Sedimentary Geochemistry: Environments and Processes Dominated by Involvement of an Aqueous Phase [and Discussion]

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GEOCHEMISTRY

Sedimentary geochemistry: environments and processes dominated by involvement of an aqueous phase

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Crust and mantle processes yield mineral assemblages which are not generally stable in Earth surface environments. Uplift to the zone of weathering therefore initiates chemical reactions which produce quite different assemblages. The precise nature of the resulting minerals depends much upon the composition of the aqueous phase present. Erosion, sedimentation and diagenesis move weathering products through a succession of chemical environments. Further solid–solution reactions occur at each stage.

Until recently, the least-well documented part of this cycle was burial diagenesis. New information provided by oil companies from their submarine exploration programmes has done much to rectify the situation. It is now possible to present a fairly complete account of the important chemical reactions occurring at each stage of the surface cycle. The major conclusion to be drawn from this exercise is that reactions involving an aqueous phase play a very important part in geological evolution as a whole.

1. Introduction

(*a*) *Objectives*

Sedimentary geochemistry is concerned with chemical investigation of geological processes and materials in low temperature and pressure environments at or relatively close to the Earth's surface. Since the theme of the meeting is both wide-ranging and forward-looking, this paper will attempt to make reference to most of the important subdivisions of sedimentary geochemical endeavour, but not to present any kind of historical review. Areas of intensive current activity and likely future expansion will be emphasized.

(*b*) *Sedimentary processes and the 'surface cycle'*

The low temperature and pressure environments and processes that are the concern of the sedimentary geochemist are represented diagrammatically in figure 1. All the principal reactants and products, solid, liquid and gaseous are included. The only region of uncertain delineation is between deep burial diagenesis and low-grade metamorphism.

A personal interpretation is that the boundary lies at the point of wholesale recrystallization. Muffler & White (1969) showed that clay minerals and carbonates in Quaternary sediments of the Colorado River Delta were converted to muscovite/chlorite assemblages below 210 °C in the Salton Sea geothermal field. Such temperatures are reached at shallow depths (1–2 km) in this region of high thermal gradient.

In Gulf Coast sediments, Perry & Hower (1970) traced the conversion of montmorillonite to illite to depths in excess of 5 km and temperatures up to 166 °C. In these sediments wholesale recrystallization does not occur. These few observations suggest that diagenetic (as distinct from metamorphic) reactions occur at temperatures up to, or perhaps a little in excess of 170 °C in burial environments where water is present as a liquid phase.

A case is made in figure 1 for recognizing three major divisions within the surface cycle. Of these, weathering and diagenesis are long-term processes where interaction between different system components takes place over considerable time intervals. The reactions that occur during erosion and deposition are by contrast rapid simply because of the transitory nature of the environment. Although it is certainly true that physical processes play a much more significant rôle during transport and deposition, some chemical reactions of import do occur (§ 3). Furthermore, all chemical sedimentation (carbonates in particular) must be considered within this division.

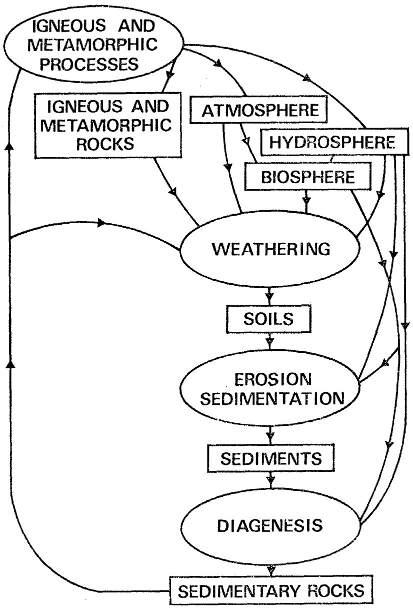

FIGURE 1. The surface geochemical cycle.

In the following sections, evidence relating to processes occurring in each of these three divisions is reviewed. Much of the information relates to present day processes but links with ancient sediments are made wherever possible. For reasons of space and time, the discussion will mostly revolve around clay-rich systems. It should be noted, however, that clay material is the most important constituent of the World's soil and weathering mantle and mudrocks constitute something over 70 % of the sedimentary column.

2. WEATHERING

(a) *Contrasting environments*

Igneous and metamorphic rocks are formed under conditions very different from those prevailing at the Earth's surface. Higher temperatures and pressures with relatively low oxygen and water activities favour minerals with low hydroxyl content, low valence states (notable Fe^{II}, Mn^{II} and S^{II}) and relatively dense crystal structures in which ionic bonding plays an important part.

In the presence of an oxygen-rich gas phase and dilute aqueous solutions, the same minerals hardly can be anticipated to be stable. These conditions will favour silicate structures determined by essentially covalent Si–O, Al–O and H–O bonding. Metals such as calcium and magnesium, sodium and potassium will tend to partition in favour of the aqueous phase since all form stable monomeric solvated species (in polar solvents). Only in evaporitic soil régimes will concentration favour precipitation of these and similar metal cations as simple salts or alumino-silicates.

(*b*) *Soil profile descriptions*

Soil scientists, geomorphologists, geologists, engineers and geochemists have studied the weathering mantle, albeit from different viewpoints, for very many years. Texts such as those by Loughnan (1969) and Carroll (1970) summarize mineralogical and chemical descriptions of soil profiles in different climatic situations and on different substrates. It seems fair to suggest, however, that many geologists and geochemists are unfamiliar with this particular facet of Earth science.

Table 1 is taken from Bunting (1965) and illustrates the effect of humid tropical weathering on basalt. Calcium, magnesium, sodium, potassium and silicon have been very extensively leached. The residuum is enriched in aluminium, iron (ferric) and water as kaolinite and soil sesquioxides (hydrated oxides of iron and aluminium). Acid igneous rocks, sediments and metamorphic rocks all are drastically and rapidly modified under humid tropical weathering conditions. Quartz is often completely removed (thereby negating the rather widespread view that it is a resistate mineral). Under cool, humid climatic conditions, quartz is relatively more stable and tends to accumulate in podsols.

Table 1. Composition of basalt and soil horizons, Kaui, Hawaii
(after Bunting 1965, p. 34)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	H_2O
soil	9.2	24.4	35.8	0.3	0.3	0.21	Nil	6.89	0.37	15.0
subsoil	9.9	28.9	35.4	0.2	0.2	0.06	Nil	5.54	0.40	17.1
mantle	32.8	24.0	21.0	3.8	2.4	0.21	0.34	3.54	0.45	10.3
rock	49.0	13.7	13.2	7.3	13.5	0.27	1.62	1.73	0.13	0.4

The most obvious approach to formulation of the chemical reactions involved in weathering is via subtractive calculations, assuming *in situ* soil formation. Bunting (1965) gives a simple explanation of such a formulation in the weathering of orthoclase to kaolinite.

$$2KAlSi_3O_{8(s)} + 11H_2O_{(l)} = Al_2Si_2O_5(OH)_{4(s)} + 4Si(OH)_{4(aq)} + 2K^+_{(aq)} + 2OH^-_{(aq)}. \qquad (1)$$

The problem with this and all similar formulations is that the resulting soils would be strongly alkaline whereas soils in general are much more commonly neutral or acid. Ionic solutions like ionic solids must preserve charge balance. This means that acid anions must be generated in weathering. Furthermore silicic acid $Si(OH)_4$ is undissociated except in alkaline solution. While providing invaluable background information, soil mineralogical studies cannot provide the key to weathering processes.

(*c*) *Aqueous phase studies*

A considerable fund of detailed compositional data exists within the literature of soil chemistry and experimental botany. The solution products of the total weathering process, however, find their way into the major rivers of the world and thence to the sea. Livingstone (1963) compiled the information then available for the composition of important freshwater bodies and table 2 summarizes his final average data.

The cations found in natural waters are the same few seen to have been obviously removed from common soil profiles. The critical new input is that the waters draining each continent are rather similar and bicarbonate, sulphate and chloride (in that order) are the important anions. Since atmospheric precipitation includes sodium chloride cycled directly from the oceans as aerosols, bicarbonate and sulphate clearly emerge as the critical anions of weathering.

Table 2. Mean composition of river waters of the World, in parts per million

	HCO_3	SO_4	Cl	NO_3	Ca	Mg	Na	K	Fe	SiO_2	sum
North America	68	20	8	1	21	5	9	1.4	0.16	9	142
South America	31	4.8	4.9	0.7	7.2	1.5	4	2	1.4	11.9	69
Europe	95	24	6.9	3.7	31.1	5.6	5.4	1.7	0.8	7.5	182
Asia	79	8.4	8.7	0.7	18.4	5.6	9.3		0.01	11.7	142
Africa	43	13.5	12.1	0.8	12.5	3.8	11	—	1.3	23.2	121
Australia	31.6	2.6	10	0.05	3.9	2.7	2.9	1.4	0.3	3.9	59
World	58.4	11.2	7.8	1	15	4.1	6.3	2.3	0.67	13.1	120
anions[1]	0.958	0.233	0.220	0.017	—	—	—	—	—	—	1.428
cations[1]	—	—	—	—	0.750	0.342	0.274	0.059	—	—	1.425

Source: Livingstone (1963, Table 81).

More recently, investigators have made studies of both solid and solution components of a weathering complex and have attempted quantitative assessments of material throughput within a given drainage basin. The work of Cleaves, Godfrey & Bricker (1970) is notable in this respect.

Similar reasoning has been applied to weathering reactions on a global scale. The aim is to quantify the total flux of materials through each stage of the surface cycle. Kinetic considerations are of paramount importance. The general principles of these approaches are outlined in Garrels & MacKenzie (1971) who have done much in this field.

(*d*) *Realistic weathering equations*

Having identified the principal solid and solution products of weathering it is possible to write chemical equations which are reasonably representative of the overall process. The first step is to establish by what means the common acid anions are introduced to the profile.

Carbon is fixed by plants from the atmospheric reservoir by photosynthesis. In so doing, the lighter stable isotope ^{12}C is enriched. Plant root respiration and microbiological degradation of plant detritus maintains high carbon dioxide partial pressures in soil pore space. Reversible dissolution and dissociation according to equation (2) takes place. The

$$H_2O_{(l)} + CO_{2(g)} \rightleftharpoons H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3(aq)}, \tag{2}$$

equilibrium constants are well known. Weathering of anorthite then can be expressed thus:

$$CaAl_2Si_2O_{8(s)} + 3H_2O_{(l)} + CO_{2(g)} \rightarrow Al_2Si_2O_5(OH)_{4(s)} + Ca^{2+}_{(aq)} + 2HCO^-_{3(aq)}. \tag{3}$$

This reaction yields the most commonly observed solid and solution products of weathering. Whether or not the soil would be acid, would depend upon the relative rate of the forward reactions (2) and (3).

It should be noted here that microbiological degradation products include many organic acids which can be extremely effective in mobilizing metal cations. A considerable amount is known about such phenomena and metal–chelate complexes have been isolated from natural systems. It is probable, however, that many of these organic molecules are relatively unstable in oxidizing surface waters and bicarbonate represents the final oxidation product.

Returning to table 2, sulphate is seen to be the second important anionic species. Some finds its way into the surface cycle by dissolution of evaporite salts but this fraction plays no part in chemical weathering. The key reaction is oxidation of sulphides of which pyrite is by far the most abundant:

$$2FeS_{2(s)} + 4H_2O_{(l)} + 7\tfrac{1}{2}O_{2(g)} \rightarrow Fe_2O_{3(s)} + 8H^+_{(aq)} + 4SO_4^{2-}{}_{(aq)}. \tag{4}$$

Ferric iron is very stable and highly insoluble in soil systems (table 1). The solution products sum to sulphuric acid which is extremely active in metal cation replacements similar to equation (3).

Equations (2) and (4) demonstrate the introduction of acids into soil profiles. It is the rate of generation of acids which is one of the most vital controls of weathering.

(*e*) *Environmental influence on weathering rate*

Once reasonable equations can be written to represent the weathering process, it is relatively simple to identify the fundamental factors governing the rate and style of chemical weathering in different environments. At the simplest level, equilibrium considerations suggest that the forward direction of equation (3) will be favoured by high activities of water and carbon dioxide (reactants) and low activities of dissolved calcium and bicarbonate (solution products). The activities of the solids cannot vary. Conditions of high rainfall, high organic productivity and good drainage (for solute removal) promote these conditions. Higher temperatures (for kinetic reasons) increase reaction rates and organic productivity. Chemical weathering is well known to be most intense in well drained areas in the humid tropics and subtropics.

Note that all reactions involve dissolved species. Removal of the aqueous phase should catastrophically reduce reaction rates. This is certainly the case in permafrost regions. Pore solutions are often present, however, in hot desert environments such that chemical weathering does take place. Links between reaction rates and environmental factors are explored more fully in Curtis (1976*a*).

(*f*) *Free energy changes*

None of the chemical weathering equations so far presented is complete in the sense that no account is taken of the energy changes that always accompany chemical reactions. Measurement, calculation and analysis of these energy changes constitutes the science of chemical thermodynamics. The application of solution thermodynamics to geology was pioneered by R. M. Garrels some 25 years ago and must rate as one of the major contributions to geochemistry.

Analysis of energy changes as a function of mineral assemblage, pore solution composition and gas phase composition enables stability relationships of different minerals to be established in terms of measurable environmental variables. The maximum concentration of silica that can stably coexist with gibbsite, for example, is minute and can be quantified (log $[Si(OH)_4] = -4.7$; Garrels & Christ 1965, p. 361). Since these concentration levels are almost invariably exceeded by orders of magnitude in diagenetic environments, gibbsite is very rarely found in sedimentary rocks even though it is a common constituent of soils in humid climates (Curtis & Spears 1971).

The rates of chemical reactions occurring in surface environments may be so slow that equilibrium is never fully attained. This has led to criticism of the use of the methods of thermodynamics in weathering situations where kinetic factors may play a dominant rôle. This is misguided criticism unless kinetic factors are totally ignored. Solution thermodynamics can establish the direction of reaction by prediction and, in many cases, this is most useful. Sedimentary geochemistry, thanks to the work of people like Garrels, is at least on the threshold of becoming a predictive science.

It has long been established that different primary minerals persist for very different times in soil profiles: some are very much less susceptible to breakdown than others. Olivines, for example, breakdown very rapidly whilst minerals like zircon and tourmaline are so resistant to weathering that they apparently survive several 'trips' through the surface cycle. Curtis (1976*b*) has shown that there is a direct correlation between mineral persistence and the free energy released (per mole) in decomposition to typical weathering products. The precise significance of this is not absolutely clear since kinetic phenomena (such as persistence) should not be simply related to thermodynamic stability.

(*g*) *Weathering mechanisms*

A case has been made for suggesting that anion production reactions, especially for bicarbonate and sulphate, are critical factors in chemical weathering. Breakdown of metal silicates, however, occurs in response to hydrogen ion input in both cases:

$$\text{silicate—O—M} + H^+ \rightarrow \text{silicate—O—H} + M^+, \tag{5}$$

with solvated metal cations removed in solution. Hydration also takes place whereby water molecules are added to the silicate 'core' to produce two hydroxides:

$$\text{silicate}{=}O + H_2O \rightarrow \text{silicate}{=}(OH)_2. \tag{6}$$

In this case one of the silicon–oxygen bonds is broken. This can be taken a stage further where monomeric silicic acid is produced:

$$\text{silicate}{=}Si{=}O + 3H_2O \rightarrow \text{silicate}{=}(OH)_2 + Si(OH)_4. \tag{7}$$

Surface hydration mechanisms of this type explain the relatively rapid dissolution of quartz in warm humid climate soil profiles.

A survey of mineral breakdown in weathering shows that three processes are particularly significant: (i) acid induced metal cation leaching; (ii) hydration; (iii) oxidation of Fe^{II} to Fe^{III}.

It is interesting to note that either hydrogen ions (protons) or electrons are involved. Transport of these subatomic particles is greatly favoured on size criteria and rapid proton or electron transfer steps may be rate determining.

(*h*) *Summary*

The products of chemical weathering are soils and aqueous solutions. The latter are continuously transported to the oceans whereas the former migrate very slowly in slope-wasting processes until some unusual storm causes erosion and the next stage of the surface cycle is entered.

The solid products, on a worldwide basis, contain much clay-sized material which includes distinct mineral species (the clay minerals) and a complex of amorphous aluminium, iron and silicon compounds together, in many cases, with significant solid organic matter. Some of these compounds are truly stable in the weathering environment, others, such as residual 'primary' minerals and organic matter persist only as a result of favourable kinetic factors.

3. Transport, deposition, halmyrolysis

The bulk of terrestrial sediment is introduced to the oceans by major river systems. Much of the solid material will have passed through several cycles of weathering, erosion and deposition before it enters the sea. Only rarely (catchments within tectonically active regions immediately adjacent to ocean basins) will 'primary' minerals escape the drastic effects of chemical weathering to be deposited more or less unaltered.

Transport and deposition processes fractionate the components of eroded soils largely on the basis of particle hydrodynamic equivalence. Clay minerals, amorphous hydroxides and organic detritus separate and accumulate as muddy sediments. Comparison of the worldwide distribution of different clay mineral types in oceanic clay sediments (Rateev *et al.* 1969) with the distribution of clays in the World's soils (Gradusov 1972) shows that sediment distributions reflect drainage patterns and further that there are no obvious changes in mineralogy between erosion and sedimentation as a result of rapid clay mineral/seawater interactions.

In order to test for less obvious but still significant reactions Russell (1970) filtered clay from the Rio Ameca (Mexico), reacted this with seawater in the laboratory and also collected clay samples from shallow water marine environments close to the rivermouth. He was able to demonstrate that, although there was no evidence for structural modification, exchangeable Ca^{2+} was rapidly replaced by K^+, Na^+ and Mg^{2+}. There was no *net* removal of cations from seawater.

Significant chemical reactions therefore do occur when soil minerals enter the sea (halmyrolysis). They probably account for the removal of much of the K^+ introduced each year to the sea in continental solution denudation. Equally, however, they increase Ca^{2+} input while not obviously altering the Na^+ and Mg^{2+} balance.

These 'balance' considerations are most important since the 'steady state' ocean model (for which there is much supportive evidence) demands that the net input of solution products of weathering is quantitatively balanced by sedimentation removal – either by reactions like that described above, or by precipitation. Biogenic calcite, aragonite, silica and organic matter are common precipitate materials and constitute a significant component of modern clay sediments at deposition.

By analogy with Russell's (1970) work (although he was unable to demonstrate it) it is probable that soil sesquioxide and organic fractions also take part in early ion-exchange reactions. It should be noted, however, that their character might be significantly different since some hydroxide soils are positively rather than negatively charged.

4. Shallow burial diagenesis

(*a*) *Introduction: ancient and modern compared*

The mineralogy of ancient shales and mudstones is, in most cases strikingly different from that of present-day surface sediments. Perhaps most obvious is the predominance of ferric iron as sesquioxides in sediments in contrast to the common occurrence of carbonates, sulphides and silicates of ferrous iron in shales and mudstones. Destruction or modification of primary detrital or precipitate phases and precipitation of new ones constitutes diagenesis.

R. M. Garrels recognized the importance of redox reactions in diagenesis (Garrels & Christ 1965). Berner (1964) investigated reduction processes in shallow marine environments and simulated diagenesis in the laboratory. He confirmed the validity of the thermochemical approach and demonstrated the particular significance of dissolved sulphide activity in early diagenetic reactions.

Curtis & Spears (1968) reviewed the published data then available for the composition of natural depositional and sediment pore waters and presented a stability field analysis which concluded that virtually all sedimentary iron minerals containing significant ferrous iron had to be formed in diagenetic rather than depositional environments.

These (and other) studies provide a reference framework within which much more sophisticated experimental and theoretical studies have been undertaken. Pore-water studies, in particular, have been pursued in numerous laboratories. These are important for two reasons:

(i) They are very sensitive indicators of solid-solution reactions.

(ii) Comparison of the actual solid assemblage with that predicted to be stable on the basis of dissolved species gives much information about the potential reactivity of the system and the extent to which kinetic factors must be considered.

(*b*) *Sulphate reduction*

Sayles & Manheim (1975) recently reviewed the results of pore-water analyses from DSDP cores distributed throughout the World's oceans. In all but pelagic clays and very slowly deposited biogenic sediments, systematic changes in pore-water composition occurred with depth below the sediment/water interface. Large sulphate depletions were almost ubiquitous and not uncommonly complete in more rapidly deposited terrigenous sediments. Sulphate depletion was invariably accompanied by enrichment in biocarbonate and ammonia; attesting to the parallel breakdown of organic matter and the very general activity of anaerobic micro-organisms.

Numerous studies have demonstrated that pyrite develops by reaction of other iron minerals and reduced sulphur species. The initial step involves sulphate reducing bacteria and can be represented as:

$$SO_4^{2-} + 2CH_2O \rightarrow HS^- + HCO_3^- + H_2CO_3, \tag{8}$$

where CH_2O represents organic matter. Reactions with ferrous iron (after reduction of sesquioxides) leads first to monosulphide (FeS) precipitation and then pyrite (FeS_2). Kinetic factors which limit the extent of pyrite development have been analysed carefully by Berner (1970). Most obvious are the amount of organic matter that can be metabolized by sulphate reducing bacteria and available iron compounds that are included within the sediment and the maximum rate at which sulphate can diffuse into the sediment from overlying depositional water.

From this and similar studies, it is clear that sulphur in pyrite is predominantly derived from the marine sulphate reservoir and that pyrite formation can only occur at relatively shallow depths where effective diffusive contact with overlying depositional water is maintained. Only when this condition is not satisfied can iron minerals other than pyrite form (Curtis & Spears 1968).

One further study of sulphate reduction demands mention. Presley & Kaplan (1968) traced the fate of different carbon isotopes during sulphate reduction in cores taken from marine basins off southern California. The familiar trend of decreasing sulphate concentration with increasing bicarbonate concentration was observed but the isotopic composition of the bicarbonate changed from $\delta^{13}C_{\text{p.d.b.}} = -1.0‰$ near the sediment/water interface to values approaching those of organic matter ($\delta^{13}C_{\text{p.d.b.}} - = -21.2‰$). The bicarbonate enrichment is due to bacterial oxidation (without fractionation) of organic matter.

(*c*) *Fermentation*

In a study of diagenesis in sediments from a reducing fjord (Saanich Inlet, British Columbia), Nissenbaum, Presley & Kaplan (1972) found complete sulphate removal from most of the cores taken and very high bicarbonate concentrations at greater than 2 or 3 m burial. Surprisingly, isotope analysis demonstrated ^{13}C enrichment with positive $\delta^{13}C_{\text{p.d.b.}}$ values (up to $+17.8‰$). Methane was observed to be present in the cores, and one sample was analysed to give $\delta^{13}C_{\text{p.d.b.}} = -55.6‰$. These findings were attributed to the activity of fermentation bacteria operating in environments free from sulphate.

Very much earlier, Oana & Deevey (1960) had demonstrated similar fractionations in freshwater (sulphate-free) systems where methane production ('marsh gas') is commonplace. Methane, in fact, turns out to be a common constituent of fairly rapidly deposited marine sediments adjacent to continental margins. Some 28 of 193 sites drilled during DSDP legs 10 to 19 encountered methane and the vast majority of samples analysed proved to be very much enriched in ^{12}C (average $\delta^{13}C_{\text{p.d.b.}}$ close to $-75‰$; Claypool, Presley & Kaplan 1973).

Without being able to write meaningful chemical equations for the fermentation process, it does seem possible to make some valid generalizations. The process occurs wherever sulphate reducing bacteria are inactive: either in anoxic freshwater sediments or in rapidly deposited marine sediments below the depth of diffusive sulphate penetration. Other factors limiting fermentation would seem to be the presence of utilizable organic matter (as in § 4*b*) and the absence of poisons – whether self-generated or otherwise.

(*d*) *Carbonates*

Bacterial processes including simple oxidation (close to the sediment/water interface), sulphate reduction and fermentation all introduce bicarbonate to the sediment/pore-water system. Thanks to stable isotope studies it is possible to distinguish between some of these contributions. The activities of aerobic and sulphate reducing bacteria introduce bicarbonate with an isotopic composition very similar to the organic substrate and very different from oceanic reservoir (table 3). Fermentation produces very light methane and heavy bicarbonate while oxidation of upward diffusing methane near the sediment/water interface can produce very light bicarbonate (Nissembaum *et al.* 1972).

All of these processes potentially are capable of causing precipitation of diagenetic carbonate phases. Pore-water cation compositional changes and calculated carbonate saturation levels both suggest carbonate precipitation (Sayles & Manheim 1975) at shallow burial depths.

Ancient sedimentary rocks provide very significant evidence of diagenetic precipitation of carbonates. Whereas $\delta^{13}C_{\text{p.d.b.}}$ values of marine limestones range narrowly around zero, those from diagenetic carbonate concretions within mudrocks vary widely; from −22.7‰ (Galimov & Girin 1968) to +7.7‰ (Curtis, Petrowski & Oertel 1971). Evidence from variations of isotope ratios, carbonate content and enclosed fabric within concretions yields conclusive evidence of development at shallow burial depths (Oertel & Curtis 1972).

TABLE 3. CARBON ISOTOPE DISTRIBUTION: AVERAGE VALUES

	$\delta^{13}C_{\text{p.d.b.}}$‰	source
'magmatic' primary carbon	~ −6	*a*
marine limestones	0	*a*
kerogen (shales and sandstones)	−26	*a*
coals	−25	*a*
petroleum	−26	*a*
natural gas – ethane	−38	*b*
natural gas – methane	−49	*b*
bacterial methane (DSDP)	−75	*c*
ocean ($HCO_3^- + CO_3^{2-} + CO_2$)	0	*a*
atmosphere CO_2	−7	*a*
living matter (land)	−25	*a*
living matter (marine)	−20	*a*
dissolved organic matter (marine)	−27	*a*

Sources: (*a*) Degens (1969); (*b*) Vinogradov & Galimov (1970); (*c*) Claypool *et al.* (1973).

Sayles & Manheim (1975) also demonstrated that, in carbonate sediments where bacterial processes were less active, recrystallization of biogenic carbonates such as high magnesian calcite and aragonite was taking place and dolomite was precipitating. Shallow burial environments must therefore be considered as likely locations for the recrystallization and precipitation of various carbonate minerals with carbonate being supplied both from biogenic primary carbonates and bacterial degradation of organic matter.

(*e*) *Iron, aluminium, silicon and clay minerals*

Apart from studies of pyrite formation, most of the conclusions relating to diagenetic mineral growth at shallow burial depths stem from pore-water studies. The logic is clear; 'since the ratio of dissolved component to solid component for most constituents of the sediments is very small, reactions undetectable in the solids often have a large and readily measurable effect upon the interstitial solutions' (Sayles & Manheim 1975). On the other hand, relatively few workers have really attempted to look for changes in both solids and solutions.

One notable exception was the work of Drever (1971). He examined shallow cores beneath surface sediments already studied for changes occurring between river suspension and marine sedimentation (see §3 – Russell).

The overall proportion of different clay minerals (montmorillonite, illite and kaolinite) did not change between different environments but iron was replaced by magnesium in montmorillonites from the more strongly reducing situations. This effect was concluded to be due to iron extraction from the clay to form sulphides. A small amount of glauconite was found in pellets having the morphology of foraminiferal test fillings. It is worth noting that none of these observations would follow from routine X-ray diffractometry.

Of very great significance was Drever's decision to use selective dissolution techniques in an attempt to follow the progress of X-ray amorphous compounds of Al, Fe and Si. Systematic and very marked depletions in all three were observed in the sequence: river suspended clay–river mouth clay–core samples at surface, 50 and 100 cm depth. The depletions amounted to something like 3.5 % Al_2O_3, 8.0 % SiO_2 and 2.5 % Fe_2O_3 by mass. Such enormous changes would not have been anticipated from pore-water studies. Drever (1971) was not able to arrive at any definitive conclusion about the reactions involving these components but this work identifies an immensely important area for further research. Alumino-silicate reactions on this scale certainly could involve metal cations in such a way as to completely modify pore solution profiles. In more open marine environments amorphous silica input would be further enhanced by the tests of siliceous micro-organisms.

(*f*) *Summary*

By putting together the findings of numerous different workers using a wide range of different investigatory techniques (mostly dealing with present-day sediments but a few with ancient sedimentary rocks) it is possible to draw some fairly definite conclusions about the processes that take place in the uppermost few metres of marine clay sediments. Where organic detritus is present (the norm) bacteria thrive and their by-products are important reactants in mineral transformations. Oxidative bacteria (close to the sediment water interface), sulphate reducing bacteria (down to a few metres) and fermentation bacteria (below the level of complete sulphate depletion in more rapidly deposited sediments) all produce bicarbonate which finds its way into diagenetic carbonates: calcite, dolomite, ankerite and siderite.

In the sulphate reduction zone, all reduced iron precipitates as sulphides and the very low concentrations of ferrous iron expected under these conditions will ensure iron-poor carbonates (calcite and dolomite) will be the only ones to form (Curtis & Spears 1968). In the fermentation zone, iron-rich carbonates are possible. It seems reasonable to conclude that biological processes are immensely important early during burial diagenesis. Not only do they modify the included organic matter, but are responsible for the development of quite commonplace sedimentary minerals. In addition to sulphides and carbonates, Nissembaum *et al.* (1972) presented indirect evidence for biologically stimulated phosphate precipitation.

In these reactions, organic and inorganic compounds interact via aqueous solution species. The interaction would appear to be so involved that no single part of the sediment/porewater system can sensibly be considered in isolation from the others.

Little is known about certain aspects of early diagenesis; particularly with regard to the fate of amorphous materials which are so difficult to handle experimentally. It is also true that many of the major transformations that are known to occur before clay sediments become indurated mudstones and shales do not occur in the shallow burial environments so far considered.

5. DEEP BURIAL DIAGENESIS

(*a*) *Organic matter and carbonates*

Most of the information upon which the discussion of the previous section was based stems from oceanographic operations and the work of chemical oceanographers and sedimentologists.

In contrast, most recent information about diagenetic processes occurring at great depths emanates from commercial drillings for petroleum hydrocarbons.

Laplante (1974) investigated carbonization of Gulf Coast Tertiary sediments with burial to depths in excess of 5 km. The elemental composition of Kerogen was determined by elemental analysis and the volatile components evolved during carbonization deduced by subtractive methods. With increasing temperature, organic material starts to decompose by elimination reactions such as decarboxylation. These predominate to depths of 3 or 4 km and temperatures up to about 100 °C. Thereafter much more hydrogen than oxygen is evolved with hydrocarbon evolution: larger molecules at lower temperatures and methane at higher. These deductions were generally supported by hydrocarbon production in the holes investigated.

Tissot, Durand, Espitalié & Combaz (1974) summarized the results of experimental carbonization runs and discuss them in light of the composition of natural Kerogens taken from a wide variety of Mesozoic and Palaeozoic source rocks.

A general scheme for hydrocarbon evolution is proposed which recognizes four distinct depth zones. The first is dominated by biochemical fermentation, the second by CO_2 and H_2O elimination reactions, the third by liquid hydrocarbon evolution and the last (of significance to the oil geologist) of methane formation. These authors were careful to point out that boundaries between the various zones vary with nature of original material, burial history and geothermal gradient.

Vinogradov & Galimov (1970) described a survey of the carbon isotope constitution of hydrocarbons evolved during burial diagenesis. They found that methane associated with petroleum (as distinct from bacterial methane) had $\delta^{13}C_{\text{p.d.b.}} = -48.6‰$ (average) and ethane $-38.3‰$ with the higher paraffins approaching normal values for organic matter. These fractionations were shown to be in keeping with thermal equilibria in the 100–200 °C region.

These studies identify an additional source of carbon dioxide being produced at much greater depths than those so far considered. Continued development of diagenetic carbonates must be anticipated in these regions in consequence of essentially abiotic modification of organic matter.

(*b*) *Redox reactions and oil prospects*

In § 4*f* the results of Drever's (1971) sesquioxide determinations were summarized. Significant depletions in ferric compounds with depth were noted in the Rio Ameca Basin cores due, presumably, to pyrite growth as a result of sulphate reduction. At depths of about 1 m, the sediment clay fraction still retained more than 2 % Fe_2O_3 which could be leached by dithionite/citrate solution. To the author's knowledge, relatively few other investigations have been carried out into the distribution of ferric iron in different sediment constituents in burial sequences. Perry & Hower (1970) found that the *total* iron content of the < 1 μm fraction of deeply buried Gulf Coast sediments (2–6 km) dropped from around 6.5 % to 4.30 % but few samples were analysed, and the difference could be attributable to original composition. The present author (unpublished data) found total ferric iron to diminish systematically from about 2.0 % to 1.5 % over the same depth range in another Gulf Coast core.

This fragmentary information suggests that reduction of iron continues from shallow environments through into deep burial situations. This finding, if substantiated, is important for two separate reasons. Firstly a metal cation could be continuously produced and available for carbonate (or other diagenetic mineral) development. Secondly, reduction must be accompanied by equivalent oxidation of a reducing agent and only one is available – organic matter. The reaction could be expressed thus:

$$2Fe_2O_3 + 3H_2O + CH_2O \rightarrow 4Fe^{2+} + HCO_3^- + 7OH^-. \quad (9)$$

Reactions of this type most certainly would modify organic matter in a way not considered in the organic geochemical studies of § 5 *a*. Furthermore, the very great increase in alkalinity would encourage carbonate precipitation from pore waters.

In terms of the overall surface cycle, weathering reactions tend to introduce acids. One of the problems of 'balancing' the cycle is finding reactions in diagenesis which counter the net acid input. Reaction (9) may have great significance in this context.

(*c*) *Clay mineral transformations*

Research into the transformation of clay minerals with depth in deep burial sequences, like that of carbonization, has been supported extensively by operating oil companies. This is particularly true of Gulf Coast sequences where a strong case has been made for associating montmorillonite–illite transformations with water release, 'overpressuring' and liquid hydrocarbon migration. Burst (1969), Perry & Hower (1970, 1972), Schmidt (1973) and Perry (1974) all made significant contributions to our understanding of the chemical and mineralogical changes involved.

In a short summary it is difficult to do justice to the careful and extensive work covered in the above references. The essence seems to be that highly expandable montmorillonite or illite–montmorillonite clays persist to burial depths of 3 or 4 km. Thereafter reactions within the sediment system include decomposition of detrital mica and potassium feldspar with conversion of montmorillonite to illite layers within the illite–montmorillonite complex. Conversion spans stratigraphic intervals ranging from 1 to 3 km or even more and results in exclusion of water (from interlayer cation hydration spheres). The onset of this 'late stage' dehydration is clearly temperature dependent and is probably influenced by both pressure and sediment composition. Values in the 75 °C region for onset and 125 to 160 °C for completion (to about 80 % illite) are quoted by Perry & Hower (1972). In their earlier paper the same authors had noted that they could find no evidence of enrichment or depletion of kaolinite or chlorite. Neither clay appears to react under these conditions.

(*d*) *Compaction and pore-water exclusion*

By the time that sediments are buried to kilometre depths, much of the pore water has been excluded. Throughout diagenesis there is continuous upward migration of pore water from greater to lower pressure environments. Water movement will follow more permeable channels. It is likely that the net upward movement will include a considerable horizontal component along silt or sand units followed by structurally controlled vertical breaks. Surface escape of gas-charged water has been observed in Gulf coast bottom sediments.

The amounts of pore water present in buried sediments has been studied extensively and depth/porosity relationships treated fully by Riecke & Chilingarian (1974). Estimates used in preparing figure 2 are based on data from Dickinson (1953), Ham (1966) and Preiss (1968). Although many different factors must influence the compactive response of clay sediments to increasing overburden, it is clear that a general relationship exists and that the bulk of pore water is excluded at 1.5 km burial.

The clay fabric within muddy sediments also changes systematically with burial. At sedimentation, with porosity values in excess of 80 %, clays almost certainly are in random orientation due to 'face/edge' electrostatic interactions. Compaction strain imposes a net rotation towards the horizontal. Highly orientated fabrics result.

Oertel & Curtis (1972) used transmission X-ray methods to determine the fabric produced by kaolinite basal planes in Palaeozoic mudstones and a number of related concretionary carbonate-cemented samples. They were able to demonstrate good correlation between compaction strain deduced from fabric determinations and that deduced from carbonate-cement content assuming carbonate to have replaced pore water at some time during compaction with prevention of further dewatering strain.

The importance of this work lies in the prospect of identifying the burial depth of cementation and hence, from the composition of the carbonate cement, to make deductions concerning the pore-water composition.

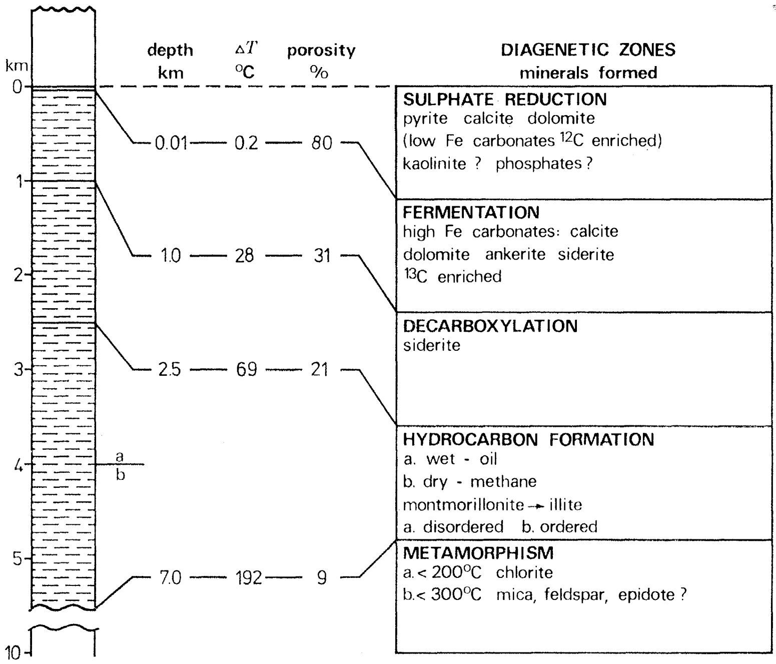

FIGURE 2. Zones or facies of diagenesis. ΔT °C = increase in temperature with depth below sediment water interface due to a gradient of 27.5 °C/km.

6. ZONES OR FACIES OF DIAGENESIS

(a) *Integration of present-day observations*

Figure 2 summarizes information 'selected' from present-day worldwide shallow oceanic cores from deep boreholes (mostly in Gulf Coast sediments). It seems plausible to recognize four (or possibly five) distinctive zones characterized by specific chemical or biochemical reactions which affect several components of the sediment system.

In the shallowest zone sulphate reducing bacteria efficiently convert seawater sulphate to dissolved sulphide species. The reactive ferric iron component of soil sesquioxide material is reduced but pyrite precipitation ensures that dissolved iron activity never exceeds extremely low levels. Carbon dioxide produced by bacterial metabolism (^{12}C enriched) may well cause calcite or dolomite to precipitate. There is also evidence of phosphate precipitation. Alkali-soluble alumina and silica are depleted: it is possible that poorly crystalline kaolinite develops.

Below about 10 m, sulphate is commonly exhausted from pore waters of organic-rich terrestrially derived clays. Fermentation takes over with organic matter degraded to methane (highly ^{12}C enriched) and carbon dioxide (^{13}C enriched). Further reduction of iron leads to ^{13}C-rich carbonates (ferroan calcite, ankerite, siderite).

Below about 1 km, bacterial processes give way to inorganic. The least stable components of the remaining organic complex break down with further generation of carbon dioxide. Precipitation of iron-rich carbonates continues.

At depths in excess of 2.5–3 km, diagenesis of the remaining organic matter changes direction and middle-range hydrocarbons evolve. This is the critical zone of liquid hydrocarbon generation. In the same depth/temperature range montmorillonite/illite transformation starts with dehydration and redistribution of metal cations. As temperatures increase, only methane is produced in the carbonization reactions, and montmorillonite/illite transformation eventually produces regularly interstratified material with about 80 % illite layers.

Between about 7 and 10 km burial, wholesale recrystallization starts. Magnesian- and iron-rich carbonates react with kaolinite to produce chlorite as the temperature rises towards 200 °C. By 300 °C illite has disappeared to be replaced by muscovite. These are metamorphic reactions.

The depths, temperatures and sediment porosity values quoted in figure 2 are no more than tentative suggestions for what might be one specific situation. Differing burial rate, thermal gradient and sediment composition are factors which are well known to affect the progress of diagenetic modification. The essence of figure 2 is the dilineation of a number of distinctive environments in a definitive sequence.

(*b*) *The end-product*

The net effect of diagenesis in any particular instance is difficult to predict because the whole sediment/pore-water system never reaches full internal equilibrium. Reactions occurring in the low temperature zones of shallow burial involve only the most unstable sediment components and are often biochemically catalysed. This also explains, of course, why many research workers have been able to reach sensible conclusions in spite of studying only one or two aspects of the overall process.

Clearly kinetic factors must play a major rôle in deciding the fate of any particular sediment. Figure 3 is an attempt to identify the effect of one particularly important factor: rate of sedimentation. The diagram should be self-explanatory. It should be noted, however, that the sulphate reduction zone is of very limited extent: effective diffusive contact is maintained over only 1 or 2 m. The other zones cover much greater depth intervals.

Only at the highest temperatures is there any evidence of movement towards full internal equilibrium. This is seen in the redistribution of elements between different silicates that occurs during late stage clay dehydration. This might be regarded as heralding the onset of metamorphism.

Sedimentologists have long recognized the upward changeover from black, pyritic shales to sideritic mudstones in cyclic sedimentation sequences. This has either been attributed to a change in depositional environment from marine to non-marine or from slower to faster depositional rate. Either one could account for the change: as can clearly be seen from figure 3. Depositional and diagenetic environments are thus seen to be linked. The former controls the rate at which the sediment passes through the latter and, thereby, the extent to which it responds to the chemical reactions that are characteristic of it.

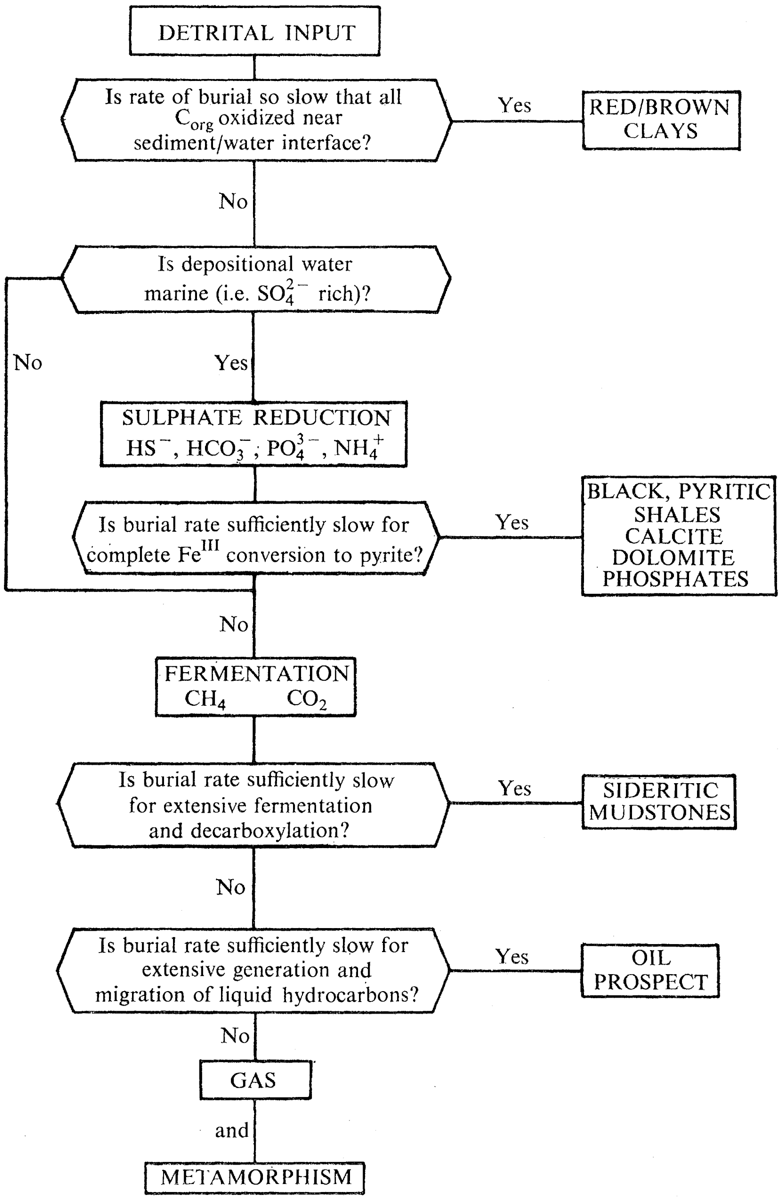

FIGURE 3. Links between sediment mineralogy and rate of burial.

(c) *Looking ahead*

A case has been made for recognizing distinctive diagenetic reaction zones akin, in certain respects, to metamorphic facies. As the findings of increasingly sophisticated studies of present-day diagenetic environments become available it should be possible to decide if distinctive zones do exist or if overlap is so great that no useful purpose can be served by their recognition.

The real difference between diagenetic and metamorphic reactions lies in the non-attainment of equilibrium in the former. Kinetic studies linking specific reactions with time, temperature and compositional controls must develop further. Accurate information on rates of burial and thermal gradients within present-day marine sediments is becoming increasingly available. Present large-scale investment by oil companies in carbonization rate studies will undoubtedly continue and should have immense value, not only in better predictions concerning petroleum evolution, but also in helping to assess kinetic controls on mineral transformations. Hopefully, there will be feedback here since the organic geochemists involved in petroleum studies seem not to recognize the possibility that redox reactions also must affect carbonization trends.

Upto the present time, there has been a tendency for oceanographers to work on present-day sediments, geologists to work with sedimentary rocks, and the two to go their own ways. Ancient mudrocks must contain valuable information about the later stages of diagenesis which are so difficult to observe directly. One obvious example is the occurrence of concretions. These offer evidence of environmental sequences as well as processes: the core material precipitating from pore solutions at one depth, outer zones precipitating in successively deeper environments. More critical studies of ancient rocks should be undertaken based on the accumulated evidence from present-day researches.

Links also must develop with hydrogeology since one very important aspect of the diagenetic process is the exclusion of massive quantities of pore fluids. Much is known in this area, but it has not been very effectively integrated with the other aspects of diagenesis.

7. Conclusions

This paper has attempted both to survey the field of sedimentary geochemistry and to make some kind of analysis as to its future development.

Diagenesis currently appears to be the most active area of enquiry and this has been discussed in some detail. The proposal for recognizing distinctive zones or facies of diagenesis has been based entirely on descriptions of phenomena in clay sediments, but extension to other types of sediment, notably coarser clastics and limestones, is entirely feasible.

Another area not touched upon is changes that have occurred throughout geological time. There can be no doubt that very significant changes to the surface cycle have occurred and quite a lot has been written about them. The view of this author is that knowledge of the surface cycle is improving to such an extent that more meaningful extrapolations will soon be feasible.

Four general conclusions about sediment geochemistry research seem worth while:

(i) It is important to study as many components of the system as possible. Separate investigations of mineralogy, pore solution chemistry or organic geochemistry all yield useful information, but interactions between these constituent parts of the sediment complex deny any possibility of making generally valid deductions from such studies.

(ii) The interactions between the various sediment constituents referred to above are best seen in pore solution investigations. This is because almost all diagenetic reactions involve hydrated reaction intermediates with at least transitory residence in the aqueous phase. Precisely the same applies in chemical weathering.

(iii) The involvement of living organisms is of paramount importance in both weathering and early diagenesis. Only microbiological factors have been dealt with in any detail in this paper, and their influence lies largely in controlling the input of anions (HCO_3^-, HS^-, PO_4^{3-}, organic acid anions) into soil or sediment systems. Also important are the activities of more complex organisms. For example, the movement of silica may very well be critically dependent upon land plants (especially grasses) during weathering and siliceous diatoms and radiolaria during sedimentation.

(iv) Separation (that is differentiation) of chemical elements in the surface cycle is dramatic. Many valuable raw materials owe their concentration to weathering or diagenetic processes. The massive differentiation of virtually all different primary rock types into kaolin/sequioxide residues and solution products in lateritic weathering must be the most efficient separation process in the whole of earth science. Chemical weathering has played a part in differentiation of the Earth's crust which probably has been grossly underestimated.

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Discussion

R. G. Burns (*Department of Earth and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts* 02139 *U.S.A.*). Soil horizons above weathered basalts in Hawaii contain concretions of manganese oxides, dominated by the mineral lithiophorite. Is any information available on the diagenesis of such tetravalent manganese oxide minerals during burial in compacted sediments?

C. D. Curtis. I am not aware of any detailed investigations of the breakdown of specific manganic compounds during burial diagenesis. It would appear (as is logical) that reduction takes place and that Mn^{2+} is incorporated into diagenetic minerals. I have not worked with the highly magnanoan carbonates that have been reported from just below the sediment/water interface in anoxic marine basins, but the manganese content of siderites is variable and the Mn^{2+}/Fe^{2+} ratio changes from the centre of concretionary bodies towards their periphery (Curtis, C. D., Pearson, M. J. & Somogyi, V. A. 1975 *Mineral. Mag.* **40**, 385–393). I think that further studies of both recent and ancient manganese-rich sediments are required before definitive statements can be made about manganese behaviour and, particularly, subtle behavioural differences between iron and manganese.

J. V. Smith (*Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois* 60637, *U.S.A.*). Two of the most important problems of the early Earth are whether the atmosphere was reducing or oxidizing, and when biological activity began to be important. Would you care to speculate, on the basis of your studies of modern sediments, what features of ancient sediments might be examined in relation to the above questions?

C. D. Curtis. At the present time (and through the Phanerozoic) almost all the oxidized iron entering the sedimentary column is reduced by organic matter via the various processes described in this paper. Rather rare circumstances allow for oxidized sediment preservation: either a lack of deposition of organic matter within rapidly deposited terrestrial detritus from arid environments or its complete destruction within the uppermost oxidizing layer of extremely slowly deposited sediments. The predominance of reduced sedimentary iron minerals within the fragmentary Pre-Cambrian record therefore is not, of itself, very convincing evidence of a reducing atmosphere.

There are, however, good examples of very ancient oxidized sediments. These may reflect an oxidizing atmosphere followed by diagenesis without reduction as described above, but they could also result from oxygen introduced directly to the hydrosphere by early photosynthetic organisms. Oxygen introduced to waters containing significant dissolved ferrous iron would be rapidly removed by oxidation and precipitation of oxidized iron minerals. Assuming that the very early atmosphere was not oxidizing and that the earliest crustal materials were almost totally reduced, the first appearance of oxidized sediments suggests a minimum age for the evolution of photosynthetic processes.

One thing is clear: it is very difficult to link the mineralogy of ancient sediments with the composition of the atmosphere – only with the combined atmosphere/hydrosphere system. The style of occurrence and mineralogy of ancient iron-rich sediments must be examined in much greater detail. The precipitation of vast amounts of siderite would imply extremely low free oxygen levels. But the Pre-Cambrian siderites could well be diagenetic.

It would seem worth while also to look carefully for evidence of concretionary bodies or horizons of the type which are referred to in the paper and which certainly occur throughout the Phanerozoic.