New Directions in Geosciences
for Unconventional Resources
OCTOBER 15-17, 2019
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Microbiological controls on marine sedimentary diagenesis

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Abstract

Throughout the sediment column, up to the temperature threshold of life, microbial activity plays an integral role in diagenesis. It is widely recognized that through their various chemoheterotrophic pathways, microorganisms are ultimately responsible for the conversion of organic carbon to CO_2 and CH_4 at temperatures <100ºC. Some aerobic bacteria use hydrolytic enzymes to break down complex molecules into simple monomers such as sugars, amino acids and fatty acids that they can then utilize, while most anaerobes are restricted to simple organic compounds (e.g., acetate, lactate, H_2) that are the by-products of fermentation (Lovley and Chapelle, 1995). Typically, the more labile materials (e.g., proteins, carbohydrates) are degraded in near-surface sediments on time scales of days to years, more refractory materials (e.g., lipids) are broken down deeper in the sediment on time scales of decades, while the most resistant materials (lignins) are transformed only on timescales of thousands to millions of years. The amount of refractory material left after microbial attack will depend on the nature of the primary producers and the degree of processing that has taken place in the river catchment area or oceanic water column. In the end, however, <1% of the original material buried into marine sediment may ultimately contribute to the sedimentary organic geochemical record (Emerson and Hedges, 1988).

Pore water and mineralogical changes during diagenesis are directly related to bacterial reduction of dissolved or solid-phase components in the sediment. The terminal electron accepting process (TEAPs) that occur at any given layer depends on what oxidants are available and, in the situation when multiple electron acceptors are present (as in the uppermost sediment layers), on the free energy yield of the specific reaction. Thus, the decomposition of freshly deposited organic material in sediments proceeds in a continuous sequence of redox reactions, with the most electropositive oxidants being consumed at, or near the surface, and progressively energetically poorer oxidants being consumed at depth until the labile organic fraction is exhausted and the deeper sediments are left with a composition very different from the sediments originally deposited [Figure 1]. When discussing sedimentary redox conditions, we employ the terms oxic, suboxic and anoxic: the distinction has traditionally been based on the amount of dissolved oxygen available, with different authors using different concentrations (e.g., oxic, >4.5 uM; suboxic, 4.5 uM – 10 nM; anoxic, < 10 nM; Morrison et al., 1999; Revsbech et al., 2009; Tyson and Pearson, 1991). The terms are similarly used to refer to specific microbial metabolisms and the TEAs coupled to the oxidation of organic carbon (e.g., Froehlich et al., 1979; Canfield and Thamdrup, 2009). Thus, oxic refers to aerobic respiration (where cells use O_2), suboxic refers to using nitrate (NO_3^-) and Mn(IV) oxyhydroxides, while anoxic refers to using Fe(III) oxyhydroxides or sulfate (SO_4^{2-}) (Konhauser, 2007).

Physical and macrofaunal processes will subsequently cause the net transport of these reduced species (e.g., HCO_3^-, Mn^{2+}, Fe^{2+}, NH_4^+, NO_2^-, HS^-, HPO_3^{2-} and CH_4) from the deeper layers towards the sediment surface, where residing anaerobic and aerobic chemolithoautotrophic bacteria use them as metabolic reactants. Alternatively, their presence in pore waters may trigger important abiotic

reactions between the solid and dissolved phases leading to secondary mineral formation, i.e., cementation.

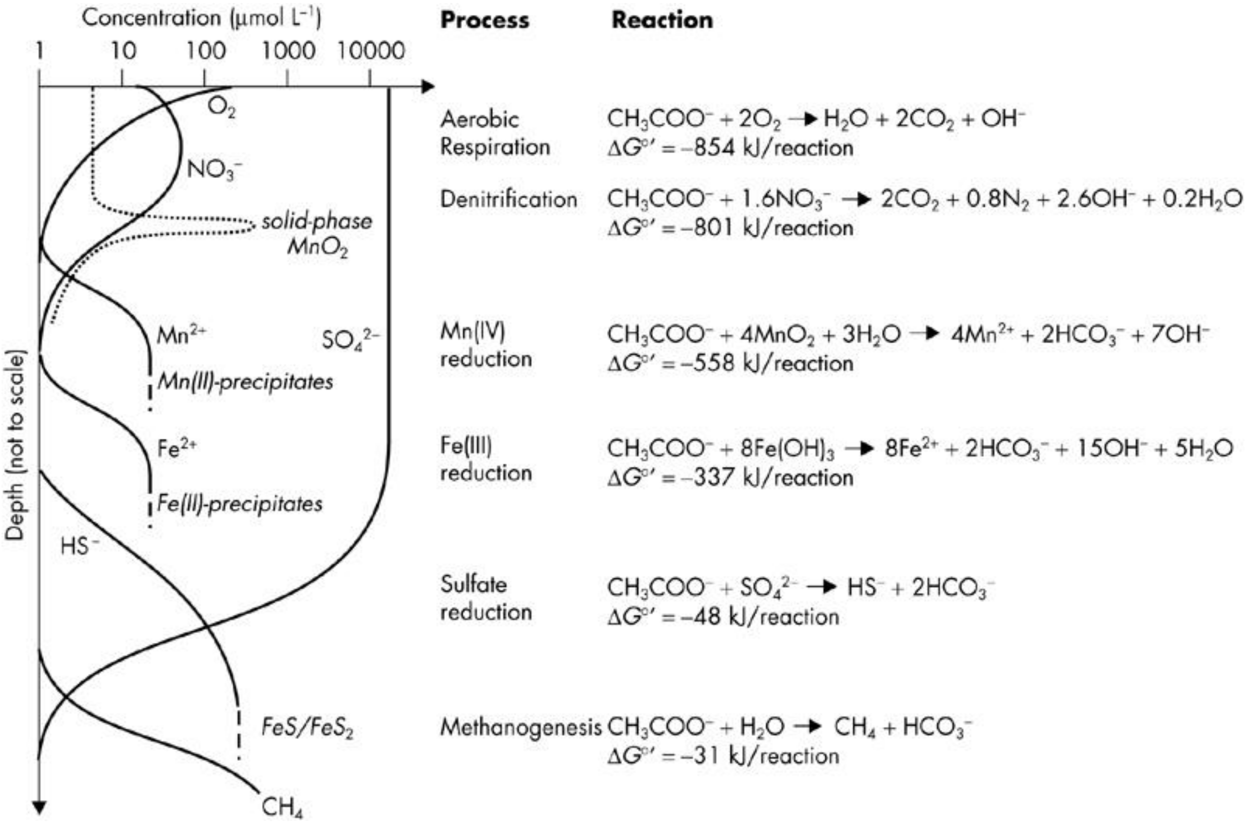

Figure 1: Idealized pore water and solid-phase profiles based on the successive utilization of terminal electron acceptors during the decomposition of marine sedimentary organic matter. From Konhauser (2007)

Oxic zone reactions

The sediment-water interface is the site of most intense heterotrophic activity. Aerobic respiration [reaction 1] is the first used metabolic pathway for the degradation of organic matter, not only because it has the greatest energy yield per amount of organic carbon oxidized, but the aerobes are equipped with a full suite of extracellular enzymes capable of degrading complex organic polymers into simpler substrates (e.g., cellulose into glucose).

[1] $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

$\Delta G^0 = -2872$ kJ/mol glucose or -240 kJ/2e$^-$

It is estimated that on a global scale, the majority of all particulate organic carbon (POC) deposited is aerobically respired; the percentage varies amongst different marine environments, with aerobic respiration accounting for >90% of the organic carbon oxidized in deep sea sediments (e.g., Bender and Heggie, 1984), while O_2 is the TEA in only 45% of coastal marine settings and freshwater lakes (e.g., Jones, 1985).

In marine sediment, one of the primary factors controlling the patterns above is the composition of the organic material and the rate at which it is deposited. Plankton-derived organic matter, rich in lipids and cellulose, exhibit significantly higher reactivities than land-derived organic material consisting of vascular plants rich in lignins (Hedges et al., 1988). Accordingly, in coastal settings, a significant fraction of POC may be relatively difficult to decompose. Furthermore, under the high deposition rates characteristic of coastal settings (1 mm yr^{-1}), O_2 diffusion is very shallow and the oxic zone may only extend down a few millimetres in depth, although physical stirring of surface sediments by waves and currents, circulation of overlying water through animal burrows that are connected to the sediment-water interface (known as irrigation) and bioturbation of surface sediments may locally increase that depth to several centimetres (e.g., Hammond et al., 1985). Therefore, with high accumulation rates, freshly deposited organic matter passes through the oxic zone on the orders of 1-10's of years, leaving a significant amount of carbon intact to support fermentative and anaerobic heterotrophic populations (Canfield, 1993). By contrast, the influx rate of POC and nutrients decreases with distance from land and water depth. This results in a progressive diminishment of macrofaunal and planktonic species, leading to low organic matter accumulation rates in the deep sea. Coupled with the low sedimentation rates associated with the open ocean (<0.01 mm yr^{-1}), the organic fraction will remain exposed to oxygenated waters for thousands of years, leading to almost complete oxidation by O_2 - only the most refractory fractions will remain available for other TEAs in the deeper sediments (Murray and Grundmanis, 1980).

O_2 is also consumed by a vast number of chemolithoautotrophic bacteria that metabolize upwardly diffusing reductants (such as HS^-, NH_4^+, Fe(II) etc). Therefore, as reduced metabolites from anaerobic respiratory pathways diffuse upwards, a fraction of the oxygen consumed in the surface layers is diverted away from aerobic respiration, towards the re-oxidation of the reduced species. As a consequence, the depth of O_2 penetration correspondingly decreases. In fact, some diagenesis models show that the amount of O_2 partitioned to organic carbon oxidation in coastal sediments can be <1%, with nitrification or hydrogen sulfide oxidation comprising the major O_2 sinks (e.g., Blackburn and Blackburn, 1993).

Suboxic zone

Nitrification-denitrification

Nitrogen cycling in aquatic sediments is relatively complex, with nitrate pore water concentrations governed by the balance between nitrification in the oxic zone and denitrification in the suboxic zone. The amount of nitrification is regulated by the concentration of pore water ammonium (NH_4^+), which largely depends on the C:N ratio of the sedimentary organic carbon being oxidized, and the amount of O_2 penetration (Blackburn and Blackburn, 1993). In the presence of O_2, ammonium is first oxidized to nitrite by ammonium-oxidizing bacteria (e.g., *Nitrosomonas* sp.), and the nitrite is then further oxidized to nitrate by nitrite-oxidizers (e.g., *Nitrobacter* sp.). Collectively, these processes [reaction 2] cause a subsurface peak of nitrate in the pore water (Mortimer et al., 1999).

[2] $NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$

The opposing processes in marine N-cycling is denitrification (loss of NO_3^- to N_2) and nitrate ammonification (loss of NO_3^- to NH_4^+). Denitrifiers most closely resemble aerobic respirers in that they are capable of completely degrading complex organic matter to carbon dioxide [reaction 3].

[3] $2.5C_6H_{12}O_6 + 12NO_3^- \rightarrow 6N_2 + 15CO_2 + 12OH^- + 9H_2O$
$\Delta G^0 = -2715$ kJ/mol glucose or -226 kJ/2e$^-$

In coastal sediments, these bacteria reduce nitrate to negligible levels within 1-10 centimetres of the sediment-water interface. No nitrate occurs below this depth except where burrows, lined with nitrifying bacteria, irrigate oxygenated water to depths well below the oxic-suboxic boundary (Hansen et al., 1981). In deep sea sediment, the vertical zone of all TEAs are expanded, and for nitrate, concentrations may not become negligible until depths of >1 meter. Denitrification fluxes range over several orders of magnitude in marine sediments, between values as low as 1 µmol m^{-2} day^{-1} in deep sea sediments (Bender and Heggie, 1984) to over 1 mmol m^{-2} day^{-1} in some estuarine and coastal waters (e.g. Devol, 1991).

The flux of N_2 escaping from sediments is often higher than predicted biological or inorganic denitrification rates based solely on pore water nitrate concentrations. This means that in the sediments, excess N_2 is being formed independent of a nitrate intermediate. One way this occurs is through the anammox process, where shunting nitrogen directly from ammonium to N_2 [reaction 4] can promote ammonium deficiencies in sediments where this process plays a key role in nitrogen cycling (Thamdrup and Dalsgaard, 2002).

[4] $NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$

Ammonium can also react inorganically with MnO_2 to form N_2 instead of nitrate [reaction 5]. The Mn(II) formed in this reaction is biologically oxidized by Mn(II)-oxidizing bacteria (see below), with O_2 as the TEA, generating more reactive MnO_2 to continue the oxidation of the soluble ammonium (Luther et al., 1997). Field evidence suggests that this reaction can out-compete the direct oxidation of NH_4^+ by O_2 to NO_3^- in Mn-rich coastal sediments, and in doing so, potentially account for 90% of N_2 formation. In essence, this process short-circuits the traditionally considered nitrification-denitrification process.

[5] $2NH_4^+ + 3MnO_2 + 4H^+ \rightarrow 3Mn^{2+} + N_2 + 6H_2O$

Manganese cycling

Detrital mineral phases that survive transport and deposition are for the most part an unreactive component of the bottom sediment. The oxides and hydroxides of manganese and iron are the exceptions. These phases are stable under the oxygenated conditions encountered in the water column, but they quickly become unstable after burial below the oxic layers of sediment. Following denitrification, reduction of Mn(IV) oxides (typically written as MnO_2) to dissolved Mn^{2+} becomes the most energy-efficient bacterial respiratory process [reaction 6].

[6] $CH_3COO^- + 4MnO_2 + 3H_2O \rightarrow 4Mn^{2+} + 2HCO_3^- + 7OH^-$
$\Delta G^0 = -558$ kJ/mol acetate or -139 kJ/2e$^-$

In most sediments, the limited amount of manganese (and iron) oxides deposited in sediment, as well as the slower rates of burial of these oxides compared to the downward diffusion of O_2, NO_3^- and SO_4^{2-}, generally makes their reduction of minor importance (<10%) in terms of the amount of total organic carbon oxidized (Burdige, 1993). There are, however exceptions to this generalization, i.e., some lakes and marine hydrothermal settings, where high rates of metal oxide reduction are driven by a combination of relatively high metal inputs and active macrofaunal activity that mix suboxic sediment with oxygenated bottom waters, thereby re-oxidizing dissolved Mn^{2+} (and Fe^{2+}) to MnO_2 or $Fe(OH)_3$ (Aller, 1990).

In typical marine sediments, the concentration of Mn^{2+} is negligible at the sediment surface, but at some depth between the NO_3^- maximum and zero NO_3^-, it begins to increase towards its maximum values. Despite forming near the base of the nitrate reduction zone, its concentration is never highest at that depth because the Mn(II) that diffuses upwards is biologically re-oxidized and precipitated as fresh MnO_2 at the sediment surface, suggesting that the TEA can be either nitrate or oxygen (Froelich et al., 1979). A characteristic feature of Mn(II)-oxidation is the upward convexity of the pore water Mn^{2+} profile and the discrete layer of MnO_2 forming at the base of the oxic zone [recall Figure 1]. By contrast, downward diffusion of Mn(II), and its reaction with HCO_3^-, most commonly results in the formation of manganous carbonates, such as rhodochrosite ($MnCO_3$).

Anoxic zone

Iron cycling

Below the zone of dissimilatory manganese reduction, and at the depth of complete nitrate removal from pore waters, is where Fe(III)-reduction takes place [reaction 7]. Ferrihydrite [$Fe(OH)_3$] is the least crystalline, most reactive and easily reducible iron oxide phase, with rates of Fe(III)-reduction in sediment declining rapidly with depth as these poorly crystalline phases become depleted (Lovley and Phillips, 1986).

[7] $CH_3COO^- + 8Fe(OH)_3 \rightarrow 8Fe^{2+} + 2HCO_3^- + 15OH^- + 5H_2O$
$\Delta G^0 = -337$ kJ/mol acetate or -84 kJ/2e$^-$

Despite the lower reactivity of crystalline phases, in sediment where ferrihydrite has either been depleted or where crystalline iron oxides are inherently more abundant, the latter can serve as significant source of reducible iron that couples the oxidation of buried organic material. According to experimental observations, Fe(III)-reducing microorganisms developed three different strategies to cope with the difficulty of transferring electrons from the cell to the surface of a barely soluble electron acceptor (see Lovley et al. 2004 for review). First, physical contact between the cell surface and ferric iron allows direct delivery of electrons. Second, iron chelators increase the solubility of Fe(III) and hence alleviate the need for Fe(III) reduction. Third, electron-shuttling compounds transfer electrons from the cell to Fe(III) oxide surface without the necessity of physical contact between cells and mineral. Considering the complexity of natural environments and the wealth of microbial capabilities, it is not surprising that different organisms, as well as single organisms, developed different strategies in order to reduce diverse Fe(III) compounds under varying conditions. For example, some evidence indicates that *Geothrix fermentans* produce and release both Fe(III)-chelators and electron shuttles (Nevin and Lovley 2002). Furthermore, studies with *Geobacter* sp. indicate that different cellular compounds are involved in reduction of dissolved Fe(III)-citrate and barely soluble ferrihydrite (e.g., Leang et al. 2005).

The reduction of ferric iron minerals increases the concentration of Fe(II) in suboxic sediment pore waters, with a peak in concentration at the boundary between the Fe(III) and sulfate reduction zones. Some of this ferrous iron may diffuse upwards to be re-oxidized to ferric hydroxide inorganically by either NO_2^-, MnO_2 or O_2 (e.g., Myers and Nealson, 1988), and it is likely that in some lakes with near-surface sediment, phototrophic Fe(II) oxidation should take place. Some Fe(II) also precipitates as mineral phases. In iron-rich sediments, the high reactivity of Fe^{2+} and the general availability of HCO_3^- in suboxic and anoxic pore waters tends to cause ferrous iron to precipitate quickly as a micritic cement in the form of siderite ($FeCO_3$). By contrast, when sulfate reduction rates exceed Fe(III) reduction rates (see below), enough HS^- is produced to react preferentially with any ferrous iron to precipitate iron monosulfide minerals instead (FeS has lower solubility than $FeCO_3$). Therefore, the precise juxtaposition of iron reduction and sulphate reduction in marine sediments controls whether siderite and/or pyrite may form (e.g., Coleman, 1985). The formation of vivianite [$Fe_3(PO_4)_3$] in many ways resembles that of siderite, namely Fe(II) concentrations must exceed those of HS^-. It also requires that soluble phosphate is made available through oxidation of organic matter, the dissolution of phosphorous-bearing solid phases or through reduction of phosphorous-adsorbing Fe(III) oxides (Krom and Berner, 1980).

Sulfate reduction

Below the suboxic layers is a highly reducing, oxygen-free zone under which sulfate reduction predominates. In marine sediments, this is the principal process by which simple fermentation products are oxidized [reaction 8], accounting for approximately 50% of the carbon oxidation in coastal marine sediments (Jørgensen, 1982), but <10% in deep sea and freshwater environments (Bender and Heggie, 1984; Jones, 1985).

[8] $CH_3COO^- + SO_4^{2-} \rightarrow HS^- + 2HCO_3^-$
$\Delta G^0 = -49$ kJ/mol acetate or -12 kJ/2e$^-$

Its relative importance in marine environments compared to freshwater environments is based simply on the higher concentrations of dissolved SO_4^{2-} (~28 mM) at the sediment-water interface, some 50 times greater than the combined sum of all other electron acceptors with higher electrode potentials. Moreover, external electron acceptors that yield more energy than SO_4^{2-} typically disappear within the first few centimetres of sediment depth, leaving sulfate as the dominant TEA for most of the sediment column (D'Hondt et al., 2002).

The rates of dissimilatory sulfate reduction are proportional to the quantity and reactivity of organic matter entering the anoxic sediments - the greater the amount of aerobic decomposition, the less labile organic matter remains available for sulfate reduction, and the more refractory the residual material becomes (Westrich and Berner, 1984). As a result of natural variations in the above, sulfate reduction rates in marine sediments can vary by six orders of magnitude, with the highest in rapidly deposited coastal and lagoonal sediments, where it occurs just below the sediment-water interface (> 1 mM cm^{-2} yr^{-1}) and the lowest levels in deep sea sediments, where rates may be <10^{-5} mM cm^{-2} yr^{-1} (Canfield, 1993).

The product of sulfate reduction is hydrogen sulfide, and as mentioned above, can lead to the formation of iron sulfide minerals. The amount and reactivity of the detrital iron phases dictates how much pyrite will form, commonly referred to as the 'degree of pyritization'. In slowly accumulating sediments (i.e., the deep sea), little labile organic matter is buried, sulfate reduction rates are slow, less HS^- is available for reaction with detrital iron, so less ferric iron is eventually converted to pyrite.

Since the saturation state of the pore waters with respect to iron monosulfides controls the pore water concentrations of dissolved iron and sulfide, limited HS^- means that pore water Fe(II) will increase in concentration. By contrast, in rapidly accumulating sediments, more labile organics are buried, near-surface sulfate reduction rates are high, HS^- is abundant, and more of it is available for reaction with dissolved Fe(II) and solid-phase ferric iron (Berner and Raiswell, 1983). Nonetheless, not all ferric iron phases are pyritized because some ferric iron minerals react only very slowly with dissolved sulfide, and complete pyritization becomes impossible in the time span over which sulfate reduction occurs in the sediment (Canfield et al., 1992).

Only a fraction of the HS^- that forms via bacterial sulfate reduction is actually precipitated as pyrite sulfur (Berner, 1982). Instead, some 90% of the HS^- is re-oxidized to sulfate. Although O_2, NO_3^-, Mn(IV)- or Fe(III)-oxides are the ultimate oxidants in sedimentary systems, there exists a dynamic S-subcycle that involves a number of sulfur intermediate product, with thiosulfate appearing to be the most significant (Jørgensen, 1990). In addition, some of the HS^- that ultimately escapes the thiosulfate subcycle provides a useable source of reducing power for various chemolithoautotrophs, most of which gain energy from oxidizing sulfide, with O_2 as the TEAP [reaction 9].

[9] $H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$

Methanogenesis

The terminal step in the anaerobic degradation of organic material is methanogenesis [reactions 10 and 11]. As the least energetically favourable process of organic degradation, the reaction product, methane (CH_4), actually stores a major part of the energy available for aerobically respiring species, i.e., methanotrophs.

[10] $CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$
$\Delta G^0 = -31$ kJ/reaction
[11] $4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$
$\Delta G^0 = -34$ kJ/reaction

On average, methanogenesis is responsible for 5-10 times less organic carbon degradation than sulfate reduction, and it is only important in sediments where a significant amount of relatively fresh organic material is delivered rapidly enough to pass through the sulfate reduction zone that it takes on any prominence (Canfield, 1993). Indeed, methane does not accumulate in sediments until more than 90% of the dissolved sulfate has been reduced (Martens and Berner, 1974). This is unsurprising given that the growth of methanogens is inhibited by SRBs because the latter have a higher affinity for the oxidizable substrates than do the former (Lovley et al., 1982). In other words, methanogens prosper when subsurface activity of SRBs is high and pore water SO_4^{2-} becomes diminished.

The CH_4 generated by methanogens in the underlying sediment subsequently diffuses upwards towards the sulfate-rich sediments, where it serves as an electron donor in the sulfate reduction-methane oxidation transition zone [reaction 12].

[12] $CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$

In some marginal marine sites, it has been estimated that nearly 100% of the downward SO_4^{2-} flux and the upward CH_4 flux can go towards anaerobic CH_4 oxidation. Comparison of these fluxes to open ocean sites even suggests that anaerobic methane oxidation might be the dominant sink for sulfate in marine sediments relative to organic carbon oxidation (D'Hondt et al., 2002). The diffusive flux of CH_4 upwards is usually inadequate to completely reduce pore water sulfate, and hence, accumulate above the CH_4-SO_4^{2-} transition zone. Yet, it has been observed in some rapidly depositing shallow water sediments that methane saturates pore waters and ultimately may escape the sediment by bubble ebullition, without complete oxidation by sulfate (Martens and Klump, 1984).

Diagenetic carbonate mineralisation

The saturation state of sediment pore waters with respect to various carbonate minerals is directly related to the metabolic process responsible for organic matter oxidation. Aerobic respiration typically results in the complete oxidation of organic carbon to CO_2, thereby promoting the dissolution of biogenic carbonate both above and below the calcite saturation horizon (Archer et al., 1989). In fact, diagenesis has been shown to result in the dissolution of a large fraction of the $CaCO_3$ raining onto the seafloor from carbonate-secreting plankton (Emerson and Bender, 1981). Anaerobic respiration, on the other hand, releases bicarbonate into the pore water system. Increased alkalinity can cause the equilibrium ion activity product for calcium carbonate to be exceeded, leading to the precipitation of early diagenetic carbonate minerals that are relatively stable once formed and not subject to rapid recycling by redox reactions in the same way as sulfides and oxides (Irwin et al., 1977). Such processes become most predominant at depth, in particular within the sulphate reduction zone, because that metabolic process increases alkalinity.

A characteristic sequence of different terminal electron accepting processes can be distinguished on both mineralogical and stable isotopic grounds in environments where precipitation of carbonate minerals is possible [Figure 2]. Although aerobic respiration induces calcite dissolution, other aerobic processes can actually facilitate the precipitation of non-ferroan calcite (no dissolved iron is present under oxic conditions), with a stable carbon isotopic composition ($\delta^{13}C$) of 0‰. For instance, chemolithoautotrophic oxidation of NH_4^+ and H_2S, at the base of the oxic zone, actually leads to a rise in pH because these reactions effectively remove protolytic species from solution, resulting in a pH higher than predicted from the reaction stoichiometries (Boudreau and Canfield, 1993). Nitrate reduction does not produce carbonate minerals with characteristic chemistry. Manganese and ferric iron reduction produce rhodocrosite and siderite, respectively, with increasingly negative $\delta^{13}C$ (typically -2 and -10‰, respectively) due to the incorporation of an increasing component of biogenic carbonate that has a $\delta^{13}C$ signature of -20 to -30‰. Sulfate reduction produces non-ferroan calcite because any available iron reacts preferentially with sulfide. These calcites have an even more negative $\delta^{13}C$ signature (typically -15‰). Finally, below the zone of sulfate reduction, methanogenesis leads to the production of ferroan carbonates (siderite) with a characteristic positive $\delta^{13}C$ signature due to coupling of methane oxidation with reduction of residual iron minerals (Curtis et al., 1986).

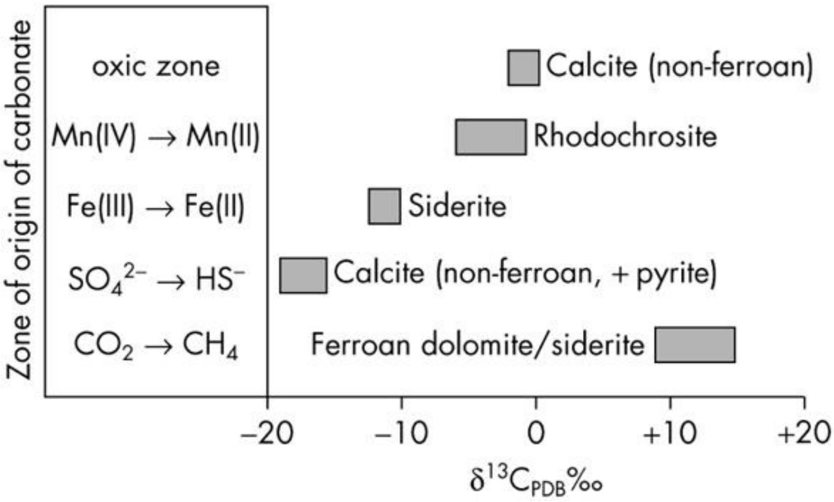

Figure 2: Carbon isotopic composition of various diagenetic carbonates formed during progressive burial in marine sediments. From Konhauser (2007)

During burial, the carbonate minerals formed may be subject to further alterations. The pore water may change its temperature and CO_2 concentration with time, so that the precipitates are in contact with alternately unsaturated and supersaturated solutions. Thus, ions of the mineral can move from one grain to another, permitting large crystals to grow at the expense of more soluble small ones. One product of such fluid flow are concretions. These hard, rounded masses form by the precipitation of a cementing agent around some form of nucleus. Siderite cements are most prominent in fresh and brackish aqueous environments, where alkalinity is generated in part by sulphate reduction, but Fe(III)-reduction rates are higher to preclude sulphide mineralisation. Conversely, pyrite and calcium carbonates are more often encountered in marine sediments.

Once the nucleus is established, further growth proceeds when the ions comprising the concretion diffuse towards the reactive site by either dissolution of exiting minerals within the sediment (diagenetic redistribution) or they may be transported from a more distant source (see Berner, 1980 for details). It is also important to point out that the chemical composition, and even mineralogy, of the concretion can change through burial, or even within the same sediment layers, as the concentrations of the constituent cations change (e.g., Al-Agha et al., 1995). For example, as Fe(III)-reduction ceases due to consumption of available reactive ferric iron, Ca^{2+} ions may subsequently replace Fe^{2+}, leading to a Ca-rich siderite or calcium carbonate precipitation instead. Rates of carbonate concretion formation range from 10-1000s of years. Water moving through the unconsolidated sediment may additionally carry dissolved ions capable of reacting with $CaCO_3$ grains. One such solute is Mg^{2+}, that under some conditions can react with calcite to form dolomite. Collectively, these processes gradually fill in the inter-grain spaces and enlarge or replace existing crystals, leading to lithification (Machel, 2004).

Current research related to banded iron formation diagenesis

Banded iron formations (BIF) are iron rich (20-40% Fe) and siliceous (40-50% SiO_2) sedimentary deposits that precipitated throughout much of the Precambrian. They are characteristically laminated, with alternating Fe-rich and Si-rich layers that can be observed on a wide range of scales. The mineralogy of the least metamorphosed BIF consists of chert, magnetite, hematite, carbonates (siderite, dolomite-ankerite), greenalite, stilpnomelane and riebeckite, but it is generally agreed that these minerals reflect both diagenetic and metamorphic overprinting: the primary iron minerals were most likely ferric hydroxide, greenalite, siderite, and amorphous silica (see Konhauser et al., 2017 for review). This mineralogy dictates that some oxidation of Fe(II) was necessary for formation, and it is generally agreed that the most likely mechanisms involved the metabolic activity of planktonic bacteria in the ancient oceans' photic zone (e.g., Konhauser et al., 2002).

If a biological mechanism was important in the initial process of Fe(II) oxidation in the ancient ocean water column, it is expected that biomass would have settled to the seafloor along with the Fe(III) minerals. This organic carbon would subsequently have served as an oxidizable substrate during diagenesis and metamorphism, but the relevant question is what terminal electron acceptors were present at the seafloor? The paucity of O_2 would have meant minimal nitrate and sulfate availability. By contrast, there was abundant ferric hydroxide deposited as BIF, and given the presence of partially reduced iron phases such as magnetite and siderite, a microbial process coupling the oxidation of organic carbon to the reduction of ferric iron mineral phases seems very likely. Recent models suggest that as much as 70% of biologically formed Fe(III) could have been recycled back into the water column via fermentation and organic carbon oxidation coupled to microbial Fe(III) reduction, with some fraction of the original biomass being consumed via methanogenesis, i.e., coupling the oxidation of acetate or H_2 to methane formation (Konhauser et al., 2005). Coupling the reduction of Fe(III) minerals to the oxidation of organic matter not only explains the low content of organic carbon in the BIF via the consumption of carbon (BIF have on average <0.5 wt% organic carbon), but it also explains the textural features in the reduced iron minerals in BIF, such as magnetite overgrowths (Li et al., 2013).

Coupled with actual BIF analyses, my colleagues at the University of Tubingen have been conducting a number of diagenesis experiments aimed at replicating the conditions under which BIF minerals formed. One of those studies involved incubating mixtures of ferrihydrite (as proxy for biogenic Fe(III) oxyhydroxide minerals) and glucose (as a proxy for degradation phases of microbial biomass) in gold capsules at 1.2 kbar and 170ºC to mimic diagenesis (Posth et al., 2013). Under these conditions, ferrihydrite ($Fe(OH)_3$) transforms to hematite, magnetite, and siderite; silica-coated ferrihydrite yielded hematite and siderite, but not magnetite. The results showed that electron transfer from organic carbon to Fe(III) minerals and between transitional Fe phase minerals during temperature/pressure diagenesis can drive the production of key BIF minerals. Importantly, we demonstrated that BIF mineralogy does not directly archive the oceanic or atmospheric conditions present on Earth during their lithification, i.e., carbonate minerals such as siderite can be formed independent of elevated atmosphere CO_2 concentrations. In another study, we showed that siderite spherulites, which are found in many BIF, can form by reacting ferrihydrite with glucose at similar pressures and temperatures as above (Köhler et al., 2013). Depending on the optical properties of the siderite, we found that it was even possible to draw conclusions about the Fe(III):C ratio of the initial ferrihydrite-biomass sediment. More recently, Halama et al. (2016) showed that magnetite formation was limited to samples containing ferrihydrite and glucose, but no magnetite was formed from Fe(III) minerals when microbial biomass was present. This is probably due to biomass-derived organic molecules binding to the mineral surface and preventing solid-state conversion of the minerals to magnetite.

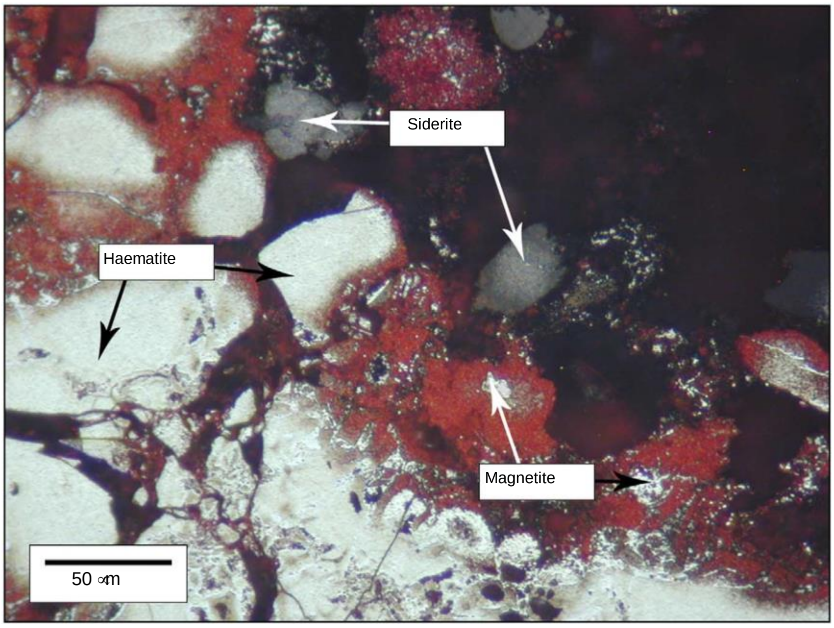

Figure 3: Ferrous and ferric iron minerals formed during pressure temperature diagenesis. Reflected light microscopy image of a mixture of ferrihydrite and glucose after 1 day of pressure and temperature treatment at 1.2 kbar and 170ºC, respectively. Hematite and magnetite have formed along with siderite, and all three minerals can be found in close association with each other. From Kohler et al. (2013).

Current research is being directed at carrying out series of well-constrained, large-scale laboratory bioreactor incubations to quantitatively evaluate the fate of phytoplankton biomass and its utilization by microbes in iron-rich marine sediments while simultaneously measuring changes in the composition of trace metals and dominant microbial metabolisms.

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