Geochemistry of Diagenetic Non-Silicate Minerals Kinetic Considerations [and Discussion]

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Geochemistry of diagenetic non-silicate minerals: kinetic considerations

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The early stages of burial diagenesis involve the reactions of various oxidizing agents with organic matter, which is the only reducing agent buried with the sediment. In a system in which a local equilibrium is established, thermodynamic principles indicate that, *inter alia*, manganese, iron and sulphate should each be consumed successively to give rise to a clearly characterized vertical zonation. However, ferric iron may not react fast enough and the relative rates of reduction of Fe^{III} and sulphate not only control the formation of iron sulphide and associated carbonate but also may lead to extreme chemical and isotopic dis-equilibrium. This produces kinetically controlled 'micro-environments'. On a larger scale, sulphide will diffuse upward to a zone in which its oxidation leads to a reduction of pH. The various dramatic changes in chemical environment across such an interface cause both dissolution and precipitation reactions. These explain common geological observations: the occurrence of flint nodules (and their restriction to chalk hosts) and the association of phosphate with glauconite.

1. Introduction

When the constituents of what later becomes a sedimentary rock are first assembled at the sediment–water interface they comprise a chemically metastable assemblage. This paper attempts to formalize some of the routes they take to approach chemical equilibrium. One of the main controls on diagenetic processes is the composition of the sediment; this may be related to depositional environment. However, to correlate different environments a classification scheme must relate the diagenetic mineral assemblage to specific processes. The aim, therefore, is to characterize these diagenetic minerals. By doing so, it is possible to investigate the controls on precipitation of diagenetic phases and assess the relative importance of depositional environment as opposed to processes common to all sediments on burial.

The materials of relevance here are the carbonate minerals produced by oxidation of organic matter and any other inorganic phases produced as a result of the diagenetic environment. Of particular interest are the relatively large concretionary bodies that consist very largely of diagenetic precipitates. They offer two advantages; they are large enough to be conspicuous (thus easily collectable) and they may preserve compositional variations reflecting either spatial or temporal changes in pore-water composition during growth of the concretion. Although they are oddities they give information about the system in general, but the reason for their specific localization also must be explained.

Their chemical and isotopic compositions can be used to deduce the environment of growth by comparison with modern analogues (Irwin *et al.* 1977; Coleman & Raiswell 1981). The fundamental basis of this work was the recognition of a scheme of reactions in pore-water samples (e.g. Presley & Kaplan 1968; Nissenbaum *et al.* 1972), which give a distinct vertical zonation and was summarized succinctly by Curtis (1977). This scheme will be discussed in greater detail in §2.

The reaction scheme, when applied to marine pore-water systems, has already been discussed and modelled by many workers (see, for example, Boström 1967; Ben-Yaakov 1973; Froelich *et al.* 1979); but in most cases an assumption of chemical equilibrium has been made. For example, the carbonate buffer tends to minimize pH variations in sea water and this concept has been used to show that large variations should not occur. This certainly is true if the system is averaged over a large enough volume of sediment and a sufficiently long time-span. Nevertheless, local perturbations in the isotropic blandness (both temporal and spatial) produce transient environments in which diagnostic minerals precipitate and remain subsequently. These perturbations and their products are the main subject of this paper. The structure within which this is discussed is as follows: a section on the accepted microbial–chemical basis of diagenetic zonation; a more detailed examination of the interactions of the various processes (and the consequent implications); and examples of the expression of these reactions as characteristic diagenetic assemblages in specific geological environments.

2. Fundamental basis for the sequence of reactions

(*a*) *Sequential organic-matter degradation processes*

The initial ingredients of a sediment can be regimented into three main groups; water and its solutes, inorganic detrital particles and organic matter. Generally, the only reducing agent buried with the sediment is organic matter. This is not surprising because detrital particles are carried in oxygenated river water, a strongly oxidizing system. To be incorporated in the sediment, organic matter must be either refractory or produced locally. The most reactive organic matter is produced within the water column.

Table 1. Zonal reaction scheme

(After Froelich *et al.* 1979.)

environment	diagenetic zone	zone code	$-\Delta G/[\mathrm{kJ\ (mol\ C_{org})^{-1}}]$
oxic	aerobic oxidation	Ox	530
sub-oxic	manganese reduction	MnR	485–515
	nitrate reduction	NR	460–505
	ferric iron reduction	FeR	220–235
anoxic	sulphate reduction	SR	65
	methanogenesis	Me	60
	decarboxylation	D	$\leqslant$ 60

The diagenetic zonal scheme of Curtis (1977) was extended by observations of variation of pore-water chemistry in pelagic sediments (Froelich *et al.* 1979). The succession of reactions (table 1) seems generally applicable. Organic matter is oxidized initially by aerobic bacteria and subsequently by successive microbial reactions involving other oxidizing agents, each being used to exhaustion before the next one is used. Oxidation reactions are followed by two further successive processes that separate reduced and oxidized carbon species; microbial methanogenesis and abiological decarboxylation.

It can be seen from table 1 that the reactions apparently follow an order dictated by the magnitude of the energy released. After removal of oxygen in the oxic zone there is no chemical thermodynamic reason why this should be so; all the other components would have to be in mutual equilibrium. The hierarchy of chemical reactions is controlled by the rate constant, which depends on the activation energy of the reaction. Similarly, it is not immediately obvious why each oxidant should be consumed totally before the next one is used. The involvement of bacteria in most of these reactions can be used to explain this paradox. The bacterial metabolic process that produces the greatest free energy per mole of organic carbon will be at a competitive advantage and will dominate the consumption of suitable organic matter until the supply of its oxidant is exhausted. At this stage it will be superseded by the next most efficient process. Although bacteria are assumed to be involved in all these reactions, their role in ferric iron (Fe^{III}) reduction is not clear (see J. G. Jones, this symposium) and it is possible that inorganic reduction may occur also. The effects of this possibility will be dealt with later.

(*b*) *Isotopic and chemical characterization of diagenetic carbonates*

The eventual product of oxidation of organic carbon may be an authigenic carbonate mineral. In all reactions, except that of methanogenesis, it will retain the negative $\delta^{13}C$ isotopic value characteristic of organic matter (see table 1). The substitution of iron in the carbonate lattice, together with carbon isotopic composition, enabled Curtis (1977) to propose a scheme to characterize the three most common sources of authigenic carbonates in mudstones; these are sulphate reduction, methanogenesis, decarboxylation. In the first case the presence of sulphide, which preferentially reacts with available iron (forming FeS and later FeS_2, pyrite), leaves a non-ferroan carbonate with a negative $\delta^{13}C$. Methanogenesis and decarboxylation both may give ferroan carbonates but are differentiated by their respective positive and negative $\delta^{13}C$ compositions. The validity of the scheme was confirmed by Irwin *et al.* (1977) for carbonates in the Kimmeridgian type section (Late Jurassic, SW England). The products of successive diagenetic zones were shown to have been formed at increasing depths of burial, as indicated by oxygen isotope temperatures. Berner (1981) developed a mineralogical classification of early diagenetic environments based on the same sequence of reactions and the classification was extended by Maynard (1982) who included carbon isotopic compositions.

(*c*) *Control of dominant diagenetic process*

Two factors determine which particular process dominates the degradation of organic matter in a sediment. For each of the processes involving oxidation, the oxidant is consumed totally. Therefore, the organic content of a sediment will be important. If it is present in sufficiently high concentration then there will be sufficient remaining after consumption of dissolved oxygen to be available for subsequent reactions. However, dissolved oxygen, nitrate and sulphate can be replenished by diffusive supply from overlying water. The efficiency of the replenishment will depend on the relation of two rates: consumption of oxidant and burial. In a rapidly buried, organic-rich sediment there will still be considerable amounts of organic matter at such depths that diffusive supply cannot satisfy demand. The subsequent process will then gain ascendency. The rate of burial was proposed as the major control by Curtis (1977) and Coleman *et al.* (1979) and obviously is so in comparing sediments of equal organic contents. However, diffusive supply from above is not relevant to Mn^{IV} or Fe^{III} reduction where the oxidant is buried with the sediment. The control of their importance relative to other reactions obviously is a more complex matter. Nevertheless, confirmation of the importance of rate of burial was provided by the data of Pisciotto & Mahoney (1981) who showed a distinctive variation of $\delta^{13}C$ of authigenic carbonates with sedimentation rate, for samples from D.S.D.P. Leg 63. At sedimentation rates of approximately 20 m Ma^{-1}, negative $\delta^{13}C$ values indicated aerobic oxidation or sulphate reduction, highly positive values at 150 m Ma^{-1} related to methanogenesis while a return to more negative compositions at 200 m Ma^{-1} showed the onset of decarboxylation.

(*d*) *Examples of distinctive diagenetic products*

Although carbonates resulting from nitrate reduction cannot be distinguished by their chemical composition, the other early diagenetic processes produce characteristic compositions. In figure 1 the chemical and isotopic compositions of distinctive authigenic carbonates can be related to specific zones. The wide range of ages and locations attest to the universal nature of the system. It is interesting to note that the carbon isotope compositions represent various mixtures of primary marine ($\delta^{13}C \approx 0‰$) with organogenetic carbonate ($\delta^{13}C = -20$ to $-30‰$). A larger component of the former is present in shallower burial products. This shows the greater efficiency of diffusive transport (of marine bicarbonate in this case) to the site of organic diagenesis at low rates of burial.

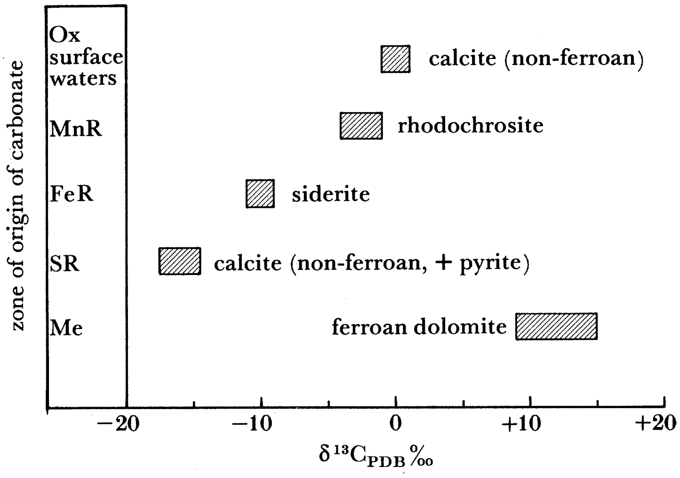

FIGURE 1. Carbon isotopic composition of authigenic carbonates related to the zone of formation. Isotope data from Becker & Clayton (1972), Coleman *et al.* (1982), Coleman (unpublished data), Irwin *et al.* (1977) and Walker (1984). Isotope values are given relative to the international standard, PDB.

The schemes described above are satisfactory, but they do have some disadvantages. They apply best to organic-rich mudstones. The systems of Curtis (1977) and Maynard (1982) rely on the preservation of carbonate minerals that can be analysed isotopically. In some environments either the absence of necessary constituent elements or an unfavourable environment (pH, *Eh*) may militate against precipitation of the characteristic phases for Berner's classification (Berner 1981). An attempt to broaden the classification is described in this paper.

3. Controls on precipitation of diagenetic minerals

(*a*) *Availability of iron*

It is apparent from a closer examination of the diagenetic zonation that the sequence of reactions cannot be followed perfectly. Iron reduction occurs in a specific zone where siderite, $FeCO_3$, can be precipitated. However, Fe^{II} obviously is available during all the subsequent burial history, helping to form pyrite and ferroan dolomite in the sulphate reduction and later zones, respectively. The source of this iron is a problem. The relative stabilities of ferroan phases is shown by the presence of non-ferroan calcite in association with pyrite (Irwin *et al.* 1977; Hudson 1977); thus the formation of pyrite by replacement of siderite in the presence of H_2S can be postulated. This does not explain the formation of ferroan carbonates later in burial. It appears that iron survives in ferric form, beyond the point where thermodynamic equilibrium indicates it should have reacted, and is actively reduced in subsequent zones.

There is no clear evidence for the mechanism of preservation of metastable Fe^{III} but a few possibilities can be presented. First, there is doubt about the extent and type of microbial involvement in the reaction (J. G. Jones, this symposium). The rate of the inorganic reaction would probably be considerably less than the bacterial equivalent. This would be analogous to the case of sulphate reduction. Dissolved sulphate at room temperature is stable in the presence of organic matter under sterile conditions, but experiments by Nakai & Jensen (1964) showed that bacteria indigenous to bottom sediment reduced sulphate in a first-order reaction, with a rate constant of approximately $2.3 \times 10^{-7}\ s^{-1}$ at 32 °C. Secondly, there is the problem of mobility of iron and organic matter. Unlike the other oxidant species, which are soluble, iron and manganese are introduced to the sediment as insoluble, detrital oxide–hydroxides. The reaction mechanism then requires other steps, each of which may impose a rate-controlling effect. Soluble organic matter has to be transported to the iron minerals and the iron-bearing minerals may have to be altered before iron is made available for reaction. However, Cronin & Morris (1982) have shown that smaller, potentially soluble, organic molecules can be incorporated into insoluble high molecular mass molecules within a few years of deposition in the sediment. Each of these factors, individually or severally, may allow iron reduction to proceed simultaneously with other reactions.

(*b*) *Evidence for burial of ferric iron*

An example of metastable retention of iron is given by Curtis *et al.* (1985), who analysed siderite concretions from Westphalian age coal measures. The porosity of the host sediment at the time of carbonate precipitation was calculated from the volume of authigenic carbonate. It can be seen (figure 2*a*) that the molar ratio, Mn:Fe, in the earliest-formed carbonates is almost an order of magnitude greater than that of detrital input. The siderites assume the Mn:Fe values typical of detrital input (Trefry & Presley 1982) at a porosity of about 50%, equivalent to a few tens of metres depth. These values continue in all the deeper-formed carbonates. Although the very low calculated porosities may be subject to error, they must represent depths of at least two kilometres.

Thus it seems that the carbonate was precipitated by manganese reduction followed by long continued iron reduction. Although these processes must have occurred to produce Mn^{II} and Fe^{II}, the $\delta^{13}C$ compositions (figure 2*b*) indicate that initially the carbonate resulted mainly from methanogenesis and, later, an increasingly large component from decarboxylation. These

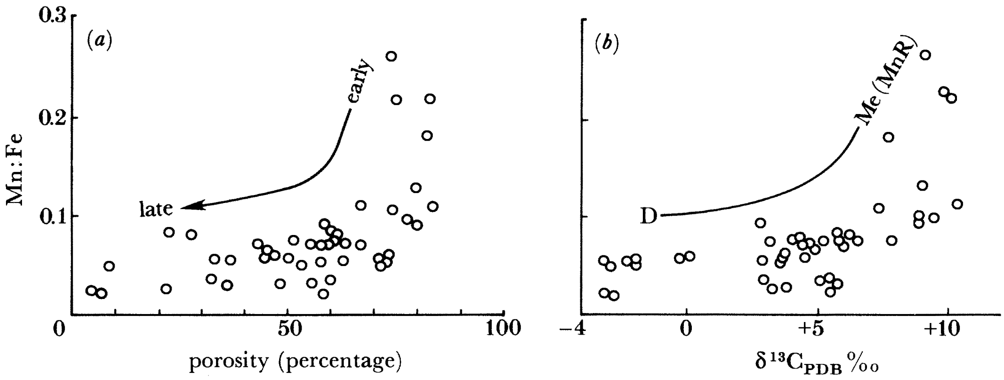

FIGURE 2. Geochemical characteristics of siderite concretions (after Curtis *et al.* 1985). Mn:Fe and porosity values show continued reduction of Fe^{III} (figure 2*a*). Isotope compositions (figure 2*b*) show that the reduction process only occurs in association with other reactions and negligibly in the FeR zone.

results show that some manganese reduction operated initially but that iron reduction accompanied methanogenesis. In these non-marine sediments, the effective absence of sulphate precluded its reduction. The Mn:Fe ratios of the deeper-formed carbonates show that the detrital input was retained in oxidized form to great depths.

(*c*) *The role of iron reduction in carbonate precipitation*

Each of the processes listed in table 1 produces CO_2. Not all of them need precipitate carbonate. The aerobic oxidation reaction can be expressed most simply by the reaction

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \rightarrow HCO_3^- + H^+. \tag{1}$$

In an aqueous system, introduction of CO_2 will not necessarily precipitate carbonate. In fact, initially it will dissolve calcium carbonate as soluble bicarbonate or tend to reduce pH. The eventual effect of (1) in the presence of calcium carbonate can be

$$CaCO_3 + HCO_3^- + H^+ \rightarrow Ca^{2+} + 2HCO_3^-. \tag{2}$$

In marine waters, pH is buffered and rarely exceeds the range 6.9–8.3 (Ben-Yaakov 1973). However, the acids and bases involved in the buffer system are weak and the net products of each reaction can drive the equilibria towards dissolution or precipitation of carbonate. In table 2 the relative effects of each reaction can be compared; the reactions are given as mass-balance for one mole of composition CH_2O, giving one mole of HCO_3^- and ignoring H_2O.

TABLE 2. MASS BALANCE FOR REACTION OF ONE MOLE ORGANIC CARBON ($CH_2O \rightarrow HCO_3^-$) IN SUCCESSIVE ZONES

zone	oxidant	products (excluding HCO_3^- and H_2O)		
Ox	O_2	—	—	$+H^+$
MnR	$2MnO_2$	$2MnO_2$	$+3OH^-$	—
NR	NO_3^-	N_2/NH_3	$+OH^-$	—
FeR	$2Fe_2O_3$	$4Fe^{2+}$	$+7OH^-$	—
SR	$\frac{1}{2}SO_4^{2-}$	$\frac{1}{2}S^{2-}$	—	$+H^+$
Me	—	$\frac{1}{2}CH_4$	—	$+\frac{1}{2}H^+$
D	—	R-CH_3	—	$+H^+$

Bicarbonate is precipitated as carbonate in the presence of a cation (such as Ca^{2+}) in an alkaline environment, which is the counterpart to (2), i.e.

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3 + H_2O. \tag{3}$$

Equations (2) and (3) are a simplistic representation of the carbonate buffer. Nevertheless, they indicate whether each reaction in table 2 tends to drive the equilibrium towards net dissolution or precipitation of carbonate.

The sub-oxic zone reactions are the only ones that individually can precipitate carbonate. Because of the low reaction rate of iron reduction, only manganese and nitrate reduction are effective and even these are important only in pelagic or non-marine environments with a low sedimentation rate. In contrast, the products of anoxic zone diagenesis are volumetrically important in sedimentary rocks and investigation of the exact mechanism of their precipitation is an illuminating exercise. Curtis (1977) pointed out the importance of the iron reduction mechanisms (see table 2) in producing alkalinity and thus allowing precipitation of carbonate. The metastable survival of ferric iron permits its reduction to accompany any of the subsequent reactions and thus preserve isotopically and chemically distinctive carbonate. Equally, its absence may lead to a characteristic diagenetic mineral assemblage.

(*d*) *Relation of iron reduction to sulphate reduction*

The association of iron reduction with sulphate reduction is implicit because the latter is recognized by the presence of diagenetic pyrite. The reaction in table 2 shows sulphide ion as the product of sulphate reduction. Four situations can be envisaged concerning the relation of accompanying iron reduction; i.e. before sulphate reduction, simultaneously with it, after reduction and not all.

(i) *Absence of iron*

With no iron available, sulphide is not precipitated and is lost from the system as H_2S. The reaction then can be rewritten as

$$S^{2-} + 2H_2O \rightarrow H_2S + 2OH^-; \tag{4}$$

thus, with the sulphate-reduction reaction in table 2,

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^-. \tag{5}$$

The implication is that some carbonate may be precipitated and that it will be non-ferroan. H_2S will escape and will diffuse in solution into other zones. Only if its concentration is sufficient to saturate the solution will its direction of movement be constrained, as rising gas bubbles. The importance of free H_2S is that it is a mobile reducing agent, unlike organic matter, which may be insoluble.

H_2S will diffuse along a concentration gradient established by its reaction with oxidizing agents or with ferrous iron (to produce insoluble sulphide). Oxidation of H_2S by dissolved oxygen (plausibly a bacterial action) will produce a marked reaction front characterized not only by the redox change but also by the effects on the pH buffer. The net reaction has the potential to lower pH dramatically, i.e.

$$H_2S + O_2 \rightarrow SO_4^{2-} + 2H^+. \tag{6}$$

There is also the possibility of direct (non-bacterial) reaction with ferric-iron minerals. This would be important if the reason for the slow rate of iron reduction were immobility of suitable organic matter. The effects of absence of iron on sulphate reduction will occur also where iron is limiting and has been exhausted (see §4*d*).

(ii) *Reduction of iron before sulphate reduction*

Iron reduction will produce siderite with a negative $\delta^{13}C$ (Walker 1984; Maynard 1982). If there is sufficient suitable organic matter, H_2S will be produced subsequently. The relative stabilities of iron sulphide and carbonate are such that non-ferroan calcite is associated with pyrite (Irwin *et al.* 1977) implying the preferential reaction of Fe^{II} with sulphide. Although there is no evidence for the reaction, it is plausible to postulate the reaction of H_2S with previously formed siderite to give iron sulphides. In the SR (sulphate-reduction) zone non-ferroan calcite could form if no residual Fe^{III} remained (as in §3*d*i).

Kantorowicz (1982) analysed spherulitic siderites from the Middle Jurassic Ravenscar Group of Yorkshire. The average $\delta^{13}C$ composition was $-16.2‰$. They occurred as siderite, rimmed by pyrite crystals, which in turn formed the core to a spherulith of radiating elongate siderite crystals. The texture and isotopic composition suggest that a period of sulphide replacement of carbonate occurred during siderite growth in the FeR (iron-reduction) zone as a result of an influx of H_2S.

(iii) *Reduction of iron simultaneously with sulphate*

The combination of equations for iron and sulphate reduction (FeR and SR, table 2) in the ratio 1:8 will give FeS, the common precursor of FeS_2 (pyrite). Carbonate will be dissolved to maintain pH. We have

$$2Fe_2O_3+4SO_4^{2-}+9CH_2O\rightarrow 4FeS+9HCO_3^-+4H_2O+H^+. \tag{7}$$

The reduction of sulphate to S^0 to convert FeS to FeS_2 can be shown as

$$4SO_4^{2-}+6CH_2O\rightarrow 4S^0+6HCO_3^-+2H_2O+2OH^-. \tag{8}$$

Thus pyrite precipitation will be associated with dissolution of carbonate followed by its precipitation. It is possible that the two processes are interdependent. The reduction of sulphate, like any other chemical process may be controlled by the build-up of the product, H_2S. The removal of H_2S by Fe^{II} may imply that the rate of iron reduction to a certain extent controls that of sulphate reduction.

(iv) *Reduction of iron after sulphate reduction*

The effects in the SR, FeR, and Ox (oxic) zones will be as indicated in §§3*d*i, ii. However, the reduction of iron simultaneous with production of bicarbonate in the Me (methanogenesis) and D (decarboxylation) zones (see table 2) explains why the carbonate precipitated is usually ferroan dolomite or ankerite. In marine waters calcite rather than dolomite is the usual precipitate. This occurs despite the higher concentration of Mg relative to Ca because sea water also contains dissolved sulphate which inhibits the formation of dolomite (Baker & Kastner 1981); below the SR zone, sulphate has been exhausted. All dolomite precipitated is ferroan because in the absence of iron the reactions tend towards dissolution of carbonate. When iron reduction accompanies methanogenesis the reaction can be expressed as

$$13CH_2O + 2Fe_2O_3 + 3H_2O \rightarrow 6CH_4 + 7HCO_3^- + 4Fe^{2+} + OH^-, \qquad (9)$$

and carbonate, which will accommodate Fe^{II}, will be precipitated.

(*e*) *Control parameter for carbonate precipitation and dissolution*

It was shown in §3*d* that availability of iron is necessary for carbonate precipitation in anoxic conditions. Its absence in marine pore waters will lead to the formation of free H_2S, which carries to other zones the reducing power of organic matter and the ability of the SR zone to reduce pH. Thus, in the absence of iron, carbonate dissolution may occur and only with Fe^{III} reduction can carbonate be precipitated in the Me and D zones. Two factors control this aspect of the diagenetic environment; the availability of sufficient reducible Fe^{III} and a sufficient rate of reduction. Examination of table 2 shows that the proportions in which the equations are combined is the factor that affects the overall chemical environment. The single practical expression of this control is the rate of iron reduction relative to that of the reaction pertinent to the particular zone. The iron reduction quotient, ρ, is defined here as

$$\rho_{\mathrm{z}} = \ln\,(8r_{\mathrm{FeR}}/r_{\mathrm{z}}), \qquad (10)$$

where r_{FeR} and r_{z} are the rates of consumption of organic carbon by iron reduction in zone z, and consumption by the reaction specific to zone z, respectively (z is SR, Me, etc.). Therefore, negative ρ values imply low relative rates of iron reduction and positive values the reverse. The factor of 8 means that a zero value for ρ_{SR} indicates that reduced iron is produced at a rate just sufficient to satisfy sulphide in producing FeS; a plausible condition (see §3*d*iii). Although z is constrained to the anoxic zones, a negative ρ_{SR} will affect shallower zones as free H_2S is released. The equivalent logarithmic quotient of the rates of iron reduction in its own zone and in other zones is denoted by ρ'_{z}.

Both the depositional environment and rate of burial will control ρ. For example, tidal or fluviatile sediments may have high Fe^{III} contents and, if buried sufficiently rapidly, will evince positive ρ_{z} values but negative ρ'_{z} values. If sulphate is absent, positive ρ_{Me} or ρ_{D} will ensue. The relevance of the parameter is that it relates directly to the diagenetic environment and thus to the characteristic diagenetic products. Similar ρ_{SR} values may result in near-shore sediments where fresh water has diluted marine pore fluids and in the fully marine equivalent when sulphate has been partially consumed. Thus ρ will vary in time within one zone and may even vary spatially within a zone at one time.

The value of ρ that would allow precipitation or dissolution of carbonate in various zones is shown in figure 3. The vertical scale is calculated as the molar ratio of carbonate:organic carbon consumed in that zone that would have to be precipitated to maintain the pH buffer. For the zones shallower than the SR zone the effect is from migrated H_2S and is shown for various values of ρ_{SR} for the Ox zone and of ρ'_{SR} for the FeR zone. It can be seen that lack of available iron will have the least effect on the precipitation of Me zone carbonate.

(*f*) *Precipitation of phosphate and silica*

A potential problem in recognizing the results of negative ρ_{SR} is that the tendency to lower pH ensures that no carbonate is precipitated. However, for two different reasons both phosphate

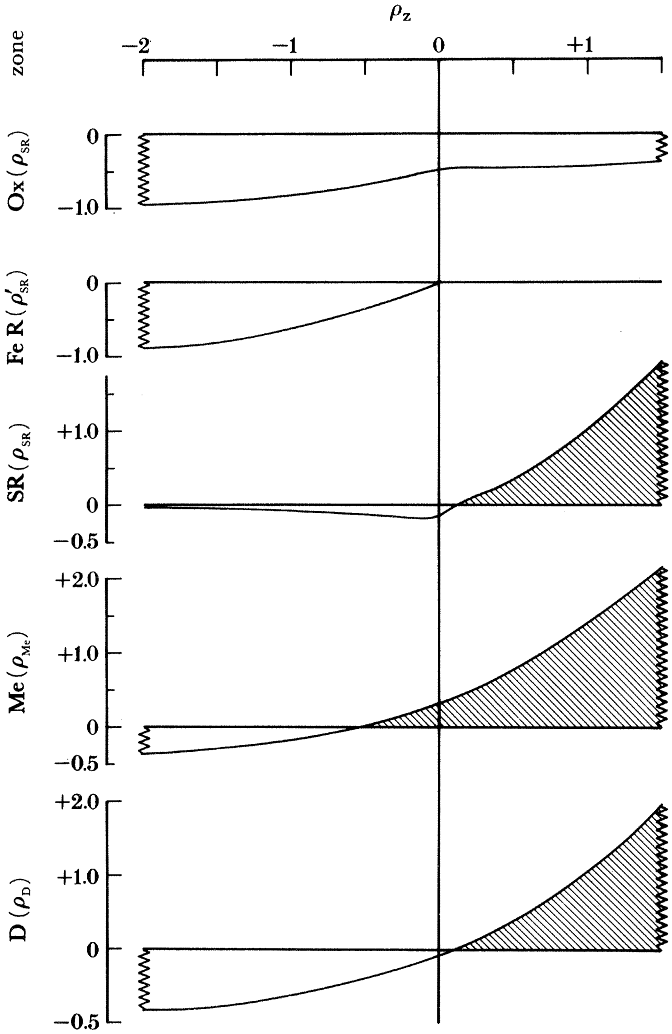

FIGURE 3. The effect of ρ on the ability of a zonal reaction to precipitate or dissolve carbonate. Vertical scale is molar ratio, carbonate: C_{org} consumed. Negative values imply dissolution.

and silica may precipitate in this environment. The work of Nathan & Sass (1981) showed that a lower pH increased the stability of apatite and francolite (carbonate–fluorapatite) relative to that of carbonate. In a situation where carbonate may be dissolved, phosphate may be preferentially precipitated or preserved.

The precipitation of silica is a more complex matter. Although the mechanism of the reaction has not been explained satisfactorily, Lovering & Patten (1962) defined conditions in which silica precipitates. Supersaturated solutions (0.1 %) were stable in the presence of air but precipitated two-thirds of the silica under an atmosphere of CO_2. The effect is similar to that engendered in synthesis of quartz for isotopic fractionation calibrations; sodium bicarbonate is added as a 'mineralizing agent' to ensure crystallization of silica. An account of geological environments that exemplify the conditions in which diagnostic diagenetic minerals form follows in §4.

4. Geological examples

(*a*) *Evidence for oxidation of hydrogen sulphide*

The isotopic composition of sulphur allows a test of the concept of reflux and oxidation of H_2S that should be associated with a reduction of pH (see equation (6)). The process of bacterial sulphate reduction imposes a large isotopic fractionation. The product sulphide has a $\delta^{34}S$ value at least 20‰ less than the original sulphate but fractionation of about -40‰ is more common (Rees 1973). In contrast, microbial oxidation of both pyrite and elemental sulphur to sulphate only produce fractionations of -0.3 to -1.7‰ (Nakai & Jensen 1964). Thus, oxidation of sulphide produces sulphate that is isotopically very negative relative to the original sulphate. The production of isotopically negative *sulphide*, however, in the original reduction process, leaves the residual sulphate isotopically positive after partial reaction. The $\delta^{34}S$ compositions in the SR and Ox zones are characterized by being different from each other and from the original sulphate.

Seawater-sulphate isotope composition provides a useful base value with which to compare diagenetically modified sulphate. Although seawater $\delta^{34}S$ has fluctuated during geological time, the long residence time of sulphate (*ca.* 20 Ma) compared with its mixing time (*ca.* 2×10^{-3} Ma), results in uniform isotopic composition at any one time (Claypool *et al.* 1980).

A possible example of sulphide oxidation was recorded by Goldhaber & Kaplan (1980) in pore-water analyses from a core from Gulf of California. H_2S was present from a depth of 0.35 m to just more than 30 m. The pore water from the core immediately above this interval contained sulphate different from that in sea water; the sulphate concentration was 15% greater and its isotopic composition 4‰ more negative than in sea water. Both of these anomalies can be explained by addition of a contribution of diagenetic sulphate from sulphide oxidation.

(*b*) *Phosphate–glauconite assemblage*

The phosphate mineral francolite (carbonate–fluorapatite $(Ca, Mg, Sr, Na)_{10}(PO_4, SO_4, CO_3)_6F_{2-3}$), offers a unique opportunity to define diagenetic environments. Its structure can accommodate minor but significant amounts of sulphate and carbonate, 2–3% and 6.5–8%, respectively. The $\delta^{13}C$ and $\delta^{34}S$ compositions of the substituents in this accommodating mineral were used to characterize the genetic origin of various phosphorites (Benmore *et al.* 1983; Benmore 1983). The data could be grouped according to the various combinations of isotopic compositions and are listed in table 3 together with the diagenetic zone, ρ and implied relative rate of burial (note that the $\delta^{34}S$ values are given with respect to contemporaneous seawater

Table 3. Characterization of phosphates by isotopic composition of substituted carbonate and sulphate

mode of occurrence	$\delta^{13}C_{P.D.B.}$ range	$\delta^{34}S^*_{c.s.w.}$ range	zone of phosphatization	ρ_{SR} range	relative rate of burial
replacing carbonate	-1.2–-0.2	-1.5–$+0.5$	Ox	< -2	slow
authigenic + Fe^{III} oxides + glauconite (+ pyrite sometimes)	-4.5–$+0.3$	-11.5–-10.5	Ox	0–-1	fast
authigenic + Fe^{III} oxides + glauconite + free H_2S + trace pyrite	-9.5–-8.9	-7.6–-2.0	FeR	-2–-1	fast
replacing carbonate + pyrite	-8.0–-3.8	$+4.3$–$+5.3$	SR	-0.5–$+0.1$	fast

* $\delta^{34}S$ with respect to contemporaneous seawater sulphate.

sulphate; Claypool *et al.* 1980). It can be seen that the low-pH environment, necessary for phosphate precipitation, may occur in different zones depending on the ρ value. The evidence for the lower pH is shown either by negative $\delta^{34}S_{c.s.w.}$ in the FeR zone (oxidation of sulphide) or replacement of carbonate in the Ox and SR zones (preferential preservation of phosphate relative to carbonate). Thus, at the same rate of burial, the variation of ρ_{SR} will control the depth at which phosphatization occurs.

Further evidence for oxidation of sulphide is given by the common association of glauconite with phosphate to form a characteristic mineral assemblage (see table 3). Glauconite, a mica mineral, is an unusual low-temperature phase in that it contains both Fe^{II} and Fe^{III} and thus reflects an unusual redox environment. It seems most likely that it will form in the FeR zone after partial reduction of Fe^{III}. Equally, partial iron reduction may occur in any of the subsequent zones but in all cases there will be competition for the Fe^{2+} ion from sulphide or carbonate. In the FeR zone, oxidation of sulphide may reduce pH so that carbonate is not a stable phase although phosphate might be so. The system requires a negative ρ_{SR} and also $\rho'_{SR} > \rho_{SR}$; a suitable environment would be one with low iron input and a relatively low rate of burial, to ensure diagenesis of organic matter in the shallower zones. An example of such a system has been described recently by Krajewski (1984) who observed phosphate cements in glauconitic limestone. Evidence for the rate of burial is that the Albian age limestone forms a condensed sequence. Both in this case, and where the phosphate–glauconite assemblage is associated with hard grounds in the chalk (see, for example, Jarvis *et al.* 1982), it is probable that some of the primary carbonate of the sediment has been lost by dissolution in the low-pH conditions.

(*c*) *Creation and maintenance of sub-oxic environments*

The sub-oxic zones, as a group, occupy a precarious position sandwiched between the more substantial Ox and SR zones. At first it seems unlikely that the specific environment that they comprise could be maintained in one part of the sediment column except under stable conditions of sediment accumulation. This may be the case for the environment of formation of phosphate (off-shore Peru–Chile) described by Burnett *et al.* (1980). The phosphates are forming at the periphery of a sub-basin of anoxic sediments. However, catastrophic events during deposition may create a situation where sulphate reduction and oxic conditions are juxtaposed, producing oxidation of H_2S and concurrence of Fe^{II} and Fe^{III}. Many possible examples can be envisaged in which oxygenated water is given access to the SR zone, such as decrease in water depth and increased wave action or emergence and introduction of fresh water to the formation. Near-shore and inter-tidal sediments may be subjected to alternation of anoxic pore water and fresh water and the interface between the two will pass through the same sediment many times. The implicit dynamic nature of the environment may explain why glauconite, the characteristic zone mineral, usually occurs as microcrystalline aggregates rather than as the larger euhedral forms of other phases.

The high reactivity of Fe^{2+} and the fact that it is often produced in association with a suitable reagent such as HCO_3^- may indicate that it will have a limited mobility in a diagenetic environment because it is precipitated rapidly. Large crystals may not form under these conditions. This is a plausible explanation for the observation that most diagenetic siderite is micritic. It may be that only with a low activity of HCO_3^- and S^{2-} can iron silicates form (for example, berthierine, see C. D. Curtis, this symposium).

It can be seen that the essence of the sub-oxic environment is the confrontation of sulphate reduction and oxic conditions. This has been described above as catastrophic introduction of oxygenated water or vertical migration of H_2S. §4*d* and §4*e* describe the effects of radial diffusion of H_2S into relatively high-Fe and low-Fe environments, respectively.

(*d*) *Carbonate–pyrite concretions*

Sub-spherical calcite concretions with pyrite rims occur in beds of the Toarcian (Late Lias) shales of NE England (the Jet Rock) and were described by Raiswell (1976). Coleman & Raiswell (1981) reported their isotopic geochemistry and considered that they represented successive concentric growth zones that had sampled variations in pore-water chemistry during burial. However, Coleman & Raiswell (1985) have reinterpreted the data and a summary of some of their findings follows.

The sediments were deposited in anoxic bottom-waters in which sulphate reduction was occurring. In the water and shallowest part of the sediment, ρ approximated to unity as framboidal pyrite was precipitated and primary carbonate was dissolved: ammonites are present as pyrite casts. Early in the burial history concretionary growth was initiated and pyrite concentration increases from the centre of the concretion to its rim, which may contain as much as 60% pyrite. Sulphur isotope data indicate that the fine-grained pyrite in the host sediment and the centre of the concretion was precipitated in a system open to sulphate replenishment. The concretion pyrite resulted from a closed system. Radially from the centre of the concretion the isotope data indicate progressive depletion of sulphate but even at the rim there was still at least 30% of the sulphate remaining. This implies that availability of iron decreased during sulphate reduction and eventually ρ_{SR} became sufficiently negative to allow non-ferroan carbonate to precipitate (see §3*d*i and figure 3).

It appears that localization of sulphate reduction after open-system reduction ceased (subsequently the concretion centres) produced local, negative ρ_{SR} conditions. Because it is unlikely that the rate of sulphate reduction increased it must have been because of exhaustion of locally available Fe. The volume of the environment was defined by the centripetal diffusion of H_2S and its fixing as a spherical shell of sulphide. Carbonate was precipitated within this shell; beyond it the low pH inhibited its precipitation.

(*e*) *Silica concretions*

The Late Cretaceous Chalk of NW Europe is a fairly pure carbonate rock in which the most obvious diagenetic products appear as bedded or nodular chert, flint. A model for flint formation has been proposed recently by Clayton (1984) who developed his concepts from a geochemical investigation of the origin of paramoudras (these are tubular or barrel-shaped flints, often up to 30 cm in diameter). The flint occupies an annular volume around a central core of chalk, centred on a very narrow vertical burrow. The burrow contains pyrite while the chalk around it has disseminated pyrite and glauconite. This chalk, unlike the surrounding host chalk, is very heavily cemented (with non-ferroan calcite). The model requires a high concentration of organic matter in the burrow, producing in it sulphate-reducing conditions, while the surrounding chalk is still oxic. The low availability of Fe ensures that ρ_{SR} becomes negative with a consequent loss of H_2S, allowing precipitation of the calcite cement, which has a very negative $\delta^{13}C$ value. H_2S diffuses radially from the burrow, consumes locally available iron (giving disseminated pyrite) and is oxidized. The consequent pH buffering requires dissolution of chalk carbonate. The high concentration of dissolved CO_2 or bicarbonate causes precipitation of silica (Lovering & Patten 1962) in the oxidation zone. It is important to stress that it is not the (potential) lowering of pH but the concomitant high p_{CO_2} that causes precipitation.

In this example, a chemical zonation was established radially around the burrow, which is the exact equivalent of the vertical zonation observed in normal burial diagenesis (Froelich *et al.* 1979). Silica was precipitated in the sub-oxic zones (MnR (manganese reduction), NR (nitrate reduction) and FeR of table 1) and at their interface with the oxic zone. Clayton (1984) was able to demonstrate this by chemical analysis of trace constituents in the flint of the paramoudra. Radial concentration profiles through the flint show a peak of Fe followed by one for Mn in sections from the inner edge to the periphery. There is a phosphate peak that covers the zones of high Fe and Mn and indicates sufficient lowering of pH to lead to its preferential preservation relative to carbonate (Nathan & Sass 1981). The silica has preserved the chemical zonation of the environment that caused its precipitation. Clayton (1984) used a similar model of local sulphate-reducing conditions in other burrows to explain the formation of the more common nodular flints, which also often contain a highly cemented chalk core. This elegant piece of work explains the common observation that diagenetic silica concretions occur in carbonate hosts but not mudstones or siliciclastics.

5. Conclusions

The preceding sections show the wealth of variety of diagenetic mineral assemblages that arise from a common set of processes applied to a range of sedimentary components. The main controls are ratio of organic matter to inorganic detritus, rate of burial and availability of the various inorganic oxidizing agents (especially Fe^{III} and SO_4^{2-}). Although the number of possible combinations of reactions is immense, in fact the potential complexity is reduced by the necessary relation of the diagenetic to the depositional environment. The geological situation will dictate which species are present or absent. An hypothetical example would be a series of coastal sediments that cover the range from freshwater swamps to fully marine deposits; with greatest accumulation of organic matter occurring in the mudstone units of the sediment packages. Diagenetic activity will be concentrated in those mudstones but the products may be found in other lithologies. The two main controls on diagenetic style are seen to be the availability of iron and sulphate. The freshwater system will be relatively poor in solutes and thus, if available, Fe^{2+} will dominate the cation system. In contrast, the marine system will have a high content of dissolved species, including SO_4^{2-}, Mg and Ca. Application of the reaction schemes outlined in §§3 and 4 give the range of diagenetic phases expected in each zone. This hypothetical example is illustrated in figure 4. For two reasons it would be expected that more than one phase would result even from burial at a constant rate. Although the average rate of deposition is constant, the episodic nature of most sedimentation causes variation in diagenesis. Additionally, the intercoupling of diagenetic zonal chemistries, as expounded in §3, implies simultaneous formation at different depths of burial.

A further cause for variation in diagenetic style is typified by the examples given in §4. The concretionary phases all grew as a result of localized diagenetic activity. The most dramatic effects resulted from the confrontation of different pore-water chemistries. This must be expected to occur on all scales from inter-granular pore to whole-formation size. Usually the

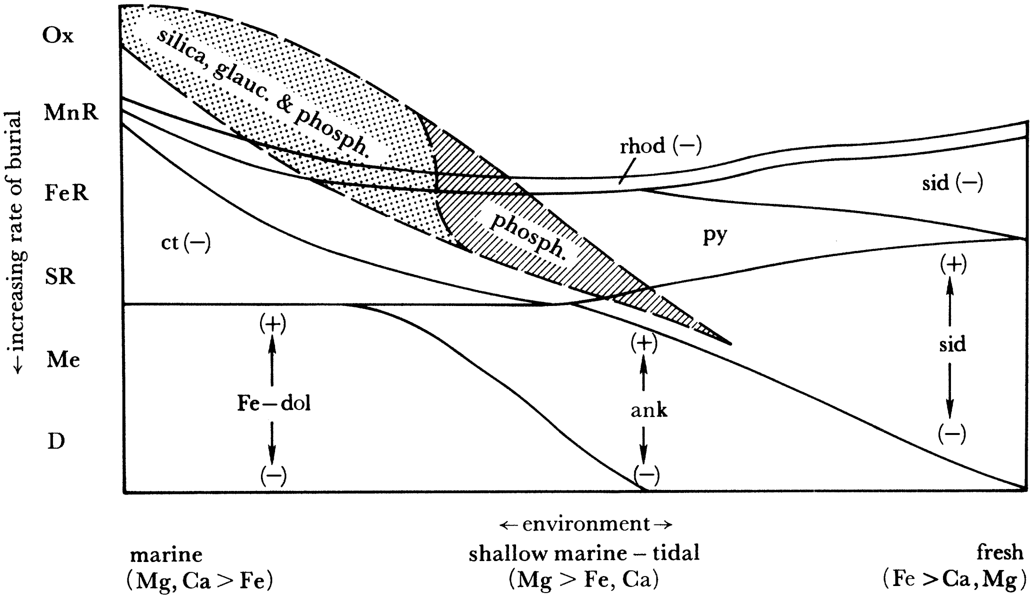

FIGURE 4. Hypothetical example of expected diagenetic assemblages resulting from the relation of diagenetic to depositional environment. The ornamented fields show minerals precipitated under low-pH conditions. The signs indicate the $\delta^{13}C$ value of carbonate materials.

cause will be heterogeneous distribution of organic matter (sometimes described as 'the dead cat in the mud concept'). This will lead to localized intense diagenetic activity and, consequently, both positive and negative diffusional gradients on all the scales mentioned above. Catastrophic changes in sedimentation rate also will lead to juxtaposition of different pore-water systems.

From these examples it can be seen that theoretical chemistry is relevant to practical geology. Diagenesis of organic matter explains a wide range of common geological observations. Apart from the occurrence of carbonate concretions the most apparent are the occurrence of flint nodules, their restriction to the chalk and the association of phosphate with glauconite.

I am indebted to my former research students, Iain Scotchman, Chris Clayton, Richard Benmore and Ian Fisher. They worked on various aspects of these problems and were bright and dedicated, sometimes both. I thank them for maintaining a high level of intellectual entropy in my laboratories. I am grateful to Maureen Sullivan and Bob Phillips for producing the drawings and to the girls of the E.P.D. typing office for fast and sympathetic preparation of the typescript. Thanks also to Chas Curtis for a constructive review.

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Discussion

R. A. Berner (*Department of Geology and Geophysics*, *Yale University*, *U.S.A.*). The amount of carbon present in the sediment controls the extent to which reduction can occur. The schemes I discussed are only valid if there is more than 1% carbon present. If less carbon is present it is possible to produce a sub-oxic or post-oxic environment, but, because of the small amount of carbon that must be present, the abundance of the characteristic diagenetic minerals will also be small. For this reason the post-oxic environment may be hard to identify. If, however, the sediment is reworked and minerals such as glauconite and phosphorite are concentrated, the environment becomes easier to recognize.

M. L. Coleman. It is important to examine the rocks petrographically as well as chemically. If, for instance, the phosphate minerals formed as a cement rather than reworked nodules, they must have been deposited *in situ*.

B. Durand (*Institut Français du Pétrole*, *Rueil Malmaison*, *France*). Most of the organic matter is insoluble, so how can it be involved in organic–inorganic interactions and how can it be used by bacteria?

M. L. Coleman. In sulphate reduction the sulphate is soluble and can therefore move to the organic matter by diffusion. However, neither iron nor manganese are soluble in their oxidized states, and this lack of solubility may explain why iron reduction often does not occur until the sulphate-reducing and methanogenic bacteria become active. Once hydrogen sulphide and methane are being produced, reduction can occur throughout the sediment. It is also possible that the considerable amount of organic material dissolved in the pore-waters can transport the reducing compounds from the insoluble organic matter to the region where ferric iron is present.

P. S. Meadows (*Zoology Department*, *Glasgow University*). Dr Coleman's comments on dissolved and insoluble organic matter are of great interest, and I would like to make two points in relation to them.

The first is that although we usually assume micro-organisms are utilizing – and hence breaking down – dissolved organic matter, there is no intrinsic reason why bacteria should not also utilize and break down insoluble organic matter. For example, there is a great deal of interesting recent work on bacteria attached to solid surfaces.

The second point is that the organic matter in sediments can be considered as being made up of two related sources; (i) that originating from the overlying matter in the form of dead organisms or their breakdown products and (ii) the cells of the sedimentary bacteria themselves.

G. Eglinton (*Organic Geochemistry Unit*, *School of Chemistry*, *University of Bristol*). As authigenic minerals grow they presumably trap both water and organic matter in fluid inclusions and on grain boundaries. Are such inclusions seen in petrographic studies of such minerals? This process could remove organic matter from further diagenesis, and could also allow the pore-water to be sampled.

M. L. Coleman. Large sparry calcite crystals often have a few inclusions within them, but the same may not be true of the fine-grained cement often found in carbonate concretions. I think a detailed study of inclusions could be very worthwhile.