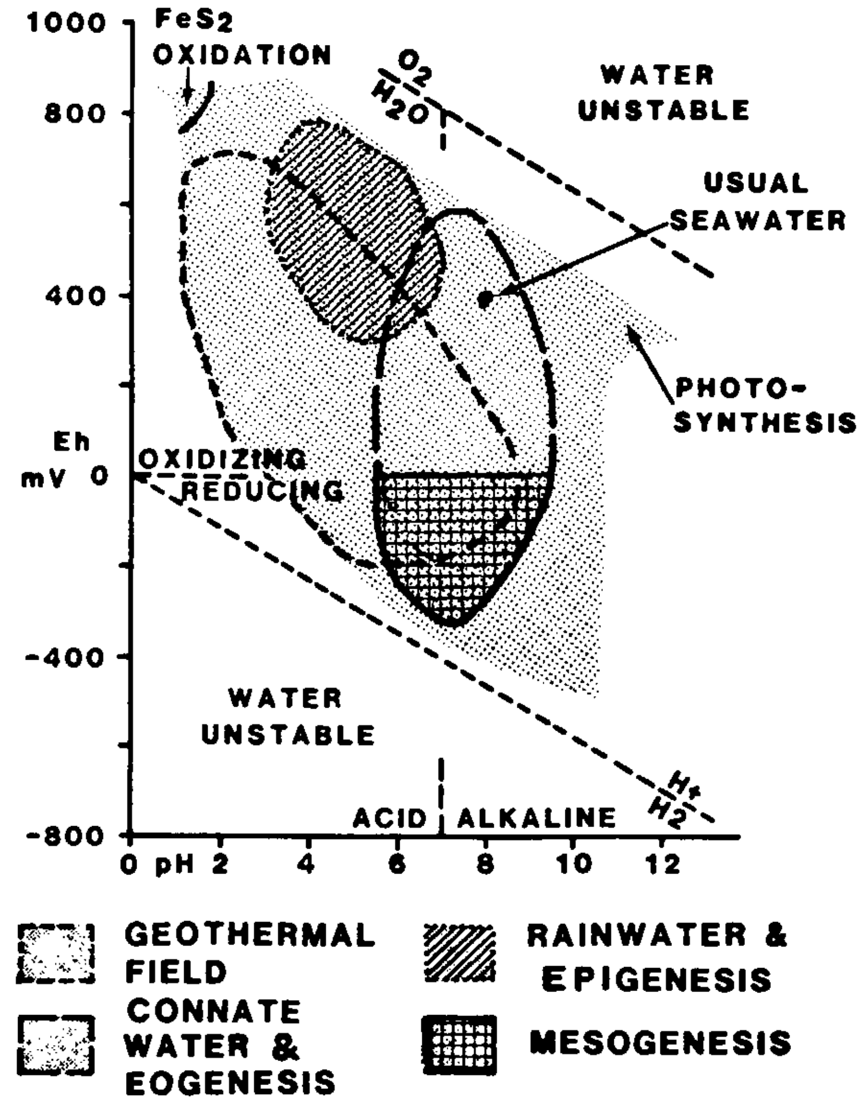


Figure 21 *pH/Eh fields of natural waters. (Adapted by V. Schmidt and the author from Fairbridge, 1967, based on data from Baas Becking* et al.*, 1960 and Garrels, 1960). Stippled area - realistic stability field of water.*

There are no known ammonia-bearing minerals in anoxic sediments except the highly unstable struvite ($NH_4Mg(PO_4) \cdot 6H_2O$) but its occurrence in modern marine sediments has yet to be demonstrated. Decrease of ammonia from its maximum in the methane generation zone can, in part, be explained by downward diffusion (Lerman, 1977). In gas hydrate-bearing sections, the decrease is partially due to dilution from hydrate water. However, the rapid drop generally seen in organic matter-rich anoxic sediments requires additional uptake by ion-exchange reactions with clays, as the effects of diffusion in dissipating concentration maxima are minor for rapidly deposited sediments. Ammonium ions are incorporated into interlayer positions of clay minerals with high layer charges, particularly illites and vermiculites as shown by Muller (1977, and references therein) for oxidized pelagic sediments of the Central Pacific. Similar reactions are likely to occur in anoxic environments leading to the fixation of dissolved ammonium in crystal lattices which will carry it to great burial depth, down to the realm of metamorphism (Itihara and Honma, 1979).

Phosphate diagenesis in rapidly deposited hemipelagic sediments of the continental margins is similar to that of ammonia (as the pore-water profiles suggest), but also different in that there are authigenic mineral phases incorporating phosphate, namely apatite ($Ca_5(PO_4)_3(OH,F)$ or its cryptocrystalline varieties collophane (carbonate-fluorapatite) and dahllite (carbonate-hydroxylapatite). Vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) is an iron-bearing phosphate. Apatite precipitation is favoured over vivianite in the presence of fine-grained calcium carbonate as nuclei. In the absence of such nuclei, apatite formation is hindered by Mg ions and vivianite may form instead. However, due to the lack of sufficient iron, supersaturation for vivianite is usually not reached (Berner, 1980). Solid phosphate minerals are often difficult to detect and a significant portion of the phosphate fixation that is required to interpret the downward decreases in the profiles of dissolved phosphate probably occurs by adsorption.

Geochemical Classification of Early Diagenetic Environments

Natural waters have been classified from a geochemical point of view in terms of their pH/Eh-fields (Figure 21). pH is the master variable controlling the solubility of many minerals under surface and subsurface conditions. Eh exerts a controlling influence on the solubility of ions which occur in more than one valence state, e.g. Fe and Mn. The classification is based on the classical work of Krumbein and Garrels (1952) and shows the field for marine connate waters (or what is the same: marine eo(dia)genesis) to cover a pH range of 6 to 9.5 and Eh levels from +600 to about 0 mV. The diagenesis of marine sediments (beyond the connate-water or eogenetic stage) occurs under a pH of 6 to 9 and Eh levels ranging from mildly reducing to about -300 mV. This classification has been useful in characterizing the stability fields of detrital and authigenic minerals in sedimentary environments (in terms of pH/Eh conditions). In practice it has not been too helpful, particularly in the study of modern unlithified sediments, as pointed out by Berner (1981), mainly for two reasons. First, the pH of most subaqueous sediments, marine and nonmarine, varies relatively little, i.e. between 6 and 8, and, in fact, 90% of Berner's measurements in modern marine sediments fell into the narrow pH-range of 6.5 to 7.5. Secondly, the Eh cannot be measured correctly because many ionic species do not easily react at a platinum or gold electrode to give off or accept electrons. Also, because of kinetic inhibition, unstable species persist into forbidden Eh-domains. The measured electrode potential, therefore, does not generally agree with the values calculated from thermodynamic data. Pt and Au eletrodes, so to speak, do not "see" ions that are not electroactive.

Berner (1981), therefore, proposed a new, more practical geochemical classification of sedimentary environments in terms of the concentration levels of dissolved oxygen and total sulphide (H_2S plus HS^-, Table 6). This scheme has the advantage of wider applicability as the two parameters used involve species which are mutually exclusive at measurable concentration levels. That is, if sulphide and dissolved oxygen are brought together at concentrations greater than 10^{-6}M, and at a pH of 6 to 8, they will react in a matter of minutes or hours, to form sulphate and water. Furthermore, the presence of one or the other, even in trace amounts, has vital (or lethal) effects on the population of organisms living in the sediment and consequently on the bacterially mediated mineralization reactions discussed before. Obligatory anaerobic bacteria cannot tolerate the presence of dissolved oxygen, even in trace amounts — they die, and sulphide minerals will be oxidized. *Vice versa*, obligatory aerobic bacteria cannot tolerate H_2S even in trace amounts and, in its presence, oxide minerals will be converted to sulphides. Dissolved oxygen and sulphide are, therefore, ideal candidates for parameters to be used in a geochemical classification of sedimentary, specifically early diagenetic environments. In the proposed classification scheme of Berner (1981) each category has its indicator minerals (Table 6) which will, at least in part, be preserved if the sediment passes from one environment to another during burial. The diagnostic value of most of these indicator minerals is evident from the discussion in the section on "early diagenetic mineralization reactions" and needs no further comment. The dividing line between the two main environments "oxic" and "anoxic" is the presence (i.e. at concentrations greater than 10^{-6}M) or absence (i.e. presence at concentrations less than 10^{-6}M) of dissolved oxygen. The anoxic environment is subdivided further into "sulphidic" and "nonsulphidic" by the same principle, i.e. presence or absence of reduced sulphur compounds. In sulphidic environments alabandite is thermodynamically stable relative to rhodochrosite only at very high H_2S concentrations. Rhodochrosite, which is the more common Mn mineral in this zone, however, is also characteristic for anoxic-nonsulphidic environments and, therefore, not diagnostic.

Further distinction of the nonsulphidic anoxic environments into "post-oxic" and "methanic" is based on the presence or absence of pyrite. The post-oxic (= "suboxic" *sensu* Froelich *et al.*, 1979, used here) environment does not contain enough organic matter for sulphate reduction to take place. Because of the lack of H_2S (and O_2) Fe^{2+} can build up to saturation with glauconite. The methanic environment, however, may follow a sulphidic anoxic stage and, therefore, contain pyrite, but this is not a necessary condition as freshwater methanic environments may be free of pyrite. Distinction between the two nonsulphidic anoxic environments, therefore, depends critically on the interpretation of types and concentrations of authigenic minerals found in paragenesis. Suboxic environments may, by definition, contain only small quantities of reduced authigenic Fe-Mn-minerals. Berner's classification is independent of pH and salinity and should, therefore, apply to all sediments, although it may be difficult to be applied to certain low-iron and low-manganese sediments.

Definition of "Early" Diagenesis

It seems that the term "early diagenesis" as generally used in the literature is rather loosely defined and, in the sense applied by the majority of authors, refers mostly to diagenetic processes that can be studied in piston cores. Even Berner (1980) in his masterly treatment of the subject leaves the definition open-ended by stating that "early diagenesis . . . refers to changes occurring during burial to a few hundred metres where elevated temperatures are not encountered. . .".

In the writer's opinion the natural incision, which occurs in burial diagenesis at about 75°C where biogenic decomposition reactions of organic matter give way to thermocatalytic reactions, is fundamental enough to be used as the lower boundary of the "early diagenetic regime". Further burial and attendant temperature increase lead to thermal maturation of kerogen and to the release of carbonic acid and organic acids. These trigger carbonate and feldspar dissolution, generate secondary porosity in sandstones, liberate potassium and aluminum and initiate the smectite to illite transformation in clayey sediments, which does not seem to start to any significant extent at temperatures less than about 75°C. A whole new set of important diagenetic reactions begins at this temperature which appears to be a threshold in terms of activation energies for thermocatalytic organic matter decomposition. The presence of this natural boundary shows up clearly on diagrams displaying the temperature variation of gas composition and yield in fine-grained, organic-matter rich sediments (Figure 22). It is therefore suggested that this temperature be used to differentiate early and intermediate diagenetic regimes. Organic geochemists, of course, use this temperature as the boundary for diagenesis versus catagenesis, the latter term being equivalent to intermediate plus advanced diagenesis in the petrologist's vocabulary. Early diagenetic burial depths range from about a 100 m for high heat-flow areas (such as the Salton Sea geothermal area) to 2 or 3 (or more) km for moderate to low geothermal gradient areas. Characteristic physical conditions of the "early diagenetic regime" defined in this way are listed in Table 7.

Table 6 Geochemical classification of early diagenetic environments
(modified after Berner, 1981)

Environment			**Diagnostic authigenic minerals and sediment characteristics**
Molar concentration	O_2	H_2S	
Oxic	$\geq 10^{-6}$	$< 10^{-6}$	Hematite, goethite, MnO_2 minerals, (no reactive organic matter)
Anoxic	$< 10^{-6}$		
Sulphidic		$\geq 10^{-6}$	Pyrite, marcasite, rhodochrosite, alabandite; organic matter.
Stagnant			Light $\delta^{34}S$, no bioturbation.
Oxic bottom waters			Trend towards heavier $\delta^{34}S$; bioturbated.
Nonsulphidic		$< 10^{-6}$	
Post-oxic (= Suboxic)	$< 10^{-6}$	$< 10^{-6}$	Glauconite and other Fe^{2+} – Fe^{3+} minerals; no sulfides. (Siderite, vivianite, rhodochrosite). Minor organic matter.
Methanic	$< 10^{-6}$	$< 10^{-6}$	Siderite, vivianite, rhodochrosite. Organic matter.

Another important caesura in terms of burial temperatures which is tentatively proposed as the boundary between the intermediate and advanced stages of diagenesis occurs at about 140°C where the transition from random mixed-layer smectite-illite to ordered mixed-layer clay minerals takes place. As the transition from diagenesis to anchimetamorphism may be placed around 200°C, the realm of diagenesis is subdivided into three about equal temperature intervals, but it is beyond the scope of this paper to give a more elaborate justification for the proposed boundaries (and to outline their variability).

Table 7 Early diagenesis

Temperature range:	0 to 75°C (Upper limit of 75°C is limit for biogenic methane generation)
Burial depths:	0.1 to 2-3 km
Porosity of clayey sediments:	90 (sea floor) to 30%
Vitrinite reflectance under oil:	R_o less than 0.5%
Clay minerals:	detrital parageneses, no newly formed illite

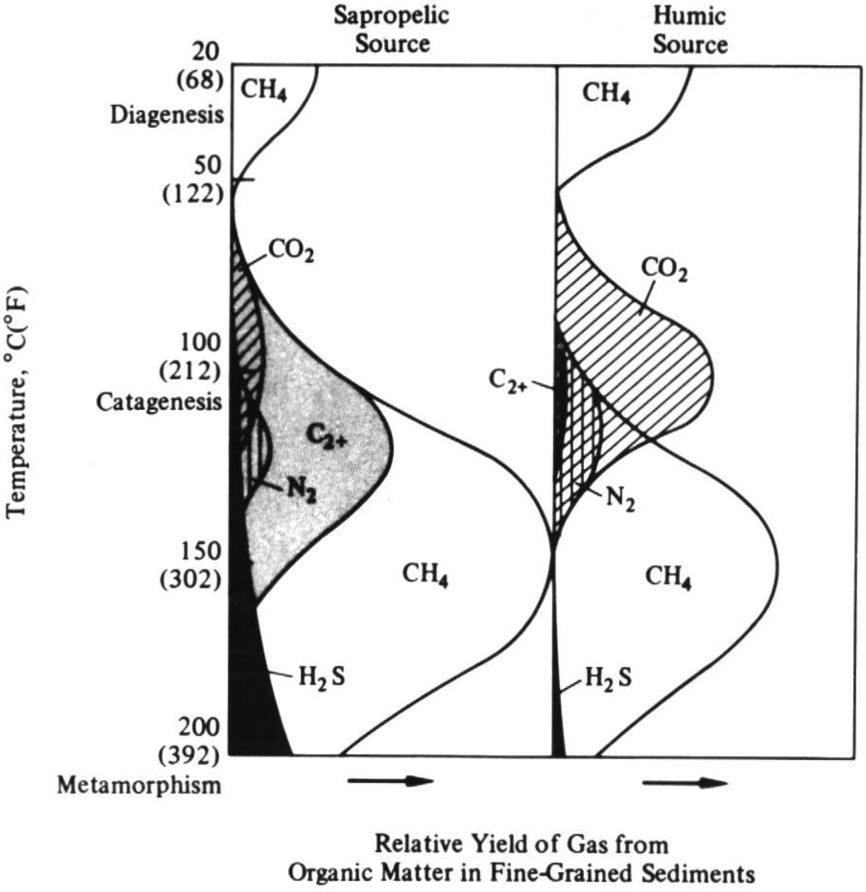


Figure 22 *Yield and composition of natural gas from different types of organic matter. (From Hunt, 1979).*

Summary and Outlook

This review of pore-water studies from modern offfshore basins shows the remarkable progress that has been achieved over the last 15 years, largely reflecting the impact of the Deep Sea Drilling Project. As a result, it appears that, for these basins, the principal trends in the chemical evolution of pore waters with progressive burial down to about 1.5 km subsurface depth are more or less established today. The observed trends provide important insights into the sources and sinks for the dissolved species and into ongoing diagenetic reactions in the subsurface.

There are, however, a few open questions, which emerge from this review and which urgently need further studies. One of these is the mass-balance problem. Can the early diagenetic mineralization products such as carbonate concretions or pyrite nodules be accounted for by relatively short-distance diffusional transport within a limited sediment volume, that is, essentially by closed-system conditions, or are open-system conditions required? The model of Wigley *et al.* (1978) for partially open-system diagenetic processes and its application by Claypool and Threlkeld (1983) are encouraging steps to tackle this problem.

A second problem, which is indirectly related to the first, concerns the role of advection as a major transport process for solutes. This problem has major geodynamic implications for trench-slope areas and fore-arc basins of island-arc/trench systems where active dewatering of the sediment prism is known to occur, but the flow patterns are not known in detail. This is a major objective for current activities of the Ocean Drilling Program.

Another big unknown concerns the effects of lithologic alternations on pore-water chemistry, for example, of interstratified mud and sand layers, or interlayered hemipelagic sediments and turbidites, or any other short-distance alternations between lithologically different sediments. The works of Colley *et al.* (1984) and Wilson *et al.* (1985) show great promise in this respect. In low-sedimentation rate areas, lithologic differences between interstratified sediments in a vertical column may have no effects on pore-water chemistry whatsoever, as DSDP site 495 shows, because diffusion (or convection) may dissipate any chemical gradients or changes in the pore-water profiles. The situation may be quite different, however, for sand/mud alternations with their porosity and permeability contrasts (as shown by DSDP sites 499 and 500, Harrison *et al.*, 1982). Here, the problem is a technical one, that is, of obtaining uncontaminated water samples from the sand layers. These questions are of considerable interest for the petroleum industry.

None of the studies described in this article is of purely academic interest. As has become obvious, organic matter plays the key role in early diagenetic pore-water/sediment interaction. The early diagenetic changes that affect the dispersed organic matter in the sediment have important consequences for what happens later during burial, when the sediment enters the "oil window". Organic matter that has lost most of its oil-generating capacity before reaching the "oil window" because of intense early diagenetic modifications including biogenic methane production, obviously is of less interest from an economic point of view than that which passes through the early diagenetic stage with less severe alteration.

Acknowledgements

This work and the author's research on gas hydrates, pore waters and carbonate concretions was funded by the Natural Sciences and Engineering Research Council of Canada. J.M. Gieskes, B. Hitchon, L. Land, E. McBride, A. Mucci and another reviewer of the Journal provided helpful critical comments at various stages on earlier versions of the manuscript. A. Kosowski typed the manuscript and R. Yates did the photographic and drafting work. This help and support is gratefully acknowledged.

References

General

These cover the sections including Introduction, Terminology, Sources of Pore-Water Data, Diagenetic Regimes of Pore-Fluid Evolution in Modern Offshore Basins, Geochemical Classification of Early Diagenetic Environments, Definition of Early Diagenesis, Summary and Outlook)

Baas Becking, L.G.M., Kaplan, I.R. and Moore, D., 1960, Limits of the natural environments in terms of pH and oxidation-reduction potentials: Journal of Geology, v. 68, p. 243-284.

Berner, R.A., 1980, Early diagenesis. A theoretical approach: Princeton Series in Geochemistry, Princeton University Press, 241 p.

Berner, R.A., 1981, A new geochemical classification of sedimentary environments: Journal of Sedimentary Petrology, v. 51, p. 359-365.

Bischoff, J.L., Greer, R.E. and Luistro, A.O., 1970, Composition of interstitial waters of marine sediments; temperature of squeezing effect: Science, v. 167, p. 1245-1246.

Carpenter, A.B., 1978, Origin and chemical evolution of brines in sedimentary basins, *in* Johnson, K.S. and Russell, J.A., eds., Geology of Industrial Minerals, 13th Annual Forum, Oklahoma Geological Survey, Circular 79, p. 60-77.

Case, L.C., 1955, Origin and current usage of the term, "connate water": American Association of Petroleum Geologists Bulletin, v. 39, p. 1879-1882.

Claypool, G.E. and Kaplan, I.R., 1974, The origin and distribution of methane in marine sediments, *in* Kaplan, I.R., ed., Natural Gases in Marine Sediments; Marine Science, v. 3, p. 99-140.

Claypool, G.E. and Kvenvolden, K.A., 1983, Methane and other hydrocarbon gases in marine sediment: Annual Reviews of the Earth and Planetary Sciences, v. 11, p. 299-327.

Claypool, G.E. and Threlkeld, C.N., 1983, Anoxic diagenesis and methane generation in sediments of the Blake Outer Ridge, DSDP Site 533, Leg 76, *in* Sheridan, R.E., Gradstein, F.M., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 76, p. 391-402.

Colley, S., Thomson, J., Wilson, T.R.S. and Higgs, N.C., 1984, Post-depositional migration of elements during diagenesis in brown clay and turbidite sequences in the North East Atlantic: Geochimica et Cosmochimica Acta, v. 48, p. 1223-1235.

Curtis, C.D., 1978, Possible links between sandstone diagenesis and depth-related geochemical reactions occurring in enclosing mudstones: Journal of the Geological Society, London, v. 135, p. 107-117.

Devol, A.H., 1978, Bacterial oxygen uptake kinetics as related to biological processes in oxygen-deficient zones of the oceans: Deep Sea Research, v. 25, p. 137-146.

Emery, K.O. and Rittenberg, S.C., 1952, Early diagenesis of California basin sediments in relation to origin of oil: American Association of Petroleum Geologists Bulletin, v. 36, p. 735-806.

Fairbridge, R.W., 1967, Phases of diagenesis and authigenesis, *in* Larsen, G. and Chilingar, G.V., eds., Diagenesis in Sediments, Developments in Sedimentology, v. 8, p. 21-89.

Fanning, K.A. and Pilson, M.E.Q., 1971, Interstitial silica and pH in marine sediments: some effects of sampling procedures: Science, v. 173, p. 1225-1231.

Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B. and Maynard, V., 1979, Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis: Geochimica et Cosmochimica Acta, v. 43, p. 1075-1090.

Garrels, R.M., 1960, Mineral equilibria at low temperature and pressure: Harper and Row, New York, 254 p.

Gautier, D.L., Clayton, J.L., Leventhal, J.S. and Reddin, N.J., 1984, Origin and source rock potential of the Sharon Springs Member of the Pierre Shale, Colorado and Kansas, *in* Woodward, J., Meissner, F.F. and Clayton, J.L., eds., Source rocks of the Rocky Mountains, Rocky Mountain Association of Geologists, p. 369-385.

Gieskes, J.M., 1975, Chemistry of interstitial waters of marine sediments: Annual Reviews of the Earth and Planetary Sciences, v 3, p. 433-453.

Gieskes, J.M., 1981, Deep sea drilling interstitial-water studies: Implications for chemical alteration of the oceanic crust, Layers I and II, *in* Warme, J.E., Douglas, R.G. and Winterer, E.L., eds., The Deep Sea Drilling Project: A decade of progress, Society of Economic Paleontologists and Mineralogists Special Publication, v. 32, p. 149-167.

Gieskes, J.M., 1983, The chemistry of interstitial waters of deep-sea sediments: Interpretation of Deep Sea Drilling Data, *in* Riley, J.P. and Chester, R., eds., Chemical Oceanography, v. 8, p. 221-269.

Goldhaber, M.B. and Kaplan, I.R., 1974, The sulphur cycle, *in* Goldberg, E.D., ed., The Sea, v. 5, Marine Chemistry: John Wiley and Sons, New York, p. 569-655.

Harrison, W.E., Hesse, R. and Gieskes, J.M., 1982, Relationship between sedimentary facies and interstitial water chemistry in slope, trench and Cocos plate sites from the Mid-America Trench transect, active margin off Guatemala. Leg 67, DSDP, *in* Von Huene, R., Aubouin, J., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 67, p. 603-614.

Heath, G.R., Moore, T.C. and Dauphin, J.P., 1977, Organic carbon in deep sea sediments, *in* Andersen, N.R. and Malahoff, A., eds., The fate of fossil fuel CO_2 in the oceans: Plenum Press, New York, p. 605-625.

Hunt, J.M., 1979, Petroleum goechemistry and geology: Freeman, San Fransisco, 617 p.

Johnson Ibach, L.E., 1982, Relationship between sedimentation rate and total organic carbon content in ancient marine sediments: American Association of Petroleum Geologists, Bulletin, v. 66, p. 170-188.

Kharaka, Y.K. and Carothers, W.W., 1982, Geochemistry of oil field waters from North Slope, Alaska: U.S. Geological Survey, Professional Paper, (in press).

Kharaka, Y.K., Hull, R.W. and W.W. Carothers, 1985a, Water-rock interactions in sedimentary basins, *in* Gautier, D.L., Kharaka, Y.K. and Surdam, R.C., eds., Relationship of organic matter and mineral diagenesis, Society of Economic Paleontologists and Mineralogists Short Course, v. 17, p. 79-176.

Krumbein, W.O. and Garrels, R.M., 1952, Origin and classification of chemical sediments in terms of pH and oxidation-reduction potentials: Journal of Geology, v. 60, p. 1-33.

Li, Y. and Gregory, S., 1974, Diffusion of ions in seawater and in deep sea sediments: Geochimica et Cosmochimica Acta, v. 38, p. 703-714.

Manheim, F.T. and Horn, M.K., 1968, Composition of deeper subsurface waters along the Atlantic continental margin: Southeastern Geology, v. 9, p. 215-236.

Manheim, F.T. and Sayles, F.L., 1974, Composition and origin of interstitial waters of marine sediments, based on deep sea drill cores, *in* Goldberg, E.D., ed., The Sea, v. 5, Marine Chemistry: John Wiley and Sons, New York, p. 527-568.

Mechalas, B.J., 1974, Pathways and environmental requirements for biogenic gas production in the ocean, *in* Kaplan, I.R., ed., Natural Gases in Marine Sediments, Marine Science, v. 3, p. 11-26.

Merino, E., 1975, Diagenesis in Tertiary sandstones from Kettleman North Dome, California. II. Interstitial solutions: distribution of aqueous species at 100°C and chemical relation to the diagenetic mineraology: Geochimica et Cosmochimica Acta, v. 39, p. 1629-1645.

Muller, P.J. and Suess, E., 1979, Productivity, sedimentation rate, and sedimentary organic matter in the oceans - I. Organic carbon preservation: Deep-Sea Research, v. 26A, p. 1347-1362.

Nesbitt, H.W., 1980, Characterization of mineral-formation water interactions in Carboniferous sandstones and shales of the Illinois Sedimentary Basin: American Journal of Science, v. 280, p. 607-630.

Nesbitt, H.W., 1985, A chemical equilibrium model for the Illinois Basin formation waters: American Journal of Science, v. 285, p. 436-458.

Reeburgh, W.S., 1983, Rates of biogeochemical processes in anoxic sediments: Annual Reviews of the Earth and Planetary Sciences, v. 11, p. 269-298.

Rhoads, D.C. and Morse, J.W., 1971, Evolutionary and ecologic significance of oxygen-deficient marine basins: Lethaia, v. 4, p. 413-428.

Roedder, E., 1977, Fluid inclusions as tools in mineral exploration: Economic Geology, v. 72, p. 503-525.

Sansone, F.J. and Martens, C.S., 1981, Methane production from acetate and associated methane fluxes from anoxic coastal sediments: Science, v. 211, p. 707-709.

Sayles, F.L. and Manheim, F.T., 1975, Interstitial solutions and diagenesis in deeply buried marine sediments: Results from the Deep Sea Drilling Project: Geochimica et Cosmochimica Acta, v. 39, p. 103-127.

White, D.E., 1957, Magmatic, connate, and metamorphic waters: Geological Society of America Bulletin, v. 68, p. 1659-1682.

White, D.E., 1965, Saline waters of sedimentary rocks, *in* Young, A. and Galley, J.A., eds., Fluids in subsurface environments, American Association of Petroleum Geologists Memoir 4, p. 342-366.

Wigley, T.M., Plummer, L.N. and Pearson, F.J., Jr., 1978, Mass transfer and carbon isotope evolution in natural water systems: Geochimica et Cosmochimica Acta, v.42, p. 1117-1139.

Wilson, T.R.S., Thomson, J., Colley, S., Hydes, D.J., Higgs, N.C. and Sorensen, J., 1985, Early organic diagenesis: The significance of progressive subsurface oxidation fronts in pelagic sediments: Geochimica et Cosmochimica Acta, v. 49, p. 811-822.

Zeikus, J.G. and Wolfe, R.S., 1972, *Methanobacterium thermoautotrophicum* sp. n., an anaerobic, autotrophic, extreme thermophile: Journal of Bacteriology, v. 109, p. 707-713.

Low to Intermediate Sedimentation-rate Basins

Anderson, R.N., Hobart, M.A. and Langseth, M.G., 1979, Geothermal convection through oceanic crust and sediments of the Indian Ocean: Science, v. 204, p. 828-832.

Anderson, R.N., Langseth, M.G. and Sclater, J.G., 1977, The mechanics of heat transfer through the floor of the Indian Ocean: Journal of Geophysical Research, v. 82, p. 3391-3409.

Baker, P.A., Gieskes, J.M. and Elderfield, H., 1982, Diagenesis of carbonate in deep-sea sediments - Evidence from Sr/Ca ratios and interstitial dissolved Sr^{2+} data: Journal of Sedimentary Petrology, v. 52, p. 71-82.

Bath, A. and Shackleton, N., 1984, Oxygen and hydrogen isotope studies in squeezed pore waters, Deep Sea Drilling Project, Leg 74, hole 525B: Evidence for mid-Miocene ocean isotopic change, *in* Moore, T.C., Jr., Rabinowitz, P.D., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 74, p. 697-699.

Bender, M.L., Hudson, A., Graham, D.W., Barnes, R.O., Leinen, M., and Kahn, D., 1986, Diagenesis and convection reflected in pore water chemistry on the western flank of the East Pacific Rise, 20 degrees south: Earth and Planetary Science Letters, v. 76, p. 71-83.

Burke, W.H., Denison, R.E., Hetherington, E.A., Koepnick, R.B., Nelson, H.F. and Otto, J.B., 1982, Variation of seawater ^{87}Sr/^{86}Sr throughout Phanerozoic time: Geology, v. 10, p. 516-519.

Chamley, H. and Millot, G., 1972, Néoformation de montmorillonite a partir de diatomées et de cendres dans le sédiments marins de Santorin (Mediterranée orientale): Comptes Rendus, Academie des Sciences, Ser. D, t. 272, p. 1132-1134.

Colley, S., Thomson, J., Wilson, T.R.S. and Higgs, N.C., 1984, Post-depositional migration of elements during diagenesis in brown clay and turbidite sequences in the North East Atlantic: Geochimica et Cosmochimica Acta, v. 48, p. 1223-1235.

Donnelly, T.W. and Merrill, L., 1977, The scavenging of magnesium and other chemical species by biogenic opal in deep-sea sediments: Chemical Geology, v. 19, p. 167-186.

Elderfield, H., Gieskes, J.M., Baker, P.A., Oldfield, R.K., Hawkesworth, C.J. and Miller, R., 1982, ^{87}Sr/^{86}Sr and ^{18}O/^{16}O ratios, interstitial water chemistry and diagenesis in deep-sea carbonate sediments of the Ontong Java Plateau: Geochimica et Cosmochimica Acta, v. 46, p. 2259-2268.

Gieskes, J.M., Elderfield, H. and Palmer, M.R., 1986, Strontium and its isotopic composition in interstitial waters of marine carbonate sediments: Earth and Planetary Science Letters (in press).

Gieskes, J.M. and Johnston, K., 1984, Interstitial water studies, Leg 81, *in* Roberts, D.G., Schnitker, D., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 81, p. 829-836.

Gieskes, J.M., Johnston, K., Boehm, M. and Nohara, M., 1984, Interstitial water studies, Deep Sea Drilling Project, Leg 75, *in* Hay, W.W., Sibuet, J.-C., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 75, p. 959-963.

Gieskes, J.M. and Lawrence, J.R., 1981, Alteration of volcanic matter in deep sea sediments: evidence from the chemical composition of interstitial waters from deep sea drilling cores: Geochimica et Cosmochimica Acta, v. 45, p. 1687-1703.

Hein, J.R., Yeh, H.W. and Alexander, E., 1979a, Origin of iron-rich montmorillonite from manganese nodule belt of the north equatorial Pacific: Clays and Clay Minerals, v. 27, p. 185-194.

Helm, R., 1985, Mineralogy and diagenesis of slope sediments offshore Guatemala and Costa Rica, Deep Sea Drilling Project leg 84, *in* Von Huene, R., Aubouin, J., *et al.*, Intitial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 85, p. 571-594.

Johnson, T.C., 1976, Biogenic opal preservation in pelagic sediments of a small area in eastern tropical Pacific: Geological Society of America, Bulletin, v. 87, p. 1273-1282.

Kastner, M., 1981, Authigenic silicates in deep-sea sediments: formation and diagenesis, *in* Emiliani, C. ed., The Sea, v. 7, The Oceanic Lithosphere: John Wiley and Sons, New York, p. 915-980.

Kastner, M. and Stonecipher, S.A., 1978, Zeolites in pelagic sediments of the Atlantic, Pacific and Indian Oceans, *in* Sand, L.B. and Mumpton, F.A., eds., Natural zeolites: Occurrence, properties, use: Pergamon Press, New York, p. 199-220.

Lawrence, J.R. and Gieskes, J.M., 1981, Constraints on water transport and alteration in the oceanic crust from the isotopic composition of pore water: Journal of Geophysical Research, v. 86, p. 7924-7934.

Lawrence, J.R., Gieskes, J.M. and Broecker, W.S., 1975, Oxygen isotope and cation composition of DSDP pore waters and the alteration of Layer II basalts: Earth and Planetary Science Letters, v. 27, p. 1-10.

Lerman, A., 1975, Maintenance of steady state in oceanic sediments: American Journal of Science, v. 275, p. 609-635.

Lerman, A., 1977, Migrational processes and chemical reactions in interstitial waters, *in* Goldberg, E.D., McCave, I.N., O'Brien, J.J. and Steele, J.H., eds., The Sea, v. 6, Marine Modeling: John Wiley and Sons, New York, p. 695-738.

Lerman, A. and Lietzke, T.A., 1977, Fluxes in a growing sediment layer: American Journal of Science, v. 277, p. 25-37.

Li, Y. and Gregory, S., 1974, Diffusion of ions in seawater and in deep sea sediments: Geochimica et Cosmochimica Acta, v. 38, p. 703-714.

MacKenzie, F.T. and Garrels, R.M., 1966, Silica-bicarbonate balance in the ocean and early diagenesis: Journal of Sedimentary Petrology, v. 36, p. 1075-1084.

Mackin, J.E. and Aller, R.C., 1984, Dissolved Al in sediments of the East China Sea: implications for authigenic mineral formation: Geochimica et Cosmochimica Acta, v. 48, p. 281-297.

McDuff, R.E., 1978, Conservative behaviour of calcium and magnesium in interstitial waters of marine sediments: Identification and interpretation, unpublished Ph.D. thesis, Scripps Institution of Oceanography, University of California, San Diego, 183 p.

McDuff, R.E., 1981, Major cation gradients in DSDP interstitial waters: the role of diffusive exchange between sea water and upper oceanic crust: Geochimica et Cosmochimica Acta, v. 45, p. 1705-1713.

McDuff, R.E. and Gieskes, J.M., 1976, Calcium and magnesium profiles in DSDP interstitial waters: diffusion or reaction?: Earth and Planetary Science Letters, v. 33, p. 1-10.

Moberly, R., Jr., Kimura, H.S. and McCoy, F.W., Jr., 1968, Authigenic marine phyllosilicates near Hawaii: Geological Society of America, Bulletin, v. 79, p. 1449-1460.

Müller, P.J. and Mangini, A., 1980, Organic carbon decomposition rates in sediments of the Pacific manganese nodule belt dated by ^{230}Th and ^{231}Pa: Earth and Planetary Science Letters, v. 51, p. 94-114.

Palmer, M.R. and Elderfield, H., 1985, Sr isotope composition of sea water over the past 75 Myr: Nature, v. 314, p. 526-528.

Savin, S.M., 1980, Oxygen and hydrogen effects in low-temperature mineral-water interactions, *in* Fritz, P. and Fontes, J.C., eds., Handbook of Environmental Isotope Geochemistry: Elsevier, Amsterdam, v. 1, p. 283-327.

Sayles, F.L. and Manheim, F.T., 1975, Interstitial solutions and diagenesis in deeply buried marine sediments: Results from the Deep Sea Drilling Project: Geochimica et Cosmochimica Acta, v. 39, p. 103-127.

Scholle, P.A., Arthur, M.A. and Ekdale, A.A., 1983, Pelagic environment, *in* Scholle, P.A., Bebout, D.G. and Moore, C.H., eds., Carbonate depositional environments: American Association of Petroleum Geologists Memoir 33, p. 619-691.

Shackleton, N.J., Hall, M.A. and Boersma, A., 1984, Oxygen and carbon isotope data from Leg 74 foraminifera, *in* Moore, T.C., Jr., Rabinowitz, P.D., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 74, p. 599-612.

Stoffyn-Egli, P., 1982, Dissolved aluminium in interstitial waters of recent sediments from the North Atlantic Ocean: Geochimica et Cosmochimica Acta, v. 46, p. 1345-1352.

Stout, P.M., 1985, Chemical diagenesis of pelagic biogenic sediments from the equatorial Pacific, unpublished Ph.D. thesis, Scripps Institution of Oceanography, University of California, San Diego, 220 p.

Wilson, T.R.S., Thomson, J., Colley, S., Hydes, D.J., Higgs, N.C. and Sorensen, J., 1985, Early organic diagenesis: The significance of progressive subsurface oxidation fronts in pelagic sediments: Geochimica et Cosmochimica Acta, v. 49, p. 811-822.

High Sedimentation-rate Basins

Berner, R.A., 1980, Early diagenesis. A theoretical approach: Princeton Series in Geochemistry: Princeton University Press, 241 p.

Carson, B., 1977, Tectonically induced deformation of deep sea sediments off Washington and northern Oregon: mechanical consolidation: Marine Geology, v. 24, p. 289-307.

Carson, B., Jennwei, Y. and Myers, P.B., 1974, Initial deep-sea sediment deformation at the base of the Washington continental slope. Geology, v. 2, p. 561-564.

Claypool, G.E. and Kaplan, I.R., 1974, The origin and distribution of methane in marine sediments, *in* Kaplan, I.R., ed., Natural Gases in Marine Sediments. Marine Science, v. 3, p. 99-140.

Claypool, G.E. and Kvenvolden, K.A., 1983, Methane and other hydrocarbon gases in marine sediment: Annual Reviews of the Earth and Planetary Sciences, v. 11, p. 299-327.

Claypool, G.E. and Threlkeld, C.N., 1983, Anoxic diagenesis and methane generation in sediments of the Blake Outer Ridge, DSDP Site 533, Leg 76, *in* Sheridan, R.E., Gradstein, F.M., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 76, p. 391-402.

Claypool, G.E., Threlkeld, C.N., Mankiewicz, P.N., Arthur, M.A. and Anderson, T.F., 1985, Isotopic composition of interstitial fluids and origin of methane in slope sediment of the Middle America Trench, Deep Sea Drilling Project Leg 84, *in* Von Huene, R., Aubouin, J., *et al.*, Initial Reports of the Deep Sea Drilling Project, v. 84, p. 683-691.

Clayton, R.N., Friedman, I., Graf, D.L., Mayeda, T.K., Meents, W.F. and Shimp, N.F., 1966, The origin of saline formation waters: 1. Isotopic composition: Journal of Geophysical Research, v. 71, p. 3869-3882.

Curtis, C.D., Petrowski, C. and Oertel, G., 1972, Stable carbon isotope ratios within carbonate concretions: a clue to place and time of formation: Nature, v. 235, p. 98-100.

Davidson, D.W., Leaist, D.G. and Hesse, R., 1983, Oxygen-18 enrichment in the water of a clathrate hydrate: Geochimica et Cosmochimica Acta, v. 47, p. 2293-2295.

Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B. and Maynard, V., 1979, Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis: Geochimica et Cosmochimica Acta, v. 43, p. 1075-1090.

Gieskes, J.M., Elderfield, H., Lawrence, J.R., Johnson, J., Meyers, B. and Campbell, A., 1982a, Geochemistry of interstitial waters and sediments, Leg 64, Gulf of California, *in* Curray, J.R., Moore, D.G., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 64, part 2, p. 675-694.

Gieskes, J.M., Johnston, K. and Boehm, M., 1985, Interstitial water studies, Leg 66, *in* Huene, R., Aubouin, J., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 84, p. 961-967.

Goldhaber, M.B. and Kaplan, I.R., 1974, The sulphur cycle, *in* Goldberg, E.D., ed., The Sea, v. 5, Marine Chemistry, John Wiley and Sons, New York, p. 569-655.

Goldhaber, M.B. and Kaplan, I.R., 1980, Mechanisms of sulfur incorporation and isotope fractionation during early diagenesis in sediments of the Gulf of California: Marine Chemistry, v. 9, p. 95-143.

Harrison, W.E., Hesse, R. and Gieskes, J.M., 1982, Relationship between sedimentary facies and interstitial water chemistry in slope, trench and Cocos plate sites from the Mid-America Trench transect, active margin off Guatemala. Leg 67, DSDP, *in* Von Huene, R., Aubouin, J., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 67, p. 603-614.

Hesse, R. and Harrison, W.E., 1981, Gas-hydrates (clathrates) causing pore-water freshening and oxygen isotope fractionation in deep-water sedimentary sections of the terrigenous continental margins: Earth and Planetary Science Letters, v. 55, p. 453-462.

Hesse, R., Lebel, J. and Gieskes, J.M., 1985, Interstitial water chemistry of gas hydrate bearing sections on the Middle-America Trench Slope Deep Sea Drilling Project, Leg 84, *in* Von Huene, R., Aubouin, J., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 84, p. 727-737.

Jenden, P.D. and Gieskes, J.M., 1983, Chemical and isotopic composition of interstitial water from Deep Sea Drilling Project sites 533 and 534, *in* Sheridan, R.E., Gradstein, F.M., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 76, p. 453-461.

Manheim, F.T., 1967, Evidence for submarine discharge of water on the Atlantic continental slope of the southern United States, and suggestions for further search: New York Academy of Sciences, Transactions, Series II, v. 29, p. 839-853.

Manheim, F.T. and Chan, K.M., 1974, Interstitial waters of Black Sea sediments: New data and review, *in* Degens, E.T. and Ross, D.A., eds., The Black Sea - geology, chemistry and biology: American Association of Petroleum Geologists Memoir 20, p. 155-180.

Manheim, F.T. and Schug, D.M., 1978, Interstitial waters of Black Sea cores, *in* Ross, D.A., Neprochnov, Y.P., *et al.*, Initial Reports of the Deep Sea Drillng Project: U.S. Government Printing Office, Washington, D.C., v. 42, pt. II, p. 637-651.

O'Neil, J.R., 1968, Hydrogen and oxygen isotope fractionation between ice and water: Journal of Physical Chemistry, v. 72, p. 3683-3684.

Rosenfeld, W.D. and Silverman, S.R., 1959, Carbon isotope fractionation in bacterial production of methane: Science, v. 130, p. 1658-1659.

Sackett, W.M. and Thompson, R.R., 1963, Isotopic organic carbon compositions of recent continental shelf derived clastic sediments of the Eastern Gulf Coast, Gulf of Mexico: American Association of Petroleum Geologists Bulletin, v. 47, p. 525-531.

Schoell, M., 1983, Genetic characterization of natural gases: American Association of Petroleum Geologists Bulletin, v. 67, p. 2225-2238.

Shipley, T.H., Houston, M.H., Buffler, R.T., Shaub, F.J., McMillenik, J., Ladd, J.W. and Worzel, J.L., 1979, Seismic evidence for widespread possible gas hydrate horizons on continental slopes and rises: American Association of Petroleum Geologists Bulletin, v. 63, p. 2204-2213.

Suess, E., 1976, Porenlösungen mariner Sedimente. Ihre chemische Zusammensetzung als Ausdruck frühdiagenetischer Vorgänge, Habiliationsschrift, Universität Kiel, 193 p.

Tucholke, B., Bryan, G.M. and Ewing, J.I., 1977, Gas-hydrate horizons detected in seismic profiler data from the western North Atlantic: American Association of Petroleum Geologists Bulletin, v. 61, p. 698-707.

Evaporite Dissolution and Hydrothermal Activity

Couture, R., Miller, R.S. and Gieskes, J.M., 1978, Interstitial water and mineralogical studies, Leg 41, *in* Lancelot, Y., Seibold, E., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 41, p. 907-914.

Dickey, P.A., 1969, Increasing concentration of subsurface brines with depth: Chemical Geology, v. 4, p. 361-370.

Gieskes, J.M., 1983, The chemistry of interstitial waters of deep-sea sediments: Interpretation of Deep Sea Drilling Data, *in* Riley, J.P. and Chester, R., eds., Chemical Oceanography, v. 8, p. 221-269.

Gieskes, J.M., Graham, D. and Ellis, R., 1980, Interstitial-water studies, Deep Sea Drilling Project sites 415 and 416, *in* Lancelot, Y., Winterer, E.L., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 50, p. 691-693.

Gieskes, J.M., Kastner, M., Einsele, G., Kelts, K. and Niemitz, J., 1982b, Hydrothermal activity in the Guaymas Basin, Gulf of California: A synthesis, *in* Curray, J.R., Moore, D.G., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 64, p. 1159-1167.

Graf, D.L., 1982, Chemical osmosis, reverse chemical osmosis, and the origin of subsurface brines: Geochimica et Cosmochimica Acta, v. 46, p. 1431-1448.

Manheim, F.T. and Horn, M.K., 1968, Composition of deeper subsurface waters along the Atlantic continental margin: Southeastern Geology, v. 9, p. 215-236.

Manheim, F.T., Sayles, F.L., and Friedman, I., 1969, Interstitial water studies on small core samples, Deep Sea Drilling Project, Leg 1, *in* Ewing, M., Worzel, J.L., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 1, p. 403-407.

Manheim, F.T., Waterman, L.S., Woo, C.C. and Sayles, F.L., 1974, Interstitial water studies on small core samples, leg 23 (Red Sea), *in* Whitmarsh, R.B., Ross, D.A., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 23, p. 955-967.

McDuff, R.E., Gieskes, J.M. and Lawrence, J.R., 1978, Interstitial water studies, Leg 42A, *in* Hsü, K., Montadert, L., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 42, part 1, p. 561-568.

Menzies, M. and Seyfried, W.E., 1979, Basalt - seawater interaction: Trace element and strontium isotope variations in experimentally altered glassy basalt: Earth and Planetary Science Letters, v.44, p. 463-472.

Müller, J. and Fabricius, F., 1978, Luneburgite in Upper Miocene sediments of the eastern Mediterranean Sea, *in* Hsü, K., Montadert, L., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 42, p. 661-664.

Sayles, F.L., Waterman, L.S. and Manheim, F.T., 1972, Interstitial water studies on small core samples from the Mediterranean Sea, *in* Ryan, W.B.F., Hsü, K.J., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 13, p. 801-808.

Sotelo, V. and Gieskes, J.M., 1978, Interstitial water studies, Leg 40: Shipboard studies, *in* Bolli, H.M., Ryan, W.B.F., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 40, p. 549-554.

Waterman, L.S., Sayles, F.L. and Manheim, F.T., 1972, Interstitial water samples on small core samples, Leg 14, *in* Hayes, D.E., Pimm, A.C., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 14, p. 753-762.

Early Diagenetic Mineralization Reactions in High Sedimentation-rate Basins

Arthur, M.A., Anderson, T.F., Kaplan, I.R., Veizer, J. and Land, L.S., 1983, Stable isotopes in sedimentary geology: Society of Economic Paleontologists and Mineralogists Short Course Lecture Notes, v. 10, p. 1-151.

Baker, P.A. and Burns, S.J., 1985, Occurrence and formation of dolomite in organic-rich continental margin sediments: American Association of Petroleum Geologists, Bulletin, v. 69, p. 1917-1930.

Baker, P.A. and Kastner, M., 1981, Constraints on the formation of sedimentary dolomite: Science, v. 213, p. 214-216.

Baron, G. and Debyser, I., 1957, Sur la présence dans des vases organiques de la mer Baltique de sulfure manganeux-hexagonal, Comptes Rendues de l'Academie des Sciences Français, v. 245, p. 1148-1150.

Berner, R.A., 1967, Thermodynamic stability of sedimentary iron sulfides: American Journal of Science, v. 265, p. 773-785.

Berner, R.A., 1969, The synthesis of framboidal pyrite: Economic Geology, v. 64, p. 383-384.

Berner, R.A., 1980, Early diagenesis. A theoretical approach: Princeton Series in Geochemistry, Princeton University Press, 241 p.

Berner, R.A., 1984, Sedimentary pyrite formation: an update: Geochemica et Cosmochimica Acta, v. 48, p. 605-615.

Botz, R. and v. Rad, U., 1986, Authigenic Fe-Mn carbonates in the Cretaceous and Tertiary continental rise sediments of DSDP Site 603 off the eastern U.S.A., *in* Van Hinte, J.E., Wise, S.W., Jr., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 93 (in press).

Bramlette, M.N., 1946, The Monterey Formation of California and the origin of its siliceous rocks: U.S. Geological Survey, Professional Paper 212, 55 p.

Carroll, D., 1958, The role of clay minerals in the transportation of iron: Geochimica et Cosmochimica Acta, v. 14, p. 1-27.

Carstens, H., 1986, Displacive growth of authigenic pyrite: Journal of Sedimentary Petrology, v. 56, p. 252-257.

Claypool, G.E., Threlkeld, C.N., Mankiewicz, P.N., Arthur, M.A. and Anderson, T.F., 1985, Isotopic composition of interstitial fluids and origin of methane in slope sediment of the Middle America Trench, Deep Sea Drilling Project Leg 84, *in* Von Huene, R., Aubouin, J., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 84, p. 683-691.

Coleman, M.L. and Raiswell, R., 1981, Carbon, oxygen and sulfure isotope variations in concretions from the Upper Lias of N.E. England: Geochimica et Cosmochimica Acta, v. 45, p. 329-340.

Curtis, C.D., 1967, Diagenetic iron minerals in some British Carboniferous sediments: Geochimica et Cosmochimica Acta, v. 31, p. 2109-2123.

Curtis, C.D., Petrowski, C. and Oertel, G., 1972, Stable carbon isotope ratios within carbonate concretions: a clue to place and time of formation: Nature, v. 235, p. 98-100.

Eder, F.W., 1970, Genese riff-naher Detritus-Kalke bei Balve im Rheinischen Schiefergebirge (Garbecker Kalk): Verhandlungen der Geologischen Bundes-Anstalt, Vienna, Jg. 1970, p. 551-569.

Farrand, M., 1970, Framboidal sulfides precipitated synthetically: Mineralium Deposita, v. 5, p. 237-247.

Garrison, R.E., Kastner, M. and Zenger, D.H., 1984, eds., Dolomites of the Monterey Formation and organic-rich units: Society of Economic Paleontologists and Mineralogists, Pacific Section, Special Publication No. 41, 215 p.

Gautier, D.L., 1985, Interpretation of early diagenesis in ancient marine sediments, *in* Gautier, D.L., Kharaka, Y.K. and Surdam, R.C., Relationship of organic matter and mineral diagenesis: Society of Economic Paleontologists and Mineralogists, Short Course Lecture Notes, v. 17, p. 6-78.

Gautier, D.L. and Claypool, G.E., 1984, Interpretation of methanic diagenesis in ancient sediments by analogy with processes in modern diagenetic environments, *in* McDonald, D.A. and Surdam, R.C., eds., Clastic diagenesis: American Association Petroleum Geologists Memoir 37, p. 111-123.

Gieskes, J.M., 1981, Deep sea drilling interstitial-water studies: Implications for chemical alteration of the ocean crust, Layers I and II, *in* Warme, J.E., Douglas, R.G. and Winterer, E.L., eds., The Deep Sea Drilling Project: A decade of progress: Society of Economic Paleontologists and Mineralogists, Special Publication 32, p. 149-167.

Goldhaber, M.B., and Kaplan, I.R., 1974, The sulfur cycle, *in* Goldberg, E.D., ed., The Sea, v. 5, Marine Chemistry: John Wiley and Sons, New York, p. 569-655.

Goldhaber, M.B., and Kaplan, I.R., 1980, Mechanisms of sulfur incorporation and isotope fractionation during early diagenesis in sediments of the Gulf of California: Marine Chemistry, v. 9, p. 95-143.

Hein, J.R., O'Neil, J.R. and Jones, M.G., 1979b, Origin of authigenic carbonates in sediment from the deep Bering Sea: Sedimentology, v. 27, p. 577-591.

Hennessy, J. and Knauth, L.P., 1985, Isotopic variations in dolomite concretions from the Monterey Formation, California: Journal of Sedimentary Petrology, v. 55, p. 120-130.

Hudson, J.D., 1978, Concretions, isotpes, and the diagenetic history of the Oxford Clay (Jurassic) of central England: Sedimentology, v. 25, p. 339-370.

Irwin, H., Curtis, C.D. and Coleman, M., 1977, Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments: Nature, v. 269, p. 209-213.

Islam, S., 1981, Thermal maturation patterns in Cambro-Ordovician flysch sediments of the Taconic Belt, Gaspe-Peninsula, unpublished M.Sc. Thesis, McGill University, 191 p.

Itihara, Y. and Honma, H., 1979, Ammonium in biotite from metamorphic and granitic rocks of Japan: Geochimica et Cosmochimica Acta, v. 43, p. 503-509.

Kelts, K. and McKenzie, J.A., 1982, Diagenetic dolomite formation in Quaternary anoxic diatomaceous muds of Deep Sea Drilling Project Leg 64, Gulf of California, *in* Curray, J.R., Moore, D.G., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 64, part 2, p. 553-569.

Kharaka, Y.K., Hull, R.W. and Carothers, W.W., 1985, Water-rock interactions in sedimentary basins, *in* Gautier, D.L., Kharaka, Y.K. and Surdam, R.C., Relationship of organic matter and mineral diagenesis, Society of Economic Paleontologists and Mineralogists, Short Course 17, p. 79-176.

Kharaka, Y.K., Hull, R.W. and Specht, D.J., 1985b, SOLMNEQ II: Solution-mineral equilibrium computations: U.S. Geological Survey, Water Supply Paper (in press).

Kharaka, Y.K., Lico, M.S. and Carothers, W.W., 1980, Predicted corrosion and scale-formation properties of geopressured geothermal waters from the Northern Gulf of Mexico Basin: Journal of Petroleum Technology, v. 32, p. 319-324.

Kushnir, J. and Kastner, M., 1984, Two forms of dolomite occurrences in the Monterey Formation, California; concretions and layers - a comparative mineralogical, geochemical and isotopic study, *in* Garrison, R.E., Kastner, M. and Zenger, D.H., eds., Dolomites of the Monterey Formation and organic rich units: Society of Economic Paleontologists and Mineralogists, Pacific Section, Special Publication no.41, p.171-183.

Lerman, A., 1977, Migrational processes and chemical reactions in interstitial waters, *in* Goldberg, E.D., McCaye, I.N., O'Brien J.J. and Steele, J.H., eds., The Sea, v. 6, p. 695-738, John Wiley and Sons, New York.

Matsumoto, R., 1983, Mineralogy and geochemistry of carbonate diagenesis of the Pliocene and Pleistocene hemipelagic mud on the Blake Outer Ridge, Site 533, Leg 76, *in* Sheridan, R.E., Gradstein, F.M., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 76, p. 411-427.

Muller, P.J., 1977, C/N ratios in Pacific deep-sea sediments: Effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. Geochimica et Cosmochimica Acta, v. 41, p. 765-776.

Oertel, G. and Curtis, C.D., 1972, Claystone-ironstone concretion preserving fabrics due to progressive compaction: Geological Society of America, Bulletin, v. 83, p. 2597-2606.

Okada, H., 1980, Pebbles and carbonate nodules from Deep Sea Drilling Project Leg 56 cores, *in* Honza, E., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 56-57, p. 1089-1105.

Pisciotto, K.A. and Mahoney, J.J., 1981, Isotopic survey of diagenetic carbonates, Deep Sea Drilling Project Leg 63, *in* Yeats, R.S., Haq, B.U., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 63, p. 595-609.

Raiswell, R., 1982, Pyrite texture, isotopic composition and the availability of iron: American Journal of Science, v. 282, p. 1244-1263.

Raiswell, R. and Berner, R.A., 1985, Pyrite formation in euxinic and semi-euxinic sediments: American Journal of Science, v. 285, p. 710-724.

Ritger, S., Carson, B. and Suess, E., 1986, Methane-derived authigenic carbonates formed by subduction-induced pore water expulsion along the Oregon/Washington margin: Geological Society of America, Bulletin, v. 97 (in press).

Russell, K.L., Deffeyes, K.S., Fowler, G.A. and Lloyd, R.M., 1967, Marine dolomite of unusual isotopic composition: Science, v. 155, p. 189-191.

Schwarcz, H.P. and Burnie, S.W., 1973, Influence of sedimentary environments on sulfur isotope ratios in clastic rocks: a review: Mineralium Deposita, v. 8, p. 264-277.

Sholkovitz, E., 1973, Interstitial water chemistry of the Santa Barbara Basin sediments: Geochimica et Cosmochimica Acta, v. 37, p. 2043-2073.

Suess, E., 1979, Mineral phases formed in anoxic sediments by microbial decomposition of organic matter: Geochimica et Cosmochimica Acta, v. 43, p. 339-352.

Tassé, N. and Hesse, R., 1984, Origin and significance of complex authigenic carbonates in Cretaceous black shales of the Western Alps: Journal of Sedimentary Petrology, v. 54, p. 1012-1027.

Wada, H., Niitsuma, N., Nagasawa, K. and Okada, H., 1981, Deep sea carbonate nodules from the Middle America trench area off Mexico, Deep Sea Drilling Project Leg 66, *in* Watkins, J.S., Moore, J.C., *et al.*, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 66, p. 453-474.

Accepted, as revised, 30 July 1986.