INTERACTIONS OF MICROORGANISMS WITH RADIONUCLIDES
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Chapter 3

The role of microorganisms during sediment diagenesis: implications for radionuclide mobility

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1. Introduction

Microbial reactions control the chemical composition of the sedimentary environment during early diagenesis. These reactions involve the breakdown and hydrolysis of solid organic matter, the destruction or formation of inorganic compounds and the chemical modification of pore-waters. Although the changes in organic and inorganic chemistry are complex, transient and involve numerous recycling reactions, they produce characteristic patterns which reflect the dominant microbial assemblages growing at a particular depth of sediment. Organic byproducts (e.g. hydrogen gas, fermentation products) may in turn activate dormant microbial consortia elsewhere in the sediment profile, while inorganic byproducts (e.g. HCO_3^-, Mn^{2+}, Fe^{2+}, NH_3, NO_2^-, HS^- and HPO_4^{2-}) may trigger important abiotic reactions between the solid and dissolved phases.

In addition to their influence on the major elemental cycles (C, S, N, P and Fe), microbial activity can also greatly influence the fate and mobility of contaminants introduced into the sediments through anthropogenic activities. Radionuclides, for example, may become mobilised through direct enzymatic microbial reduction, adsorption onto free-living microbes or chelation with biogenically-generated organic ligands (see also Chapters 6, 7 and 11, this volume). Microorganisms can also cause their direct immobilisation by adsorbing contaminants to attached populations or promoting the indirect precipitation of authigenic phases that can either adsorb or co-precipitate the metals. Microbial transformation of these host phases may further mobilise the radionuclides, and their partitioning between the sediment and pore-water will be governed largely by the prevailing redox conditions. In this chapter we review some of the principal microbially-driven chemical reactions within the sediment, and consider the relationship between these and the mobility of some environmentally-important radionuclides, namely Cs, Tc, U, Np and Pu.

2. Organic geochemical signals

Organic matter input to sediments is predominantly in the form of complex polymeric and macromolecular solids. Hydrolysis and fermentation transform these polymers into simple, soluble organic molecules such as amino acids, fatty acids and hydrogen gas (H_2), which are then used by a variety of chemoheterotrophic bacteria – microorganisms that use organic molecules as both a carbon and energy source. This both decreases the total organic carbon (TOC) content of the sediment, and mobilises O, H, N, P and S associated with the organic matter (Santschi et al., 1990a). Release of organic N and P is particularly important since these nutrients drive the sedimentary N and P cycles (Martens et al., 1978; Jørgensen, 1983a; see also Chapter 1, this volume). For example, organic N released into solution as amino acids is deaminated, producing NH_4^+, which then drives the microbial nitrification-denitrification couple (Jenkins & Kemp, 1984; Santschi et al., 1990a).

Characteristic and reproducible organic geochemical signals are generated in the solid phase and pore-waters during organic matter degradation. This is particularly evident in undisturbed sediments that receive a continued input of fresh organic material to the surface. Under such conditions there is a pronounced decrease in solid phase labile organic material with depth (e.g. Hulth et al., 1996; Mortimer and Rae, 2000). However, this steady-state profile may be obscured by a number of factors, including physical mixing, variations in sedimentation rate or short-term changes in organic matter input. For instance, Hedges et al. (1988) have shown that plankton-derived organic matter exhibited approximately 5 times the reactivity of land-derived organic material, so seasonality in planktonic blooms could have a significant bearing on the organic flux to the ocean sediment. The other solid phase signal which may be evident is a change in the C:N:P ratio. Although the C:N ratio of the organic matter input will depend on the relative contribution of terrestrial and marine material (Hulth et al., 1996), there may be recognisable trends with depth in a given sediment. For example, the average elemental composition of organic matter from plankton entering marine sediment is 106C:16N:1P (Redfield, 1958), yet preferential stripping of the N into solution causes the C:N ratio of the sediment to increase with depth (Jørgensen, 1983a). This is partially counteracted by the assimilation of some of the NH_4^+ into growing bacterial cells (which are included in measurements of sediment TOC).

Blackburn (1980) showed that the actual C:N ratio of organic matter mineralised in the upper sediment was lower than that of the average organic detritus present at that depth, whereas the opposite case was true deeper in the sediment. This serves to illustrate how microbial cells themselves should be viewed as an integral component of the sedimentary package. Although there is clear evidence for changes in the C:N ratio during early diagenesis, there is debate as to whether or not preferential stripping of P also occurs, increasing C:P or whether this is partially counteracted by the assimilation of PO_4^{3-} into cells (Jørgensen, 1983a; Ramirez & Rose, 1992).

Degradation of organic matter produces soluble products which are rapidly utilised by other bacteria. Acetate is probably the most important fermentation product (Lovley & Phillips, 1989; Parkes et al., 1989), and hence attempts have been made to determine its concentration in pore-water profiles (Balba & Nedwell, 1982). Nevertheless, current sampling methods produce elevated acetate concentrations that overestimate bioavailability (Shaw & McIntosh, 1990; Wellsbury & Parkes, 1995). Measurements of organic

degradation products are therefore limited to turnover rates (Reeburgh, 1983), rather than concentration-depth profiles.

3. Major inorganic geochemical signals

Pore-water and mineralogical changes in sediments are dominated by the activity of chemoheterotrophic microorganisms in all environments at near-neutral pH and ambient surface temperature. The types of organic compounds that can be oxidised vary for different microorganisms; some microorganisms use hydrolytic enzymes to break down complex molecules into simple monomers such as sugars, amino acids and fatty acids which they can then utilise, while others are restricted to simple fermentation products. The electron acceptors used by bacteria in dissimilative metabolism depend on both what candidates are available and, in the situation when multiple terminal electron acceptors (TEAs) are present, on the energy yield of the reaction (Lovley & Chapelle, 1995). For example, using acetate as the organic substrate at pH 7, most energy is obtained via aerobic respiration (reaction 1). As soon as oxygen is depleted, anaerobic respiration takes over, with nitrate reduction (reaction 2); manganese reduction (reaction 3); iron reduction (reaction 4); and sulfate reduction (reaction 5) being used successively.

$$CH_3COO^- + 2O_2 \rightarrow H_2O + 2CO_2 + OH^- \quad (1)$$
$$\Delta G = -856 \text{ kJ/mol } CH_3COO^-$$

$$CH_3COO^- + 1.6NO_3^- \rightarrow 2CO_2 + 0.8N_2 + 2.6OH^- + 0.2H_2O \quad (2)$$
$$\Delta G = -806 \text{ kJ/mol } CH_3COO^-$$

$$CH_3COO^- + 4MnO_2 + 3H_2O \rightarrow 4Mn^{2+} + 2HCO_3^- + 7OH^- \quad (3)$$
$$\Delta G = -569 \text{ kJ/mol } CH_3COO^-$$

$$CH_3COO^- + 8Fe(OH)_3 \rightarrow 8Fe^{2+} + 2HCO_3^- + 15OH^- + 5H_2O \quad (4)$$
$$\Delta G = -361 \text{ kJ/mol } CH_3COO^-$$

$$CH_3COO^- + SO_4^{2-} \rightarrow HS^- + 2HCO_3^- \quad (5)$$
$$\Delta G = -48 \text{ kJ/mol } CH_3COO^-$$

Chemoautotrophs have evolved the metabolic capacity to oxidise inorganic substances for cellular energy, with carbon dioxide as their source of carbon. The reduced chemical species used include H_2S, elemental S, NH_3, NO_2^-, Mn^{2+} and Fe^{2+}. Their oxidation by some of the terminal electron acceptors illustrated above produces characteristic chemical and mineralogical signals, particularly in sediments where environmental parameters (e.g. pH, oxygen fugacity) deviate from normal conditions, as for example, in acid mine drainage waters (Ledin & Pedersen, 1996; Freise et al., 1998).

Signals caused by chemoheterotrophs

Biogeochemical zones

Organic matter degradation in sediments is controlled predominantly by terminal electron accepting processes, which in turn are based on the potential thermodynamic yield of the various metabolic processes. Biogeochemical zones of differing terminal electron accepting pathways form the framework for describing early diagenesis of aquatic sediments. Evidence for the existence of these sequential microbial processes has been known for more than half a century (Mortimer, 1941), but a formalised depth-related scheme was not developed until the 1970s (Claypool & Kaplan, 1974; Froelich et al., 1979). This scheme, which represents the microbial degradation of organic matter using successively less energy efficient electron acceptors, is shown in Fig. 1. During the last 20 years, this sequential framework has been used successfully to describe the degradation of organic matter in a variety of aquatic environments, from hypertrophic systems (Barica & Mur, 1980; Klump & Martens, 1981; Canfield et al., 1993) to the oligotrophic deep ocean (Froelich et al., 1979, Christensen et al., 1987; Hulth et al., 1997). Although the depths over which these zones occur may vary from a few mm or cm in coastal sediments with a high organic carbon flux to several metres in the deep ocean where the carbon flux is lower, they occur in any system where the supply of labile organic matter outpaces diffusion of oxygen into the sediment (Jørgensen, 1983a). The reactions which occur in these biogeochemical zones are important not only because they are responsible for the degradation and transformation of organic matter, but also because they play a crucial role in the formation of early diagenetic minerals (Coleman, 1985). In simple terms, for any given system, the depth range of each zone can be determined from a characteristic sequence of chemical changes in the sediment pore-water which occur as electron acceptors are used up and reduced products are formed.

Aerobic respiration

Aerobic respiration is the most energy efficient mechanism for the degradation of organic matter, and therefore represents the first biogeochemical zone. Microorganisms that use oxygen as their terminal electron acceptor completely oxidise a wide variety of natural and synthetic organic compounds to carbon dioxide, water and cell biomass. Aerobic metabolism involves enzymes that selectively degrade individual classes of compounds. For example, the degradation of cellulose involves the activity of a number of hydrolase enzymes, each specific to the breakage of a particular bond (Senior & Balba, 1990). The breakdown of more refractory compounds, such as lignin, is made possible by the use of highly reactive oxygen-containing radicals, such as the superoxide radical (O^{2-}), hydrogen peroxide (H_2O_2) and hydroxyl radicals (OH); each generated through the biochemical reduction of O_2 (Senior & Balba, 1990).

Aerobic respiration has been shown to be the most important terminal electron accepting process in many environments, oxidising >90% of the organic carbon in pelagic marine sediments (Bender & Heggie, 1984) and approximately 45% in marginal marine and freshwater lake environments (Jørgensen, 1983a; Jones, 1985). Oxygen consumption rates in sediments typically range from 3 to 4500 mg m^{-2} day^{-1} for freshwater and marine environments (Reeburgh, 1983), and depend on the carbon source, oxygen concentration

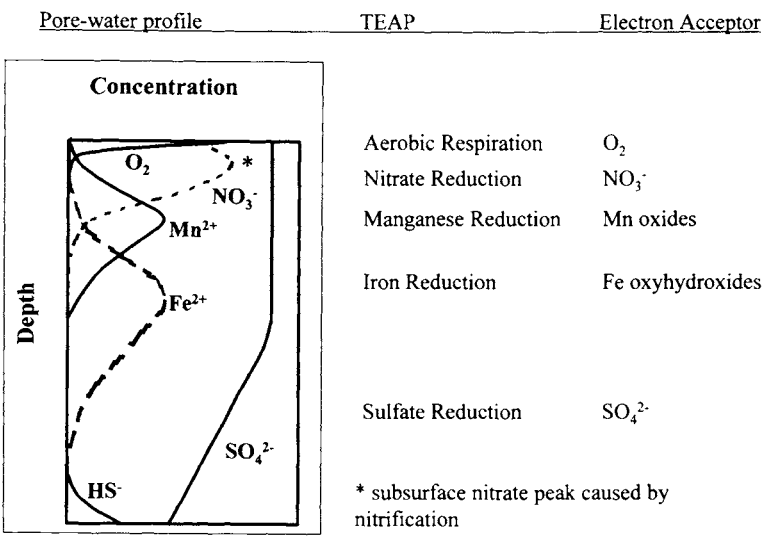

Fig. 1. Hypothetical pore-water profiles produced by successive terminal electron accepting processes (TEAPs) during decomposition of organic matter by chemoheterotrophs. Note also the subsurface nitrate peak caused by chemoautotrophic nitrification (modified from Burdige, 1993).

in the overlying water, the physical regime of the environment and the sedimentation rate (Burdige, 1993; Canfield, 1994). In particular, aerobic respiration rates show a good correlation with sedimentation rates, whereby carbon oxidation is reduced by a factor of 4.8 for every factor of 10 increase in sedimentation rate (Canfield, 1993). Under the low sedimentation rates associated with pelagic marine sediments, little organic matter is deposited and enough time exists for almost complete decomposition via aerobic respiration. At high deposition rates (e.g. continental margins), abundant organic matter is buried and the organic-rich sediment accumulates rapidly enough to pass through the oxic zone. It is estimated that only 45% of the carbon oxidised in these marine settings occurs by aerobic processes, an observation supported by models which suggest that aerobic carbon oxidation dominates when the sedimentation rate is below 0.01 cm y^{-1}, whereas anaerobic carbon oxidation dominates at higher deposition rates (Boudreau & Canfield, 1993; Canfield, 1994). Oxygen is typically used up within the upper few mm of sediment in hypertrophic environments where consumption is faster than resupply (Jørgensen & Revsbech, 1985), but may persist to half a metre or more in pelagic environments (Murray & Grundmaris, 1980). Bioirrigation by macrofauna may introduce oxygenated water to depth, thereby locally increasing the depth of the oxic zone (Hammond et al., 1985).

Nitrogen cycling

Nitrogen cycling in aquatic sediments is relatively complex, with nitrification and dissimilatory nitrate reduction mainly controlling nitrate pore-water profiles. The former is a chemoautotrophic process, and hence will be discussed later. Dissimilatory nitrate reduction most closely resembles aerobic respiration in that nitrate-reducing bacteria

(which reduce nitrate to ammonia) or denitrifying bacteria (which reduce nitrate to N_2) are capable of completely degrading complex organic matter to carbon dioxide, with the concomitant depletion of pore-water nitrate. Dissimilatory nitrate reduction generally occurs at the depth where oxygen is used up, although in some instances O_2 can substitute when it is available, thereby reducing both O_2 and nitrate simultaneously (Tiedje et al., 1982). In coastal sediments, dissimilatory nitrate reduction reduces nitrate to negligible levels within the first couple of centimetres of the pore-water profile. No nitrate occurs below this depth except where burrows introduce oxygenated water which oxidises any ammonia present (Hammond et al., 1985; Mortimer et al., 1999). Nitrate may also be reduced to organic nitrogen by assimilatory nitrate reduction (Jørgensen, 1983a), although in most environments this process is of minor importance (Tiedje et al., 1982). Rates of nitrate reduction 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 & Heggie, 1984) to over 10 mmol m^{-2} day^{-1} in coastal sediments (Seitzinger, 1988). One of the main factors controlling the relative significance of nitrate reduction is the NO_3^- to O_2 concentration ratio (Canfield, 1993), and in estuarine sediments where water column nitrate levels are similar to dissolved O_2 levels, nitrate reduction is responsible for more carbon oxidation than aerobic respiration (Jørgensen & Sørensen, 1985). In freshwater lake sediments with high nitrate, nitrate reduction may be responsible for the oxidation of up to 20% of the organic carbon (Jones, 1985).

Neither aerobic respiration or dissimilatory nitrate reduction have a significant impact on sediment mineralogy. However, the subsequent terminal electron accepting processes described below involve important mineral dissolution and precipitation reactions (Fig. 2). The pathways for organic matter oxidation by most anaerobic microbial processes are very different from those for aerobic respiration or dissimilatory nitrate reduction. Anaerobic decomposition of organic matter is not generally accomplished by a single organism, but instead by a consortium of interdependent microorganisms (see Chapter 1, this volume). These are very limited in the types of organic compounds that they can oxidise, but together can exploit simple organic acids, long chain fatty acids and monoaromatic compounds (Lovley & Chapelle, 1995). Thus in suboxic to anoxic sediments, much of the organic matter released from hydrolysis of complex organic matter is first metabolised via fermentative microorganisms. Some of the primary fermentative byproducts include acetate, lactate, propionate, butyrate and H_2. Because fermentative microorganisms do not completely oxidise organic matter to CO_2, other types of microorganisms operate in conjunction to bring about complete oxidation of organic matter. Fermentation can in fact be inhibited by a high concentration of fermentable byproducts (Schink, 1988; Senior & Balba, 1990) because their accumulation makes the reactions thermodynamically unfavourable (Canfield, 1994).

Reduction of Fe and Mn

Following dissimilatory nitrate reduction, reduction of manganese oxides becomes the most energy-efficient bacterial respiratory process (Santschi et al., 1990a). The principal mineralogical change associated with manganese reduction is dissolution of Mn oxides to produce dissolved Mn^{2+} (Myers & Nealson, 1988), which often diffuses upwards and reprecipitates as fresh Mn oxides at the sediment surface (Burdige, 1993). Downward diffusion of Mn^{2+} most commonly results in the formation of rhodocrosite ($MnCO_3$)

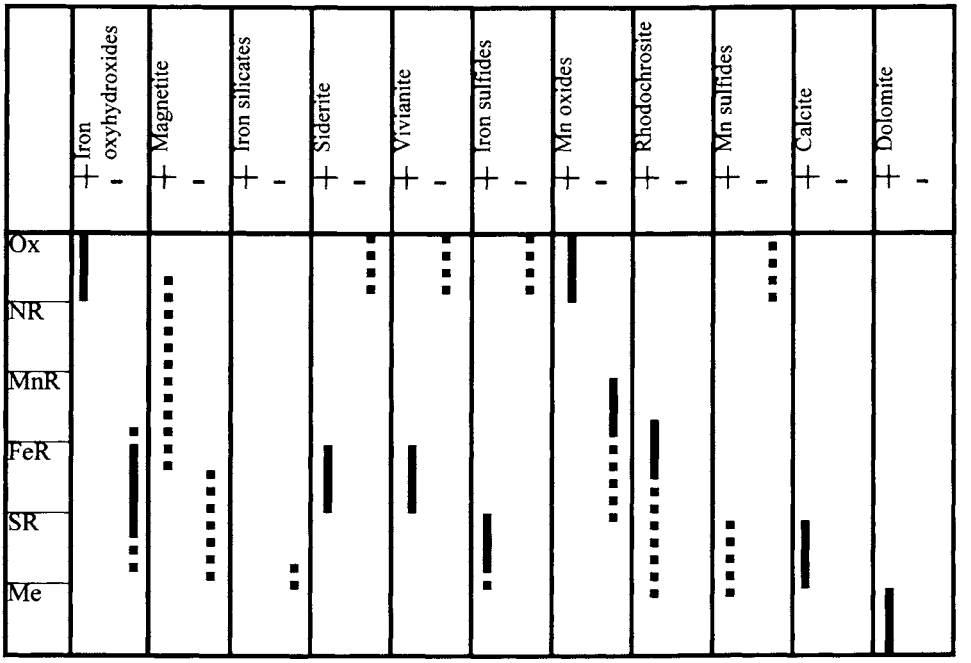

Fig. 2. Hypothetical depth profiles illustrating zones where principal authigenic minerals may precipitate (+) or be dissolved (–) within organic-rich sediments. Both microbial/inorganic precipitation and reductive dissolution reactions have been included. Solid lines indicate depth intervals over which minerals are commonly precipitated or dissolved. Dashed lines indicate other depths where these processes may occur. Ox = aerobic respiration; NR = nitrate reduction; MnR = manganese reduction; FeR = iron reduction; SR = sulfate reduction; Me = methanogenesis.

(Emerson, 1976; Burdige, 1993) or other Mn-carbonates such as kutnahorite and manganoan calcite (Aller & Rude, 1988). Although rhodocrosite has been seen to form in cultures of Mn-reducing bacteria (Lovley & Phillips, 1988) and its formation in lakes and marine sediments has been attributed to bacterial activity (Sokolova-Dubina & Deryugina, 1967; Suess, 1979), it is not known whether the bacteria play a role in mineral formation beyond supplying the ions necessary for precipitation. In environments where pore-water Mn^{2+} concentrations are relatively high, such as in the Baltic Sea basins, MnS may form (Suess, 1979). Because of the limited amount of manganese deposited in sediment, Mn reduction is of minor importance in terms of the amount of total organic carbon oxidised, generally <5% in most environments (Jørgensen, 1983a; Bender & Heggie, 1984; Jones, 1985).

Below the zones of dissimilatory nitrate reduction and manganese reduction, when nitrate has been exhausted and Eh drops accordingly, iron reduction occurs. Dissimilatory iron reduction is broadly distributed amongst several known bacterial genera (Fredrickson & Gorby, 1996). *Geobacter metallireducens* (Lovley & Phillips, 1988) and *Shewanella putrefaciens* (Lovley et al., 1989a) were among the first bacteria studied in pure culture that could gain energy from coupling the oxidation of organic matter and/or H_2 to Fe(III)

reduction. Since then, many more species, including some known sulfate reducers, such as *Desulfuromonas* sp. (Roden & Lovley, 1993) and *Desulfovibrio* sp. (Coleman et al., 1993), have shown the ability to reduce ferric iron. Iron reduction has potentially the most significant impact on sediment mineralogy. Amorphous to poorly-crystalline iron hydroxides, such as ferrihydrite and lepidocrocite, are considered the most important source of Fe(III) for iron reduction, with the rates of reduction declining rapidly with depth as they become depleted (Lovley & Phillips, 1986a, b, 1987). More crystalline Fe(III) oxides (e.g. hematite and goethite) are also microbially reducible, and recent experimental observations suggest that these minerals may provide energy for cellular growth comparable to that derived from the poorly crystalline phases (Roden & Zachara, 1996). Other studies have shown that a variety of microorganisms can even reduce Fe^{3+} in both magnetite (Kostka & Nealson, 1995) and smectite clays (Kostka et al., 1999), clearly indicating that a wide array of iron minerals can be used by Fe(III)-reducing bacteria. The rates of iron reduction are dependent upon a number of factors, including the surface area and site concentration of the solid iron phase, the composition of the aqueous solution in which the microbes grow and the amount of Fe^{2+} sorbed to the oxide surface (Roden & Zachara, 1996; Fredrickson et al., 1998; Urrutia et al., 1998).

Removal of Fe from solution

The reduction of ferric iron minerals produces an increase in the concentration of ferrous iron in the pore-water. Some of this ferrous iron may diffuse upwards to be reoxidised, but most is removed from solution by precipitation of metal sulfides at depth. There is often a pore-water ferrous iron maximum at the boundary between the iron reduction and sulfate reduction (SR) zones (Jørgensen, 1983a; Burdige, 1993). Below this depth, the iron is removed from solution by reaction with sulfide produced by sulfate-reducing bacteria (SRB) below. This forms metastable iron monosulfide minerals such as greigite and mackinawite which are precursors to pyrite (FeS_2) (Postma, 1982; Berner, 1984). The precise mechanism for the transformation of monosulfides into pyrite, however, remains poorly understood (Benning et al., 2000).

In addition to sulfide formation, iron may be removed from solution by the abiogenic or biogenic precipitation of hydroxide, mixed valence oxide, carbonate, phosphate and silicate minerals, depending on the chemical conditions of the particular sediment (Santschi et al., 1990a; Lovley, 1991). The biologically-induced formation of epicellular iron hydroxide by bacteria can occur either passively or actively (Konhauser, 1997, 1998; Ferris et al., 1999). In the first instance, the oxidation and hydrolysis of cell-bound ferrous iron and/or the alteration of local pH and redox conditions around the cell due to metabolic activity can all induce transformation to insoluble hydroxide forms. Alternatively, ferrous iron diffusing upwards into more oxidising sediment spontaneously reacts with dissolved oxygen (or potentially NO_3^- or MnO_2) to precipitate rapidly (abiotically) as ferric hydroxide on available nucleation sites (Burdige, 1993; Canfield, 1993). Bacteria passively act as such sites, and over a short period of time the microbes can become completely encrusted in amorphous iron as abiological surface catalysis accelerates the rate of mineral precipitation. Indeed, ferrihydrite develops on the organic remains of dead cells, implying that iron mineralisation can occur independent of cell morphology, trophic classification or physiological state (Ferris et al., 1989). It has also been suggested that under circumneutral pH any bacterium

that produces acidic, extracellular polymers will nonspecifically adsorb positively charged Fe-hydroxides (Ghiorse, 1984) since the point of zero charge (pH where the mineral has zero charge) of amorphous Fe-hydroxides lies in the range of 5.3–7.5 for natural samples (Schwertmann & Fechter, 1982). Reactive organic sites can therefore scavenge ferric iron from the surrounding waters. The active process by which iron hydroxides form stems from the ability of Fe(II)-oxidising bacteria to oxidise ferrous iron as an energy source (see below).

In suboxic sediments there is clear evidence for authigenic magnetite (Fe_3O_4) formation (Karlin et al., 1987), although its actual origin is uncertain because a variety of potential precipitation mechanisms exist (Lovley, 1991). The biogenic magnetite fraction is commonly single domain, with a high natural magnetic remanence, and is known to proceed under both 'biologically controlled' and 'biologically induced' conditions (see Blakemore & Frankel, 1989). In the first instance, magnetotactic bacteria produce intracellular chains of single, pure magnetite crystals (35–120 nm in diameter), under precise biochemical, chemical and probably genetic control (Mann et al., 1990; Bazylinski, 1996). Magnetotactic bacteria are common in aquatic habitats, their greatest abundance being at the oxic–anoxic boundary (Bazylinski, 1995). Obligately microaerophilic bacteria, such as *Aquaspirillum magnetotacticum* strain MS-1, use oxygen, nitrate (Bazylinski & Blakemore, 1983) and possibly ferric iron (Blakemore & Frankel, 1989) as terminal electron acceptors. In contrast, pure cultures and consortia of iron reducers have been shown to produce magnetite crystals quite different from those formed under controlled conditions. This magnetite is extracellular, there is no evidence of cellular material associated with it, and the crystals typically consist of a mixture of round and oval particles that range in size from 10–50 nm (Lovley et al., 1987). It remains unclear whether the iron reducers produce magnetite enzymatically or whether they simply create the necessary chemical conditions for abiotic precipitation to proceed (Lovley, 1991). However, since the magnetite produced is crystalline, and not particularly reducible, iron-reducing bacteria effectively convert part of the labile iron oxide pool into a more refractory one.

Other minerals which have been observed to form in cultures of iron-reducing bacteria are siderite ($FeCO_3$) (Lovely & Phillips, 1986a; Mortimer & Coleman, 1997; Mortimer et al., 1997) and vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$) (Fredrickson et al., 1998; Zachara et al., 1998). As with magnetite, it is unclear whether microorganisms enzymatically catalyse the precipitation reactions or simply produce chemical conditions to make abiotic precipitation favourable. Siderite formation has been linked to the activity of sulfate-reducing bacteria and methanogens, as well as iron reducers (Coleman, 1985; Lovley, 1991; Coleman et al., 1993). Since iron reduction produces both ferrous iron and bicarbonate, conditions may become favourable for the precipitation of siderite. However, in marine sediments, sulfate reduction produces sulfide which will preferentially react with any ferrous iron to precipitate iron monosulfide minerals. Therefore, siderite is more common in freshwater environments (Postma, 1982); the precise juxtaposition of iron reduction and sulfate reduction in marine sediments controls whether siderite and/or pyrite may form (Coleman, 1985; Coleman et al., 1993). Vivianite forms under anoxic conditions where sufficient phosphate and iron are present and the sulfide activity is low enough to preclude formation of iron sulfides (Hearn et al., 1983). Precipitation is extremely slow and may be inhibited by the presence of ferric hydroxides which will react with phosphate to form insoluble ferric

hydroxy-phosphates (Emerson & Widmer, 1978; Postma, 1981). Vivianite has been observed in the upper iron reduction zone in anaerobic lake sediments (Emerson & Widmer, 1978), in freshwater swamps (Postma, 1982) and in river sediments (Hearn et al., 1983). Indirect evidence has also shown that it may form under marine conditions before the onset of sulfate reduction (Martens et al., 1978).

When the sediment receives significant input of detrital material and/or biogenic silica (e.g. diatom frustrules) their dissolution may lead to reprecipitation of authigenic aluminosilicates. Biogenic iron silicate minerals are ubiquitous in freshwater sediments, and precipitate when dissolved silica and aluminum react with cellularly bound iron via hydrogen bonding between the hydroxyl groups in the bound iron and the hydroxyl groups in the silica and aluminum (Konhauser & Urrutia, 1999). This is not unusual, as ferrihydrite commonly adsorbs large quantities of silica in natural mineral deposits (Carlson & Schwertmann, 1981). Over time, these hydrous compounds dehydrate, with some phases converting to more stable crystalline forms. Authigenic formation of iron silicates in the marine environment has also been recently reported from the Amazon delta, where Michalopoulos & Aller (1995) reported authigenic K–Fe–Mg clays contributing >3% of sediment weight.

With respect to the percentage of total organic carbon oxidised, the importance of iron reduction compared to other terminal electron accepting pathways varies according to the environment. It is also difficult to assess because methods used to estimate iron reduction are generally flawed and tend to underestimate rates (Lovley, 1991). However, iron reduction is known to be an extremely important process in soils (Ponnamperuma, 1972) and in tropical sediments rich in ferric oxyhydroxide, such as those along the Amazon Shelf (Aller et al., 1986, 1998). It has also been shown to be important in temperate marine and freshwater environments (Jones et al., 1984; Sørensen & Jørgensen, 1987; Lovley et al., 1990; Coleman et al., 1993; Hines et al., 1997).

Other electron acceptors

In addition to Fe(III) and Mn(IV), some bacteria may use other metals as electron acceptors. In cultures of *G. metallireducens*, the *c*-type cytochromes were oxidised by gold, silver and mercury, although whether the reduction of these metals can function to support growth was not determined (Lovley et al., 1993). The microbial reduction of selenate (SeO_4^{2-}) to selenite (SeO_3^{2-}) or elemental selenium has been shown in anoxic sediments and culture (Macy et al., 1989; Oremland et al., 1989). Other microbial taxa have been shown to reduce As(V) to As(III) (Ahmann et al., 1994; Newman et al., 1997); Cr(VI) to Cr(III) (Wang et al., 1989); V(V) to V(IV) (Yurkova & Lyalikova, 1991); Mo(VI) to Mo(V) (Sugio et al., 1988); and Cu(II) to Cu(I) (Sugio et al., 1990). The likely effects of microbially mediated reduction on the solubility of radionuclides will be discussed in more detail below.

Interestingly, many of the microbially-mediated metal reductions can be coupled to the oxidation of organic contaminants or humic compounds. Lovley et al. (1989b) and Lovley & Lonergan (1990) have shown that, in contaminated groundwater, *G. metallireducens* could couple the oxidation of synthetic aromatic hydrocarbons, such as benzoate, toluene, phenol and *p*-cresol, to Fe(III) reduction. Purified enrichment cultures metabolised other aromatics such as syringic acid, ferulic acid, nicotinic acid, *m*-cresol and a variety of mono-

and dihydroxybenzoates (Lonergan & Lovley, 1991). The reductive dehalogenation of chlorinated organic compounds, e.g. tetrachloromethane, has similarly been demonstrated for pure cultures of *S. putrefaciens* (Picardal et al., 1993). Kazumi et al. (1995) have suggested that a consortium of microorganisms may be involved in the degradation of chlorinated aromatics, with one or more microbes being responsible for dehalogenating the substrate, while other microbes utilise the aromatic ring and degradation products. Iron reducers can, however, also contribute indirectly to organic oxidation reactions by forming chemically reactive forms of Fe(II). Klausen et al. (1995) have shown that surface-bound Fe(II) species, because of their significantly lower reduction potential compared with aqueous Fe(II), contributed to the reduction of nitroaromatic compounds to amines and anilines.

Until recently, humic substances were considered resistant to bacterial degradation. However, Lovley et al. (1996) established that cell suspensions of *G. metallireducens* and *Shewanella alga* were able to use humic substances as electron acceptors for the anaerobic oxidation of organic compounds. Microbial humic reduction also mediated the reduction of Fe(III) oxides. First, the bacteria oxidised acetate or lactate with the humics as intermediate electron acceptors. Second, the reduced humic acids donated electrons to Fe(III), thereby regenerating the humic substances in an oxidised form to accept, once again, electrons from the humic-reducing bacteria. In essence, the humics served as electron shuttles between the microbes and the solid iron oxide. In a subsequent study, Coates et al. (1998) demonstrated that humic-reducing bacteria of the *Geobacteraceae* family could be recovered from a variety of sediment types, suggesting that the potential for humic substances to actively enhance microbial reduction processes was widespread.

Sulfate reduction and sulfidation

Below the zones described by Froelich et al. (1979) as 'suboxic' (nitrate-reducing, manganese-reducing and iron-reducing), is the 'anoxic' sulfate reduction zone. Sulfate reduction only occurs when all other available terminal electron acceptors have been exhausted. In marine environments, where there is a high concentration of dissolved sulfate, it is quantitatively a very important process of organic matter degradation and may occur over a considerable thickness of sediment (Jørgensen, 1983a). It has been estimated that sulfate reduction is responsible for nearly all organic carbon oxidation in euxinic sediments (Canfield, 1993), approximately 50% of the organic carbon oxidation in coastal marine sediments (Jørgensen, 1983a), but $<10\%$ in pelagic and freshwater environments (Bender & Heggie, 1984; Jones, 1985). Some freshwater environments such as swamps, which are very organic-rich and hence have substantial releases of S from organic matter, may support increased sulfate reduction (Berner, 1980). The rate of sulfate reduction is proportional to the quantity and reactivity of organic matter entering the sulfate reduction zone, which in turn is a function of the extent to which this organic matter was first degraded in the oxic zone (Westrich & Berner, 1984). Sulfate 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 accumulating hemipelagic sediments, and lowest levels in deep-sea pelagic sediments (Canfield, 1993).

Sulfate reduction results in an increase in pore-water sulfide at the expense of sulfate. Dissolved H_2S can be extremely toxic to sulfate-reducing bacteria because it combines with the iron of cytochromes (Postgate, 1984). On the other hand, reaction with extracellular iron is a common detoxification mechanism for sulfide in the environment through formation of insoluble iron monosulfides (FeS), and eventually pyrite. Initially, this process is driven by reaction of the biogenic sulfide with dissolved ferrous iron diffusing down from the iron-reducing zone above. However, as the sulfide produced overwhelms the ferrous iron available, sulfide accumulates in the pore-water up to the base of the iron-reducing zone and is removed more slowly by abiotic reaction with ferric iron minerals (Canfield, 1989). This liberates further ferrous iron, leading to the formation of additional iron sulfide, and eventually pyrite. The amount and reactivity of iron phases dictates how much pyrite will form (Canfield, 1989; Canfield et al., 1992). In very rapidly accumulating sediments (>1 mm y^{-1}), there may be insufficient interstitial dissolved sulfide at depth to allow reaction with all detrital iron minerals. In other words, there is an over abundance of iron minerals deposited. By contrast, at lower sedimentation rates, potentially all of the Fe supplied to the sediments may become pyritised because the supply of dissolved sulfide exceeds the amount of iron initially deposited, although this does not generally happen because some Fe phases react only very slowly. For example, Canfield et al. (1992) have shown that ferrihydrite has a half-time for reaction of 4 hours. Lepidocrocite, goethite, hematite, magnetite and sheet silicates are increasingly less reactive, with the latter having a reaction half-time of 100,000 years. Those minerals which are most reactive to sulfide can also be readily utilised by iron-reducing bacteria, suggesting that the two processes may act in competition. In addition to reacting with iron minerals, sulfide may reduce manganese oxides in a similar fashion (Aller & Rude, 1988; Santschi et al., 1990a). These reactions highlight the importance of sulfate reduction with respect to the sediment mineralogy; along with iron reduction, it is responsible for the predominant mineralogical transformations during early diagenesis and the oxidation of most, if not all, remaining organic matter left in the sediments.

Methanogenesis

In some instances, the terminal step in the anaerobic degradation of organic material is methanogenesis. The methanogens are strictly limited in the types of compounds that they can metabolise (Madigan et al., 1997) and most use CO_2 (as HCO_3^- at circumneutral pH) as both their terminal electron acceptor and carbon source, while H_2 serves as the electron donor (reaction 6). A second class of reactions involves the reduction of compounds containing the methyl functional group, such as methanol (CH_3OH) and methylamine (CH_3NH_2) to methane (reaction 7). Other methanogens disproportionate acetate to give methane and bicarbonate (reaction 8). Methanogens cannot use long chain fatty acids and aromatic compounds so, under anoxic conditions where methanogens grow, the homoacetogenic bacteria, are also required. These bacteria convert fatty acids and aromatics to acetate and H_2, which are then consumed by the methanogens.

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \qquad (6)$$
$$\Delta G = -131 \text{ kJ/mol } CH_4$$

$$4CH_3OH \text{ (methanol)} \rightarrow 3CH_4 + CO_2 + 2H_2O \quad (7)$$
$$\Delta G = -106 \text{ kJ/mol } CH_4$$

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^- \quad (8)$$
$$\Delta G = -31 \text{ kJ/mol } CH_4$$

Methanogenic activity is particularly abundant in fresh- and brackish-water sediments, such as peat deposits, tidal estuaries and eutrophic lakes (Smith & Klug, 1981; Williams & Crawford, 1984; Avery & Martens, 1999), or in some rapidly depositing shallow water marine sediments (Canfield, 1993), where the accumulation of organic material exceeds decay by conventional terminal electron acceptors, particularly sulfate. By contrast, marine waters contain sufficiently high levels of sulfate such that SRBs effectively out compete the methanogens for available acetate or H_2 in the sediments (Lovley et al., 1982; Lovley & Klug, 1986). This pattern largely stems from the thermodynamic and kinetic advantages sulfate-reducing bacteria have over methanogens, as indicated by the standard Gibbs free energy change of the oxidation of the substrates (Rinzema & Lettinga, 1985) and the higher affinity sulfate-reducing bacteria have for the oxidisable substrates (Lovley & Klug, 1983). Because of this competitive disadvantage, the major precursors of methane production in marine environments are compounds which are inefficiently used by sulfate-reducing bacteria, i.e. the methylated compounds (King, 1984).

Carbonate minerals and sediment hydrogen concentrations

The pore-water and mineralogical signatures described in the previous sections outline the major chemical and mineralogical changes that occur with depth through successive biogeochemical zones. However, both carbonate mineral formation and microbial oxidation of hydrogen may occur in any biogeochemical zone, and these are worth describing separately.

The saturation state of sediment pore-waters with respect to calcium carbonate is dependent on organic matter oxidation during diagenesis (Van Cappellen & Gaillard, 1996). Aerobic respiration results in the complete oxidation of organic carbon to CO_2 and hence may promote the dissolution of biogenic carbonate (Archer et al., 1989). Anaerobic respiration, on the other hand, generates bicarbonate and potentially drives the precipitation of early diagenetic carbonate minerals (Boudreau & Canfield, 1993). These minerals are relatively stable once formed and are not subject to further rapid recycling by redox reactions in the same way as sulfides and oxides. Therefore, a characteristic sequence produced by different terminal electron accepting processes can be distinguished on both mineralogical and stable isotopic grounds in environments where precipitation of carbonate minerals is possible, e.g. organic-rich muds (Berner, 1981; Maynard, 1982; Coleman, 1985; Fig. 3). Aerobic respiration produces non-ferroan calcite because there is no dissolved iron present under oxic conditions. This calcite has a stable carbon isotopic composition ($\delta^{13}C_{PDB}$) of 0‰ (as do all primary marine carbonates). Nitrate reduction does not produce carbonate minerals with characteristic chemistry. Manganese and iron reduction produce rhodocrosite and siderite, respectively, with increasingly negative $\delta^{13}C_{PDB}$ (typically –2 and –10‰, respectively) due to the incorporation of an increasing component of organogenetic carbonate which has a $\delta^{13}C_{PDB}$ signature of –20 to –30‰. Sulfate reduction produces non-ferroan

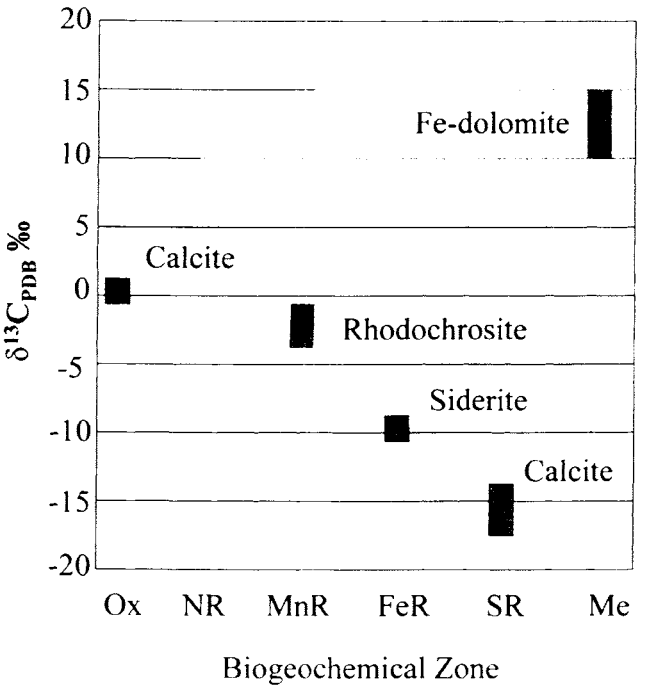

Fig. 3. Characteristic chemical and carbon isotopic composition of authigenic carbonate minerals produced in different biogeochemical zones (after Coleman, 1985).

calcite because any available iron reacts preferentially with sulfide. These calcites have an even more negative $\delta^{13}C_{PDB}$ signature (typically −15‰). Finally, below the zone of sulfate reduction, methanogenesis leads to the production of ferroan carbonates (siderite or ferroan dolomite) with a characteristic positive $\delta^{13}C_{PDB}$ signature due to coupling of methane oxidation with reduction of residual iron minerals (Irwin et al., 1977; Coleman, 1985).

As discussed above, the dominant terminal electron accepting pathways are generally segregated into distinct zones in sediments based on the potential thermodynamic yield of the various metabolic processes. However, reactions yielding less energy should also take place as long as they are energetically favourable and segregation can perhaps be more accurately explained on the basis of competition between different types of microorganisms for electron donors (Lovley & Phillips, 1987; Lovley et al., 1994; Lovely & Chapelle, 1995). For example, microorganisms may couple the oxidation of hydrogen to the reduction of nitrate, manganese, iron, sulfate or carbon dioxide and this is the predominant control on the concentration of dissolved hydrogen gas in aquatic sediments. Lovley & Goodwin (1988) also showed that microorganisms oxidising H_2 with the reduction of more electrochemically positive terminal electron acceptors can maintain lower hydrogen concentrations than microorganisms using terminal electron acceptors which yield less energy. Therefore, sediments in which nitrate and/or manganese reduction were the dominant terminal electron accepting pathway had the lowest hydrogen concentrations

(<0.05 nM), and these levels increased through iron reduction (0.2 nM), sulfate reduction (1–1.5 nM) and methanogenesis (7–10 nM). This pattern of H_2 concentrations can be ascribed to the physiological capabilities of the microorganisms growing in the sediments. Microorganisms that use Fe(III) for H_2 oxidation can metabolise it to concentrations lower than those that can be utilised by sulfate reducers, and the sulfate reducers can metabolise the same substrates to concentrations below those usable by methanogens. These findings are consistent with observations of sediments where sulfate is not reduced, and methane not produced until the reducible Fe^{3+} has been converted to Fe^{2+}. Thus, when the availability of Fe(III) does not limit the rates of microbial Fe(III) reduction, sulfate reduction and methane production are inhibited because of the iron reducers' competitive advantage in using available substrates at much lower concentrations (Lovley & Phillips, 1987). Trace metals are subject to similar forms of competition, with for example, the presence of nitrate inhibiting As(V) reduction, while sulfate reduction is inhibited by the presence of As(V) (Dowdle et al., 1996).

Problems with the biogeochemical zone scheme

There are a variety of potential problems with the simple zonal scheme. Natural aquatic environments contain complex microbial communities rather than a simple succession of 'pure cultures', and hence there is potential for overlap of the processes described above (Canfield et al., 1993, Postma & Jakobsen, 1996). In addition, microenvironments may form, allowing the coexistence of suboxic and anoxic processes at the same sediment depth (Goldhaber et al., 1977). There may also be complex and continuous recycling reactions occurring which are simply not seen because their net effects cancel each other out.

Our understanding of the individual microbial reduction reactions which form the basis of the biogeochemical zone scheme is incomplete, particularly in the case of iron and manganese reduction. For instance, we have known for more than a decade that ferric oxides persist at depth below the iron reduction zone, even in the presence of labile organic matter and microorganisms (Canfield, 1989; Lovley et al., 1990), but we do not know why iron reduction ceases. There is growing evidence for complex cycling of Mn–Fe–S rather than a simple succession of manganese reduction, iron reduction and sulfate reduction. Canfield et al. (1993) challenged the view that the sequence of Mn^{2+} and then Fe^{2+} in pore-water was indicative of a change from manganese reduction to iron reduction because Mn oxides may oxidise Fe^{2+} to Fe^{3+} oxides, releasing Mn^{2+} into solution. Similarly, reduced sulfur species, specifically S^0, organic S and/or FeS, can be used by chemoautotrophic bacteria to reduce Mn-oxides completely under anoxic conditions, thereby complicating measurement of the actual sulfate reduction rate (Aller & Rude, 1988). Canfield (1989) also showed that it is possible to have pore-waters rich in Fe^{2+}, but low in H_2S, despite active sulfate reduction. This is due to the reaction of ferric oxyhydroxides with H_2S which forms iron sulfides, leaving Fe^{2+} in solution. He invoked microenvironments to explain the contradictory findings that iron reduction was the major source of pore-water Fe^{2+} but most ferric oxides were reduced by H_2S. In one microenvironment, iron reduction released Fe^{2+} into solution, whereas in the other, ferric oxides were reduced by H_2S, with the Fe^{2+} generated quickly reacting with additional H_2S to precipitate iron sulfides. More recently, it has been shown that sulfate reduction may occur in Fe-rich environments (Jakobsen & Postma, 1994), and that sulfate-reducing bacteria are able to switch to the reduction of

ferric iron (Coleman et al., 1993). It has also been observed that certain nitrate-reducing bacteria are capable of iron reduction (Sørensen, 1982, 1987; Lovley & Phillips, 1988; Ehrlich, 1990) and that fermenters can reduce manganese and ferric iron (Jones, 1985).

Recent advances in sampling both pore-water geochemistry and microbiological populations also suggest that the sequential scheme of biogeochemical zones is an oversimplification. Techniques described in Chapter 2 of this volume, such as signature lipid biomarkers, can now be used to distinguish in situ microbial biomass, community structure and nutritional status (White, 1993). Nucleic acid sequence analysis of genes also allows characterisation of community structure and function (Muyzer et al., 1993). This has led to the development of 'gene probes' to sample for specific groups of microorganisms. These technologies have been used in redox stratified environments (Coleman et al., 1993; Duan et al., 1996) to show that siderite-iron monosulfide concretions, present in anoxic salt-marsh sediments, were caused by direct enzymatic reduction of Fe(III) by sulfate-reducing bacteria (*Desulfovibrio*), rather than the iron-reducing populations.

New methods have also been devised to sample pore-water chemistry at higher resolution than previously possible. The two principal new approaches are microelectrodes (Brendel & Luther, 1995) and gel probes (Davison et al., 1991, 1994; Krom et al., 1994; Zhang et al., 1995; Mortimer et al., 1998). Microelectrode profiling of redox species in cores from continental margin sites off the coast of Nova Scotia has recently revealed evidence for complex interactions between the manganese and nitrogen cycles (Luther et al., 1997, 1998), whereby Mn^{2+} did not appear until many millimetres below the oxic layer. Those studies used field data and laboratory evidence to suggest that dinitrogen could be produced by the oxidation of ammonia and organic-N with MnO_2 in air, and that dissolved Mn^{2+} could abiotically reduce nitrate to dinitrogen. Direct evidence for close coupling between Mn and N has also recently been obtained in laboratory experiments (Hulth et al., 1999).

Signals caused by chemoautotrophs

During chemoheterotrophic activity, reduced byproducts such as NH_3, Mn^{2+}, Fe^{2+}, H_2S and CH_4 are generated below the oxic–suboxic boundary. Physical and macrofaunal processes will cause the net transport of these reduced species from the deeper layers towards the sediment surface. As a result, a fraction of the oxygen consumed in the surface layers is diverted away from aerobic respiration toward the reoxidation of reduced species by chemoautotrophic bacteria (Van Cappellen & Gaillard, 1996). The impact of chemoautotrophic bacteria on sediment mineralogy and pore-water chemistry is variable, and generally site specific. Bacterial nitrification often occurs in sediments between the zones of aerobic respiration and nitrate reduction. Nitrifying bacteria develop especially well in lakes and streams that receive inputs of ammonia-rich sewage or at sites beneath planktonic blooms where extensive protein decomposition occurs (ammonification). Methanotrophs occur wherever stable sources of methane are present. In more extreme environments, such as those associated with acid mine waters or under low oxygen concentrations, iron and sulfur-oxidising bacteria play a major role in the localised Fe and S cycles.

Just below the sediment–water interface, ammonia diffusing up from depth comes into contact with oxygen in the oxic layer and is converted to nitrate by the process of nitrification (Hansen et al., 1981). The ammonium is first oxidised to nitrite by ammonium-oxidising bacteria (e.g. *Nitrosomonas*) (reaction 9), and this is then further oxidised to nitrate by nitrite oxidisers (e.g. *Nitrobacter*) (reaction 10); no bacterium is known that will carry out the complete oxidation of ammonia to nitrate (Madigan et al., 1997). Combined, these processes cause a subsurface peak of nitrate in the pore-water (Fig. 1). In coastal sediments with a high carbon flux and relatively low nitrate concentration in the overlying water, this nitrification peak is often very close to the sediment–water interface (Mortimer et al., 1999).

$$NH_3 + 1.5O_2 \rightarrow NO_2^- + H_2O + H^+ \quad (9)$$
$$\Delta G = -96 \text{ kJ/0.5 mol } O_2$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \quad (10)$$
$$\Delta G = -74 \text{ kJ/0.5 mol } O_2$$

Although methane is a relatively stable compound, a variety of bacteria, the methanotrophs, utilise it as an electron donor for energy generation and as their sole source of carbon. These bacteria are all obligate aerobes and they grow abundantly at the chemocline in lakes and sediment, where methane from the underlying anoxic zone diffuses upwards to the overlying oxic zone. Methanotrophs are also able to oxidise ammonia, although they cannot grow with it as the sole electron donor (Madigan et al., 1997).

In acid mine drainage, *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* catalyse the reaction between iron and oxygen, leading to the formation of ferric iron minerals (reaction 11). Because very little energy is generated in the oxidation of ferrous to ferric iron (with oxygen as the electron acceptor), these bacteria must oxidise large quantities of iron in order to grow. For example, it has been estimated that a consumption of 90.1 mol of Fe^{2+} is required to assimilate only 1.0 mol of carbon (Ehrlich, 1990). Consequently, even a small number of bacteria can be responsible for precipitating vast amounts of iron.

$$2Fe^{2+} + 0.5O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \quad (11)$$
$$\Delta G = -54 \text{ kJ/0.5 mol } O_2$$

At neutral pH, Fe(II) oxidation by *Sphaerotilius natans*, *Leptothrix ochracea* and *Gallionella ferruginea* occurs under partially reduced conditions, with an Eh range of +200 to +320 mV and oxygen levels of 0.1–1.0 mg of O_2 per litre (Ehrlich, 1990). The existence of these microaerophilic bacteria depends on their oxidising efficiency relative to abiotic oxidation at low oxygen fugacity. Although there is no conclusive evidence that iron bacteria other than the acidophiles derive energy from Fe(II) oxidation, *Gallionella ferruginea*, for example, can grow autotrophically with Fe^{2+} as its sole energy source at a pH just below 7 (Hallbeck & Pedersen, 1991). Straub et al. (1996) also demonstrated that the biological oxidation of ferrous iron in the absence of oxygen was possible using nitrate instead as the electron acceptor. This observation, that nitrate reducers, which had never previously been grown in iron media, exhibited a capacity for ferrous iron oxidation, implies that this

form of microbial oxidation of ferrous iron may be common in the suboxic zone of aquatic environments.

The role of sulfur-oxidising bacteria in controlling sediment mineralogy and pore-water chemistry is also limited to environments where the spontaneous reaction of sulfide with oxygen is inhibited (e.g. where the oxygen concentration is low). This includes being just above the oxic/anoxic boundary, or living at hot springs, where the solubility of oxygen at elevated temperatures is low. The oxidation of hydrogen sulfide normally occurs in stages, with sulfate generally the final end product. Microaerobic bacteria such as *Beggiatoa* sp., *Thiovulum* sp. and *Thiothrix* sp. are specifically dependent on H_2S and are commonly found in sediments at the transition between O_2 and H_2S (Jørgensen, 1983a; Jørgensen & Revsbech, 1983; Nelson & Jannasch, 1983). *Beggiatoa* sp. oxidise H_2S to elemental sulfur (reaction 12), which may then be further oxidised to SO_4^{2-} (reaction 13) by other bacteria, such as *Thiobacillus thiooxidans*, which grows attached to the mineral surface and uses it as an electron donor (Madigan et al., 1997). It is unclear whether *Beggiatoa* gain energy or whether these H_2S oxidisers produce intracellular sulfur for other reasons, e.g. to protect the cell from harmful oxygen compounds such as hydrogen peroxide (Kuenen & Beudeker, 1982) or as an electron acceptor, whereby it may be reduced back to H_2S if conditions become anaerobic (Jørgensen & Revsbech, 1983). Another interesting type of metabolism is shown by *Thioploca* sp., which grow as thick mats on the ocean floor. These cells can migrate upwards as much as 10 cm above the surface to accumulate NO_3^- intracellularly within vesicles and then migrate back downwards where they reduce it with the concomitant oxidation of hydrogen sulfide (Fossing et al., 1995).

$$H_2S + 0.5O_2 \rightarrow S^0 + H_2O \qquad (12)$$
$$\Delta G = -209 \text{ kJ/0.5 mol of } O_2$$

$$S^0 + H_2O + 1.5O_2 \rightarrow SO_4^{2-} + 2H^+ \qquad (13)$$
$$\Delta G = -195 \text{ kJ/0.5 mol of } O_2$$

The sulfur oxidisers also include those bacteria that inhabit the low pH environments associated with acid mine drainage environments. *Thiobacillus thiooxidans* enzymatically oxidises sulfide, sulfur, thiosulfate and other reduced sulfur compounds for cellular growth (Kuenen & Beudeker, 1982; Jørgensen, 1983b).

4. Radionuclide contaminants

The biogeochemical behaviour of radionuclides is becoming increasingly important due to the issues of their disposal as nuclear wastes, their long-term containment and ultimately their movement through the environment. Important radionuclides in the environment include high yield fission products such as radiocaesium and technetium, as well as the actinide elements, including uranium, plutonium and neptunium. The nuclear properties of significant isotopes of these elements, as well as an indication of their oxidation states and typical environmental concentrations of some contaminated areas are included in Table 1.

Table 1
Nuclear properties, oxidation states and environmental concentrations of key environmental radionuclides of Cs, Tc, U, Pu and Np

Element	Isotope	Half-life (y)	Environmental oxidation state	Major decay mode	Sample type	Concentration range
Caesium	134	2.06	I	Gamma	[a]Seawater (Irish Sea)	5.0×10^{-3}–100 Bq l^{-1}
	*137	30.17		Gamma	[b,c]Pore waters	2.8×10^{-3}–2.3×10^{-1} Bq l^{-1}
					[c,d]Sediment	0.1– 3.5×10^{4} Bq kg^{-1}
Technetium	99	2.15×10^{5}	IV, VII**	Beta	[e]Seawater (Irish Sea)	1–340×10^{-3} Bq l^{-1}
					[f]Surface water (fallout)	5.0×10^{-5}–6.3×10^{-4} Bq l^{-1}
					[d,g]Sediment	0.1–60.4 Bq kg^{-1}
Uranium	238	4.47×10^{9}	IV, VI**	Alpha	[h]Seawater (average)	3 μg l^{-1}
					[h]Surface waters	0.1–500 μg l^{-1}
					[i]Sediment	1.2–120 μg g^{-1}
Neptunium	237	2.14×10^{6}	IV, V**, VI	Alpha	[j]Seawater (Irish Sea)	8.0×10^{-5}–1.4×10^{-3} Bq l^{-1}
					[k]Sediment (Irish Sea)	1.2×10^{-2}–13 Bq kg^{-1}
Plutonium	238	87.7	III, IV**, V, VI	Alpha	[l]Seawater	1.0×10^{-5}–5.0×10^{-2} Bq l^{-1}
	*239, 240	2.41×10^{4}, 6.55×10^{3}		Alpha	[l]Surface waters	3.7×10^{-6}–4.8×10^{-3} Bq l^{-1}
	241	14.4		Beta	[m]Porewaters (Irish Sea)	2.0×10^{-3}–6.4×10^{-2} Bq l^{-1}
					[l]Sediment	1.6×10^{-1}–1.3×10^{4} Bq kg^{-1}

* Isotopes for which concentration data are quoted; ** Indicates the most common oxidation state in the natural environment.
[a] Kershaw et al., 1992; [b] Comans et al., 1992; [c] Sholkovitz & Mann, 1984; [d] Morris et al., 2000; [e] Leonard et al., 1997; [f] cited in Wildung et al., 1979; [g] Morita et al., 1993; [h] cited in Murphy & Shock, 1999; [i] Langmuir, 1997; [j] Pentreath & Harvey, 1981; [k] Assinder et al., 1991; [l] cited in Sholkovitz, 1983; [m] Livens et al., 1994.

Caesium

Large amounts of radiocaesium (predominantly ^{137}Cs and ^{134}Cs) have been deposited in the environment from nuclear weapons testing, nuclear accidents and in waste effluents associated with nuclear fuel reprocessing (Choppin et al., 1995). Radiocaesium has a relatively short half-life, and is a major contributor to the radiotoxicity of spent nuclear fuel in the first 300 years or so after removal from the nuclear power station. The extent of incorporation of $^{134,137}Cs$ into sediment burial is limited by their relatively short half-lives. For particle associated radiocaesium and other short lived (half-life <30 years) radionuclides, high sedimentation rates are required if the radionuclides are to be fully incorporated into biogeochemical cycles associated with sediment deposition.

The majority of radiocaesium (oxidation state +1) behaves conservatively in the environment, although it interacts strongly with clay minerals in soils and sediments (Evans et al., 1983; Cremers et al., 1988). Thus, radiocaesium may be removed from the water column during settling of suspended sediment, resulting in reduced mobility and bioavailability (Santschi et al., 1988; Santschi et al., 1990b). In certain sediments, this situation may be complicated by changes in pore-water chemistry during sediment burial and early diagenesis resulting in a remobilisation of radiocaesium (Sholkovitz, 1985). For example, Comans et al. (1989) reported in-situ solid/liquid distribution coefficients (Kd values) for radiocaesium in lake sediment contaminated by Chernobyl derived ^{137}Cs. They showed that the Kd values for radiocaesium in a sediment core decreased with depth, suggesting a decline in sediment-associated ^{137}Cs with burial. The binding mechanism for caesium in natural systems is regulated by a small number of highly selective ion exchange sites located at the edges of clay minerals (Sawhney, 1970). In natural waters, monovalent ions with a low ionic radius such as K^+ and NH_4^+ are expected to compete with Cs for these sites (Sawhney, 1972) and, in the sediment profile described by Comans et al. (1989), NH_4^+ showed a significant negative linear relationship with the Kd values for ^{137}Cs. The authors concluded that the decrease in the observed ^{137}Cs Kd values with depth was caused by the ion exchange of radiocaesium bound to sediments for pore-water NH_4^+. Therefore, production of NH_4^+ via microbial metabolic activity may well lead to post depositional remobilisation of ^{137}Cs from sediments (Zwolsman et al., 1993; Kaminski et al., 1994).

Technetium

There are no stable isotopes of Tc, but one isotope, ^{99}Tc, is a long-lived (half-life 2.1×10^5 y), high yield fission product which is produced in kilogram quantities in nuclear reactors. Technetium is important as an environmental contaminant because it is one of the most mobile radionuclides (Garland et al., 1983). It has been released to the environment primarily as a result of nuclear weapons testing and fuels reprocessing and, due to its long half-life, will be an important component of high level wastes when they are finally disposed (Wildung et al., 1979; Bird & Evenden, 1996).

Technetium is present in the environment in one of two oxidation states, Tc(IV) and Tc(VII), the latter forming the pertechnetate (TcO_4^-) anion (Wildung et al., 1979). Tc(IV) is only formed under neutral pH and conditions where Eh values lie below approximately +220 mV (Brookins, 1988; Sparkes & Long, 1988). Studies on the behaviour of ^{99}Tc in

the natural environment have been limited due to the low concentrations generally found in environmental materials and due to numerous difficulties associated with its analysis (Holm, 1993). In oxic waters, the majority of technetium exists as pertechnetate and is expected to remain in solution until it decays (Beasley & Lorz, 1986). This is because the TcO_4^- anion is highly soluble and poorly sorbed by soils and sediments due to its predominantly negatively-charged surfaces (Walton et al., 1986; Elwear et al., 1992). In fact, TcO_4^- is often used as a conservative tracer for water transport studies (Leonard et al., 1997). In contrast, Tc(IV) reacts readily with mineral surfaces, i.e. iron oxyhydroxides and sulfides, or insoluble humic substances (Lieser & Bauscher, 1988; Sparkes & Long 1988), both of which may lead to decreased solubility. Only when Tc(IV) reacts with low molecular weight, soluble, organic ligands may its solubility be increased (Wildung et al., 1979; Sheppard et al., 1990).

The variability in the chemical behaviour of Tc is highlighted by the observed Kd values. Values range from <10 ml g^{-1} (Kershaw et al., 1992) to, rather more infrequently, values as large as 1000 ml g^{-1} reported for anaerobic sorption experiments (Lieser & Bauscher, 1987). The low values reflect the limited retention of Tc in oxic environments, whereas the higher values point to immobilisation under reducing conditions. For example, a soil core profile containing ^{99}Tc and other artificial radionuclides from Sellafield waste effluents, including ^{137}Cs, was taken at an intertidal salt marsh in west Cumbria (Morris et al., 2000). The marsh is relatively well characterised and due to its hydrology, remains suboxic throughout the year (Keith-Roach et al., 2000). The ^{99}Tc profile in the core strongly resembled both the ^{137}Cs profile and the Sellafield discharge history for ^{137}Cs. From this, Morris et al. (2000) concluded that the majority of ^{99}Tc input to the marsh was particle associated, and that the profile had a qualitative relationship with historical discharges of Tc from Sellafield. The mechanisms by which ^{99}Tc became incorporated into the particulate input remain unidentified, but microbially-mediated reductive sorption in reducing microenvironments prior to transport to the marsh may explain the pattern of retention seen in these suboxic sediments.

The association of technetium with anaerobic microorganisms can be demonstrated by considering the reported concentration ratios (Bq g^{-1} dry weight in organism/Bq ml^{-1} in solution) for a range of microbes and for aquatic organisms. For sulfate-reducing bacteria, reported concentration ratios range from 5750 ml g^{-1} (for indirect sulfide precipitation; Lloyd et al., 1998) to 12,850 ml g^{-1} (for dissimilatory TcO_4^- reduction; Lloyd et al., 1999). These compare to concentration ratio maxima for aquatic organisms of 1000–1500 ml g^{-1} (Masson et al., 1989) and Kd values for bulk sediments of 10–1000 ml g^{-1}. The concentration ratios for sulfate-reducing bacteria are at least an order of magnitude higher than values reported for aquatic organisms or sediments suggesting a very strong association (either directly or indirectly) of technetium with sulfate-reducing bacteria.

The actinide elements

The actinide elements can be treated as a group in terms of their geochemical behaviour, but the sources of these elements in the natural environment are very different. Uranium is a primordial radioactive element which is ubiquitous in the environment and has a crustal abundance of 2.3 mg kg^{-1} (Krauskopf, 1988). Naturally occurring uranium comprises

of three isotopes, ^{234}U, ^{235}U and ^{238}U, all of which decay by α-emission. Uranium is exploited in the nuclear industry, and uranium milling and mining has led to locally enhanced concentrations of uranium and U-series radionuclides (Krauskopf, 1988; IAEA, 1999). In addition, significant quantities of uranium associated with the nuclear fuel cycle will eventually be disposed of in nuclear repositories. Other environmentally significant actinides, e.g. Np and Pu, are produced in nuclear reactors via neutron capture and β^--decay reactions. They have been released to the natural environment via nuclear weapons and accidents, as well as in effluents associated with nuclear fuel reprocessing (Hanson, 1980). The principal isotopes of the transuranic elements are α-emitters, with half-lives ranging from 8.77×10^1 to 2.14×10^6 years (Table 1).

Extensive reviews of the complex geochemical behaviour of the actinides are included in Morse & Choppin (1991) and Dozol et al. (1993) and an overview is given in Chapter 4 of this volume. Briefly, oxidation states of +3 to +6 inclusive may be encountered in the environment (Dozol et al., 1993). The lower valence states form simple cations, M^{3+} and M^{4+}, which are easily hydrolysed due to their high charge density, and are readily lost from solution by reaction with solid surfaces (Nelson & Lovett, 1978). The higher valence states form the dioxo- cations MO_2^+ and MO_2^{2+}, which are more soluble due to both their lower charge density and their ready complexation with common oxygen-containing ligands, such as CO_3^{2-}, to give neutral and anionic carbonate-complexes (Morse & Choppin, 1991; Clark et al., 1995). Thus, for the actinide elements, there is a clear distinction between 'reduced', relatively insoluble species, and 'oxidised', relatively soluble species (Nelson & Lovett, 1978).

The relative solubilities of U, Np and Pu in the environment are primarily governed by the dominant oxidation state(s) of the element (Table 1). In most geochemical systems, the dominant form of uranium is expected to be the relatively soluble uranyl ion, UO_2^{2+}. The relatively insoluble U(IV) is only expected in strongly reducing conditions where it forms uraninite (UO_2) (Suzuki & Banfield, 1999). The transuranic elements display different behaviour depending on their accessible range of oxidation states. Plutonium potentially has access to all four oxidation states in redox conditions found in the natural environment (Dozol et al., 1993), although in sedimentary environments, Pu^{4+} is thought to dominate, with PuO_2^+ present as the metastable soluble form in seawaters (Nelson & Lovett 1978; Morse & Choppin, 1991). Neptunium displays an intermediate range of oxidation states with Np^{4+}, NpO_2^+ and NpO_2^{2+} all possible species at environmental redox potentials. In oxic to mildly reducing environments NpO_2^+ is thought to dominate (Lieser & Muhlenweg, 1988; Morris & Livens, 1996); indeed, Np(V) is not effectively removed from waste effluents via typical physicochemical or biotechnological processes (Lloyd et al., 2000). Thus, neptunium is the most mobile of the transuranic elements in oxic environments, with plutonium displaying lower solubility as it is more prone to reductive sorption (Hursthouse & Livens, 1993). This general environmental behaviour is reflected in published Kd values for Np and Pu of 10^4 and 10^5 ml g^{-1}, respectively (Morse & Choppin, 1991; Kershaw et al., 1992).

5. Biogeochemical processes affecting radionuclide mobility

The fate of radionuclides in the sedimentary environment is a complex function of both

abiotic and biotic factors. Abiotic factors such as pH, ionic strength and the presence of competing and complexing ions are important in controlling radionuclide speciation. These factors, in turn, control their mobility in the environment (Santschi & Honeyman, 1989; Pedersen, 1993). Microbial activity may affect actinide mobility via a number of processes including (i) direct mechanisms, such as enzymatic reduction or sorption on to microbial biomass, and (ii) indirect mechanisms, such as mineral dissolution/precipitation reactions or interactions with organic and inorganic metabolites. The biogeochemical behaviour of a radionuclide will also depend on the form in which it is released and upon its initial associations. For example, different radionuclides may be released as refractory oxides or in the elemental form, or upon release, they may become preferentially associated with clay mineral fractions, organic matter and iron/manganese hydroxides (Choppin & Stout, 1989; Santschi et al., 1990b).

Direct enzymatic reduction

Microorganisms can, in principle, obtain energy to support growth from the dissimilatory reduction of redox active radionuclides including Tc, U, Np, and presumably Pu (Lovley, 1995; Lloyd & Macaskie, 1996; Lloyd et al., 2000; see also Chapters 7, 8, 11 and 12, this volume). In one of the first studies that examined the potential for soil microorganisms to affect technetium solubility, Henrot (1989), found that in aerobic cultures there was little bioaccumulation of Tc (as TcO_4^-) on bacterial surfaces. By contrast, in a mixed anaerobic inoculum, a substantial fraction of the Tc became associated with the biomass in the growth medium, presumably as Tc(IV). If pertechnetate was added to a mixed anaerobic culture medium after bacteria had been removed by filtration, there was no removal of TcO_4^-. This suggested that direct enzymatic reduction of Tc(VII), and subsequent adsorption on to microbial surfaces was responsible for the changes in Tc solubility. Lloyd & Macaskie (1996) subsequently demonstrated that the dissimilatory metal-reducing bacteria *G. metallireducens* and *S. putrefaciens* could enzymatically reduce pertechnetate in the presence of acetate and lactate. In those pure culture experiments, the reduced Tc products were species-specific: *S. putrefaciens* produced soluble reduced Tc species in the supernatant, whereas *G. metallireducens* precipitated appreciable quantities of technetium as a low valence, insoluble oxide, hydroxide or oxohydroxo compound (e.g. Tc_2O_5 or TcO_2). Lloyd et al. (1997) further established that anaerobic cultures of *Escherichia coli* were able to couple the oxidation of formate or hydrogen directly to the reduction of pertechnetate, while Lloyd et al. (1999) reported that a range of electron donors could be utilised by *D. desulfuricans*, with TcO_4^- as the sole electron acceptor in non-sulfidogenic cultures.

Enzymatic reduction of U(VI) has been suggested as a pathway for U(VI) immobilisation in sediments (Barnes & Cochran, 1993) and aquifers (Lovley et al., 1993). Direct dissimilatory reduction of U(VI) coupled to the oxidation of organic substrates, and the subsequent extracellular precipitation of the insoluble U(IV) mineral uraninite (UO_2), has been demonstrated for a number of pure culture species, including *Clostridium*, *Desulfovibrio*, *G. metallireducens* and *S. putrefaciens*, (Lovley et al., 1991, 1993; Gorby & Lovley, 1992; Lovley, 1993; Francis, 1994). The enzymatic reduction of U(VI), as the soluble uranyl ion, UO_2^{2+}, by *G. metallireducens* and *S. putrefaciens*, occurs via the following reactions (equations modified from Lovley et al., 1991; Lovely & Phillips, 1992):

$$CH_3COO^- + 2UO_2^{2+} + H_2O \rightarrow 2UO_2 + HCO_3^- + 4H^+ \quad (14)$$
$$\Delta G = -158 \text{ kJ/mol } CH_3COO^-$$

$$H_2 + UO_2^{2+} \rightarrow 2H^+ + UO_2 \quad (15)$$
$$\Delta G = -82 \text{ kJ/mol } H_2$$

Aqueous uranyl can also be reduced by mixed cultures of Fe- and sulfate-reducing bacteria (Ganesh et al., 1997; Abdelouas et al., 2000), although attempts to grow SRB's with UO_2^{2+} as the sole electron acceptor have been largely unsuccessful (Suzuki & Banfield, 1999). The free energy yield per mole of acetate, coupled to U(VI) reduction, is -158 kJ mol^{-1}, a value which lies between the yields for the reduction of Mn(IV) and Fe(III).

Dissimilatory reduction of Np(V) in the presence of *S. putrefaciens* has recently been observed in a series of batch experiments (Lloyd et al., 2000). The majority of the reduced Np(IV) remained soluble in the culture medium (>85%) and was thought to be present in a microcolloidal form. These results were not surprising considering that *S. putrefaciens* has been shown to reduce Fe(III), U(VI) and Tc(VII) enzymatically, and the redox couple for Np(V)/Np(IV) (+0.74 V) lies between the redox couples for U(VI)/U(IV) (+0.32 V) and Fe(III)/Fe(II) (+0.77 V). Following reduction, indirect bioprecipitation of Np(IV)-phosphate was then induced by Citrobacter sp. in the presence of glycerol-2-phosphate as the source of PO_4^{3-}. Lloyd et al. (2000) also performed a bioreduction experiment in conditions related to the behaviour of Np(V) in natural waters (i.e. in carbonate buffer and at a reduced concentration of neptunium). In these experiments a substantial fraction of the Np(V) appeared to be directly reduced by *S. putrefaciens* to an insoluble, unidentified Np species.

The biological reduction of plutonium has also been described. Iron-reducing *Bacillus* strains were able to solubilise up to 90% of Pu(IV) hydrous oxide in the presence of nitrilotriacetic acid (NTA); only 4.5% of the plutonium was solubilised in uninoculated NTA media (Rusin et al., 1994). Analysis of the solution phase, however, did not reveal the presence of a Pu(III)-NTA complex. Instead, the authors suggested that the soluble Pu(III)-NTA formed during microbial reduction spontaneously reoxidised to Pu(IV)-NTA, and thus remained in solution. Although the mechanism of Pu(IV) solubilisation in the presence of NTA and iron reduction remains unidentified, the results are of importance as they suggest that the microbially mediated reduction of highly insoluble Pu(IV) oxyhydroxide (K_{sp} $10^{-56.8}$ to $10^{-57.8}$) to the more soluble Pu(III) hydroxide (K_{sp} = $10^{-22.6}$) may increase the solubility of plutonium in the environment.

Biosorption

At the normal growth pH (between 5 and 8), structural polymers that reside in the cell wall and surrounding fabric of bacteria are naturally anionic (Beveridge, 1989). By virtue of their small size, bacteria also have the largest surface area to volume ratio of cellular life forms. This property offers bacteria a remarkable potential to sequester and accumulate an assortment of metals onto their surfaces. Furthermore, bacteria are found in every environment where liquid water is freely available. They are not only ubiquitous, but are also found in vast numbers, more than 10^8 cells g^{-1} in marine muds and garden

soils, 10^5 cells ml^{-1} in river waters and 10^8 cells cm^{-2} in biofilms (Geesey et al., 1978; Ehrlich, 1990). The combination of cell reactivity and abundance implies that the biomass associated with microorganisms can have a direct effect on contaminant solubility.

Microorganisms have been shown to biosorb radionuclides (Francis, 1990; Avery, 1995), a property that lends itself to bioremediation strategies for the removal of such contaminants (Voleski & Holan, 1995; Lovley & Coates, 1997; Eccles, 1998). The similarity in ionic radius of Cs^+ to that of other monovalent cations, particularly K^+, leads to higher levels of uptake than would be expected from passive sorption processes alone (Avery, 1995). Potassium is an essential macronutrient, and microorganisms accumulate K^+ intracellularly via metabolism-dependent transport systems (Avery et al., 1992). Therefore, caesium may be incorporated into the uptake cycle for potassium, although the extent of incorporation is variable for different microorganisms and it can be affected by the presence of other monovalent cations. Biomass accumulations of ^{137}Cs have been reported for bacteria, cyanobacteria, algae, yeast and fungi (Avery, 1995), with particularly high Cs accumulations of 56 g kg^{-1} (dry weight) associated with bacteria (*Rhodococcus* sp.) isolated from ^{137}Cs-enriched soils (Tomioka et al., 1992). Similarly, unexpectedly strong retention of radiocaesium derived from Chernobyl was attributed to microbial activity in organic-rich layers of upland soils (Johnson et al., 1991).

For the actinide elements, accumulation in cells is thought to occur predominantly via metabolism-independent biosorption (Pentreath, 1981; Scoppa, 1984; Suzuki & Banfield, 1999). Biosorption is defined as the passive sorption and complexation of metal ions by microbial biomass or material derived from this. Indeed, the metal biosorption capacity of non-living biomass can be greater than that of living cells: cellular degradation increases the availability of functional groups capable of binding metals (Ferris et al., 1988) and the protons generated by membrane respiration in living cells no longer compete with dissolved metals for binding sites (Urrutia et al., 1992). In some cases, microbial biomass may even have a greater capacity for metal adsorption than inorganic fractions such as ferric oxides or clays (Berthelin et al., 1995). Studies on the biosorption of uranium have reported uptake by different microorganisms ranging from 23–9000 g kg^{-1} biomass (Eccles, 1998). For neptunium, biosorption levels for aerobic microorganisms are low (11–15 g kg^{-1} biomass) suggesting that, as expected from the geochemical behaviour of NpO_2^+, the adsorption of Np(V) is less effective than that of other radionuclides (Strandberg & Arnold, 1988). Wahlgren et al. (1980) tentatively related the observed pattern of plutonium cycling in Lake Michigan to seasonal differences in accumulation in phytoplankton. Recently, Keith-Roach (2000) used lipid biomarkers to examine the variation in microbial population in a marsh where Am, Pu and Np concentrations were measured in pore-waters over an annual cycle. The study suggested that seasonal variations in transuranic element concentrations in pore-waters were related to changes in aerobe biomass in the marsh. For example, the concentrations of plutonium and americium were at a minimum in periods where microbial biomass was at a maximum, presumably due to passive sorption. As the relative biomass concentration declined in the marsh due to cell degradation, the plutonium and americium concentrations in pore-waters subsequently increased. Although this pattern was complicated in winter months by other factors, this study suggests that direct sorption of actinide elements by microbial biomass may have a significant short-term effect on actinide solubility in the environment.

Organic metabolites

Fermentation products formed during diagenesis may act as ligands with actinide ions (Munier-Lamy & Berthelin, 1987; Berry et al., 1991; Gadd, 1997). Although such reactions are expected to increase actinide solubility, in sedimentary environments many of the organic byproducts of microbial metabolism are rapidly utilised by other bacteria and their effect on actinide solubility may be considered transitory. The consumption of hydrogen, or other fermentation products, during diagenesis also regulates the redox potential of the local environment, and subsequently has the potential to shift the oxidation state distribution of the multivalent actinides (Silva & Nitsche, 1995; Choppin & Bond, 1996). This ultimately leads to differences in their environmental behaviour. For example, the greater susceptibility of Pu(V) to redox processes implies that it may be reduced to Pu(IV) more readily than Np(V) or U(VI) (Morse & Choppin, 1991). Generally, as sediment burial occurs, and a more reducing environment develops, the actinides are expected to become reduced and therefore less soluble.

In addition to the organic degradation products produced in diagenesis, bacteria and fungi may, under stress of iron deficiency, produce specific iron chelators such as siderophores. These highly specific, low molecular weight chelating agents allow Fe(III) to be sequestered and delivered into cells via active transport systems. Although virtually specific for Fe(III), siderophores can complex certain other metals including the tetravalent actinides (Birch & Bachofen, 1990; Macaskie & Dean, 1990; Brainard et al., 1992; Neu et al., 2000). Some siderophores are also capable of complexing U(VI) (Macaskie & Dean, 1990). The binding constants for the tetravalent actinides are similar to those for Fe(III) (e.g. desferrioxamine B-Fe(III) = $10^{30.6}$; desferrioxamine B-Pu(IV) = $10^{30.8}$) (Neu et al., 2000). The concentrations of these chelating agents in the environment are estimated to be very low, typically 0.01–3.0 μmol kg^{-1} in soils (Brainard et al., 1992; Neu et al., 2000). This is approximately 3–4 orders of magnitude lower than concentrations of other organic complexing agents such as organic acids or humic substances. However, Brainard et al. (1992) showed that a specific siderophore (enterobactin), at low concentrations (0.1 mM), was equal to or better than a series of strong chelators such as oxalic acid, citric acid or EDTA at concentrations three orders of magnitude higher at solubilising hydrous PuO_2. In addition to the environmental significance of these sequestering agents, biotechnological actinide remediation treatments using siderophores have also been suggested (Birch & Bachofen, 1990).

Inorganic metabolites

During diagenesis, inorganic metabolites such as bicarbonate, phosphate, ferrous iron and hydrogen sulfide are released into sediment pore-waters. These metabolites may in turn affect the speciation and mobility of the actinide elements. For example, in a closed aqueous system, increased levels of carbon dioxide produced through organic degradation may increase the solubility of actinides by forming neutral or anionic actinide-carbonate complexes such as $M(VI)O_2(CO_3)_3^{4-}$ and $M(V)O_2(CO_3)^-$ in solutions with pH > 6 (Clark et al., 1995; Banaszak 1998; Suzuki & Banfield, 1999). Some cells also produce phosphatase enzymes that release phosphate (HPO_4^{2-}) from organic compounds

(Suzuki & Banfield, 1999). This has biotechnological applications because the phosphate generated potentially binds and precipitates large quantities of metals including actinides. For instance, a copper tolerant bacterium, *Citrobacter* sp., which produced three times more phosphatase than the parent strain, accumulated up to 9 g U kg^{-1} dry cell weight as insoluble hydrogen autinite (HUO_2PO_4) (Macaskie, 1990; Macaskie et al., 1990). The biomineralisation of insoluble actinide phosphates via *Citrobacter* sp. has also been demonstrated for Pu(IV) and Np(IV) (Macaskie et al., 1994; Lloyd et al., 2000; see Chapters 11 and 12, this volume).

Ferrous iron also plays a role in the reduction of U(VI). In a series of batch experiments, uranium reduction rates ranged from greater than 3 days in the presence of 1 mM soluble Fe^{2+} to less than a few hours in the presence of both soluble Fe^{2+} and colloidal hematite (Liger et al., 1999). In the case of the latter experiments, the pseudo first order rate constants for U(VI) reduction were of the same order of magnitude as the highest corresponding rate constants for direct enzymatic reduction of U(VI). This suggests that abiotic surface catalysed reduction of U(VI) may be a major pathway for reductive immobilisation during diagenesis. The inorganic formation of a reduced TcS_2-like phase via co-precipitation of TcO_4^- with FeS (mackinawite), has also recently been observed, (Wharton et al., 2000). Interestingly, on reoxidation of the TcS_2-FeS phase, the technetium remained in an insoluble TcO_2-like phase, i.e. the Tc(IV) failed to reform into Tc(VII) on reoxidation and remained insoluble. This implies that when technetium is reduced to insoluble TcS_2 in a sulfidic environment it may remain insoluble as Tc(IV)-oxide even if the sediment is subsequently exposed to aerobic conditions (Wharton et al., 2000).

A number of workers have demonstrated that dissolved sulfide reacts only slowly with U(VI) (Kochenov et al., 1977; Mohagheghi et al., 1985). In particular, Lovley et al. (1993) showed that at circumneutral pH, the rate of abiotic uranyl reduction in the presence of HS^- was very much slower than the measured rates of direct enzymatic uranium reduction. Uranium(VI) reduction may also be catalysed by mineral, and even bacterial surfaces (Kochenov et al., 1977; Mohagheghi et al., 1985). Sulfide minerals such as pyrite and galena can reduce U(VI) under anoxic conditions (Wersin et al., 1994), and interestingly, are frequently found in close association with supergene uranium deposits (Brookins, 1988). The production of H_2S in sulfidic environments also effects technetium speciation. Henrot (1989) reported that in single culture experiments the sulfate-reducing bacteria *Desulfovibrio vulgaris* and *Desulfovibrio gigas* converted up to 70% of pertechnetate to adsorbed and/or insoluble forms. Similarly, Lloyd et al. (1998) observed that the production of H_2S by cultures of *Desulfovibrio desulfuricans* led to the extracellular precipitation of insoluble technetium sulfides. The Tc:S ratio of 1:5 in the precipitates suggested that either TcS_2 or Tc_2S_7 were formed. Moreover, the lack of intracellular precipitation of Tc noted in the sulfidogenic cultures indicated that it was unlikely that Tc was directly reduced within the cell.

Mineral precipitation/dissolution reactions

The solubility of radionuclides is affected by the precipitation and/or dissolution of oxidised mineral phases. In the first instance, the solubility of actinide elements is often limited by adsorption onto solid surfaces such as iron oxyhydroxides (Keeny-Kennicutt

& Morse, 1984, 1985; Hsi & Langmuir, 1985; Hursthouse et al., 1991). The accumulation of metals by bacteriogenic iron oxides has clearly been demonstrated (Clarke et al., 1997), and recently, Ferris et al. (1999, 2000) suggested that the relative proportion of bacterial organic matter in biogenic Fe oxides affected the solid phase uranium enrichment. A number of studies have also presented evidence that scavenging of plutonium and americium by ferric hydroxides occurs at sediment/water interfaces in marine environments (Sholkovitz & Mann, 1984; Malcolm et al., 1990), although the possible role of microorganisms in the precipitation of these ferric iron phases was not discussed.

Secondly, ferric hydroxide reduction may affect actinide solubility by releasing adsorbed radionuclides from ferric oxide phases (Sholkovitz, 1983). Barnes & Cochran (1993) reported that uranium was desorbed from sediments during the reduction of Fe/Mn hydroxides. The subsequent exposure to a reducing environment may result in the actinide ions becoming reduced, and subsequently adsorbing on to new mineral surfaces. Morris et al. (2001) reported that plutonium underwent seasonal cycling in salt marsh pore-waters, and that maximum plutonium solubility appeared to coincide with minimum iron and manganese solubility in marsh pore-waters. Interestingly, Eh measurements at the site were relatively constant over an annual cycle, suggesting that the observed cycling of Pu, Fe and Mn was complex. In other environments, no obvious link between actinide solubility and Fe/Mn oxide cycles has been observed (Sholkovitz & Mann, 1984; Malcolm et al., 1990).

6. Summary

Microbial metabolism is the predominant control on sediment mineralogy and pore-water chemistry in aquatic environments. Although changes in organic and inorganic chemistry are complex, transient and involve numerous recycling reactions, both produce characteristic patterns. Chemoheterotrophic bacteria use a sequence of terminal electron accepting processes which produce successive changes in the pore-water chemistry and associated mineralogy. These processes are integrally linked to bulk changes in sediment and soluble organic matter. The contribution of chemoautotrophic bacteria in most aquatic sediments is limited to nitrification, but they become more important at low pH and oxygen levels, or in organic-rich sediments that generate methane.

Environmental radioactivity and an understanding of the fate of radionuclides in the natural environment are of great importance when considering the legacy of nuclear waste and the future potential exploitation of nuclear power. As we have discussed, the fate of radionuclides in the natural environment cannot be considered without examining the role that microbial activity plays in either enhancing their mobility or causing their immobilisation. Because of the low concentrations of radionuclides in the natural environment, and the radiotoxicity of these elements, few studies on biogeochemical cycles of the artificial radionuclides have been performed. However, it is clear that a further understanding of the rates of movement, the pathways and the reservoirs of contaminant radionuclides in the environment continues to be one area of biogeochemical research which has contemporary relevance.

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