Chapter 6: Redox Evolution in Surface and Groundwaters

Four billion years of photosynthetic activity has created an oxygenated surface environment for the Earth. While oxygen produced during the first billion and a half years was consumed in oxidizing most of the iron in the oceans, the activity of blue-green algae ultimately built up O_2 levels in the atmosphere to 21%. It has remained close to this steady-state value since Precambrian time, held in check largely by bacterial oxidation of the algal biomass that generates it. Atmospheric oxygen is the primary and most thermodynamically-efficient electron acceptor available in natural waters. However, below the water table where access to atmospheric gases becomes highly restricted, O_2 concentrations can drop off as it is consumed by aerobic bacteria during respiration of available substrates (reduced compounds such as organic carbon, sulfide and reduced metals like Fe^{2+} and Mn^{2+} used by bacteria for food and cell synthesis). As it does, bacteria using other decreasingly-efficient electron acceptors like NO_3^-, Fe^{3+} and SO_4^{2-} become competitive. The sequence of these steps towards lower and lower redox potential along a groundwater flow path or with depth in some lakes constitutes redox evolution. Redox evolution has great importance for the solubility of certain minerals and the production of some hazardous compounds including H_2S, CH_3Hg and methane. The availability of accessible substrates is a critical component for redox evolution. The ubiquity of dead vegetation, whether in saturated soils, swamps or sedimentary aquifers, makes organic carbon the primary substrate driving the evolution of redox in most natural waters.

REDOX EVOLUTION THROUGH OXIDATION OF ORGANIC CARBON

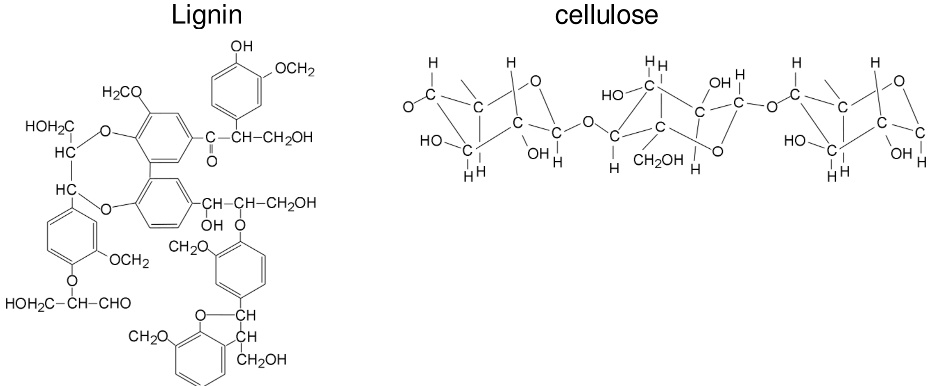
Dissolved organic carbon (DOC) is gained by groundwaters during infiltration through soils, although concentrations are generally less than 1 to 2 mg-C/L. It can also be found within the aquifer as sedimentary organic carbon (SOC) including peat beds, coal laminations, organic-rich clays, and hydrocarbon. Surface waters contain dissolved and particulate organic carbon (DOC and POC) that support redox reactions. DOC is highly concentrated in landfill leachates, reaching 100s to 1000s of mg-C/L. Similarly, groundwaters and runoff from agricultural landscapes may have DOC > 10 to 100 mg-C/L from crop residues and manure spread on fields.

Aerobic biodegradation and generation of DOC

The organic carbon geochemistry of natural waters begins photosynthesis in air and surface waters, where CO_2 is converted to organic or "fixed" carbon through the exchange of four electrons:

$$CO_2 + H_2O \rightarrow O_2 + CH_2O$$

Here, fixed carbon is simplistically represented as carbohydrate. While this is a reasonable approximation of the C, O and H content of vegetation, it belies the great variety of organic carbon compounds synthesized by plants. The most abundant compound is cellulose — chains of sugar molecules bundled by hydrogen bonding between chains into stable and resistant structures (Fig. 6-1). Lignin is a minor component of biomass, comprising carbon ring structures in an acid-insoluble polymer that cements plant cells together. Plant protein, while only a minor component of plant biomass, is the principal reservoir of nitrogen used in cell structures and plant function. It is comprised essentially of the amine —NH_2 functional group attached to carbon. Organic sulfur is present in plant cells as well as Ca, K, Mg and P. Trace elements or micronutrients include B, Cl, Cu, Fe, Mn, Mo and Zn.



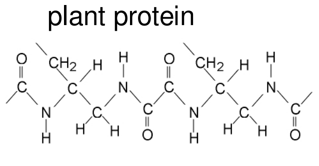


Fig. 6-1 Primary components of vegetation including cellulose - C-O bonded chains of carbohydrate, lignin – complexes of aromatics with carbohydrate functional groups, and plant protein – C-N bonded into chains of amino [$-NH_2$] acids. Sources: the Lignin Institute (www.lignin.info), Drever (1997).

Dissolved organic carbon (DOC) in groundwaters and surface waters is generated through the degradation of dead biomass by bacteria and fungi. The process generally begins under aerobic conditions in the soil surface or in aerated surface and soil waters where aerobic bacteria degrade and metabolizing the more labile components of biomass. The carbon pool evolves towards more recalcitrant humic substances with production of CO_2 and release of energy.

The great energy yield from the oxidation of fixed or reduced carbon by O_2 sustains aerobic bacteria in their activities of metabolism and cell construction. As presented earlier in Chapter 2, the overall redox reaction can be written as: the

$$O_2 + CH_2O \rightarrow CO_2 + H_2O \qquad \text{with } \Delta G^\circ_r = -501.8 \text{ kJ/mol}$$

The negative free energy of the reaction indicates that the reaction is exothermic. Further, the very high reaction constant demonstrates that carbohydrate be thermodynamically stable only in the absence of O_2.

While the general reaction for respiration is simply the reverse of photosynthesis, there is a transformation of the primary components of vegetation (Fig. 6-1) towards more stable aromatic structures — the humic substances. These refractory compounds are less accessible to degradation and accumulate in soils. Their solubility is largely a function of soil pH and their molecular weight. Fulvic acids are lighter (some 500 to 2500 atomic mass units, amu) and soluble over the range of pH in natural waters. Humic acids are larger molecules (up to 1,000,000 amu) and become insoluble at low pH. Humin is the amorphous dark brown to black substance in soils that makes up much of the soil carbon reservoir.

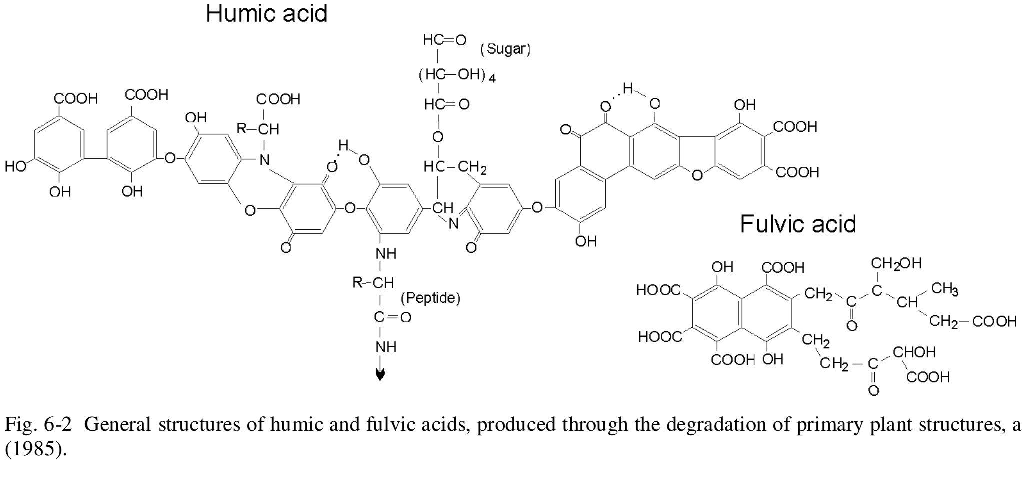


Fig. 6-2 General structures of humic and fulvic acids, produced through the degradation of primary plant structures, after Stephenson (1985).

An important process in the biodegradation of plant debris is the release of nutrients back into the root zones for re-uptake. Nitrogen as ammonium, NH_4^+ and nitrate, NO_3^- from amino acids are essential to plants incapable of their own nitrogen fixation — a process limited to only a few plants such as clover and legumes.

The composition of DOC in aerobic groundwater recharged through unsaturated soils is comprised largely of humic and fulvic acids. Concentrations are typically below 10 ppm C and most often less than 1 to 2 ppm. Accompanying these large organic components are low molecular weight fatty acids such as acetate, CH_3COOH. However, these are labile compounds that can be readily metabolized by aerobic bacteria, and so if present constitute only a minor component of DOC. Thus, at the point of recharge in aerated recharge environments, groundwater moves away from open-system conditions with respect to atmospheric O_2 with a residual concentration of generally recalcitrant DOC. Such groundwaters generally recharge with a significant residual dissolved oxygen (DO) concentration. Without a source of labile carbon for bacteria, the system remains aerobic, which is an unfavorable state for pathogens such as *E. coli* and *Heliobacter*, which thrive under anoxic conditions. This represents the greatest majority of shallowly circulating groundwater flow systems, making them of high quality for drinking water.

Exceptions occur in soils where recharge is rapid and biodegradation is incomplete, such as in some agricultural regions, waterlogged soils or recharge from wetlands. In such cases, the load of dissolved organics is not consumed by respiration prior to recharge due to the poor access to atmospheric O_2. This leads to new steps down the thermodynamic scale of redox reactions, involving secondary electron acceptors and different strains of anaerobic bacteria.

Anaerobic biodegradation and generation of DOC

Water-saturated environments greatly diminish the supply of atmospheric O_2 and the activity aerobic bacteria. In such cases, biodegradation of the organics follows different pathway of geochemical reactions. Anaerobic biodegradation is common in tundra soils, wetlands and marshes, but also occurs in aquifers that contain significant amounts of organic carbon such as buried peat beds in sediments. However, biodegradation of the labile carbohydrate $[CH_2O]$ compounds occurs through a series of fermentation reactions — disproportionation of the primary carbon compounds into lighter weight organic acids, hydrogen, carbon dioxide and methane. The result is a much higher concentration of DOC in the water and much slower rate of degradation. Redox conditions are at the bottom of the scale, where methane and even hydrogen gas exist.

$$2CH_2O \rightarrow CH_3COOH_{\text{acetatic acid}}$$

$$4CH_2O \rightarrow CH_3CH_2COOH_{\text{propionic acid}} + CO_2 + H_2$$

$$6CH_2O \rightarrow CH_3(CH_2)_2COOH_{\text{butyric acid}} + 2CO_2 + 2H_2$$

Acetate and hydrogen accumulate in solution from degradation of these higher molecular weight organic acids:

$$CH_3(CH_2)_2COOH_{\text{butyric acid}} + 2H_2O \rightarrow 2CH_3COOH_{\text{acetic acid}} + 2H_2$$

$$CH_3CH_2COOH_{\text{propionic acid}} + 2H_2O \rightarrow CH_3COOH_{\text{acitic acid}} + CO_2 + 3H_2$$

These substrates in turn support bacteria that mediate fermentation and carbonate reduction reactions to produce methane as the final product of anaerobic degradation of organic carbon:

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad \textit{Acetate fermentation}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \textit{CO}_2\textit{ reduction}$$

The rates of reaction and abundance of terminal and intermediary compounds depend on environmental factors including temperature, seasonality, availability of substrates, nutrients, etc. Organic N and S are released to the water in reduced forms. Further, the recalcitrant products of biodegradation such as humic and fulvic acids can also be produced anaerobically and accumulate in the water. The result is a highly heterogeneous mixture of humic, fulvic and fatty acids, plus reduced N and S compounds including ammonia and sulfides. DOC concentrations in such environments can exceed 10 to 100 ppm C, and with high dissolved methane.

The availability of labile organic carbon generated through anaerobic biodegradation is of great benefit to anaerobic bacteria. These operate using less thermodynamically-favourable electron acceptors in the anoxic realm,, where aerobic bacteria cannot compete for substrate.

Electron acceptors and redox evolution

Within the p*e* – pH constraints for the stability of water, we can have a host of aqueous redox reactions. Each will be defined by its own p*e* – pH stability line. The differences in redox potential governs which redox pair will be active. The redox evolution of groundwaters from the infiltration of water through organic rich and aerated soil zone to depth within an aquifer follows a series of steps from redox pairs that release the greatest amount of free energy to those that release very little. Aerobic oxidation of organics is the first in this chain. We saw above that oxidation of carbohydrate with O_2 releases some 502 kJ per mole. Here we will look at the energy releases during oxidation of organics with subsequent redox pairs.

Natural and contaminated waters follow a chain of redox reactions which consume organic matter. As the most viable electron acceptor becomes depleted (O_2 being the first in line), the electron acceptor with the next greatest energy release will begin to function. Thus, the redox evolution of water will proceed in steps to lower Eh potentials until either the organic substrate or the available electron acceptors are consumed.

Electron acceptors and their associated reduced form make a redox pair. The common pairs in natural waters, according to their respective energy releases, include:

O_2/H_2O

NO_3^-/N_2

Mn^{4+}/Mn^{2+}

Fe^{3+}/Fe^{2+}

SO_4^{2-}/HS^-

CO_2/CH_4

Each of these redox pairs will operate at a successively lower electrical potential, measured in volts. Note that most of these pairs involve the non-metallic elements O, N, S and C – elements which have a range of oxidation states (Periodic Table 3-1) and are also ubiquitous in natural waters.

The redox potential of water will have an impact on redox-sensitive metals that may be present as sorbed or precipitated phases in the aquifer, or bottom sediments in the case of surface waters. Changing the redox state of such metals, including the transition metals – V, Cr, Mn, Fe and Co, and some heavy metals such as U, greatly affects their solubility.

Although natural waters seldom achieve redox equilibrium, the equilibrium thermodynamic approach used for acid – base reactions in Chapter 3 allows us to see the direction in which redox evolution is moving and what mineral phases are stable. It also provides us with a method to measure redox potential in solutions – Eh, a parameter that will be important for geochemical modeling.

Denitrification

The Haber-Bosch process to synthesize ammonia from N_2 increased by 10-fold global agricultural yields and is the single most important development behind our exponential increase in population. So where does all this ammonia end up? Bacteria such as *Nitrosomonas* and *Nitrobacter* use oxygen to nitrify it to NO_3^-. Releases from fertilizers, manure and sewage effluent now make nitrate one of the most pervasive regional pollutants of groundwaters.

Nitrate is one of the most soluble anions, and its removal from surface and groundwaters is mainly achieved by reduction to elemental nitrogen N_2 – the process of denitrification. In this reaction, an electron donor such as organic carbon is oxidized. The resulting release of energy is significant and so is mediated by bacteria.

$$CH_2O + \tfrac{4}{5}\,NO_3^- + \tfrac{4}{5}\,H^+ \rightarrow \tfrac{2}{5}\,N_2 + CO_2 + \tfrac{7}{5}\,H_2O$$

$$\begin{aligned}\Delta G^\circ_r &= \tfrac{2}{5}(0) + (-137.17) + \tfrac{7}{5}(-237.14) - (-129.7) - \tfrac{4}{5}(-108.74) + \tfrac{4}{5}(0)\\ &= -252.47 \text{ kJ/mol}\end{aligned}$$

The stability field for the redox pair NO_3^-/N_2 can be determined following the same approach used for the stability of water (Fig. 6-5), and using $P_{N_2} = 1$ atmosphere:

$$NO_3^- + 5e^- + 6H^+ \Leftrightarrow \tfrac{1}{2}\,N_2 + 3H_2O$$

$$\log K = -\frac{3(-237.14) - (-108.74)}{5.708} = 105.6$$

$$10^{105.6} = \frac{P_{N_2}^{1/2} \cdot a_{H_2O}^3}{a_{NO_3^-} \cdot a_{e^-}^5 \cdot a_{H^+}^6}$$

$$105.6 = \tfrac{1}{2}\log P_{N_2} - \log a_{NO_3^-} - 5\log a_{e^-} - 6\log a_{H^+} \qquad \textit{and using } P_{N_2} = 1 \textit{ atm}$$

$$pe = 21.1 + \tfrac{1}{5}\log a_{NO_3^-} - \tfrac{6}{5}\,pH$$

Creating this line for the drinking water limit of nitrate of 10 ppm as N ($a_{NO_3^-} = 10^{-3.15}$ mol/L):

$$pe = 20.5 - \tfrac{6}{5}\,pH$$

In particularly reducing environments, certain bacteria can reduce nitrate beyond elemental N, producing ammonia. Although this is a less common reaction, it can be important in anoxic, organic rich sediments. It is defined by the following reaction, and p*e* – pH relationship.

Denitrification by pyrite oxidation

Under anoxic conditions, pyrite oxidation can proceed of other electron acceptors with high redox potential are present. The process of denitrification ($NO_3^- \rightarrow N_2$) takes place at a high p*e*, near 12 in neutral pH waters, whereas sulfate reduction ($SO_4^{2-} \rightarrow HS^-$) takes place at low p*e*, below about –2. Accordingly, nitrate and sulfide together in an aqueous environment is not a thermodynamically stable configuration. Sulfide oxidation by reduction of nitrate to N_2 is an exothermic reaction and can proceed under natural conditions:

$$FeS_2 + \tfrac{14}{5}\,NO_3^- + \tfrac{4}{5}\,H^+ \rightarrow Fe^{2+} + 2SO_4^{2-} + \tfrac{7}{5}\,N_2 + \tfrac{2}{5}\,H_2O$$

$$\Delta G^\circ_r = -1194.4$$

The ferrous iron released to solution in this reaction can also act as an electron donor for denitrificationA geochemical situation where such a reaction could proceed is where nitrate contaminated groundwater encounters sulphide in the aquifer. Surface sources of nitrate include fertilizer, manure or wastewater treatment. Pyrite is commonly found in aquifers of glacial origin, such as tills, or in bedrock aquifers such as shaley limestone and crystalline rocks.

Example 6-1 Denitrification in a pyrite-bearing clastic aquifer

Drinking water for the German city of Hanover is extracted from the Fuhrberger Feld aquifer of unconsolidated glacio-fluvial sediments. However, the region supports intensive agriculture, which has added up to 200 mg/L of NO_3^- to the regional groundwater. Yet, in the Hanover water supply a sharp increase in sulfate, not nitrate, has been observed. The nitrate in the water remains below 2 mg/L, whereas less offensive sulphate has increased from about 80 to over 250 ppm (Böttcher et al., 1990).

The increase in SO_4^{2-} is attributed to denitrification based on oxidation of pyrite within the aquifer. Within the upper 5 m of the saturated zone, NO_3^- levels average near 100 mg/L, but drop to below detection near 8 m depth. Virtually all nitrate is transformed by the bacterium *Thiobacillus denitrificans* within the first 10 m below the water table. The principal lines of evidence include:

The exponential increase in both $\delta^{15}N$ and $\delta^{18}O$ values of the residual nitrate (Fig. 6-3) can only be due to fractionation during denitrification. Attenuation of the high nitrate concentrations with depth cannot simply be mixing with low-NO_3^- groundwater.

The $\delta^{34}S$ of the increasing dissolved sulfate is low and in the range of the pyrite found as disseminated grains in the unconsolidated aquifer. confirms that pyrite is the denitrification substrate

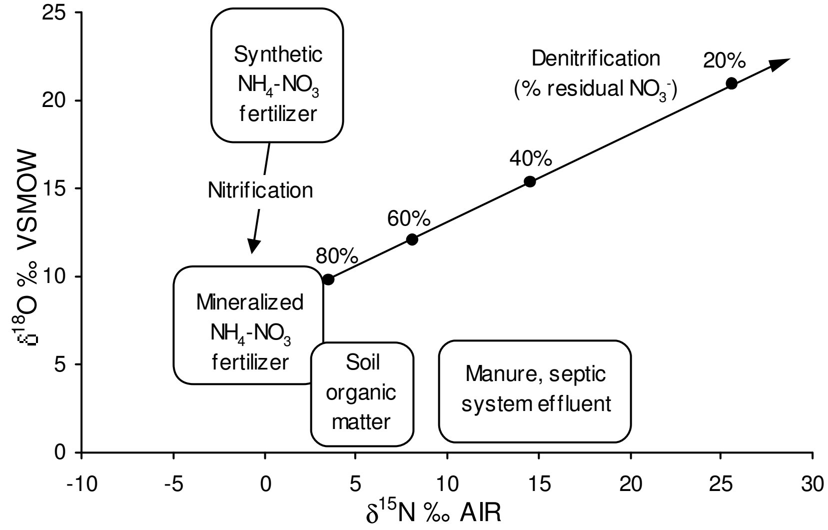


Fig. 6-3 Rayleigh enrichment of ^{15}N and ^{18}O in NO_3^- is clear evidence for microbial denitrification in the Fuhrberger Feld aquifer (modified from Böttcher et al., 1990).

Manganese reduction

Like iron, manganese is a transition element with two principal oxidation states beyond that of metallic Mn. These are Mn^{2+} and Mn^{4+}. Although less abundant in soils and aquifers than Fe, manganese reduction buffers pH at a higher p*e*. The manganese oxide pyrolusite [MnO_2] is the common mineral form, found as a cement or heavy mineral in clastic aquifers.

$$CH_2O + 2MnO_2 + 4H^+ \rightarrow CO_2 + 2Mn^{2+} + 3H_2O \qquad \Delta G^\circ_r = -107.64$$

Species	Mn_{metal}	Mn^{2+}	$MnO_{2\,pyrolucite}$	CH_2O	CO_2	H_2O
ΔG°	0	–228.1	–465.14	–129.7	-394.37	–237.14

$$MnO_2 + 2e^- + 4H^+ \Leftrightarrow Mn^{2+} + 2H_2O$$

$$\log \mathrm{K} = -\frac{-237.24}{5.708} = 41.6$$

$$10^{41.6} = \frac{a_{\mathrm{Mn}^{2+}} \cdot a^{2}_{\mathrm{H_2O}}}{a_{\mathrm{MnO_2}} \cdot a^{2}_{e^-} \cdot a^{4}_{\mathrm{H}^+}}$$

$$41.6 = \log a_{\mathrm{Mn}^{2+}} - 2 \log a_{e^-} - 4 \log a_{\mathrm{H}^+}$$

$$\mathrm{p}e = 20.8 - \tfrac{1}{2} \log a_{\mathrm{Mn}^{2+}} - 2\ \mathrm{pH}$$

and fixing the dissolved Mn^{2+} concentration at 10^{-6}, this becomes

$$\mathrm{p}e = 23.8 - 2\ \mathrm{pH}$$

Reduction of ferric iron

In the absence of MnO_2, or when the supply has been exhausted, the oxidation of residual organic matter will jump down to a lower p*e* buffered by the next most energy-yielding redox pair. If ferric iron species are present, then this will be the reduction of Fe^{3+} to Fe^{2+}. In circum-neutral pH waters, ferric iron is very insoluble, so the reaction will involve the precipitated phase, ferrihydrite:

Species		Fe^{2+}	Fe^{3+}	$Fe(OH)_{3\ \mathrm{ferrihydrite}}$	CH_2O	CO_2	H_2O
ΔG°	0	–82.88	–8.56	–692.07	–129.7	-394.37	–237.14

The energy released per mole of CH_2O oxidized is rather substantial:

$$\mathrm{CH_2O + 4Fe(OH)_3 + 8H^+ \rightarrow CO_2 + 4Fe^{2+} + 11H_2O} \qquad \Delta G^\circ_r = -436.45\ \mathrm{kJ/mol}$$

$$\mathrm{Fe(OH)_3} + e^- + \mathrm{3H^+} \Leftrightarrow \mathrm{Fe^{2+} + 3H_2O} \qquad \Delta G^\circ_r = -102.23\ \mathrm{kJ/mol}$$

$$\log \mathrm{K} = -\frac{\Delta G^\circ_r}{5.708} = -\frac{-102.23}{5.708} = 17.9$$

$$10^{17.9} = \frac{a_{\mathrm{Fe}^{2+}} \cdot a^{3}_{\mathrm{H_2O}}}{a_{\mathrm{Fe(OH)_3}} \cdot a_{e^-} \cdot a^{3}_{\mathrm{H}^+}} = \frac{a_{\mathrm{Fe}^{2+}}}{a_{e^-} \cdot a^{3}_{\mathrm{H}^+}}$$

$$17.9 = \log a_{\mathrm{Fe}^{2+}} - \log a_{e^-} - 3 \log a_{\mathrm{H}^+}$$

$$\mathrm{p}e = 17.9 - \log a_{\mathrm{Fe}^{2+}} - 3\mathrm{pH}$$

To plot this line on our p*e* – pH diagram, let’s set the activity of ferrous iron at 10^{-6} mol/L. This gives us the following line defining the boundary between the Fe^{2+} and the $Fe(OH)_3$ stability fields:

$$\mathrm{p}e = 23.9 - 3\mathrm{pH}$$

Sulfate reduction

The reduction of sulfate to sulfide is one of the most common redox buffers, owing to the high solubility and variety of sources of SO_4^{2-} in natural waters. In marine settings, the high sulfate content in seawater provides a large reservoir of this electron acceptor, giving it an important role in diagenetic reactions involving sedimentary organic carbon. In aquifers, sulfate can be found as gypsum deposits in fractures or in sedimentary horizons. It can be derived from oxidation of pyrite if present within the oxidizing zone of aquifers. Sulfate also is supplied by high salinity brines found in deep crystalline settings and deep sedimentary basins.

Sulfate reduction is a common reaction that is mediated by a group of bacteria referred to simply as sulfate reducing bacteria or SRBs. They can operate on very different organic substrates ranging from fixed organic carbon (oxidation state of 0, e.g. CH_2O) sources such as peat and soil organics to reduced organic carbon (oxidation state of –IV) including petroleum, bituminous solids and methane. Sulfate reduction involves an 8 electron transfer, from S^{6+} to S^{2-}.

Species	SO_4^{2-}	HS^-	H_2S	CH_2O	CH_4	CO_2	H_2O	HCO_3^-
$\Delta G°_r$	–744.0	12.2	–-27.7	–129.7	–50.72	-394.37	–237.14	–586.8

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \qquad \Delta G°_r = -197.9$$

$$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O \qquad \Delta G°_r = -17.02$$

The sulfate reduction half reaction can be written as:

$$SO_4^{2-} + 8e^- + 9H^+ \rightarrow HS^- + 4H_2O \qquad \Delta G°_r = -192.36 \text{ kJ/mol}$$

$$\log K = -\frac{\Delta G°_r}{5.708} = -\frac{-192.36}{5.708} = 33.7$$

$$10^{33.7} = \frac{a_{HS^-} \cdot a_{H_2O}^4}{a_{SO_4^{2-}} \cdot a_{e^-}^8 \cdot a_{H^+}^9}$$

$$33.7 = \log a_{HS^-} - \log a_{SO_4^{2-}} - 8 \log a_{e^-} - 9 \log a_{H^+}$$

$$pe = 4.21 + \tfrac{1}{8} \log \left(\frac{a_{SO_4^{2-}}}{a_{HS^-}} \right) - \tfrac{9}{8} \text{ pH}$$

When there the two redox species are both dissolved, the stability line is generally drawn for the case where they have equal concentrations, and so their activity ratio is 1.

$$pe = 4.21 - \tfrac{9}{8} \text{ pH}$$

In this case, less energy is released per mole of CH_2O and the reaction has a lower equilibrium constant. Clearly, sulfate reduction will only take place when the more favored reaction – O_2 respiration – is precluded by anaerobic conditions. For this reason sulfate reducing bacteria become dormant under oxidizing conditions, leaving the oxidation of organics to aerobic bacteria.

The sulfide product of sulfate reduction, as either HS^- or H_2S, is toxic to most organisms. Hydrogen sulfide has a high solubility unless there are metals present in solution to form sulphides such as FeS ($K_{sp} = 10^{-3.92}$), PbS ($K_{sp} = 10^{-12.8}$), or ZnS ($K_{sp} = 10^{-9.05}$).

^{34}S and ^{18}O tracers of sulfate reduction

The reduction of SO_4^{2-} to dissolved sulfide (H_2S or HS^-) is accompanied by a significant fractionation for ^{34}S . For abiotic reduction (e.g. geothermal systems), the equilibrium enrichment factor is on the order of 70‰. When bacteria mediate the sulfate reduction reaction, the dissolved sulfide is depleted in ^{34}S by about 25 ±10‰ (Krouse, 1970).

The process of sulfate reduction, however, can have an even stronger effect on the partitioning of ^{34}S and ^{18}O due to the effect of an isotope fractionating reaction on a diminishing reservoir. This "Rayleigh" distillation effect is presented at the end of Chapter 1, and for the case of $\delta^{18}O$ evolution during rainout (Chapter 3). In the case of sulfate reduction, bacteria preferentially reduced the isotopically light SO_4^{2-} to HS^- and H_2S, leaving behind the ^{34}S- and ^{18}O-enriched SO_4^{2-} in the residual sulfate reservoir (Fig. 6-4). A strong enrichment in $\delta^{34}S_{SO_4^{2-}}$ and $\delta^{18}O_{SO_4^{2-}}$ is a clear sign that sulfate reducing bacteria (SRBs) are at work.

The enrichment for ^{18}O during sulfate reduction is capped at value that represents an equilibrium with $\delta^{18}O$ of the water. Although the sulfate ion is unwilling to exchange its oxygen with water at low temperatures, it seems that during microbially-mediated sulfate reduction, such exchange can take place (Fritz et al., 1989). For this reason, the Rayleigh enrichment seen in Fig. 6-4 is less dramatic for ^{18}O than for ^{34}S.

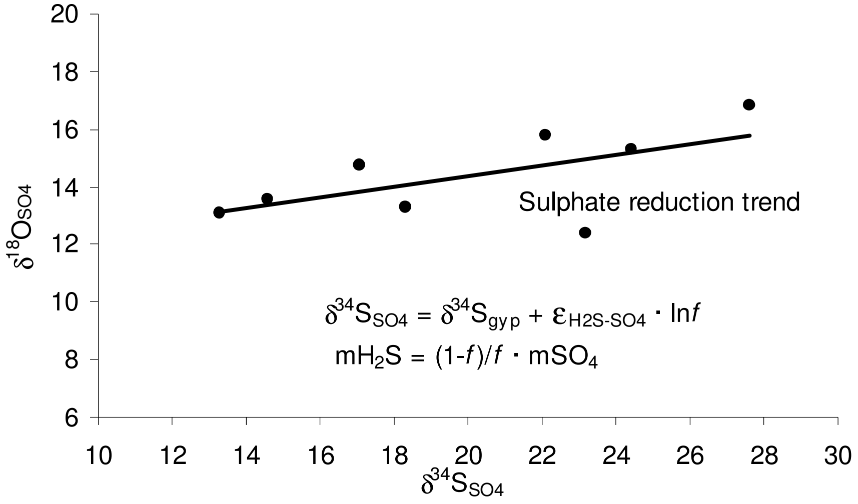


Fig. 6-4 Sulfate reduction trend observed for $\delta^{34}S$ and $\delta^{18}O$ in the residual sulfate in artesian groundwaters from Oman. These groundwaters have several ppm H_2S. Gypsum in the Cretaceous aquifer is the source of sulfate.

Methanogenesis

The last of the redox reactions that can occur in this scenario of redox evolution driven by excess organic carbon is that of methanogenesis. This is in fact a complicated series of complementary reactions whereby the organic carbon itself plays the opposing roles of electron acceptor and electron donor. This sounds improbable, but does occur and involves the formation intermediary organic carbon species with varying associated free energies.

Methanogenic reactions occupy the last rung of the redox ladder, and so offer a minimum of energy to the bacteria that facilitate them. Nonetheless, in the absence of the forgoing electron acceptors, from O_2 to SO_4^{2-}, bacterial methanogenesis is both viable and ubiquitous. Virtually all water-saturated environments, from wetlands and tundra to landfills and manure piles, host the suite of bacteria capable of producing methane. Various reactions degrade the complex organic molecules of vegetation to simpler compounds, with by products including acetate CH_3COOH, CO_2 and H_2. Complementary bacterial reactions can then ferment acetate to produce methane, or reduce CO_2 using H_2 to produce methane.

The two commonly accepted pathways for bacterial methanogenesis, presented by Klass, 1984:

$CH_3COOH \rightarrow CH_4 + CO_2$ Acetate fermentation

$\Delta G^\circ_r = (-50.7 - 394.4) - (-396.46) = -48.64$ kJ/mol

and $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ CO_2 reduction

$\Delta G^\circ_r = (-50.7 + 2\ (-237.14)) - (-394.4 + 04\ (0)) = -130.58$ kJ/mol

The overall reaction can be written simply as the oxidation and reduction of different forms of carbohydrate:

$$2CH_2O \rightarrow CH_4 + CO_2 \qquad \text{methanogenesis}$$

$$\Delta G^\circ_r = (-50.7 - 394.4) - 2\,(-129.7) = -316.28 \text{ kJ/mol}$$

Writing this as a redox half-reaction with electrons on the left side as conventionally expressed:

$$CO_2 + 8\,e^- + 8H^+ \rightarrow CH_4 + 2\,H_2O \qquad \Delta G^\circ_r = -130.58 \text{ kJ/mol}$$

$$\log K = -\frac{\Delta G^\circ_r}{5.708} = -\frac{-130.58}{5.708} = 22.9$$

$$10^{22.9} = \frac{P_{CH_4} \cdot a^2_{H_2O}}{P_{CO_2} \cdot a^8_{e^-} \cdot a^8_{H^+}}$$

$$22.9 = \log P_{CH_4} - \log P_{CO_2} - 8 \log a_{e^-} - 8 \log a_{H^+}$$

$$pe = 2.86 + \tfrac{1}{8} \log P_{CH_4} + \tfrac{1}{8} \log P_{CO_2} - pH$$

Creating the stability line for atmospheric conditions where P_{CO_2} and $P_{CH_4} = 1$ gives the equation:

$$pe = 2.86 - pH$$

Plotting each of these redox half-reactions on a p*e* – pH diagram with the stability field of water shows the evolution of redox conditions in natural waters with excess organic matter.

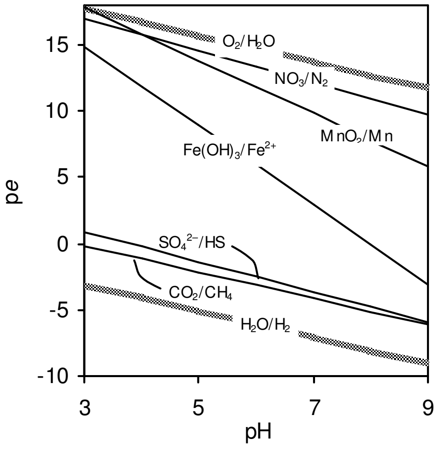


Fig. 6-5 p*e* – pH diagram for principal redox buffering pairs in water

OXIDATION REACTIONS WITH ELEMENTAL OXYGEN — O_2

A consequence of our oxygen-rich atmosphere is that most surface waters and shallow groundwaters contain significant levels of dissolved oxygen that maintain an oxidizing redox environment at the Earth's surface. As discussed above, aerobic respiration is the dominant pathway for biodegradation. However, in addition to oxidation of organic carbon, other substrates exist and are exploited by aerobic bacteria. Any reduced compounds such as organic N, ammonia, ferrous iron minerals, organic sulfur and sulfides are susceptible to oxidation by reaction with atmospheric O_2. Moreover, oxidation with O_2 as the electron acceptor yields the greatest energy output, and so is exploited by aerobic bacteria in almost every near-surface hydrological setting.

Pyrite oxidation

Sulfide minerals are common phases that can be oxidized by elemental oxygen or other electron acceptors. Ferrous iron is another, as is elemental iron such as found in well casings and landfills. When present, these species can control the redox of water and buffer Eh. The rule is that oxidation of a given compound can only be done by an electron acceptor (oxidant) of higher electropotential. For example, ferrous iron is readily oxidized by O_2 or NO_3^- but not with SO_4^{2-}, which is reduced to sulfide at a lower p*e* than at which oxidation of Fe^{2+} occurs (Fig. 6-5).

Sulfide, whether in the form of H_2S or minerals such as pyrite FeS_2 is formed at low redox potential. Of the common minerals and compounds found in the environment, only fixed or reduced carbon compounds (e.g. CH_2O or CH_4) have a greater energy release during oxidation. For this reason, sulfide ores can ignite during mining and milling. In the presence of electron donors of higher electropotential, sulfides are a good substrate for redox reactions.

Pyrite oxidation by O_2 or Fe^{3+}

The most common and most problematic oxidation reaction is the oxidation of pyrite when waste rock and tailings are left at the surface in base metal mining camps. Removal of sulfide rich rock from a deep, anoxic environment to the high P_{O_2} surface setting unleashes the following reactions:

$$FeS_2 + 3\tfrac{1}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad \textit{Thiobacillus thiooxidans}$$

The ferrous iron in this reaction is also oxidized by O_2, producing Fe^{3+} according to the biologically mediated reaction:

$$Fe^{2+} + \tfrac{1}{4}\,O_2 + 2\tfrac{1}{2}H_2O \rightarrow Fe(OH)_3 + 2H^+ \qquad \textit{Thiobacillus ferrooxidans}$$

These complementary reactions are acid generating and can quickly lower the pH of the aqueous setting. As the pH is lowered, $Fe(OH)_3$ becomes more soluble, releasing Fe^{3+} and allowing a second pyrite oxidizing reaction to proceed:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad \text{abiological}$$

As this latter does not require atmospheric O_2, it can proceed under saturated conditions, providing there is an available source of ferric iron.

While these pyrite oxidizing reactions are most commonly observed in mining areas, they also take place in other geochemical settings. Glacial till is a common material to find pyrite, usually as disseminated grains, from the mechanical erosion of sulfide-bearing bedrock. Limestone and crystalline rocks can often have minor pyrite that is accessible to groundwaters.

IRON REDOX EQUILIBRIA AND SOLUBILITY

Iron is the crust's 4th most abundant element, yet is rarely found in surface or groundwaters at concentrations over 1 ppm. Sources of Fe in natural waters include the weathering of common mafic silicates such as amphiboles and pyroxenes, weathering of pyrite, and magnetite. However, Fe solubility is controlled by the two fundamental conditions of aqueous geochemistry – redox and pH.

Under the oxidizing conditions of most near surface weathering environments, Fe concentrations are limited by the low solubility of ferric oxyhydroxide minerals. Amorphous forms have the general formula of $Fe(OH)_3$ and are known as limonite or ferrihydrite. Through burial and heating, water is lost and crystalline forms develop, including goethite (FeOOH) and hematite (Fe_2O_3). Under reducing conditions, Fe^{2+} dominates and the hydroxide $Fe(OH)_2$ is much more soluble than ferrihydrite.

The distribution of the various dissolved ferric and ferrous iron hydroxide species is naturally very sensitive to pH. At low pH, species such as Fe^{3+} and $Fe(OH)^{2+}$ dominate. At circum-neutral pH, $Fe(OH)_{3\ \mathrm{ferrihydrite}}$ precipitation will limit dissolved Fe concentrations to less than 0.001 mg/L. At higher pH, $Fe(OH)_4^+$ becomes stable and again increases the solubility of ferric iron. A similar pattern is observed for reduced iron, although ferrous iron hydroxide precipitate $Fe(OH)_2$ is only stable above ~ pH 9.

*Fe solubility with pH and p*e

The pH and p*e* controls on iron solubility become clearer by looking at the individual reactions. Let's start with oxidizing conditions and look at the ferric (Fe^{3+}) iron hydroxide species in equilibrium with ferrihydrite precipitates in aquifers. This is a common setting, as almost all soils will have some ferrihydrite coatings on mineral grains. The following calculations determine the concentration of the main dissolve ferric hydroxide species in equilibrium with $Fe(OH)_{3\ \mathrm{ferrihydrite}}$.

Species	Fe^{2+}	Fe^{3+}	$Fe(OH)_{3\ \mathrm{ferrihydrite}}$	$Fe(OH)_3^\circ$	$Fe(OH)_2^+$	$Fe(OH)^{2+}$	$Fe(OH)_4^-$	$Fe(OH)_{2\ \mathrm{solid}}$	$HFeO_2^-$
ΔG°	–82.88	-8.56	–692.07	–648.3	–450.5	–233.2	–833.83	–486.5	–379.0
Species	HCO_3^-		$FeCO_3$	FeS	HS^-				
ΔG°	–586.8		–673.05	–93	12.1				

$$\begin{aligned}
Fe(OH)_{3\ \mathrm{ferrihydrite}} &\Leftrightarrow Fe(OH)_3^\circ \\
K &= 10^{-7.67} \\
\log a_{Fe(OH)_3^{\circ\circ}} &= -7.67
\end{aligned}$$

$$\begin{aligned}
Fe(OH)_{3\ \mathrm{ferrihydrite}} &+ H^+ \Leftrightarrow Fe(OH)_2^+ + H_2O \\
K &= \frac{a_{Fe(OH)_2^+}}{10^{-pH}} = 10^{-0.78} \\
\log a_{Fe(OH)_2^+} &= -0.78 - pH
\end{aligned}$$

$$\begin{aligned}
Fe(OH)_{3\ \mathrm{ferrihydrite}} &+ 2H^+ \Leftrightarrow Fe(OH)^{2+} + 2H_2O \\
K &= \frac{a_{Fe(OH)^{2+}}}{10^{-2pH}} = 10^{2.70} \\
\log a_{Fe(OH)^{2+}} &= 2.70 - pH
\end{aligned}$$

$$\begin{aligned}
Fe(OH)_{3\ \mathrm{ferrihydrite}} &+ 3H^+ \Leftrightarrow Fe^{3+} + 3H_2O \\
K &= \frac{a_{Fe^{3+}}}{10^{-3pH}} = 10^{4.89} \\
\log a_{Fe^{3+}} &= 4.89 - 3pH
\end{aligned}$$

$$\begin{aligned}
Fe(OH)_{3\ \mathrm{ferrihydrite}} &+ H_2O \Leftrightarrow Fe(OH)_4^- + H^+ \\
K &= a_{Fe(OH)_4^-} \cdot 10^{-pH} = 10^{-16.71} \\
\log a_{Fe(OH)_4^-} &= -16.71 + pH
\end{aligned}$$

Plotted on a diagram of pH vs dissolved iron concentration, these lines give the concentration of each ferric hydroxide species in equilibrium with ferrihydrite. The sum of these individual concentrations gives the total ferric iron concentration in solution under oxidizing conditions (Fig. 6-6). Clearly, in oxidizing waters at circum-neutral pH, iron has a very low solubilty.

We can carry out similar calculations to see Fe solubility under reducing conditions. In this case, the solid phase is $Fe(OH)_2$, which dissociates under neutral pH conditions completely to produce dissolved Fe^{2+}. Under very alkaline conditions, the anion $HFeO_2^-$ becomes stable and increases Fe solubility.

$$Fe(OH)_{2\,\text{solid}} + 2H^+ \Leftrightarrow Fe^{2+} + 2H_2O$$
$$K = a_{Fe^{2+}} \cdot 10^{2pH} = 10^{12.38}$$
$$\log a_{Fe^{2+}} = 12.38 - 2pH$$

$$Fe(OH)_{2\,\text{solid}} \Leftrightarrow HFeO_2^- + H^+$$
$$K = a_{HFeO_2^-} \cdot 10^{-pH} = 10^{-18.83}$$
$$\log a_{HFeO_2^-} = -18.83 + pH$$

Plotting these relationships on a pH vs. Fe_{total} diagram shows that the solubility of Fe^{2+} hydroxide is much greater than Fe^{3+} hydroxide (ferrihydrite) over the pH range of most natural waters. In fact, at pH 7, the concentration of Fe^{2+} can exceed 1000 ppm. However, there are anions other than hydroxide, which can limit Fe^{2+} solubility – CO_3^{2-} and HS^-.

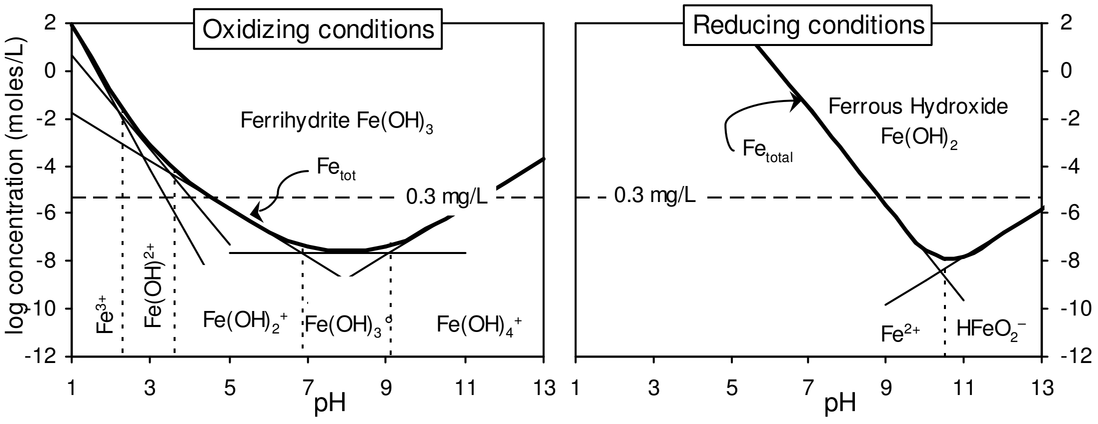


Fig. 6-6 Solubility of ferric iron (left diagram) and ferrous iron according to pH. The WHO water quality objective of 0.3 mg/L for total dissolved iron is shown.

Ferrous iron carbonate – siderite solubility

The reduction of ferric iron to Fe^{2+} is often driven by oxidation of organic carbon. The reaction increases DIC and pH, which favors CO_3^{2-} in the distribution of dissolved inorganic carbon species. Increasing both Fe^{2+} and CO_3^{2-} moves the system towards saturation with siderite [$FeCO_3$] which will control Fe solubility.

$$FeCO_3 + H^+ \Leftrightarrow Fe^{2+} + HCO_3^-$$
$$K = \frac{a_{HCO_3^-} \cdot a_{Fe^{2+}.}}{10^{-pH}} = 10^{-0.59}$$
$$\log a_{Fe^{2+}} = -0.59 - \log a_{HCO_3^-} - pH$$

If we are to plot this on a pH – Fe solubility diagram, the activity of bicarbonate must be fixed. As there are other controls such as calcite solubility which limit HCO_3^- and CO_3^{2-}, the concentration of HCO_3^- is often found within the range of 100 to 300 mg/L. For this example, $a_{HCO_3^-}$ is set at $10^{-2.5}$ (200 mg/L).
0

Fig. 6-7 shows that in waters with a reasonable carbonate alkalinity, siderite precipitation constrains the solubility of ferrous iron to a much lower level than does ferrous iron hydroxide. Above pH 7, Fe^{2+} concentration is less than 1 mg/L, and less than the drinking water objective of 0.3 mg/L above pH 7.2.

Ferrous iron sulfide – amorphous FeS

Any well owner with a hydrogen sulfide problem is familiar with the black FeS precipitate that encrusts their pump and well casing. In the absence of O_2, steel will oxidize to Fe^{2+} by reducing H^+ to H_2. In the presence of H_2S and HS^- from sulfate reduction, the Fe^{2+} will precipitate to as an amorphous ferrous iron sulfide. Crystalline forms such as pyrrhotite [FeS] and pyrite [FeS_2] are thermodynamically more stable, but require time and higher temperature to form, and so are not controlling phases in near surface geochemical environments.

To see how effective FeS is at limiting Fe^{2+} concentrations in water, lets presume that a groundwater with excess organic carbon has reduced ferrihydrate [$Fe(OH)_3$] in the subsurface and is now reducing sulfate. Sulfate reduction is an acid-consuming reaction and so the pH will generally be above 7, making HS^- the dominant species. The following mineral dissociation reaction will control the solubility of Fe^{2+} and HS^-:

$$FeS + H^+ \Leftrightarrow Fe^{2+} + HS^-$$

$$K_{sp} = \frac{a_{Fe^{2+}} \cdot a_{HS^-}}{a_{H^+}} = 10^{-3.89}$$

$$\log a_{Fe^{3+}} = -3.89 - \log a_{HS^-} - pH$$

As with siderite, the activity of HS^- must be specified in order to determine FeS solubility with pH. For this example, let's set the concentration of HS^- at 10 mg/L ($3.03 \cdot 10^{-4}$ or $10^{-3.5}$ mol/L) and use the simplification that $a = m$.

The results of this calculation, plotted in Fig. 6-7 show that at a reasonable level of HS^-, FeS is a highly limiting Fe phase. In this example, Fe^{2+} is below 0.3 mg/L at all pH values above 5. Note that FeS has much lower solubility than siderite. Thus, in the presence of dissolved sulfide, siderite will be dissolved and the Fe^{2+} reprecipitated as FeS.

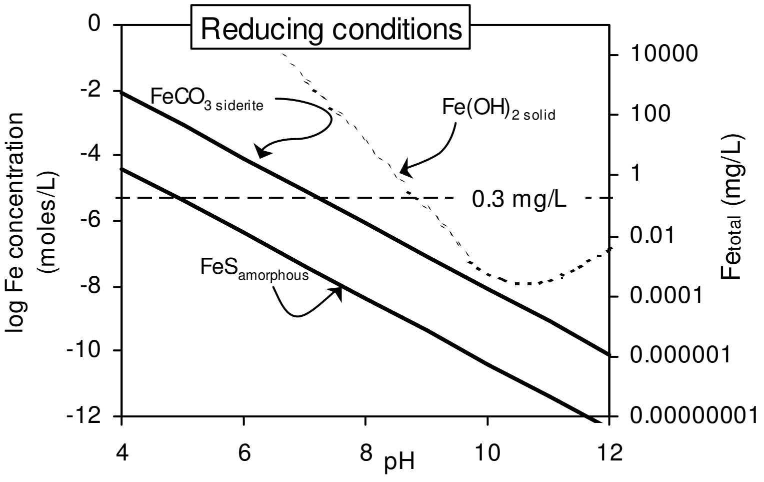


Fig. 6-7 Solubility of iron under reducing conditions (Fe^{2+}) in the presence of DIC ($m_{HCO_3^-}$ = 200 mg/L) and in the presence of hydrogen sulfide (m_{HS^-} = 10 mg/L).

Oxidation of zero-valence iron

The oxidation of metallic, or zero-valence, iron — Fe° is an important reaction in certain groundwaters. Natural native iron occurrences are rare, with examples from the iron mining regions in Sweden, and perhaps the Thule iron meteorite of the western Greenland coast that provided early Inuit with iron for arrow and harpoon points. However, steel well casings and the use of zero valence iron with in-situ contaminant attenuation substrates provide sites where Fe° oxidation reactions occur. The reaction can proceed aerobically, as we all know from rusted cars:

$$Fe^\circ + \tfrac{3}{4}O_2 + 1\tfrac{1}{2}H_2O \rightarrow Fe(OH)_3$$

and anaerobically, with the production of elemental hydrogen:

$$Fe^\circ + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$$

In the anaerobic case, there is an increase in pH through the production of hydroxide, which limits the solubility of ferrous iron through the precipitation of $Fe(OH)_2$ – an amorphous black precipitate.

Summary of iron solubility

Iron solubility can be limited by phases other than hydroxide, carbonate and sulfide. If present at significant concentrations other ligands can complex and precipitate iron from solution. Phosphate species ($H_2PO_4^-$ and HPO_4^{2-}) form stable ferrous iron minerals including vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$] with $K = 10^{-25.76}$ (Al Borno and Thompson, 1994). While SO_4^{2-} often has a high concentration in water, jarosite minerals [$(K,Na)Fe_3(SO_4)_2(OH)_6$] ($K_{sp} = 10^{-93}$ to 10^{-75}; Langmuir, 1997) limit ferric iron solubility at low pHs where ferric iron hydroxides are soluble, and melanterite [$FeSO_4 \cdot 7H_2O$] is soluble at most pHs ($K_{sp} = 10^{-2.21}$; Reardon and Beckie, 1987).

Some geochemical conditions can increase iron solubility above that of these controlling phases. One is the rate of mineral precipitation, which can sometimes exceed the residence time of water in a given system. Iron supersaturation can be created if precipitation is impeded by adsorption of organics or other complexes on the nucleation surface. In waters with dissolved organics and other ligands (phosphates, F^-), both ferric and ferrous iron complexes and colloids can form (Hem, 1972) thus increasing dissolved Fe concentrations.

Nonetheless, most surface waters and shallow groundwaters are oxygenated, and iron concentrations are limited by ferric iron hydroxide - ferrihydrite, generally to less than 0.1 mg/L. Amorphous ferrihydrite precipitates are commonly found as flocs and gels in sediments where they can harden into cements. They have a high sorption capacity and so are very effective in removing a host of metals from solution. Only under conditions of extreme pH such as found in mine settings (acid mine drainage) or in highly alkaline ($pH > 10$) will ferric iron be soluble.

When concentrations of dissolved Fe exceed about 0.1 mg/L, this usually signifies reducing conditions where ferrous iron dominates. In organic rich sediments or groundwaters where sulfate is reduced to HS^-, black FeS precipitate forms. In non-sulfur settings, siderite [$FeCO_3$] becomes the limiting phase. Both phases, however, are more soluble at lower pH.

High Fe^{2+} groundwaters pose a significant problem to the water well industry due to screen and pump fouling by iron bacteria. The locally aerobic conditions established in the aquifer around the well is conducive to the oxidation of Fe^{2+} – a reaction that is mediated by a host of microbes who thrive off the energy released and create a slimy red precipitate of ferric hydroxide and organics.

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PROBLEMS

1. **(3)** Write the two complementary redox half-reactions for (i) the oxidation of hydrogen — H_2 by O_2 and (ii) oxidation of methane — CH_4, with O_2. Determine the Gibb's free energy for each overall reaction. Which would provide more energy to bacteria, per mole of O_2 consumed.

$$\begin{array}{lll} \text{(i)} & H_2 \rightarrow 2H^+ + 2e^- & \\ & \underline{2H^+ + 2e^- + \tfrac{1}{2}O_2 \rightarrow H_2O} & \\ & H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O & \Delta G^{\circ}_r = -237.14\ \text{kJ/mol}\ H_2 \\ & & \quad = -474.28\ \text{kJ/mol}\ O_2 \end{array}$$

$$\begin{array}{lll} \text{(ii)} & CH_4 \rightarrow C^{4+} + 4H^+ + 4e^- & \\ & \underline{4H^+ + 4e^- + O_2 \rightarrow 2H_2O} & \\ & CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O & \Delta G^{\circ}_r = -817.93\ \text{kJ/mol}\ CH_4 \\ & & \quad = -408.97\ \text{kJ/mol}\ O_2 \end{array}$$

Hydrogen oxidation provides more energy per mole of O_2 consumed.

2. **(4)** A groundwater was sampled from a confined aquifer. The temperature was measured at 25°C, and the water had a pH of 8.15 and Eh of –0.27 V. The geochemical analysis for this water is as follows (in mg/L):

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Fe^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	HS^-	DOC
mg/L	68.71	0.34	95	5.7	<0.001	31.0	2.34	300	4.1	6.8
mmol/L	1.71	0.014	4.13	0.15	<2E–5	0.51	0.066	3.13	0.12	0.57

Calculate an Eh for this water from the sulfate/sulfide redox couple (don't forget to use activities). What is the calculated p*e* for this water? How does your calculated Eh compare with your measured Eh? Write the geochemical reaction that seems to be buffering redox.

Note that this water contains no detectable ferrous iron. What solid phase would be limiting it's concentration, and what should be the equilibrium concentration of Fe^{2+}?

$$I = \tfrac{1}{2}(4\times1.71 + 4\times0.014 + 4.13 + 0.15 + 0.51 + 0.066 + 4\times3.13 + 0.12)\cdot 10^{-3}$$
$$= 0.0122$$

$$\log\gamma_{SO_4} = \frac{-0.5z^2\sqrt{I}}{1+\sqrt{I}} + 0.3I = \frac{-0.5\cdot4\sqrt{0.0122}}{1+\sqrt{0.0122}} + 0.3\cdot0.0122 = -0.195$$

$$\gamma_{SO_4} = 0.64$$
$$a_{SO_4} = m_{SO_4}\cdot\gamma_{SO_4}$$
$$= 0.00313\cdot0.64$$
$$= 0.00199$$

$$\log\gamma_{HS} = \frac{-0.5\cdot1\sqrt{0.0122}}{1+\sqrt{0.0122}} + 0.3\cdot0.0122 = -0.046$$

$$\gamma_{HS} = 0.89$$
$$a_{HS} = m_{HS}\cdot\gamma_{HS}$$
$$= 0.00012\cdot0.89$$
$$= 0.000112$$

$$SO_4^{2-} + 8e^- + 9H^+ \rightarrow HS^- + 4H_2O \qquad \Delta G^\circ_r = -192.36 \text{ kJ/mol}$$

$$K = -\frac{\Delta G^\circ_r}{5.708} = 10^{33.7}$$

$$10^{33.7} = \frac{a_{HS^-}}{a_{SO_4^{2-}}\cdot a_{e^-}^8\cdot a_{H^+}^9}$$

$$pe = 4.21 + \tfrac{1}{8}\log\frac{a_{SO_4^{2-}}}{a_{HS^-}} - \tfrac{9}{8}\,pH$$
$$= 4.21 + \tfrac{1}{8}\log\frac{0.00199}{0.000112} - \tfrac{9}{8}(8.15)$$
$$= -4.8$$

$$Eh = 0.059\,pe$$
$$= 0.059\,(-4.8)$$
$$= -0.28 \text{ volts}$$

The calculated Eh is almost identical to the measured Eh, indicating the bulk Eh is controlled by the SO_4^{2-}/HS^- redox couple.

The redox reaction that seems to be buffering Eh at this low value is sulfate reduction:

$$SO_4^{2-} + 8e^- + 9H^+ \rightarrow HS^- + 4H_2O$$

(WHAT ABOUT SIDERITE?) The low Fe concentration suggests that any Fe^{2+} that may be released by reduction of ferric iron oxyhydroxides (ferrihydrite) is being precipitated as a sulfide. At low temperature, pyrite is unlikely to form, although FeS can precipitate as mackinawite. The solubility of Fe^{2+} in association with HS^- and FeS is controlled by the reaction:

$$Fe^{2+} + HS^- \Leftrightarrow FeS + H^+ \qquad \Delta G^\circ_r = -93 + 82.88 - 12.1 = -22.2 \text{ kJ/mol}$$

$$K = 10^{3.89} = \frac{a_{FeS} \cdot a_{H^+}}{a_{Fe^{2+}} \cdot a_{HS^-}} = \frac{10^{-8.15}}{a_{Fe^{2+}} \cdot 0.00011}$$

$$a_{Fe^{2+}} = 8.3 \cdot 10^{-9}$$

As this is less than 1 ppb, it was not detected in the analysis done for this water.

3. **(3)** The oxidation of ammonium by O_2 is an important reaction in soils and surface waters that releases NO_3^- to the environment. Write a redox equation for the oxidation of ammonium ($\Delta G^\circ_{NH4+} = -79.31$ kJ/mol) to nitrate and determine the p*e* - pH relationship that defines the equilibrium for this redox pair at an ion activity ratio of 1 (i.e. for $a_{NO3-} / a_{NH4+} = 1$)

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \qquad \Delta G^\circ_r = -266.57$$

Now writing the redox half reaction for ammonium oxidation,

$$NH_4^+ + 3H_2O \rightarrow NO_3^- + 8e^- + 10H^+ \qquad \Delta G^\circ_r = 681.99$$

$$K = 10^{-119.48} = \frac{a_{NO_3^-} \cdot a_{H^+}^{10} \cdot a_{e^-}^{8}}{a_{NH_4^+}}$$

$$-119.48 = -8pe - 10pH + \log\frac{a_{NO_3^-}}{a_{NH_4^+}}$$

and for a $\frac{a_{NO_3^-}}{a_{NH_4^+}}$ activity ratio equal to 1,

$$pe = 14.94 - \tfrac{5}{4}pH$$

at pH = 7, p*e* = 6.18