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C-S-Fe Geochemistry of Some Modern and Ancient Anoxic Marine Muds and Mudstones [and Discussion]

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C–S–Fe geochemistry of some modern and ancient anoxic marine muds and mudstones

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Most sedimentary C, S and Fe occurs in marine muds and is originally present as an unstable mixture of dissolved sulphate, organic matter and detrital Fe minerals. During early diagenesis, key reactants are either destroyed (reduction of Fe(III) and SO_4^{2-} to form pyrite), created (organically bound sulphur (OBS)) or preserved (Fe-bearing silicates). Pyrite formation is commonly limited not by sulphide availability but by the rate at which detrital Fe minerals react with sulphide. At low temperatures, detrital Fe(II) and Fe(III)-bearing clay minerals react very slowly with sulphide and are buried intact. The uptake of sulphur into organic matter is not, as commonly assumed, sulphide-limited. We believe that polysulphides react rapidly with organic matter and that the availability of reactive polysulphides may also influence the sulphur content of kerogen. Polysulphide formation is favoured at stable aerobic–anaerobic interfaces and sediments deposited under weakly oxygenated bottom waters are most likely to contain sulphur-rich kerogen.

Deep burial (greater than 70 °C) C–S–Fe diagenesis is characterized by the loss and partial reduction of Fe(III) from smectitic and illitic clays and the conversion of limited amounts of OBS to lower molecular mass S compounds. Pyrite formation is volumetrically insignificant. More than 90% of OBS remains within organic-rich mudrocks during petroleum generation and expulsion, preserving a sulphur-enriched residual kerogen. The extent to which OBS is eventually converted to H_2S, and at what level of thermal maturity, is unclear. If, as may be likely, much of the sulphur in residual kerogen is thiophenic, it will be stable to at least 200 °C.

1. Introduction

Carbon, sulphur and iron are abundant and chemically active elements in sedimentary basins. Most of the iron and reduced carbon in basins, plus a major fraction of the sulphur, occur in mudrocks. Most muds are deposited on continental margins and initially comprise an unstable assemblage of soil-derived material and organic matter, plus dissolved sulphate and oxygen. Diagenetic redox reactions, mainly between C, S and Fe, are a response to this inherent instability. Our principal aim here is to describe the main reactions involving C, S and Fe during both the early and deep burial diagenesis of mudrocks, and to explore the crucial influence of early diagenetic reactions on deeper processes.

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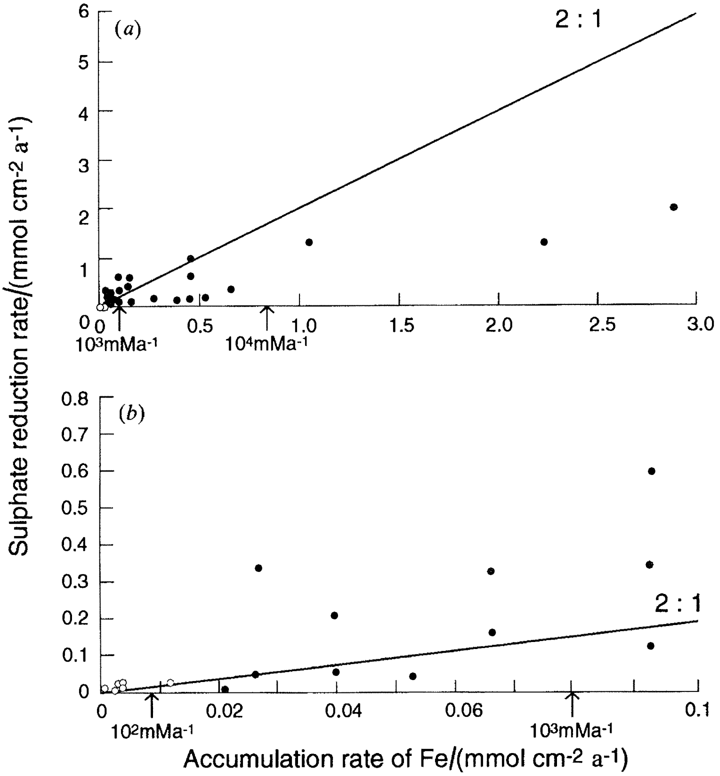

Figure 1. Comparison of the rates of sulphate reduction and of accumulation of detrital iron in sediments deposited on continental shelves and margins (data from Canfield 1989). In sediments plotting above the line, sufficient sulphide is produced to pyritize, potentially, all detrital iron. Figure 1*b* is a blow-up of the area of (*a*) close to the origin; ○, euxinic sediments.

2. Early diagenesis: destruction, production and preservation of key reactants

Microbially mediated sulphate reduction is a ubiquitous process in anoxic marine muds. Sulphide is the result of sulphate reduction and may react: (1) with detrital Fe phases to form pyrite (Berner 1970); (2) by diffusing or mixing back towards the sediment–water interface where it is reoxidized to elemental sulphur, polysulphides and sulphate (Jørgensen 1977; Berner & Westrich 1985); (3) along with its partial oxidation products, with organic matter to form organically bound sulphur (OBS; Aizenshtat *et al.* 1983; Sinninghe Damste *et al.* 1989; Mossmann *et al.* 1991).

Understanding the fate of early diagenetic sulphide is important because the phases into which it may be bound behave in very different ways during deeper burial diagenesis. For example, reaction of sulphide with Fe(III) phases not only removes an important mineral oxidant from the sedimentary system but also locks sulphide into a phase (pyrite) which is stable to at least 200 °C. In contrast, low temperature incorporation of sulphide into organic matter produces a material which may decompose at higher temperatures to give sulphide.

(*a*) *Pyrite formation*

The ultimate potential for pyritization depends on the relative rates at which sulphide is produced by sulphate reduction and at which detrital Fe minerals

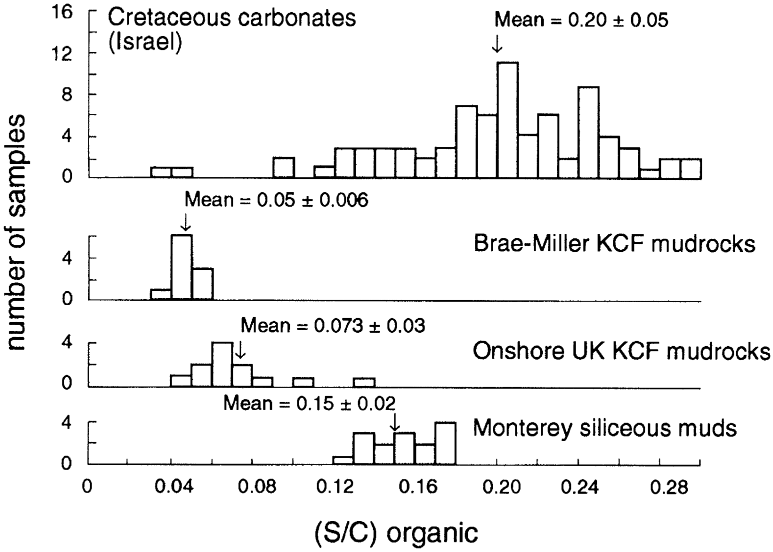

Figure 2. S/C ratios of kerogens isolated from petroleum source rocks. Previously published data from Orr (1986) and Bein *et al.* (1990).

accumulate. The actual degree of pyritization is also influenced by the rate at which Fe phases react with sulphide (Canfield *et al.* 1992); if an Fe-bearing mineral passes through the sulphate reduction zone faster than it can react with sulphide, pyrite will not form. Also, pyritization is inhibited where sulphide is rapidly removed from surface sediments by bioturbation.

The rate of sulphate reduction in marine sediments is proportional to the quantity and reactivity of organic matter entering the sulphate reduction zone (Westrich & Berner 1984). This in turn is a function of both the amount of reactive organic matter arriving at the sediment–water interface and the extent to which this organic matter is first degraded by oxic respiration. Sulphate reduction rates in marine sediments vary by six orders of magnitude and are highest in rapidly deposited continental shelf sediments, with intermediate levels in more slowly deposited hemipelagic and continental margin sediments and with the lowest levels in deep sea sediments (Berner 1978; Canfield 1989, 1991).

Since sulphate reduction rates are positively correlated with sediment (and Fe) accumulation rates, the ultimate potential for pyritization depends on the relationship between the rates of sulphate reduction and sedimentation accumulation. Canfield (1989) has compiled a list of studies in which rates of both sulphate reduction and sediment accumulation were determined in sediments deposited on the continental shelf and margin, at water depths of a few metres to several hundred metres. Assuming that the sediment supply contained 4 wt % Fe, we have calculated the rate of Fe accumulation in these sediments and have compared them with the rates of sulphate reduction (figure 1). In very rapidly accumulating sediments (greater than 10^3 m Ma^{-1}), rates of sulphide production are insufficient to pyritize the influx of detrital Fe phases. At lower sediment accumulation rates, more typical of average rates for most mudrocks, there is generally sufficient sulphide produced to pyritize, potentially, all of the Fe supplied to the sediment. However, numerous studies have shown that it is exceptionally rare to find sediments in which pyrite is the sole Fe phase (e.g. Raiswell *et al.* 1988). In these cases, pyritization is incomplete because the rates of the reaction between sulphide and certain Fe phases are so slow that pyritization is impossible in the timespan over which sulphate reduction occurs in marine sediments.

At low temperatures, half-lives for Fe minerals in the presence of 1 mM sulphide vary from less than a day (ferrihydrite) to perhaps millions of years (some sheet and framework silicates; Canfield *et al.* 1992). Particles deposited on continental shelves and margins reside in the sulphate reduction zone between 10 and 2×10^6 years. Canfield *et al.*'s (1992) data therefore imply that oxihydroxides, goethite and haematite will rarely, if ever be preserved in anoxic sediments. In contrast, most Fe-bearing silicates will generally be preserved intact (e.g. Mossmann *et al.* 1991).

Sediments deposited under well-oxygenated bottom waters are often highly bioturbated by benthic macrofauna. Rates of sulphate reduction may be enhanced in bioturbated sediments through the biological mixing of reactive organic matter down into the zone of sulphate reduction (Berner & Westrich 1985). However, only a small fraction of the produced sulphide is eventually buried as pyrite (Jørgensen 1977; Berner & Westrich 1985). Sulphide is effectively unavailable for reaction with detrital Fe minerals because it is rapidly reoxidized by O_2 mixed into the sediment. The overall effect of these competing processes is that a smaller fraction of detrital Fe minerals is buried as pyrite in highly bioturbated sediments compared to non-bioturbated sediments (Raiswell *et al.* 1988).

(*b*) *Incorporation of sulphur into organic matter*

Twenty years ago Gransch & Posthuma (1973) published an influential paper in which they argued that sulphur was incorporated into sedimentary organic matter (principally kerogen) during early diagenesis. These authors noted that many sulphur-rich crude oils are generated from iron-poor carbonate and siliceous source rocks. Assuming a direct correlation between the sulphur contents of oil and source kerogen, Gransch & Posthuma (1973) proposed that S-rich kerogens occur in Fe-poor source rocks through the partitioning, during early diagenesis, of a finite reservoir of bacterially produced sulphide between detrital iron minerals (forming pyrite) and kerogen. According to this model, iron-poor, fine-grained sediments should contain sulphur-rich organic matter.

Several studies of modern sediments have confirmed that sulphur is indeed incorporated into kerogen within metres of the sediment–water interface, although the rates and mechanisms remain obscure (Aizenshtat *et al.* 1983; Sinninghe Damste *et al.* 1989; Mossmann *et al.* 1991). Nevertheless, there is sufficient circumstantial evidence to suggest that Gransch & Posthuma's (1973) model, although widely accepted, is over-simplified. In particular, we have already shown that more sulphide is produced in many anoxic sediments than that required to completely pyritise detrital Fe minerals (figure 1). In these sediments, sulphide availability is unlikely to control the extent of sulphur incorporation into kerogen.

Testing of Gransch & Posthuma's (1973) hypothesis has been hampered by a lack of data for the sulphur content of kerogens. In figures 2 and 3 we present new and recently published data for organic S/organic C ratios for organic-rich sediments from five locations: Pliocene–Recent siliceous muds from the Peru–Chile Margin (Mossmann *et al.* 1991); Miocene siliceous muds of the Monterey and Sisquoc Formations in California (Orr 1986); Upper Jurassic mudrocks of the Kimmeridge Clay formation (KCF), from both southern England and the North Sea Basin; and Upper Cretaceous carbonates from Israel (Bein *et al.* 1990). Organic S/Organic C

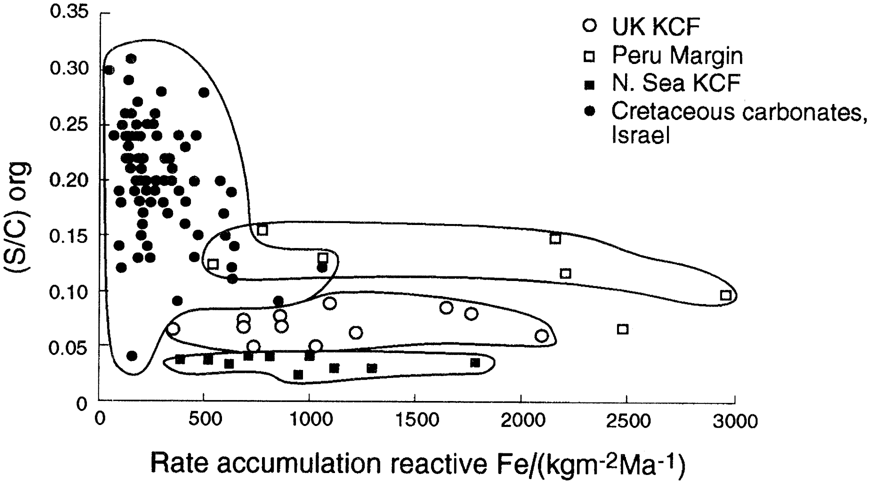

Figure 3. S/C ratios of kerogens against the rate of accumulation of HCl-soluble iron in some petroleum source rocks. Previously published data from Bein *et al.* (1990) and Mossmann *et al.* (1991). KCF, Kimmeridge Clay Formation.

ratios vary from 0.04 to 0.30 and are generally highest in the more Fe-depleted sediments from Israel, California and Peru. Although these results support Gransch & Posthuma's supposition that kerogens in biogenic source rocks are sulphur-rich, they do not constitute strong evidence that sulphide availability controls the sulphur content of kerogen. A better test of this hypothesis is to plot the sulphur contents of kerogen as a function of the *accumulation rate* of Fe (figure 3). A negative relationship between these two parameters would support the idea that a finite volume of early diagenetic H_2S is partitioned between detrital Fe minerals and kerogen: no such relationship is apparent.

One of the most intriguing facets of this dataset is the relatively low sulphur contents of kerogens within the KCF mudrocks from the North Sea Basin. Of the five locations for which we have organic S/organic C data, these sediments are the only ones which were deposited under sulphidic bottom waters. All the rest show evidence of limited benthic activity and were probably deposited under poorly oxygenated bottom waters. Since iron accumulated quite slowly in these KCF mudrocks it is very likely that dissolved sulphide was abundant when the sediments were deposited. Despite this, the sulphur contents of kerogens are relatively low and are much lower than those in other sediments, for example on the Peru–Chile Margin, in which Fe accumulated more rapidly. These data strongly suggest that neither the availability of sulphide nor the rate of accumulation of Fe are the sole controls on the extent to which sulphur is incorporated into kerogen.

There is a strong possibility that low temperature incorporation of sulphur into sedimentary organic matter may be achieved by reaction with polysulphides (Lalonde *et al.* 1987; Kohnen *et al.* 1989). Polysulphides are reactive, partial oxidation products of sulphide oxidation. They can be formed chemically, by reaction with oxygen or ferric iron, and also by microbiologically catalysed reactions at aerobic–anaerobic interfaces. Polysulphide abundances have rarely been determined in pore-waters but one may speculate that they will be most abundant where upwardly diffusing sulphide meets downwardly diffusing oxygen. Sulphide-oxidizing bacteria colonize these aerobic–anaerobic interfaces and enhance the rates

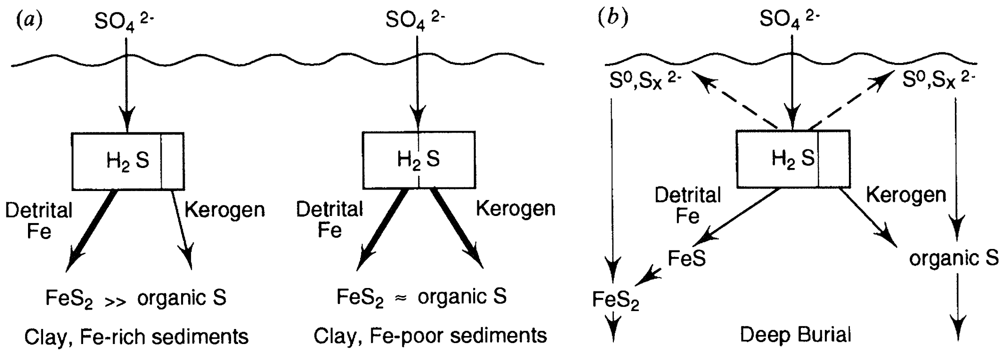

Figure 4. Two models for the early diagenetic incorporation of sulphur into kerogen. In the conventional model (*a*), the sulphur content of kerogen is controlled by sulphide availability, which is itself controlled by the sediment's detrital Fe content. In a second (*b*), sulphur uptake is effected by reactions involving both sulphide and polysulphide and the sulphur content of kerogen is influenced by local environmental factors favouring the occurrence of polysulphide.

of sulphide oxidation many orders of magnitude above that driven by chemical oxidation by ferric iron (Jørgensen 1982). Polysulphides will therefore be most abundant in localized environments close to the surface of sediments accumulating under *oxygenated* bottom waters. They will be much less abundant in environments, like euxinic sediments, where the only significant oxidant is ferric iron. One explanation for the surprisingly low concentrations of organic sulphur in euxinic sediments is that sulphur can be incorporated into organic matter both by rapid reaction with polysulphides and by slower reaction with sulphide (figure 4). Sulphur uptake into organic matter would then be favoured in sediments deposited under weakly oxygenated bottom waters, where stable anaerobic–aerobic interfaces can be maintained for significant periods of time.

It is notable that all the sediments containing sulphur-rich kerogen were deposited under oxygen-bearing bottom water. Iron-poor, carbonate or siliceous sediments may contain sulphur-rich kerogen not because they are iron-poor, but because they tend to accumulate on open marine shelves and margins where euxinic conditions are unlikely to develop. In contrast, small basins, like present-day fjords, are more likely to fill with clastic debris and, under the correct oceanographic conditions, to develop sulphidic bottom waters. Relatively sulphur-poor kerogens appear to result under these conditions.

Relatively little is known about the extent to which the nature of the organic matter itself may influence its reaction with sulphur species. Many individual organic sulphur compounds have been detected and have been related to precursor molecules, principally unsaturated lipids, known to exist close to the sediment–water interface (Sinninghe Damste *et al.* 1989). However, much of the sulphur in kerogen remains poorly characterized and the link between these lipids and the bulk of the insoluble sedimentary organic sulphur is unclear.

3. Deep burial diagenesis

Organic carbon, ferric iron and OBS are the main redox sensitive species buried within sedimentary basins. In this section we explore the behaviour of these species in deeply buried sediments using data for mudrocks of the KCF.

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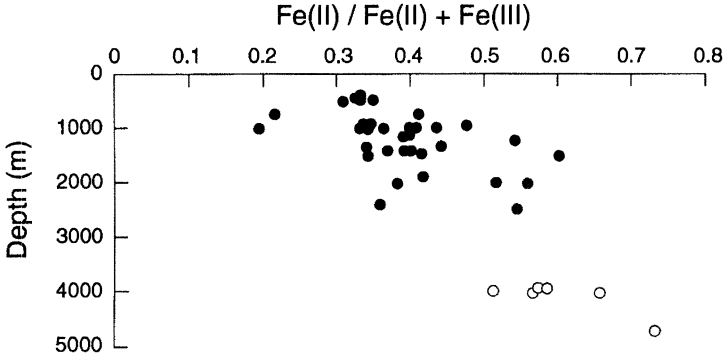

Figure 5. Ferric iron/total iron ratios in the silicate fraction of Kimmeridge Clay Formation mudrocks as a function of burial depth. Samples are from English successions and sediment cores from the North Sea Basin (open circles).

(*a*) *Iron*

Curtis (1985) has stressed the potential importance of ferric iron as a mineral oxidant in sedimentary basins and has summarized data from the Gulf Coast and Sverdrup Basins which imply that iron is lost from illite/smectite during the gradual conversion of smectite to illite. The diagenetic development of Fe-rich chlorite in Gulf Coast mudrocks indicates that at least part of the iron in Gulf Coast shales buried to above 100 °C occurs in the reduced, ferrous form (Hower *et al.* 1976). If, as Hower *et al.* suggested, the iron in chlorite was derived from detrital I/S, and if the iron in the detrital I/S was in the ferric form (as might be expected in a weathering product), then a reduction reaction is implied.

The general consequences of iron reduction can be explored by constructing a general chemical equation for the above reaction. For example:

$$\underset{\text{‘illite’}}{K_2(Fe^{(III)})_4[Si_6Al_2O_{20}](OH)_4} + CH_2O + 1.727H_2O \rightarrow$$

$$\underset{\text{Fe chlorite}}{0.3636(Fe^{(II)}{}_{8.75}Al_3)[Si_{5.5}Al_{2.5}O_{20}](OH)_{16}} + 4SiO_2 + 2K^+ + 0.818Fe^{2+}$$

$$+ HCO_3^- + 2.636OH^-. \qquad (1)$$

In this reaction, alkalinity is increased and carbonate precipitation is favoured. In contrast, consider a second reaction which occurs in sedimentary basins and in which Fe-rich chlorite is formed through the reaction between siderite and kaolinite:

$$9FeCO_3 + 3Al_2Si_2O_5(OH)_4 + 2H_2O \rightarrow Fe_9Al_6Si_5O_{20}(OH)_{16} + SiO_2 + 9CO_2. \qquad (2)$$

In contrast to reaction (1), CO_2 is generated in reaction (2) and carbonate/silicate dissolution may be favoured.

Very little has been reported on the redox geochemistry of iron in deeply buried sediments. Accordingly, we present Fe(II) and Fe(III) data derived from samples of KCF mudrocks taken from English successions, where the KCF has been buried to between 0.5 and 2 km, and from cores from the Central Graben of the North Sea Basin, where the KCF is presently at its maximum burial depth of 4 km (about 130 °C).

Pyrite Fe, non-pyrite Fe(II) and Fe(III) were determined using the methods described by Zhabina & Volkov (1978) and Begheijn (1979). Although only 20–40 %

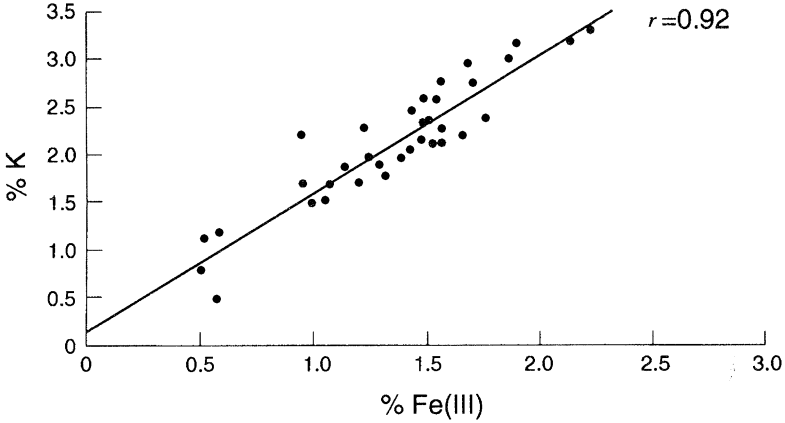

Figure 6. Ferric iron versus potassium for Kimmeridge Clay Formation mudrocks. Samples are from English successions.

of the iron in the onshore KCF occurs as pyrite, DOP is independent of total organic carbon. This relationship suggests that pyrite formation was limited by the availability of reactive Fe (Raiswell & Berner 1985). Most of the remaining Fe is contained within silicates, since siderite is scarce in most samples.

Mineralogical and microscopic investigations suggest that mixed-layer illite/smectite (I/S) is the only significant Fe-bearing mineral. Fe(III) typically comprises 50–70% of the silicate Fe (figure 5) and is strongly correlated with potassium (figure 6). Since these sediments contain very little K feldspar or mica, we interpret this trend as indicating that Fe(III) is located within mixed layer I/S. The correlation between Fe(II) and K is less good and it is unclear to what extent Fe(II) is also located within I/S, or within other phases.

In more deeply buried KCF mudrocks from the North Sea, Fe(III) comprises 30–50% of the total silicate Fe. As for the onshore samples, chlorite is rare or absent, suggesting that most of the Fe occurs in phengitic illite, which dominates the clay mineral assemblage.

Although the English and North Sea KCF mudrocks described here are lateral equivalents, we cannot unequivocally conclude that Fe reduction has occurred during silicate diagenesis of the KCF. The English and North Sea KCF mudrocks are sedimentologically distinct and may also have initially been mineralogically distinct. Nevertheless, illitic material in deeply buried, North Sea KCF mudrocks is texturally distinct from, and more compositionally homogeneous than onshore KCF mudrocks (Burley & Macquaker 1992). These data suggest that large-scale recrystallization of the illitic matrix has occurred during deep burial diagenesis of the North Sea KCF, in which case Fe reduction is a real possibility.

The extent to which Fe(III) is reduced during deep burial diagenesis remains unclear, as do the reduction mechanisms. Ferric iron undoubtedly survives diagenesis (Shaw 1956). However, in organic-rich rocks such as the KCF, there is more than enough reduced carbon to reduce all Fe(III) to Fe(II), yet reduction is incomplete below 120 °C. In contrast, in organic-lean sediments such as bentonites from the disturbed belt in Montana, reduction of Fe(III) has been demonstrated in the absence of an obvious, local reducing agent (Eslinger *et al.* 1979). Although partial reduction of Fe may be characteristic of mudrock diagenesis, the controls, rates and mechanisms remain as clear as mud!

(*b*) *Organically bound sulphur*

Thermal maturation of kerogen results in its disproportionation into relatively low molecular mass, hydrogen-rich species (petroleum) and a more condensed, hydrogen-deficient residue. We have calculated a simple mass balance for organic sulphur during the generation of petroleum from KCF mudrocks located in the Brae-Miller area of the Central North Sea. This area is ideal for such a study because source rocks and reservoir are interbedded and are presently at their maximum burial temperature (130 °C). Our approach is essentially that of Cooles *et al.* (1986), who described a simple way of calculating the volumes of petroleum expelled from source rocks. By measuring the sulphur contents of oil, gas, kerogen and source rock bitumen, this approach can be extended to construct a simple sulphur mass balance for the source rock. Oils and bitumens are an order of magnitude depleted in sulphur (around 0.5 wt%) compared to the parent kerogen (5 wt%). Only 6% of OBS is expelled as oil from these mudrocks and essentially no sulphur is expelled as H_2S. The vast bulk of the sulphur thus remains in the residual kerogen.

It is impossible to place these results in the context of the sulphur geochemistry of kerogen because little is known about it. However, thiophenic structures appear to be the dominant sulphur-bearing compounds in crude oils and asphaltenes and it is reasonable to speculate that thiophenes may comprise an even greater fraction of the sulphur in kerogens, especially within the residues remaining after oil has been generated (Waldo *et al.* 1991). However, it is unclear how much of the OBS is eventually converted to H_2S, and at what temperature. If thiophenic structures are the dominant S species in residual kerogen, their high thermal stability means that very little H_2S will be generated below 200 °C.

(*c*) *Interaction of* Fe *and* S *during deep burial diagenesis?*

It is possible that the lack of H_2S in gases generated from mudrocks reflects reaction with Fe minerals to form pyrite. Almost all deeply buried mudrocks contain more non-pyritic Fe than OBS. If an average mudrock contains 4.5% Fe, half of which is Fe(III), and 1% organic matter containing 1% S, then it contains about 200 times more Fe(III) than OBS. Even siliceous muds, which are relatively Fe-poor and extremely rich in OBS, contain more Fe(III) than OBS (Mossmann *et al.* 1991). Except in organic-rich carbonates, the potential therefore exists to react all OBS with Fe minerals to form pyrite. However, SEM observations of KCF mudrocks suggest that pyrite formation is a volumetrically unimportant process at temperatures up to at least 120 °C. If H_2S is generated from OBS and forms pyrite, it cannot be detected against the large masses of pyrite formed during early diagenesis.

4. Summary and conclusions

Most iron, reduced carbon and a significant fraction of the sulphur in sedimentary basins occurs within muds and mudrocks. Intense early diagenetic cycling of C, S and Fe in muds results in the formation of pyrite, which is stable throughout the diagenetic realm, and the incorporation of sulphur into organic matter to form OBS, which is potentially reactive during deep burial diagenesis. Pyrite formation is commonly not controlled by sulphide availability but by the rate at which sulphide reacts with certain detrital Fe phases. Fe(II) and Fe(III)-bearing silicates are thus preserved intact into deeply buried sediments.

The incorporation of sulphur into sedimentary organic matter is not limited by sulphide availability. We believe that sulphur uptake into kerogen occurs rapidly by reaction with polysulphide and more slowly by reaction with sulphide. Environments which favour polysulphide formation also favour the formation of sulphur-rich kerogens. Sediments deposited under weakly oxygenated bottom waters, where stable anaerobic–aerobic interfaces can be maintained for some time, are thus more likely to contain sulphur-rich kerogens. Carbonate and siliceous source rocks may contain sulphur-rich kerogen not because they are depleted in Fe, but because they tend to be deposited on open shelves and margins where it is difficult to develop oxygen-free bottom waters.

During deep burial diagenesis Fe is lost from illite/smectite and appears to be at least partially reduced. Reduction mechanisms are unknown. Less than 10% of OBS is expelled from source mudrocks along with petroleum; the rest remains as a sulphur-enriched kerogen residue. If, as seems likely, most of the OBS is residual kerogen occurs as thermally stable thiophenic structures, it is unlikely to break down to give H_2S below at least 200 °C.

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Discussion

D. R. Lovley. The model of sulphate reduction ($SO_4^{2-} \rightarrow S^{2-}$, then S^{2-} reduces Fe^{3+}) is probably not correct: microbes directly reduce Fe^{3+}.

A. C. Aplin. The reactions are undoubtedly more complex than suggested in the text.

P. Meadows. All sediments in the sea (continental shelf to the abyssal plains) are bioturbated to some degree. There are distinctions between anoxic and oxic bottom waters. Sulphide in pore waters may not always be low (burrow oxide linings). If you can see bioturbation in the geological record, it must be important and the top 1 m highly bioturbated. Whereas the sediment overall may be anoxic (and smell of H_2S), there may be oxidizing regions within it (burrows).

A. C. Aplin. Within the geological record, some rocks are laminated (i.e. low bioturbation). Sedimentation heterogeneity (lamination and bioturbation) varies. The concentration of sulphides tends to be lower in more bioturbated sediments.

J. Small. Can Dr Aplin comment on our present understanding of the control of Fe reduction by the maturation of organic matter during middle to late diagenesis? How can we investigate this potentially important redox control?

A. C. Aplin. Not too much is known about mechanisms or controls.

T. Lyons. Can S-isotopes be used to constrain the mechanism of sulphur incorporation via polysulphides? Does polysulphide formation require O_2 (therefore proximity to the sediment–water interface)? If so we might expect organic sulphur compounds with lighter sulphur than that in pyrite. The data suggest later incorporation in which case what is the source of polysulphides?

A. C. Aplin. We do indeed see the latter trend. However, polysulphides forming at or close to the sediment–water interface may be isotopically distinct from dissolved sulphide.

P. Aargaard. How much Fe^{3+} is preserved with burial? Does Dr Aplin have enough data to quantify this?

A. C. Aplin. Approximately 40–50% of the total Fe is Fe^{3+} in the Kimmeridge Clay Formation but this obviously depends on mineralogy. Buried Fe^{3+} is a potentially important mineral oxidant in clastic sediments.