

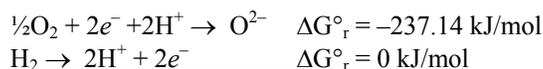
Chapter 1: Redox Evolution in Surface and Groundwaters

Four billion years of photosynthetic activity has generated 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 O₂ levels in the atmosphere to 21%. It has remained close to this steady-state value since Precambrian time, held in check largely by respiration of the biomass that generates it.

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 environment at the Earth's surface. Any reduced compounds such as ferrous iron minerals, sulfides and organic matter are susceptible to oxidation by reaction with atmospheric O₂. This is the first step in the redox evolution of surface and groundwaters. Subsequent steps occur when this electron acceptor is depleted. If waters contain significant quantities of reduced compounds, then the next available electron acceptor will be used to further drive redox reactions and push the system to a lower redox potential. Recall in Chapter 2 that the redox potential of a system can be measured as its electromotive potential compared with the standard hydrogen electrode, Eh. It is also measured by the activity of the dominant redox pairs, which provide a measurement of electron activity, or *pe*. Here we will examine the series of common redox reactions that can occur sequentially in waters with an abundance of electron donors.

Electron donors and electron acceptors in waters

Pure water, H₂O, with its dissociation products, OH⁻ and H⁺, has no redox pairs, and is inert from a redox perspective. No electron exchange reactions will take place. Add elemental oxygen, O₂, and hydrogen, H₂, and the potential to exchange electrons has developed. Oxygen in its zero valence state requires electrons to fill its outer orbit – it is an electron acceptor. Hydrogen will shed its electron to become a hydrogen ion – H⁺, and so is an electron donor. Individually, these elements represent redox half cells or pairs. Together, they can perform work through a coupled redox reaction.



Many compounds in water are electromotively inert, and do not participate in redox reactions. Ca²⁺, for example, will not accept electrons under natural conditions. Similarly, Cl⁻ is most stable in this valence state and requires considerable energy to be oxidized. However, through photosynthesis and mineral weathering, waters receive a host of other compounds that can participate in electron transfers. Table 1-1 lists the most common electron donors and electron acceptors, as well as the *pe* at which they operate. Establishing viable redox reactions becomes a simple exercise of linking electron donors with an electron acceptor that sits further up the redox scale, which will produce an exothermic reaction on which bacteria can live.

Table 1-1 Common forms and oxidation states of the important redox elements in natural waters. Valence states for these and other redox species are given in Table 2-5.

Electron acceptors (oxidants)	Electron donors (fuel)
O ₂	
NO ₂ ⁻	N ₂ O
NO ₃ ⁻	NH ₄ ⁺
MnO ₂	Mn ²⁺
Fe(OH) ₃	Fe ²⁺
SO ₄ ²⁻	H ₂ S
CO _{2(aq)}	CH ₂ O, CH ₄

 H₂

This table demonstrates the general rule for redox reactions, given that with the exception of photosynthesis, reactions will only proceed if there is an energetic gain for the mediator. Thus, common plausible reactions involve an electron donor from the left column and an electron acceptor from a lower level in the right column, but not from a higher level. For example:



OXIDATION REACTIONS WITH ELEMENTAL OXYGEN — O₂

Respiration – oxidation of organic matter with O₂

The most common redox reaction and perhaps the most important for the weathering of continental crust is the oxidation of biomass, respiration, which is mediated by bacteria in soils, groundwaters and in surface waters. It is simply the reverse reaction to photosynthesis, and one of the most energetic in natural (and polluted) waters. For this reason, aerobic bacteria out-compete others working further down the redox scale, and will dominate as long as elemental oxygen is available. This reaction is discussed in Chapter 2, and reviewed here, showing the two redox half reactions and the complete reaction.

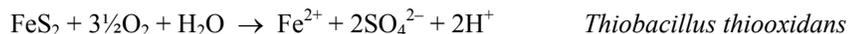


Under open system conditions, diffusion of atmospheric O₂ into the soil gas provides a continual supply for aerobic degradation of organics. Below the water table, groundwaters recharge with dissolved oxygen (DO) concentrations close to air saturated values (8.71 ppm O₂ at 25°C; Table 2-8). As most shallow groundwaters contain only a few ppm of DOC, which are generally relatively recalcitrant, they retain their DO until other electron donors are encountered along the flow path. In lakes, aerobic conditions throughout the water column are maintained by diffusion of atmospheric O₂ into the surface layer, by photosynthesis in the upper few meters, and by convection of oxygenated waters to depth during seasonal temperature inversions.

Pyrite oxidation by O₂ and Fe³⁺

Sulfide, whether in the form of H₂S or minerals such as pyrite FeS₂ is formed at low redox potential. Of the common minerals and compounds found in the environment, only fixed or reduced carbon compounds (e.g. CH₂O or CH₄) 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 electromotive potential, sulfides are a good substrate for redox reactions.

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_{O₂} surface setting unleashes the following reactions:

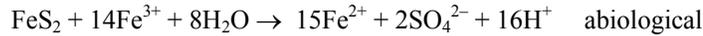


3 Chapter 6 Redox Reactions

The ferrous iron in this reaction is also oxidized by O₂, producing Fe³⁺ according to the biologically mediated reaction:



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 Fe³⁺ and allowing a second pyrite oxidizing reaction to proceed:



As this latter does not require atmospheric O₂, 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.

Example 1-1 Pyrite oxidation in glaciofluvial sediments

Groundwater recharge has been studied in an aquifer of glaciofluvial sands situated in southeastern Manitoba (Cherry et al., 2000). The aquifer is a medium grained quartz sand with 1 to 3% carbonate content. Interstratified within the glaciofluvial sands are sandy till units. The following four water quality analyses are for groundwaters taken at different depths in the upper 30 m of the aquifer:

T°C	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	SO ₄ ²⁻	Cl ⁻	HCO ₃ ⁻
25	12.50	27.9	<0.01	8.39	19.7	17.4	1.29	0.000

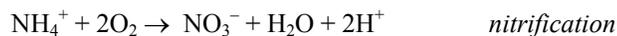
A qualitative inspection of these geochemical data allows the following interpretation:

- The shallowest groundwaters have a Ca²⁺ – HCO₃⁻ geochemical facies following infiltration through the forest soil and upper quartz sand aquifer.
- During flow through the upper 10 m, the pH . . . geochemistry . . .
- Pyrite oxidation is apparent from the increase in sulfate
- The carbonate content is buffering acidity during pyrite oxidation, which causes an increase in HCO₃⁻ activity.

Nitrification

The release of organic nitrogen in soils as well as in aerobic wastewater treatment systems occurs by the oxidation of ammonia, NH₃ or more commonly, ammonium, NH₄⁺ which is the dominant form at pH values lower than 9.2. The pathway begins during biodegradation of vegetation with the mineralization of reduced nitrogen bound in amino acids of proteins and released as NH₄⁺ (Fig. 3-3).

In the presence of abundant oxygen, mineralized ammonium is converted to nitrite and then to nitrate through the bacterially mediated pathway of nitrification.



Where elemental O₂ is restricted to low levels, it is converted to nitrite, NO₂⁻.

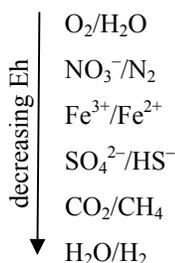


Nitrite, so produced by oxidation of ammonium, remains in solution as a highly soluble anion, or can be further oxidized to nitrate where DO levels permit. Both ammonium and nitrate in soils and surface waters can be assimilated by living vegetation, whether algae or plants, for regeneration. This is an essential step in recycling organic nitrogen back into the living biomass.

REDOX EVOLUTION IN WATER - OXIDATION OF ORGANICS

In most waters, it is the oxidation of excess organic carbon that drives redox evolution. Other electron donor substrates such as sulfides can also support redox reactions in water, but are less common. Organic carbon is ubiquitous, and provides more energy than all other electron donors encountered by groundwaters and surface waters. Dissolved organic carbon (DOC) can be gained by groundwaters during infiltration through soils, although concentrations are generally less than 1 to 2 ppm C. 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 in the water column and in bottom sediments. DOC is highly concentrated in landfill leachates, reaching >1000 ppm C. Similarly, groundwaters and runoff from agricultural landscapes may have DOC > 10 to 100 mg-C/L from crop residues and manure spread on fields.

The redox evolution of water with excess organic matter follows a series of steps from the aerated near surface zone to deeper zones where successive electron acceptors are available to oxidize organic carbon. The redox pairs that release the greatest amount of free energy are most competitive and operate ahead of those that release very little. Aerobic oxidation of organics is the first in this chain. We saw above that oxidation of carbohydrate with O₂ releases some 502 kJ per mole. Here we will look at the energy releases during oxidation of organics with the following redox pairs, presented in order of decreasing electromotive potential.



Each of these redox pairs will operate at a successively lower electromotive potential. 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.

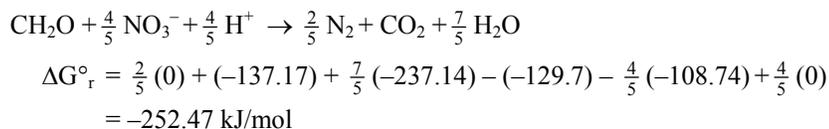
Although natural waters seldom achieve redox equilibrium, the equilibrium thermodynamic approach used for acid – base reactions in Chapter 3 allows us to see the direction in which redox evolution is moving and what mineral phases are stable. It also provides us with a method to measure redox potential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

Denitrification

The Haber-Bosch process to synthesize ammonia from N₂ increased by 10-fold global agricultural yields and is the single most important development behind the exponential increase in population. So where does all this ammonia end up? Bacteria such as *Nitrosomonas* and *Nitrobacter* use oxygen to nitrify it to NO₃⁻.

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.



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. 1-3), and using $P_{\text{N}_2} = 1$ atmosphere:

$$\begin{aligned} \text{NO}_3^- + 5e^- + 6\text{H}^+ &\Leftrightarrow \frac{1}{2} \text{N}_2 + 3\text{H}_2\text{O} \\ \log K &= -\frac{3(-237.14) - (-108.74)}{5.708} = 105.6 \\ 10^{105.6} &= \frac{P_{\text{N}_2}^{1/2} \cdot a_{\text{H}_2\text{O}}^3}{a_{\text{NO}_3^-} \cdot a_{e^-}^5 \cdot a_{\text{H}^+}^6} \\ 105.6 &= \frac{1}{2} \log P_{\text{N}_2} - \log a_{\text{NO}_3^-} - 5 \log a_{e^-} - 6 \log a_{\text{H}^+} \quad \text{and using } P_{\text{N}_2} = 1 \text{ atm} \\ pe &= 21.1 + \frac{1}{5} \log a_{\text{NO}_3^-} - \frac{6}{5} \text{pH} \end{aligned}$$

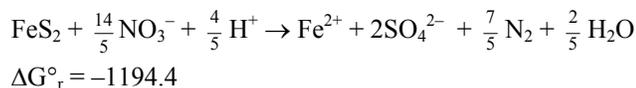
Creating this line for the drinking water limit of nitrate of 10 ppm as N ($a_{\text{NO}_3^-} = 10^{-3.15}$ mol/L):

$$pe = 20.5 - \frac{6}{5} \text{pH}$$

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 $pe - \text{pH}$ 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 ($\text{NO}_3^- \rightarrow \text{N}_2$) takes place at a high pe , near 12 in neutral pH waters, whereas sulfate reduction ($\text{SO}_4^{2-} \rightarrow \text{HS}^-$) takes place at low pe , 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:



The ferrous iron released to solution in this reaction can also act as an electron donor for denitrification. A 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 1-2 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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of the residual nitrate (Fig. 1-1) 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 $\delta^{34}\text{S}$ 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

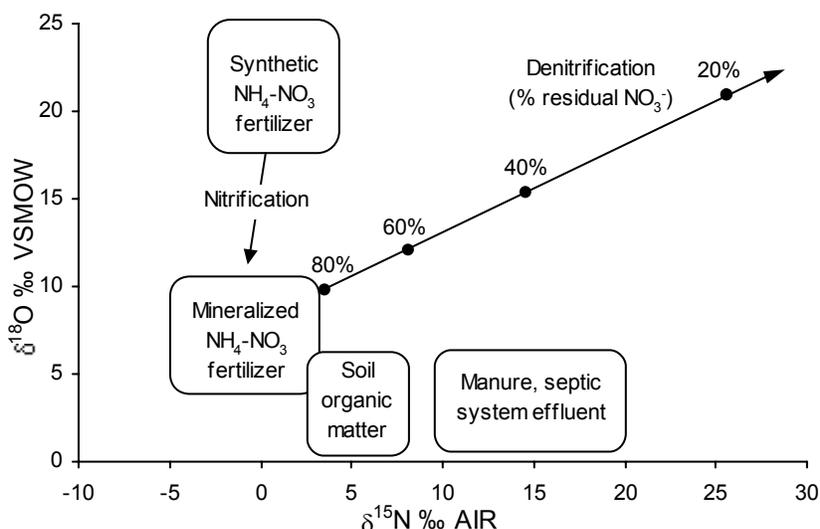


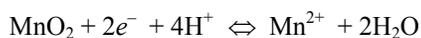
Fig. 1-1 Rayleigh enrichment of ^{15}N and ^{18}O in NO_3^- is clear evidence for microbial denitrification in the Fuhrberger Feld aquifer (modified from Böttcher et al., 1990).

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 pe. The manganese oxide pyrolusite [MnO_2] is the common mineral form, found as a cement or heavy mineral in clastic aquifers.



Species	Mn_{metal}	Mn^{2+}	$\text{MnO}_2_{\text{pyrolusite}}$	CH_2O	CO_2	H_2O
ΔG°	0	-228.1	-465.14	-129.7	-394.37	-237.14



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

$$10^{41.6} = \frac{a_{\text{Mn}^{2+}} \cdot a_{\text{H}_2\text{O}}^2}{a_{\text{MnO}_2} \cdot a_{e^-}^2 \cdot a_{\text{H}^+}^4}$$

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

$$pe = 20.8 - \frac{1}{2} \log a_{\text{Mn}^{2+}} - 2 \text{pH}$$

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

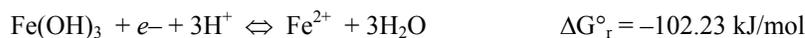
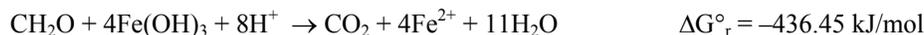
$$pe = 23.8 - 2 \text{pH}$$

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 pe 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^{3+}	Fe^{3+}	$\text{Fe}(\text{OH})_3$ 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:



$$\log K = -\frac{\Delta G_r^\circ}{5.708} = -\frac{-102.23}{5.708} = 17.9$$

$$10^{17.9} = \frac{a_{\text{Fe}^{2+}} \cdot a_{\text{H}_2\text{O}}^3}{a_{\text{Fe}(\text{OH})_3} \cdot a_{e^-} \cdot a_{\text{H}^+}^3} = \frac{a_{\text{Fe}^{2+}}}{a_{e^-} \cdot a_{\text{H}^+}^3}$$

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

$$pe = 17.9 - \log a_{\text{Fe}^{2+}} - 3\text{pH}$$

To plot this line on our $pe - \text{pH}$ 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 $\text{Fe}(\text{OH})_3$ stability fields:

$$pe = 23.9 - 3\text{pH}$$

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. CH₂O) 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 S⁶⁺ to S²⁻.

Species	SO ₄ ²⁻	HS ⁻	H ₂ S	CH ₂ O	CH ₄	CO ₂	H ₂ O	HCO ₃ ⁻
ΔG _r ^o	-744.0	12.2	-27.7	-129.7	-50.72	-394.37	-237.14	-586.8



The sulfate reduction half reaction can be written as:



$$\log K = -\frac{\Delta G_r^\circ}{5.708} = -\frac{-192.36}{5.708} = 33.7$$

$$10^{33.7} = \frac{a_{\text{HS}^-} \cdot a_{\text{H}_2\text{O}}^4}{a_{\text{SO}_4^{2-}} \cdot a_{e^-}^8 \cdot a_{\text{H}^+}^9}$$

$$33.7 = \log a_{\text{HS}^-} - \log a_{\text{SO}_4^{2-}} - 8 \log a_{e^-} - 9 \log a_{\text{H}^+}$$

$$pe = 4.21 + \frac{1}{8} \log \left(\frac{a_{\text{SO}_4^{2-}}}{a_{\text{HS}^-}} \right) - \frac{9}{8} \text{pH}$$

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.

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

In this case, less energy is released per mole of CH₂O and the reaction has a lower equilibrium constant. Clearly, sulfate reduction will only take place when the more favored reaction – O₂ 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 H₂S, 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}).

³⁴S and ¹⁸O tracers of sulfate reduction

The reduction of SO₄²⁻ to dissolved sulfide (H₂S or HS⁻) is accompanied by a significant fractionation for ³⁴S. 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 ³⁴S by about 25 ± 10‰ (Krouse, 1970).

The process of sulfate reduction, however, can have an even stronger effect on the partitioning of ³⁴S and ¹⁸O 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 $\delta^{18}\text{O}$ 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. 1-2). A strong enrichment in $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ and $\delta^{18}\text{O}_{\text{SO}_4^{2-}}$ 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 $\delta^{18}\text{O}$ 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. 1-2 is less dramatic for ^{18}O than for ^{34}S .

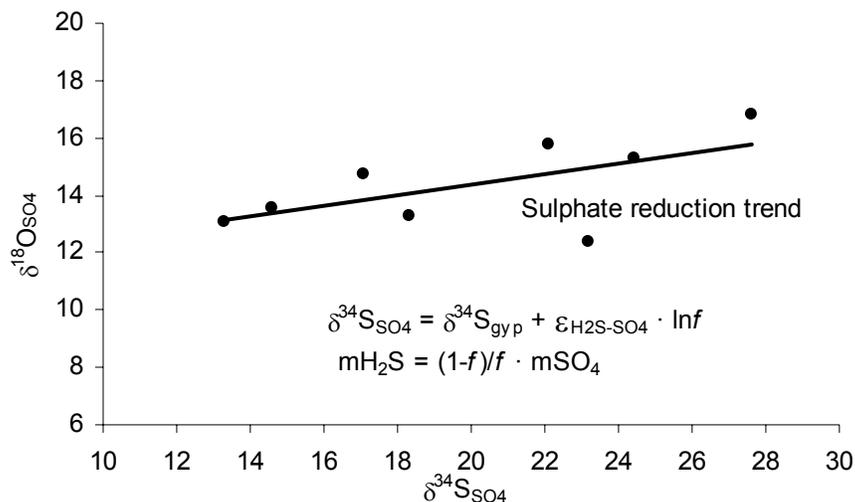


Fig. 1-2 Sulfate reduction trend observed for $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in the residual sulfate in artesian groundwaters from Oman. These groundwaters have several ppm H_2S . Gypsum in the Cretaceous aquifer is the source of sulfate.

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 catalyze 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, whether wetlands, tundra, landfills or bovine intestinal tracts, host the suite of bacteria capable of pumping out 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:



$$\Delta G^\circ_f = (-50.7 - 394.4) - (-396.46) = -48.64 \text{ kJ/mol}$$



$$\Delta G_r^\circ = (-50.7 + 2(-237.14)) - (-394.4 + 04(0)) = -130.58 \text{ kJ/mol}$$

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



$$\Delta G_r^\circ = (-50.7 - 394.4) - 2(-129.7) = -316.28 \text{ kJ/mol}$$

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



$$\log K = -\frac{\Delta G_r^\circ}{5.708} = -\frac{-130.58}{5.708} = 22.9$$

$$10^{22.9} = \frac{P_{\text{CH}_4} \cdot a_{\text{H}_2\text{O}}^2}{P_{\text{CO}_2} \cdot a_{e^-}^8 \cdot a_{\text{H}^+}^8}$$

$$22.9 = \log P_{\text{CH}_4} - \log P_{\text{CO}_2} - 8 \log a_{e^-} - 8 \log a_{\text{H}^+}$$

$$pe = 2.86 + \frac{1}{8} \log P_{\text{CH}_4} + \frac{1}{8} \log P_{\text{CO}_2} - pH$$

Creating the stability line for atmospheric conditions where P_{CO_2} and $P_{\text{CH}_4} = 1$ gives the equation:

$$pe = 2.86 - pH$$

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

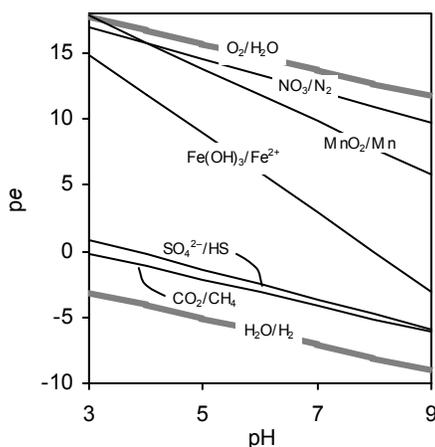


Fig. 1-3 $pe - pH$ diagram for principal redox buffering pairs in water

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.

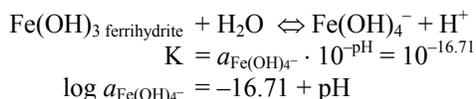
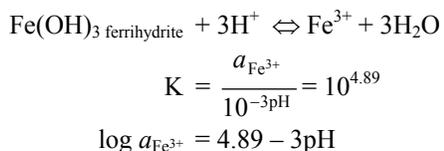
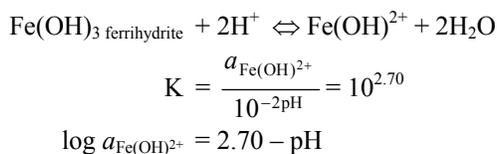
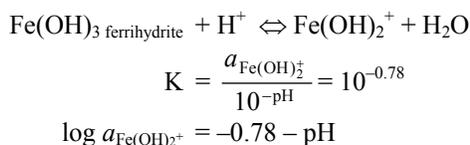
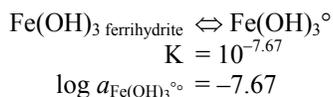
Under the oxidizing conditions of most near surface weathering environments, Fe concentrations are limited by the low solubility of ferric oxyhydroxide minerals. Amorphous forms have the general formula of $\text{Fe}(\text{OH})_3$ and are known as limonite or ferrihydrite. Through burial and heating, water is lost and crystalline forms develop, including goethite (FeOOH) and hematite (Fe_2O_3). Under reducing conditions, Fe^{2+} dominates and the hydroxide $\text{Fe}(\text{OH})_2$ 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 $\text{Fe}(\text{OH})_2^{2+}$ dominate. At circum-neutral pH, $\text{Fe}(\text{OH})_3$ ferrihydrite precipitation will limit dissolved Fe concentrations to less than 0.001 mg/L. At higher pH, $\text{Fe}(\text{OH})_4^-$ becomes stable and again increases the solubility of ferric iron. A similar pattern is observed for reduced iron, although ferrous iron hydroxide precipitate $\text{Fe}(\text{OH})_2$ is only stable above \sim pH 9.

Fe solubility with pH and pe

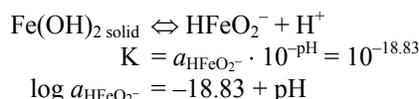
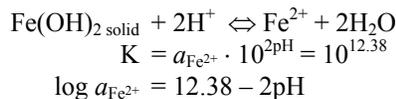
The pH and *pe* controls on iron solubility become clearer by looking at the individual reactions. Lets start with oxidizing conditions and look at the ferric (Fe^{3+}) iron hydroxide species in equilibrium with ferrihydrite precipitates in aquifers. This is a common setting, as almost all soils will have some ferrihydrite coatings on mineral grains. The following calculations determine the concentration of the main dissolve ferric hydroxide species in equilibrium with $\text{Fe}(\text{OH})_3$ ferrihydrite.

Species	Fe^{2+}	Fe^{3+}	$\text{Fe}(\text{OH})_3$ ferrihydrite	$\text{Fe}(\text{OH})_3^\circ$	$\text{Fe}(\text{OH})_2^+$	$\text{Fe}(\text{OH})_2^{2+}$	$\text{Fe}(\text{OH})_4^-$	$\text{Fe}(\text{OH})_2$ 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				



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. 1-4). Clearly, in oxidizing waters at circum-neutral pH, iron has a very low solubility.

We can carry out similar calculations to see Fe solubility under reducing conditions. In this case, the solid phase is $\text{Fe}(\text{OH})_2$, 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.



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^- .

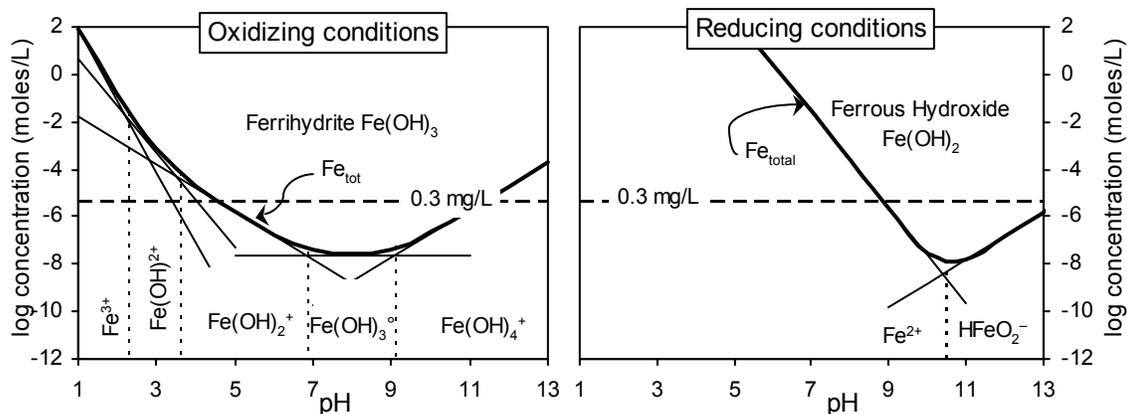
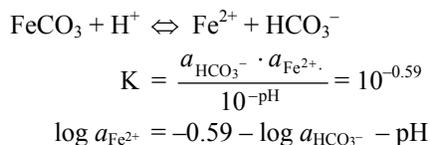


Fig. 1-4 Solubility of ferric iron (left diagram) and ferrous iron according to pH. The WHO water quality objective of 0.3 mg/L for total dissolved iron is shown.

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.



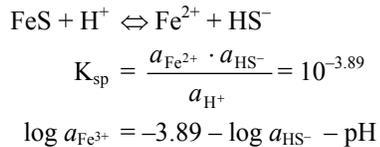
If we are to plot this on a pH – Fe solubility diagram, the activity of bicarbonate must be fixed. As there are other controls such as calcite solubility which limit HCO_3^- and CO_3^{2-} , the concentration of HCO_3^- is often found within the range of 100 to 300 mg/L. For this example, $a_{\text{HCO}_3^-}$ is set at $10^{-2.5}$ (200 mg/L).

Fig. 1-5 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 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 $[\text{FeS}]$ and pyrite $[\text{FeS}_2]$ 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, let's presume that a groundwater with excess organic carbon has reduced ferrihydrate $[\text{Fe}(\text{OH})_3]$ 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^- :



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. 1-5 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.

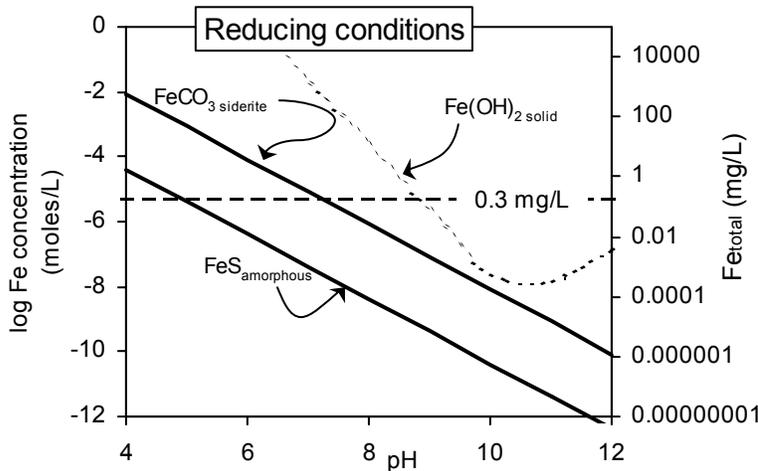


Fig. 1-5 Solubility of iron under reducing conditions (Fe^{2+}) in the presence of DIC ($m_{\text{HCO}_3^-} = 200$ mg/L) and in the presence of hydrogen sulfide ($m_{\text{HS}^-} = 10$ mg/L).

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 iron minerals including vivianite [$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$] with $K = 10^{-25.76}$ (Al Borno and Thompson, 1994). While SO_4^{2-} often has a high concentration in water, jarosite minerals [$(\text{K},\text{Na})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$] ($K_{\text{sp}} = 10^{-93}$ to 10^{-75} ; Langmuir, 1997) limit ferric iron solubility at low pHs where ferric iron hydroxides are soluble, and melanterite [$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$] is soluble at most pHs ($K_{\text{sp}} = 10^{-2.21}$; 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 ($\text{pH} > 10$) 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.

FURTHER READING

Kinetic reaction rates: Krauskopf, K.B. and Bird, D.K., 1995. Reaction Rates and Mass Transfer. Chapter 11, in: *Introduction to Geochemistry*, Third Edition, McGraw Hill, pp. 273-299

Iron and sulfur redox: Langmuir, D. 1997. Iron and Sulfur Geochemistry. Chapter 12 in: *Aqueous Environmental Geochemistry*, Prentice-Hall, 600pp.

Hackett, G. and Lehr, J.H., 1985. *Iron Bacteria Occurrence, Problems and Control Methods in Water Wells*. National Ground Water Association,

PROBLEMS

- 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 Gibbs free energy for each overall reaction. Which would provide more energy to bacteria, per mole of O_2 consumed.
- 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
68.71	0.34	95	5.7	<0.001	31.0	2.34	300	4.1	6.8

Calculate an Eh for this water from the sulphate/sulphide redox couple (don't forget to use activities). What is the calculated pe 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 its concentration, and what should be the equilibrium concentration of Fe^{2+} ?

- 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 ($\Delta G^\circ_{\text{NH}_4^+} = -79.31$ kJ/mol) to nitrate and determine the pe - pH relationship that defines the equilibrium for this redox pair at an ion activity ratio of 1 (i.e. for $a_{\text{NO}_3^-} / a_{\text{NH}_4^+} = 1$)