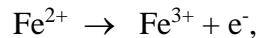


## *Oxidation-reduction reactions*

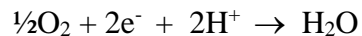
### **JB Maynard 2014**

Up to this point, we have been mainly concerned with phase transfers of organic compounds. That is the actual compounds are conserved, merely transferred from one reservoir to another. The destruction of organic compounds, that is their transformation into other substances, involves oxidation or reduction. For example, the BTEX compounds are degraded by oxidation, whereas the chlorinated solvents are degraded by reductive dechlorination.

Chemical oxidation is the process of removal of an electron from an element, whereas reduction is the addition of an electron. These reactions in reality always involve the *transfer* of an electron from one element to another, although for convenience we often portray only one-half of the process. Consider for example electron transfers involving iron, the most abundant element in the Earth's crust that readily exchanges electrons with other atoms. We can express its oxidation by the half-reaction



The most common balancing reduction reaction is consumption of oxygen:



The  $e^{-}$  in the oxidation reaction represents the removal of an electron to some electron acceptor, just as we used  $\text{H}^{+}$  to represent the removal of a proton in discussing acidity. We don't really have a pool of unattached electrons or protons in a solution, although we are used to treating aqueous solutions as though free  $\text{H}^{+}$  existed.

In natural waters, the chief driver of reduction is the oxidation of organic matter. A variety of substances can serve as the oxidant. In Figure 8-1 we show the most important ones, ranked by their characteristic potential relative to a standard hydrogen electrode. Unlike the dissociation of acids, electron transfers tend to be slow. Consequently bacterial mediation is common (and in many cases is necessary). In attacking organic matter, microbial communities will choose the reactants at the highest possible oxidation state, then, once that oxidant is exhausted, move down the chain of potentials until all of the organic matter is consumed or until the lower stability limit of water is reached.

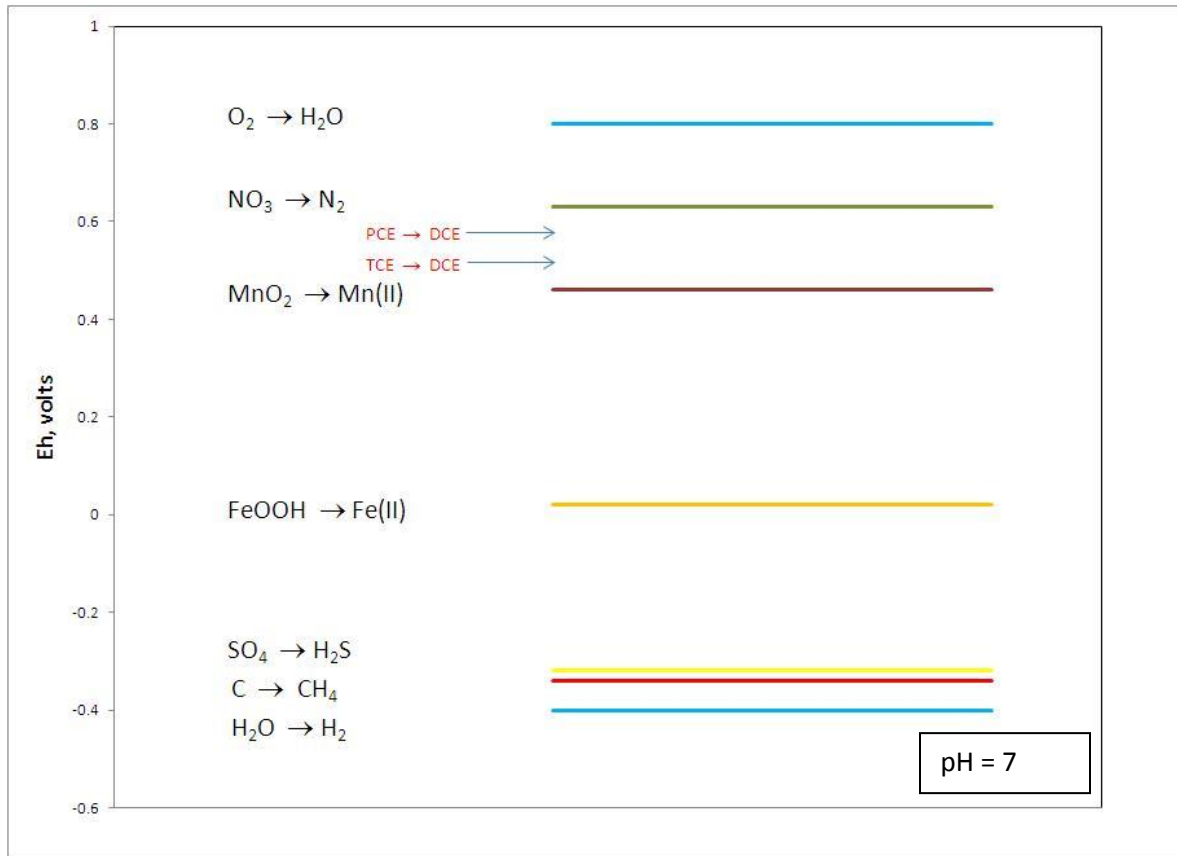


Fig. 8-1. The normal series of oxidation-reduction reactions encountered in sediments with depth below the sediment-water interface and also in aquifers along a flowpath from the recharge zone into the aquifer at circumneutral pH.

In aquifers, oxidation by free oxygen is the dominant process down to  $O_2$  levels of about 0.5 mg/L, where nitrate reduction takes over. Many aquifers, especially in the western US, have insufficient organic matter to get to this stage and remain oxic. Coastal plain aquifers of the East and Gulf Coast and glacial aquifers of the Midwest show a greater tendency to development of the anoxic facies. Apparently there was greater generation of organic debris during the deposition of these aquifers.

Distribution of redox facies by percentage of aquifers (McMahon and Chapelle, 2008, table 2)

Aquifer type	Example	$O_2$ Reduction	Suboxic Undiff	$NO_3$ Reduction	$Mn(IV)$ Reduction	$Fe(III)/SO_4$ Reduction	Methano- genesis	Mixe Proc
Sand and gravel	High plains	89.0	1.2	1.5	1.4	2.3	0.2	
Western volcanics	Columbia Plateau	88.7	0.9	1.9	1.9	1.9	0.0	
Carbonate/crystalline	NJ-NY-NE	69.9	12.0	1.3	1.8	7.7	0.0	
Carbonate	Ozarks	58.5	15.7	1.6	0.6	15.4	2.3	
Semiconsolidated SS	Coastal Plain	53.1	3.7	0.0	0.9	9.0	8.1	
Glacial deposits	Upper midwest	44.4	2.9	1.2	6.0	24.8	6.4	

### Potential-pH diagrams: Iron Oxide

The potentials shown in Fig. 8-1 are for a constant pH of 7. Let us next consider reactions at other pH values. Returning to our iron system:



we could extend the analogy to the proton by employing the activity of electrons in the solution as a variable:

$$K = (a_{\text{Fe}^{3+}} \times a_{e^{-}}) / a_{\text{Fe}^{2+}} \quad \text{or}$$

$$\text{Log } K = \text{log} a_{\text{Fe}^{3+}} - \text{log} a_{\text{Fe}^{2+}} + \text{log} a_{e^{-}}.$$

If we define a negative log of electron activity analogous to pH:

$$\text{Log } K = \text{log} a_{\text{Fe}^{3+}} - \text{log} a_{\text{Fe}^{2+}} - pe.$$

If we know  $K$ , then we can express the relative activities of ferric and ferrous iron as a function of the variable  $pe$ .

An alternative strategy is to use the Nernst equation,

$$E_h = E^{\circ} + (RT/nf) \ln(a_{\text{oxid}}/a_{\text{red}}),$$

where  $a_{\text{oxid}}$  and  $a_{\text{red}}$  are the activities of the oxidized and reduced species raised to the power of their stoichiometric coefficients,  $R$  is the gas constant,  $T$  is Kelvin temperature,  $f$  is the Faraday constant,  $n$  is the number of electrons transferred,  $E_h$  is the electrode potential relative to a standard hydrogen electrode, and  $E^{\circ}$  is the standard electrode potential.

At 25°C, this formula becomes

$$E_h = E^{\circ} + (.0592/n) \log(a_{\text{oxid}}/a_{\text{red}}).$$

If we know  $E^{\circ}$ , then we can express the relative activities of ferric and ferrous iron as a function of the variable  $E_h$ .

$K$  can be found from

$$\Delta G = -RT \ln K, \text{ which at } 25^{\circ}\text{C is } \Delta G = -5.707 \log K$$

$E^{\circ}$  can also be found from the  $\Delta G$  of the reaction via

$$\Delta G = n f E^{\circ}, \text{ which at } 25^{\circ}\text{C is } \Delta G = 96.487 n E^{\circ}.$$

From free energies we find

$$\Delta G = [-4.60 + 0] - [-78.87] = 74.27 \text{ kj.}$$

Note that  $\Delta G$  for  $e^-$  is 0, just as it is for  $H^+$ . Then we can calculate

$$\text{Log } K = -74.27/5.707 = -13.01$$

$$E^0 = 74.27/(96.487 \times 1) = .770 \text{ volts or } 770 \text{ mv}$$

Our two equations then become

$$-13.01 = \log a_{\text{Fe}^{3+}} - \log a_{\text{Fe}^{2+}} - pe \quad \text{or}$$

$$pe = 13.01 + \log(a_{\text{Fe}^{3+}}/a_{\text{Fe}^{2+}}) \quad \text{and}$$

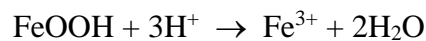
$$Eh = .770 + .0592 \log(a_{\text{Fe}^{3+}}/a_{\text{Fe}^{2+}}).$$

For the boundary of predominance between ferrous and ferric iron:

$$pe = 13.01 \quad \text{or} \quad Eh = .770 \text{ v.} \\ (8-1)$$

Note from these two expressions that  $pe = Eh/.0592$ .

The equations above account for the two soluble iron species at Earth surface conditions. What about solids? There are a great many iron minerals, a number of which are commonly encountered. One of the most important in terms of reactions in natural waters is goethite, FeOOH. We can express its dissolution to ferric iron quite simply by



$$\Delta G = [-4.60 + 2(-237.13)] - [-488.55] = +9.69 \text{ kj}$$

$$\text{Log } K = \log a_{\text{Fe}^{3+}} - 3 \log a_{\text{H}^+} = -1.70 \quad \text{or}$$

$$\text{pH} = -.566 - .333 \log a_{\text{Fe}^{3+}}.$$

In this reaction, the stability of the solid depends on both the pH and the activity of ferric iron in solution. A common concentration range of regulatory concern for metals in natural waters is between .05 and 1 ppm. For Fe and Mn the U. S. Public Health Service specifies 0.3 and 0.05 ppm. This level corresponds to an activity of about  $5 \times 10^{-6}$  for Fe and about  $0.9 \times 10^{-6}$  for Mn. Therefore, let us use  $10^{-6}$  as the cutoff point for metal solubility (see also Garrels and Christ 1965, p. 188). Using this reference value, we arrive at

$$\text{pH} = 1.43.$$

$$(8-2)$$

This answer tells us that there should be virtually no  $\text{Fe}^{3+}$  in solution in natural waters at ordinary pH values. Only under extremely acidic conditions are you likely to encounter this species.

What about  $\text{Fe}^{2+}$ ? Here we are dealing with an electron transfer. The reaction can be expressed as (again written as an oxidation):



$$\Delta G = [-488.55] - [-78.87 + 2(-237.13)] = +64.58 \text{ kJ}$$

$$\text{Log } K = 3\text{log}a_{\text{H}^+} + \text{log}a_{\text{e}^-} - \text{log}a_{\text{Fe}^{2+}} = -11.32.$$

Again using  $10^{-6}$  for the activity of the iron in solution, this expression reduces to

$$\text{pe} = 17.32 - 3\text{pH}.$$

$$(8-3)$$

We now have three equations relating the behavior of our chosen iron species, each couched in terms of the variables pH and pe. Thus we can represent the reactions on the familiar pH-pe diagrams shown below. The diagonal dotted lines show the upper and lower stability limits of water. From this diagram we see that iron will be soluble in natural waters only when it can be reduced to the ferrous form. By the same token, the appearance of significant dissolved Fe in an analysis indicates reducing conditions in the water.

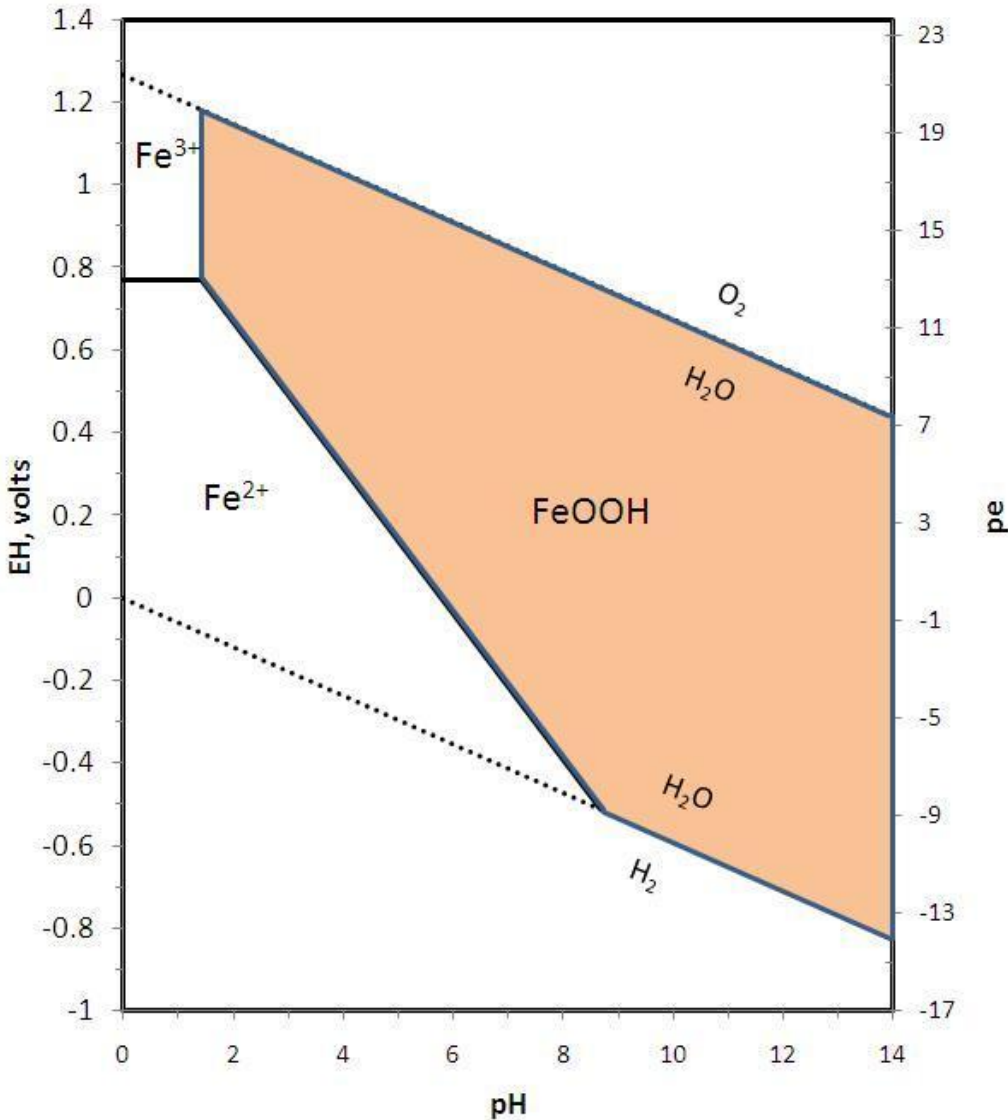


Figure 8-2. Potential-pH diagram for iron in natural waters at 25°C.

Iron reduction and oxidation in surface waters occurs rapidly at neutral and high pH, and thus is largely abiotic. However, at low pH (< ~5), oxidation is kinetically inhibited and there are communities of Fe oxidizing bacteria that catalyze the reaction to take advantage of the electron transfer. In groundwaters, both the oxidation and reduction reactions seem to proceed slowly and it is the norm to find bacterial consortia driving the reactions. Their biomass accumulation is a common source of biofouling of water production wells.

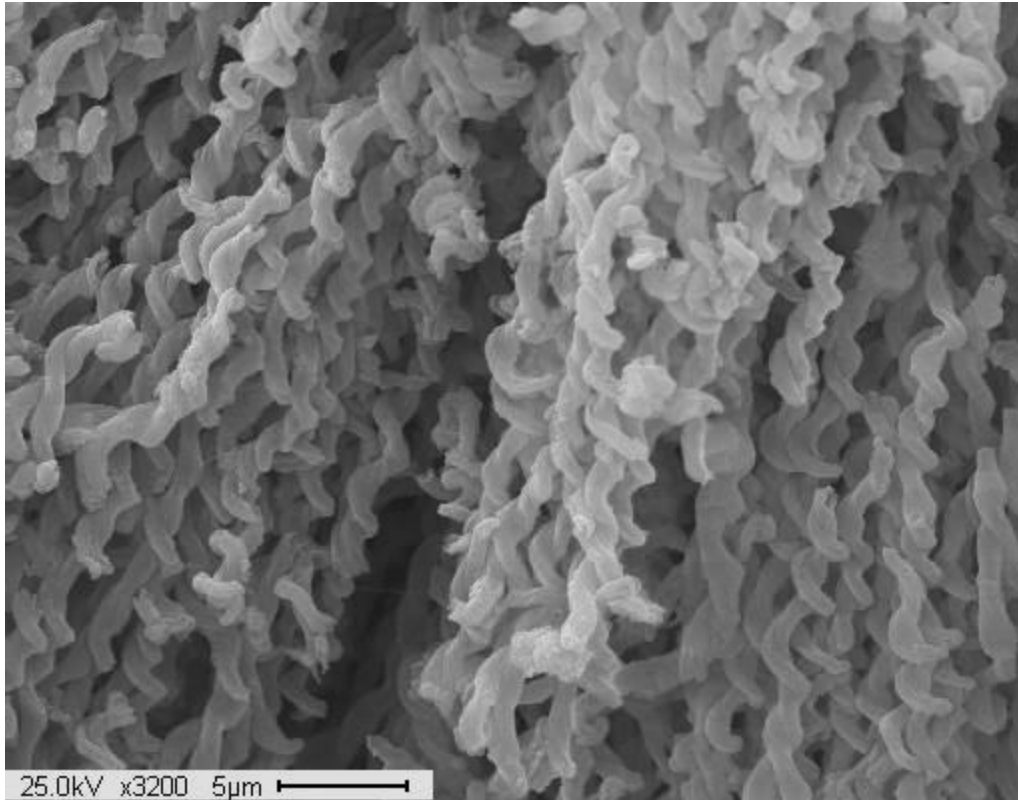
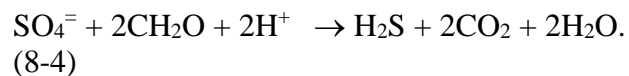


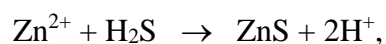
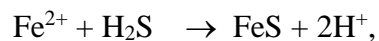
Figure 8-3. Filamentous iron-oxidizing bacteria occluding the well bore in a production well in a buried-valley production well. (University of Cincinnati)

### Potential-pH Diagrams: Sulfate-sulfide

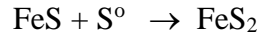
Iron is found in minerals in the ferrous as well as in the ferric state. The most reactive mineral containing  $\text{Fe}^{2+}$  is pyrite,  $\text{FeS}_2$ . In this mineral, iron occurs in the +2 state, but S is found in the -1 instead of the more common -2 state. Under oxygen-free conditions, bacteria can use the oxygen of  $\text{SO}_4^{2-}$  to oxidize organic matter (represented here in idealized form by  $\text{CH}_2\text{O}$ ):



The sulfide produced is strongly reactive towards heavy metals:

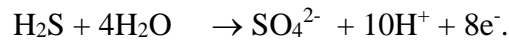


which form very insoluble sulfide compounds.  $\text{FeS}$  is unstable relative to pyrite and the further reaction, which is an oxidation of  $\text{S}^{2-}$  to  $\text{S}^-$ ,



occurs quickly in modern sediments close to the sediment water interface. As a result, ancient rocks contain almost entirely pyrite as the iron sulfide mineral. ZnS and PbS, by contrast, are quite stable and retain S in the -2 state.

Let us separate the sulfate part of reaction (8-4) and cast it as an oxidation. Then



The rather startling number of electrons involved in this reaction is typical of S. From free energy tables we find

$$\Delta G = [-744.63] - [-27.87 + 4(-237.13)] = +231.76 \text{ kJ}$$

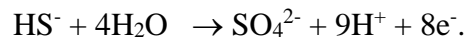
$$\text{Log } K = \log a_{\text{SO}_4^{2-}} + 10 \log a_{\text{H}^+} + 8 \log a_{\text{e}^-} - \log a_{\text{H}_2\text{S}} = -40.61.$$

If we consider the point of balance between sulfate and sulfide ( $a_{\text{SO}_4^{2-}} = a_{\text{H}_2\text{S}}$ ), then the relationship becomes

$$\text{pe} = 5.076 - 1.25\text{pH}.$$

(8-5)

In natural waters we also need to consider the dissociated form of hydrogen sulfide,  $\text{HS}^-$ . Its oxidation to sulfate is given by



$$\Delta G = [-744.63] - [12.10 + 4(-237.13)] = +191.79 \text{ kJ}$$

$$\text{Log } K = \log a_{\text{SO}_4^{2-}} + 9 \log a_{\text{H}^+} + 8 \log a_{\text{e}^-} - \log a_{\text{HS}^-} = -33.61$$

$$\text{pe} = 4.201 - 1.125\text{pH}.$$

(8-6)

Finally, the two dissolved S species are related by a reaction we have seen before:



$$\Delta G = [12.10] - [-27.87] = 39.97$$

$$\text{Log } K = \log a_{\text{HS}^-} + \log a_{\text{H}^+} - a_{\text{H}_2\text{S}} = -7.004.$$

For the point of equal predominance,  $a_{\text{H}_2\text{S}} = a_{\text{HS}^-}$ , so

$$\text{pH} = 7.00.$$



The next figure shows the distribution of the dissolved S species superimposed on the previous Fe diagram. I have omitted native sulfur, which needs to be included for S-rich systems. Note that over the pH range 6-8 the reduction of iron oxide to soluble  $\text{Fe}^{2+}$  and the reduction of sulfate to sulfide occur at about the same potential.

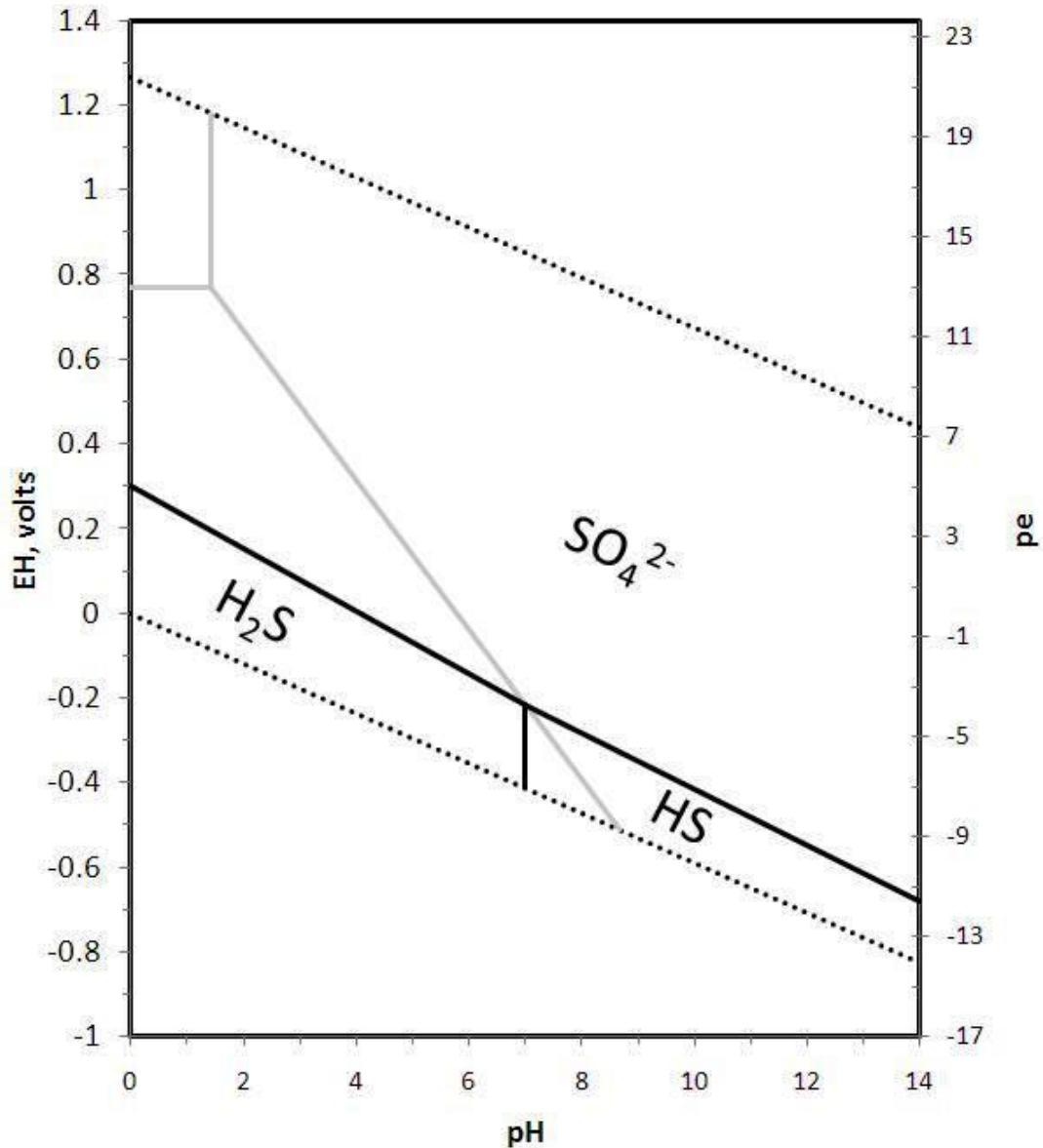


Figure 8-4. Eh-pH diagram for sulfur in natural waters at 25°C.

For the reduction of sulfate to sulfide, the reaction rate is extremely slow at temperatures less than about 100°C. Therefore all sulfate reduction in near-surface waters is bacterial. The reverse reaction can occur quite readily and so need not be bacterially mediated, but there are several important groups of micro-organisms that employ sulfide oxidation as a metabolic pathway.

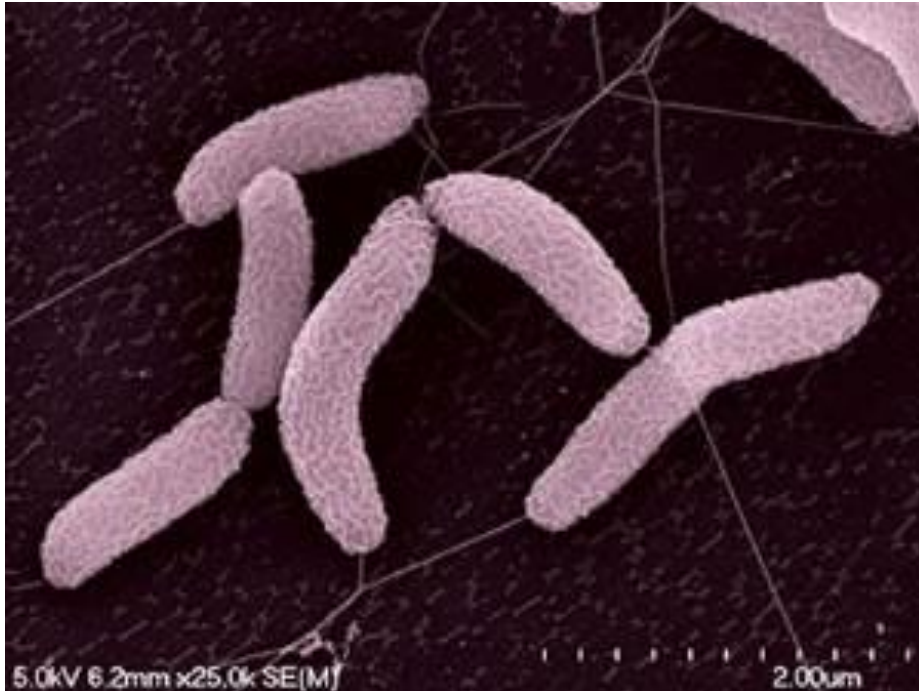
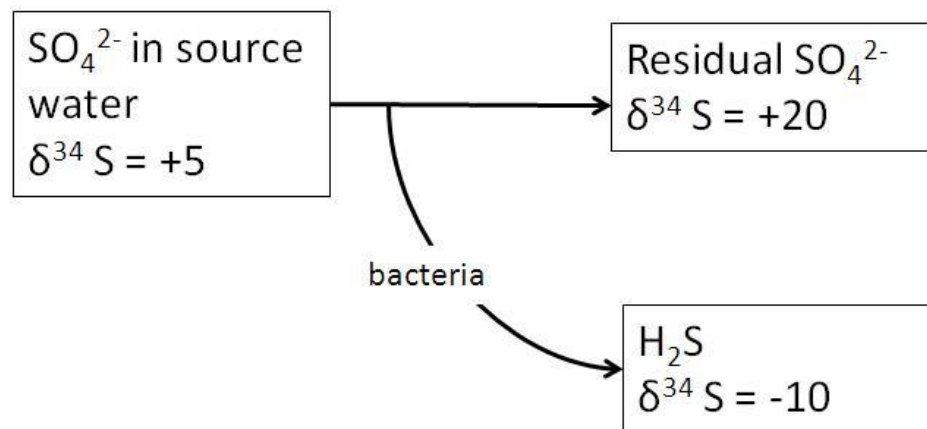


Figure 8-5. SEM photomicrograph of *Desulfovibrio*. (Lawrence Berkely)

Bacterial sulfate reduction reaction produces a strong fractionation in S isotopes because of the preference by the relevant enzymes for the lighter isotope:



The example shown is for  $\frac{1}{2}$  the sulfate converted to sulfide and a fractionation of 15 permil. For comparison, Lytle et al. ( ) reported values of  $\Delta$ sulfate-sulfide of 15 and 40 permil for iron deposits in two water distribution systems. As reduction proceeds, the residual sulfate becomes progressively enriched in  $^{34}\text{S}$ , a process often referred to as Rayleigh “distillation”. The presence of this residual heavy sulfate is one of the best indicators of significant sulfate reduction.

### Potential-pH Diagrams: Manganese

Mn is very similar to Fe in its chemical properties. For example both are commonly found in +2 and +3 valences with high spin states for the 3d electrons and with similar ionic radii.  $\text{Mn}^{2+}$  is 0.83 and  $\text{Fe}^{2+}$  is 0.78 Å, while the +3 ions are 0.70 and 0.65 Å. Accordingly, Mn is commonly found substituted in small amounts in Fe minerals. Mn, however, also has access to a higher valence state, +4, which gives rise to a plethora of complex Mn oxide minerals that do not have Fe counterparts. On the other hand, Mn sulfides are quite rare compared to their Fe cousins. The net result is a partitioning of Mn from Fe in geochemical systems towards areas of higher oxidation potential.

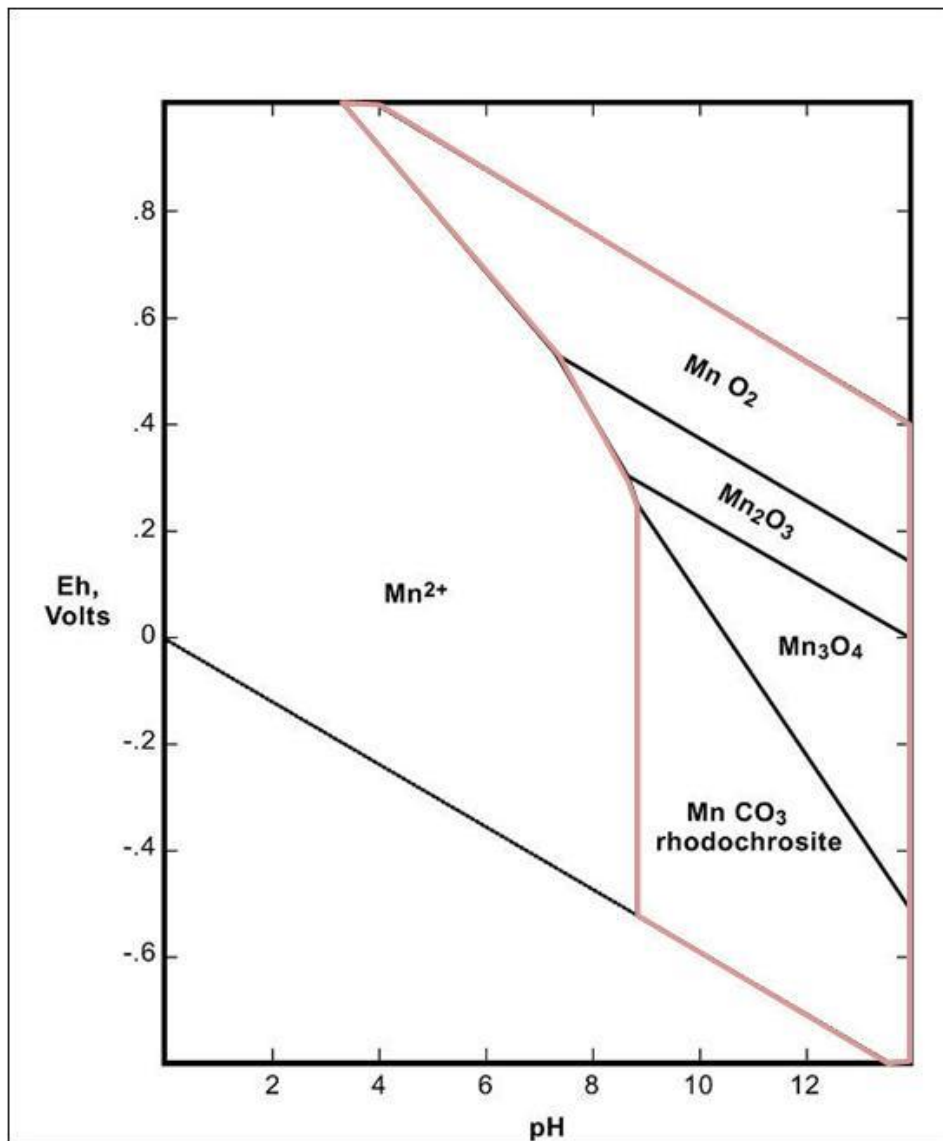


Figure 8-6. Eh-pH diagram for manganese.

Eh-pH relations for Mn show a much larger field of the soluble 2+ valence state than for Fe. This tends to make Mn more mobile. Also, Mn kinetics, both for oxidation and for reduction, are extremely slow under

abiotic conditions. Therefore almost all Mn reaction at the Earth's surface is microbially mediated. A common bacterium that can reduce both Mn and Fe, is *Geobacter*.

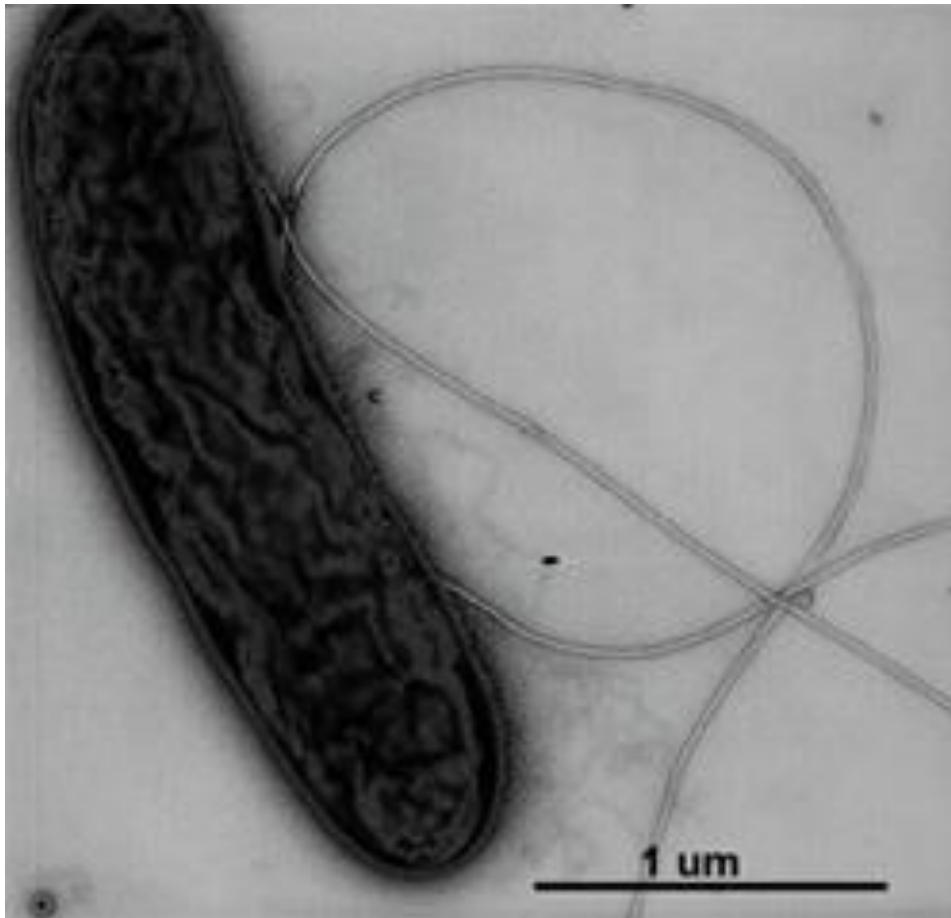


Figure 8-7. *Geobacter metalligensis*, an oxidizer of Mn and Fe

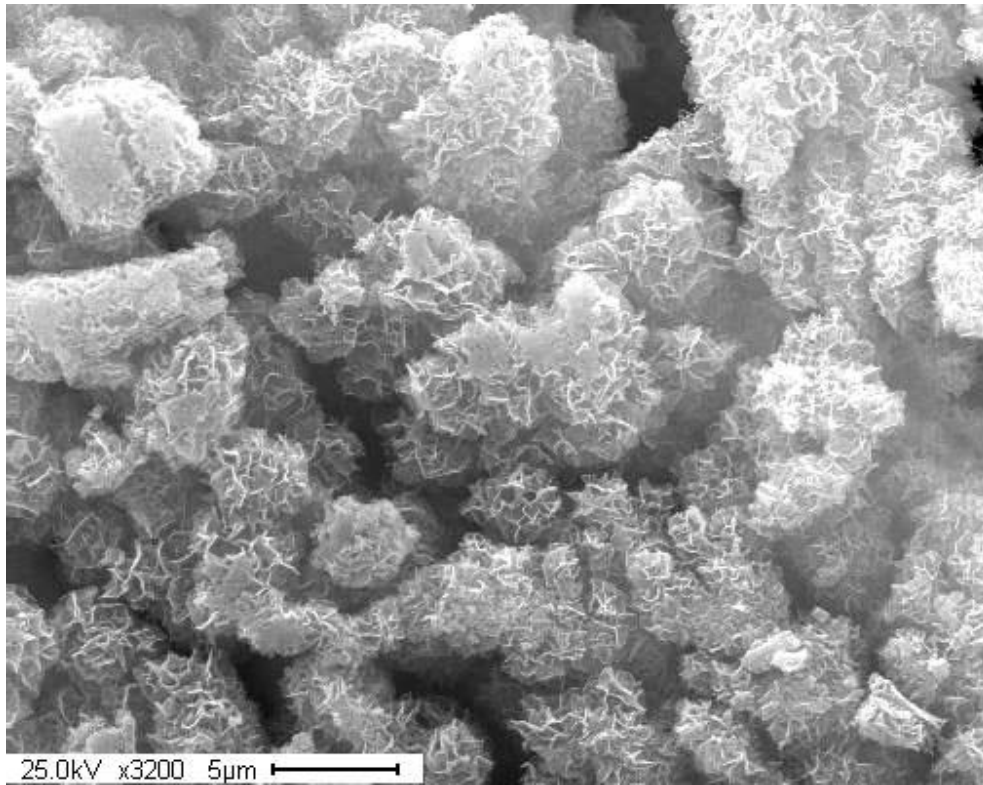


Figure 8-8. Unidentified manganese-oxidizing bacteria also occluding the well bore in a production well in a buried-valley production well (University of Cincinnati)

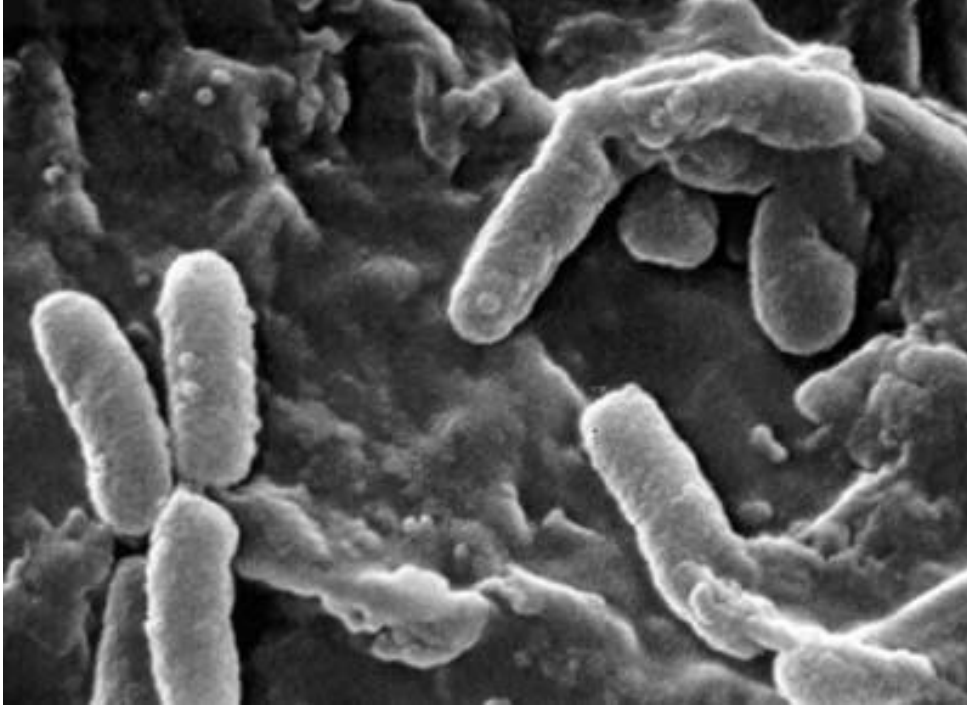
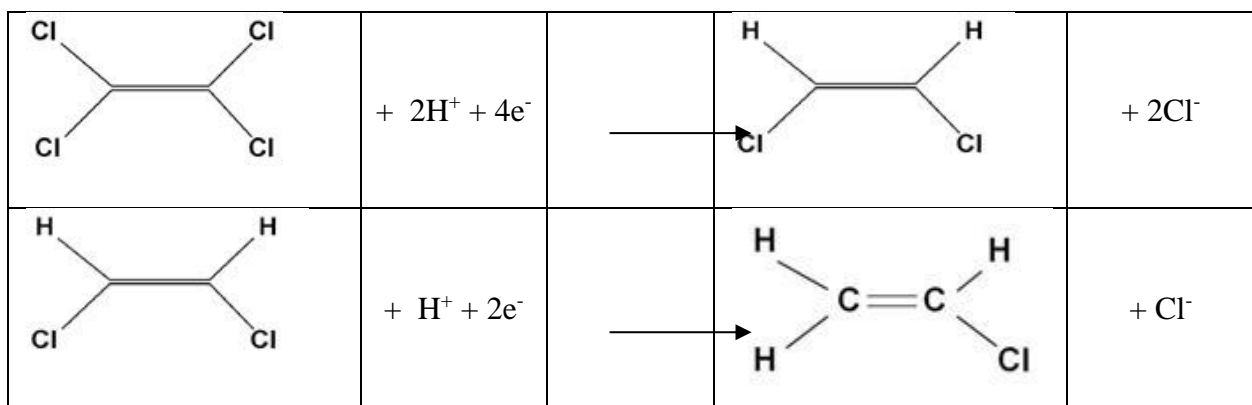
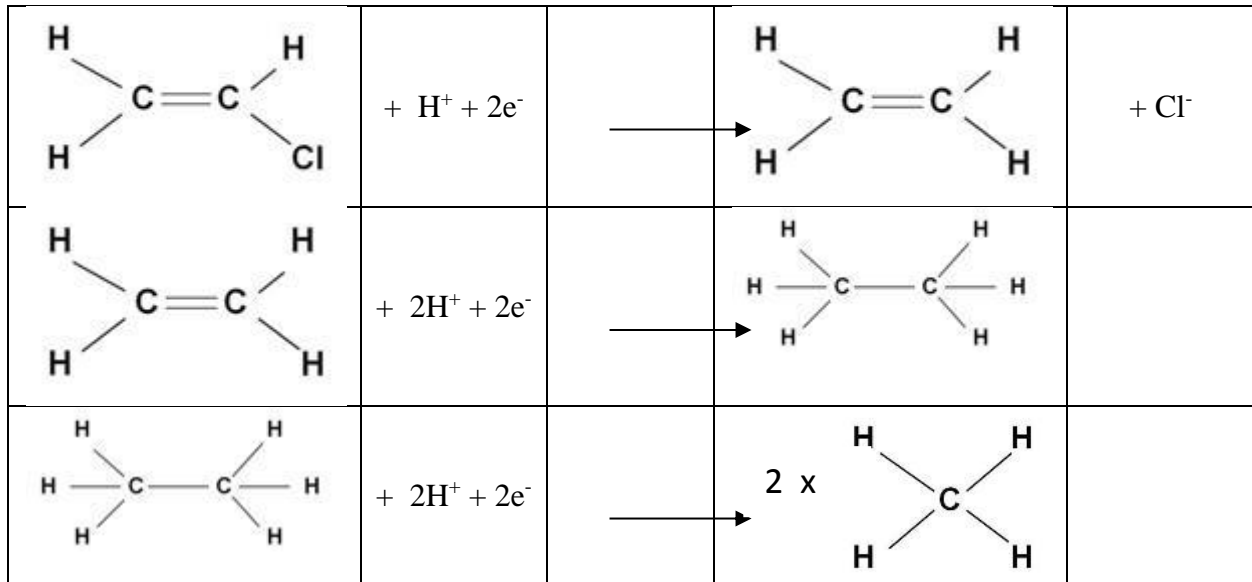


Figure 8-9. *Pseudomonas aeruginosa*, an anaerobic bacterium capable of reducing manganese.

### Reductive Dechlorination

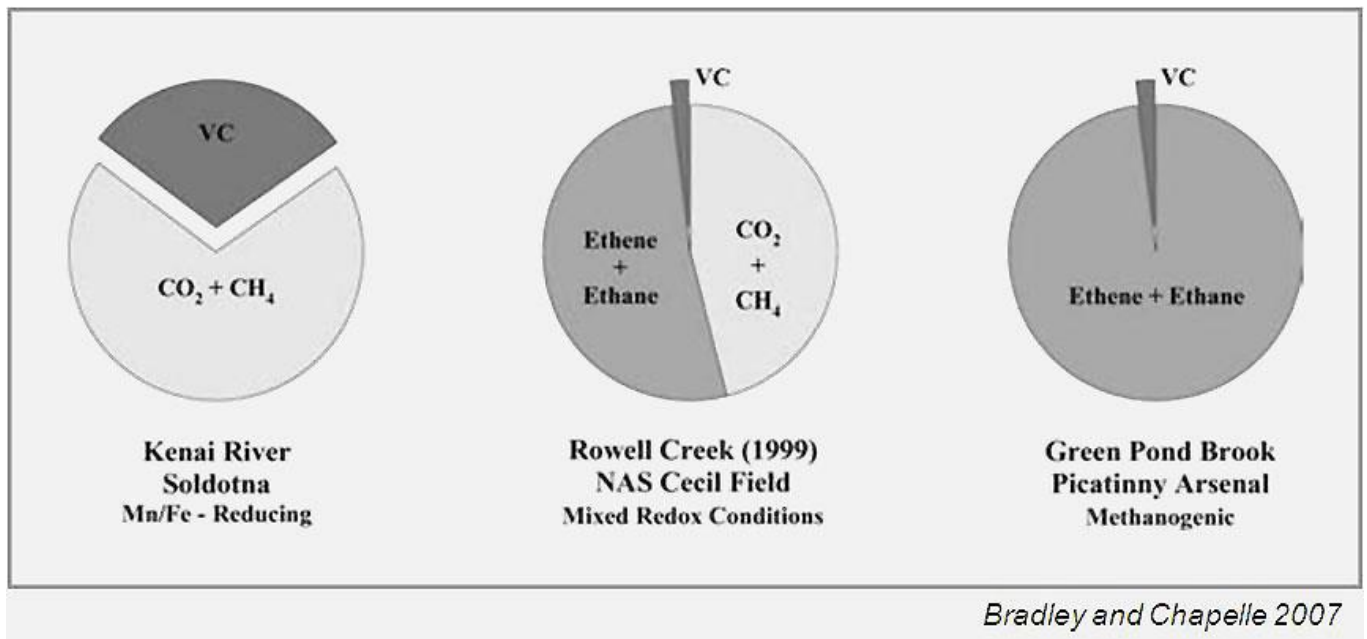
In Fig. 8-1 the potential for the first dechlorination step of TCE and PCE are shown. Many aquifers have oxidation states low enough to reach the threshold for these reactions to occur.





Any of the systems in Fig. 8-1 from Mn down are capable of supplying the needed electrons, but so many are needed the process normally does not go to completion.

The extent of the biodegradation of these compounds cannot be monitored by the disappearance of the parent because of dilution, dispersion, and sorption, but often the appearance of the daughters, especially CIS and VC are used on the assumption that their further degradation is minor. This proves not to be the case for many aquifers, however, as documented by Bradley and Chapelle (2007).



The surest indicator of biodegradation is the accumulation of  $\text{Cl}^-$  above local background, but so many localities have high natural background or the contaminant plume contains additional  $\text{Cl}^-$  from other sources, that this measure is often ineffective. The net result is that using daughter product accumulation to quantify biodegradation via reductive dechlorination will tend to underestimate the amount of intrinsic remediation going on. Hence a too-ambitious clean-up scheme could be implemented.