

UR-SISTEMAK

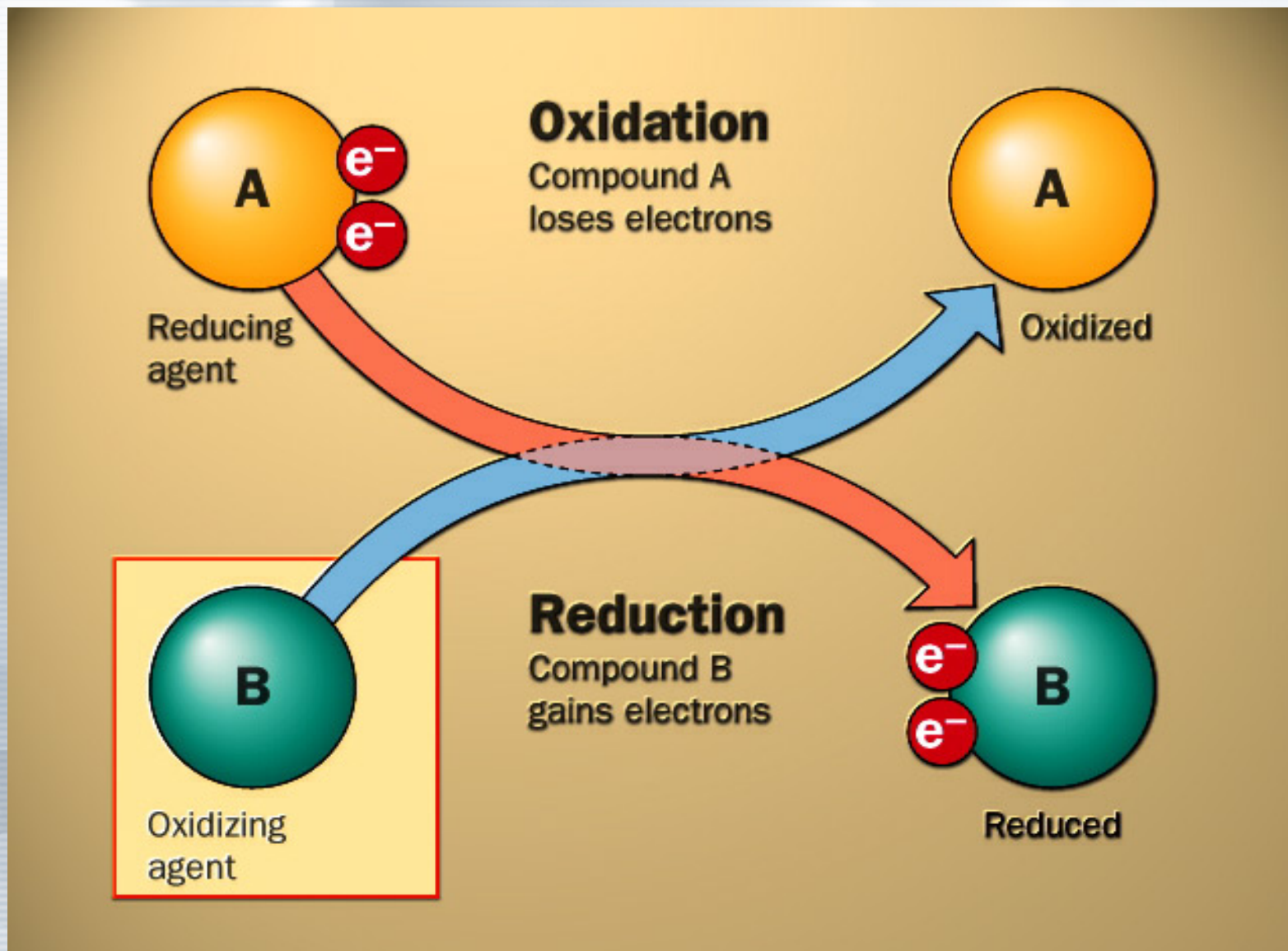
Eh-pH DIAGRAMAK



Ur Sistemetan sortzen diren mineralak ur horien Eh-pH-rekin mugatuta izaten dira. Mineral hauen baldintzak kalkulatzeko:

Eh-pH diagramak

Oxidation – Reduction Reactions



Oxidation – Reduction Reactions involve the gain and loss of electrons. The species involved in these reactions may be atoms, molecules, or ions.

Oxidation: the loss of electrons

Reduction: the gain of electrons

Reducing agent: an electron donor (it loses electrons and is oxidized.)

Oxidizing agent: an electron acceptor (it gains electrons and is reduced.)

Electromotive series: list of metals whose order indicates the relative tendency to be oxidized, or to give up electrons.

Oxidation – Reduction Reactions Listed in an electromotive series.	
Reaction	ΔG_R (kJ / mol)
$\text{Zn} + \text{Fe}^{2+} \leftrightarrow \text{Zn}^{2+} + \text{Fe}$	-68.4
$\text{Fe} + \text{Cu}^{2+} \leftrightarrow \text{Fe}^{2+} + \text{Cu}$	-144.4
$\text{Cu} + 2\text{Ag}^+ \leftrightarrow \text{Cu}^{2+} + 2\text{Ag}$	-88.7

Standard electrode potential (E°)

- ✧ is the potential of a given half-cell when all components are in their standard states
- ✧ By convention, the standard electrode potential refers to a half-reaction written as a reduction
- ✧ The voltage generated under ideal conditions at a concentration of 1M.
- ✧ is related to free energy of an oxidation reduction reaction by:

$$\Delta G_R = -nFE$$

- ✧ Where ΔG_R is the free energy for the reaction, E is the corresponding electromotive force, n is the number of electrons transferred in the reaction, and F is Faraday's constant (96.42 kJ / volt · gram equivalent).

Measurement of Standard electrode potentials (E°)

The potential of a half-cell is referenced with respect to the standard hydrogen electrode

✧ By convention:

Half-reaction

$E^\circ_{\text{half-cell}}$



0.00 V



0.00 V



A partial list of reduction potentials at 25°C.

Oxidized form	Reduced form	E^0 (volts)
$\text{Li}^+ + \text{e}^-$	Li	-3.05
$\text{K}^+ + \text{e}^-$	K	-2.93
$\text{Mg}^{2+} + 2 \text{e}^-$	Mg	-2.38
$\text{Zn}^{2+} + 2 \text{e}^-$	Zn	-0.76
$\text{Fe}^{2+} + 2 \text{e}^-$	Fe	-0.44
$2 \text{H}^+ + 2 \text{e}^-$	H_2	0.00
$\text{SO}_4^{2-} + 4 \text{H}^+ + 2 \text{e}^-$	$\text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	0.20
$\text{Cu}^{2+} + 2 \text{e}^-$	Cu	0.34
$\text{I}_2 + 2 \text{e}^-$	2I^-	0.54
$\text{Fe}^{3+} + \text{e}^-$	Fe^{2+}	0.77
$\text{Hg}_2^{2+} + 2 \text{e}^-$	2Hg	0.79
$\text{Ag}^+ + \text{e}^-$	Ag	0.80
$\text{NO}_3^- + 4 \text{H}^+ + 3 \text{e}^-$	$\text{NO} + 2 \text{H}_2\text{O}$	0.96
$\text{Br}_2 + 2 \text{e}^-$	2Br^-	1.09
$\text{O}_2 + 4 \text{H}^+ + 4 \text{e}^-$	$2 \text{H}_2\text{O}$	1.23
$\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{e}^-$	$2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$	1.33
$\text{Cl}_2 + 2 \text{e}^-$	2Cl^-	1.36
$\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^-$	$\text{Mn}^{2+} + 4 \text{H}_2\text{O}$	1.49

Measurement of Standard electrode potentials (E°)

✧ It is impossible to measure only the electromotive force of a half reaction, therefore a reference standard was created by which to compare half reactions.

✧ The potential of a half-cell is referenced with respect to the standard hydrogen electrode

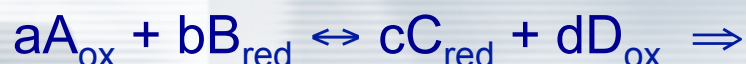
✧ By convention:

Half-reaction	$E^\circ_{\text{half-cell}}$
$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	0.00 V
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00 V

The Nernst Equation and Eh

✧ At nonstandard conditions, the cell potential may be calculated using the Nernst equation.

Consider the following generic redox reaction:



$$\Delta G_R = \Delta G_R^\circ + RT \cdot \ln([C_{\text{red}}]^c [D_{\text{ox}}]^d / [A_{\text{ox}}]^a [B_{\text{red}}]^b) \Rightarrow$$

$E = E^\circ - (RT / n F)(\ln K) =$ The Nernst Equation which can be used to calculate the emf of an oxidation – reduction reaction under any conditions.

Using log instead of ln, the Nernst equation reads:

$$E = E^\circ - (0.0592 / n)(\log K) =$$

$$E^\circ + \frac{0.0592}{n} \cdot \log \left(\frac{\text{activity product of oxidized species}}{\text{activity product of reduced species}} \right)$$

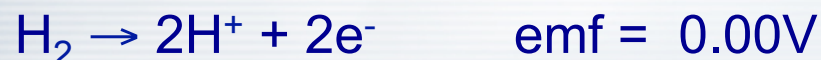


How are Eh and pH related?

Consider the following electrode:



And the standard:



Put them together in the equation:



$$\mathbf{Eh = E^\circ - 0.0592pH.}$$

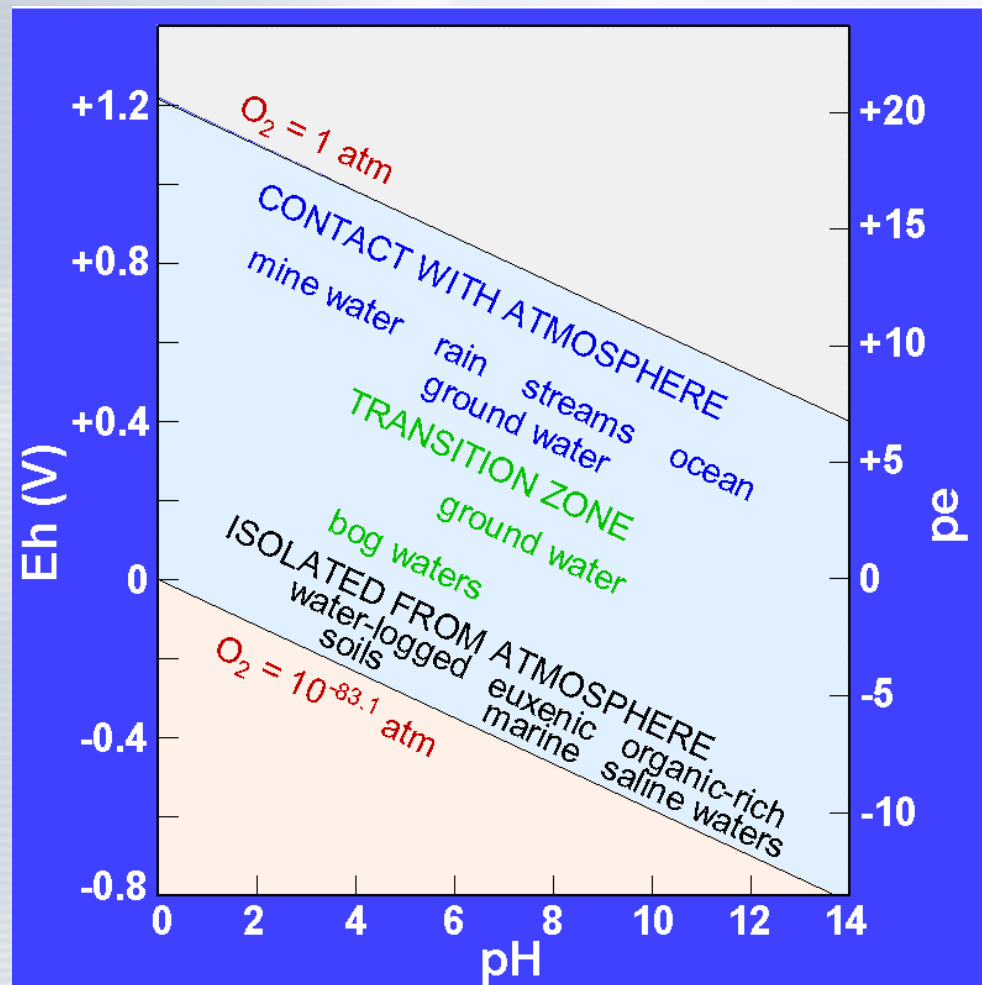
We can describe systems graphically in terms of Eh and pH.

The Eh – pH diagram

Stability limits for natural waters at the earth's surface in terms of Eh and pH at 25°C.

Think of the water electrode:

Think upper limit of H₂O where $p_{O_2} = 1$; and the lower limit as $p_{H_2} = 1$.

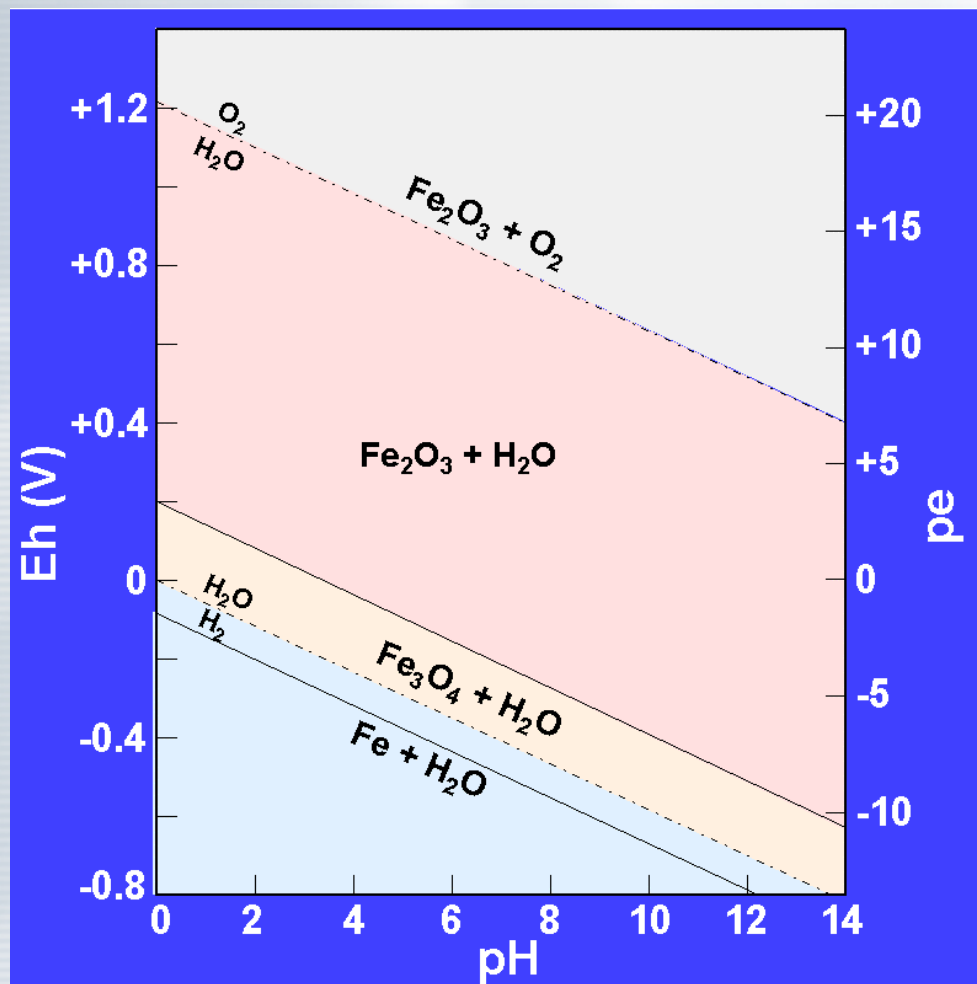


Iron Eh – pH diagram

Iron can exist in the natural environment in three oxidation states: 0, 2+ & 3+

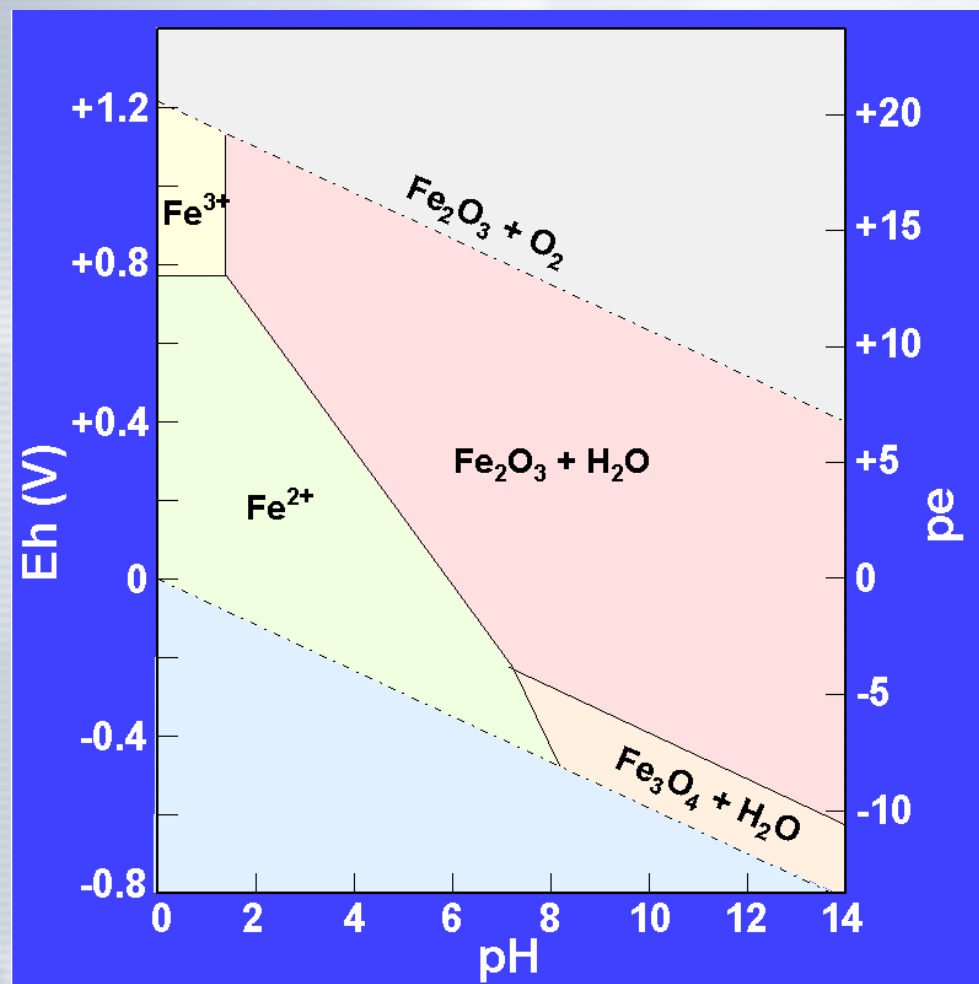
Fe_3O_4 is the mineral **Magnetite** and Fe_2O_3 is the mineral **Hematite**.

Note that native iron does not coexist with water in the natural environment.



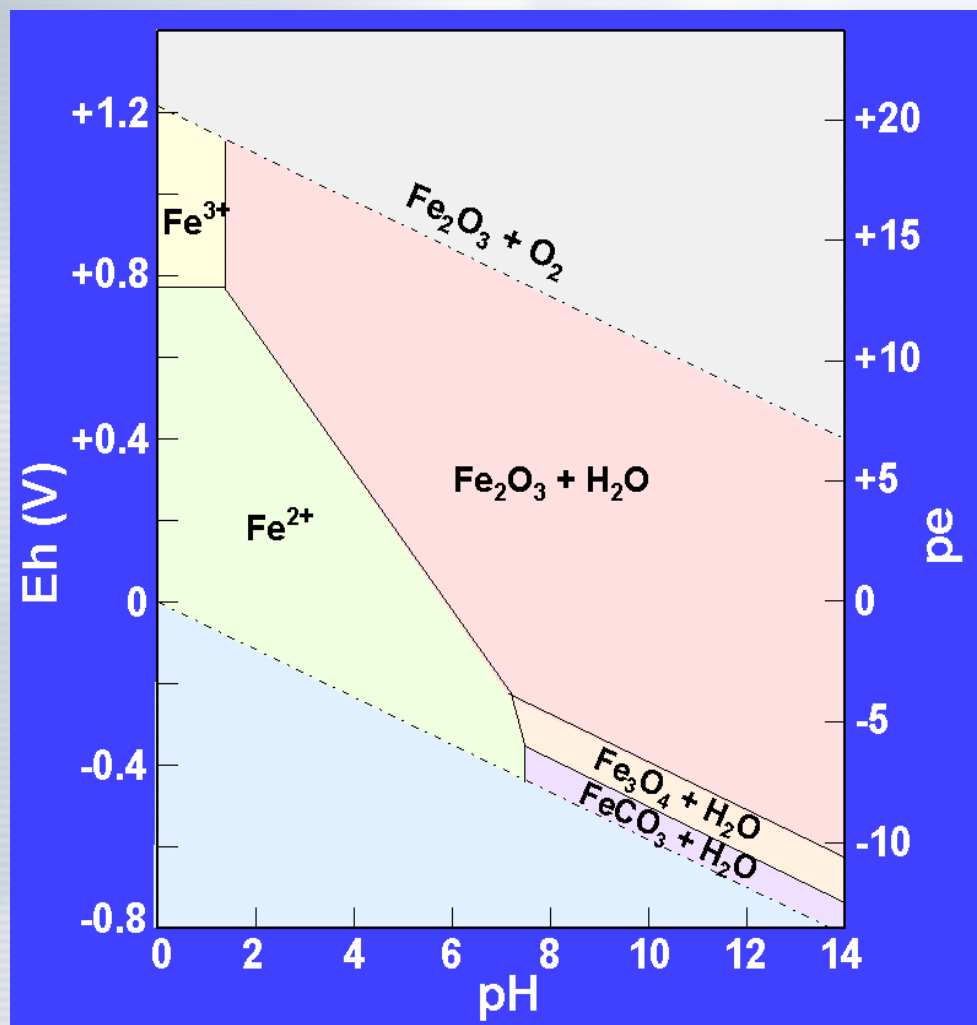
Iron Eh – pH diagram

Composite diagram showing the stability fields for **hematite** and **magnetite** as a function of Eh and pH.



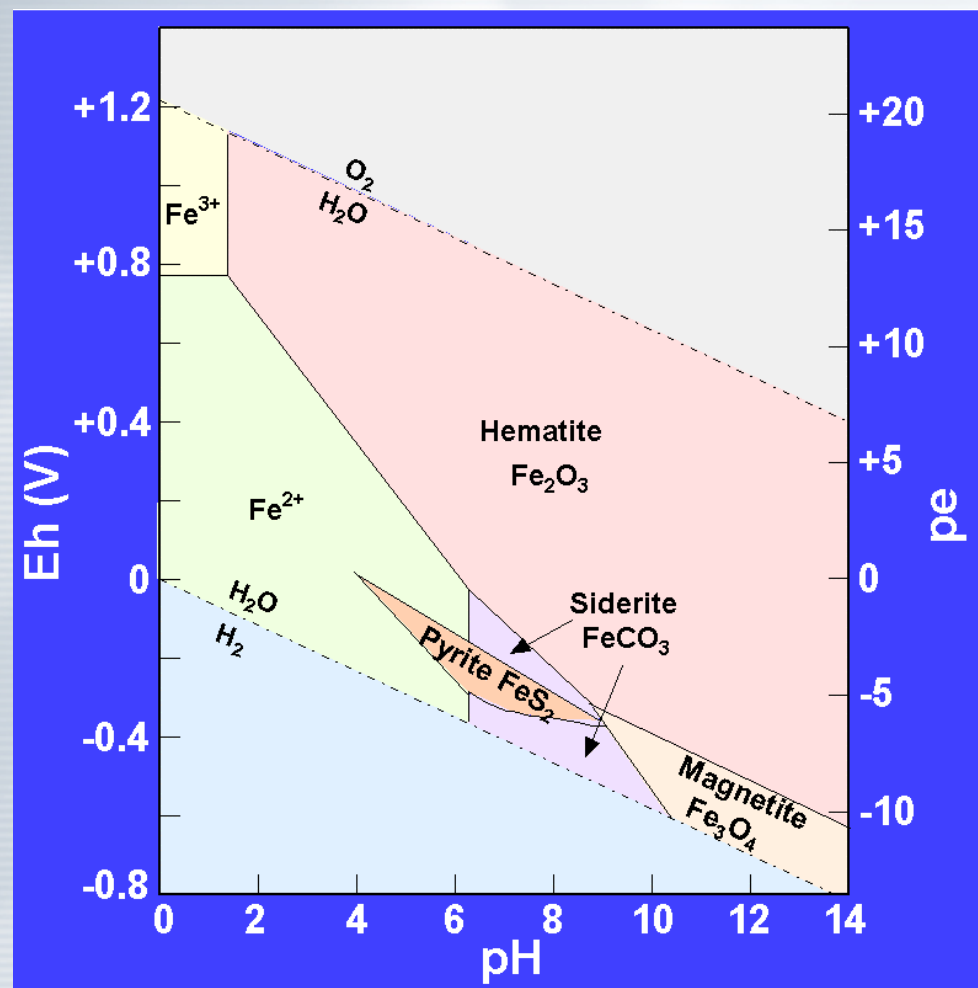
Iron Eh – pH diagram

Composite Eh-pH diagram showing the stability fields of **hematite**, **magnetite**, and **siderite** as a function of Eh and pH.



Iron Eh – pH diagram

Composite Eh-pH diagram showing the stability relations for the **iron oxides**, **carbonates**, and **sulfides** in water at 25°C.



Copper Eh – pH diagram

The stability of supergene hydrothermal minerals is typically shown on a plot of Eh (a measure of the availability of oxygen) versus pH (concentration of hydrogen ions, or acidity). The concept of this phase diagram is the same as that of a plot of pressure versus temperature.

Minerals shown are:
 Chalcocite
 Native copper
 Covellite
 Cuprite
 Malachite

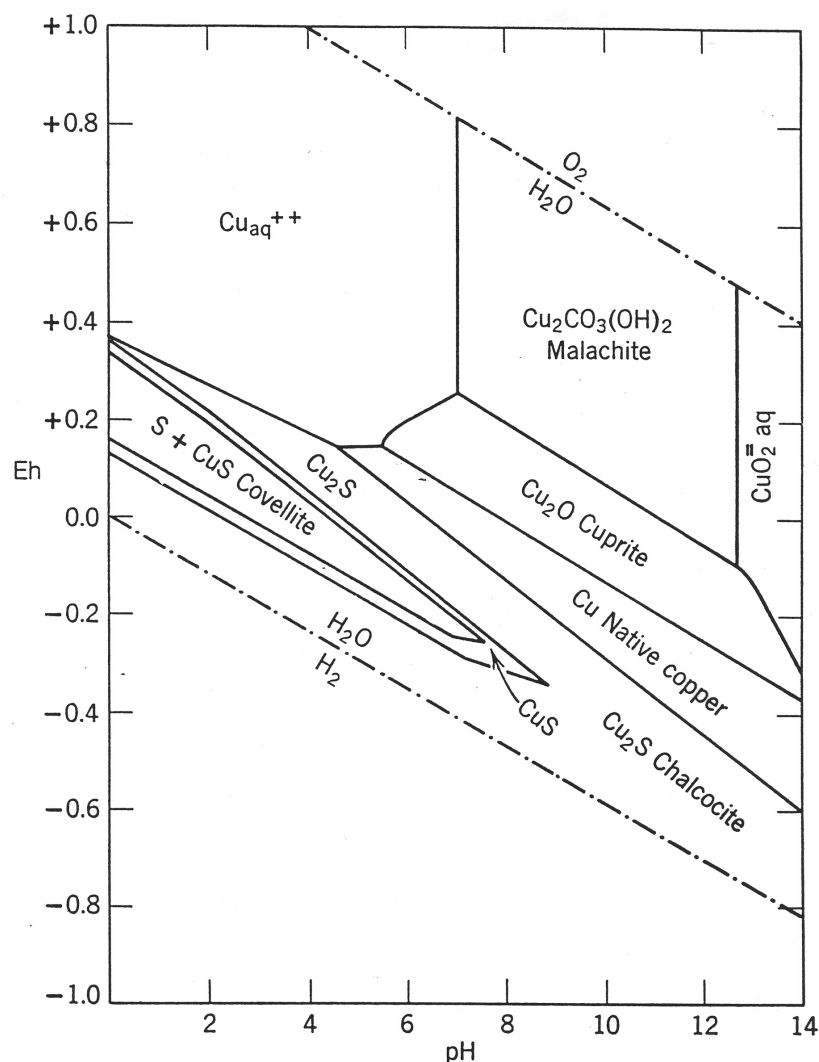


FIG. 14.22. Stability relations of some copper minerals commonly found in supergene enrichment deposits in the system Cu-H₂O-O₂-S-CO₂ at 25°C and 1 atmosphere total pressure.

Copper & iron Eh – pH diagram

