E_h-P^H CONTROL ON SEDIMENTATION

The stability of an element in a particular oxidation state depends upon the energy change involved in adding or removing electrons.

A quantitative measure of this energy change is provided by a factor known as the **Oxidation –Reduction Potential, Oxidation Potential** or **Redox Potential.**

The Oxidation – Reduction Potential of any reaction is a relative figure. The reference standard is the reaction :

$H_2 = 2H^+ + 2e$ (e=electron)

The oxidation potential of this reaction for unit activity of the reacting substances is arbitrarily fixed as 0.00 volt and the scale of oxidation potential extends on either side of zero.

Oxidation potentials are symbolisedbyE^O when the relevant reactions take place under the standard conditions of unit activity of the reacting substances and by E_h when the experimental situations deviates from these conditions.

The oxidation potential varies with varying concentration of the reacting substances .This variation with concentration is of special importance in reactions involving hydrogen or hydroxyl ions.

A variation in P^Hproduces large changes in oxidation potentials involving hydrogen or hydroxyl ions.

EFFECT ON SEDIMENTATION

1. DECOMPOSITION OF WATER AND EVOLUTION OF HUDROGEN

The range of oxidation potential of natural environments determines the reaction that may take place .Chemical reaction in aqueous media are theoretically limitedto those with oxidation potentials between the following two reactions :

$H_2O = ½ O_2 + 2H^+ + 2e,$ $E^O = 1.23$ volt (1)

$2H^+ + 2e = H_2$ $E^O = 0.00$ volt (2)

The oxidised form of any couple with a higher potential than that for (1) will theoretically decompose water with evolution of oxygen.

The reduced form of any couple with a lower potential than that for (2) will theoretically decompose water with evolution of hydrogen.

However, the chemistry of sedimentation indicates that the potentials of these two reactions do largely control **Oxidation** and **Reduction** under natural conditions.

2. E_h CONTROL PRECIPITATION OF ELEMENTS HAVING MULTIPLE VALENCY

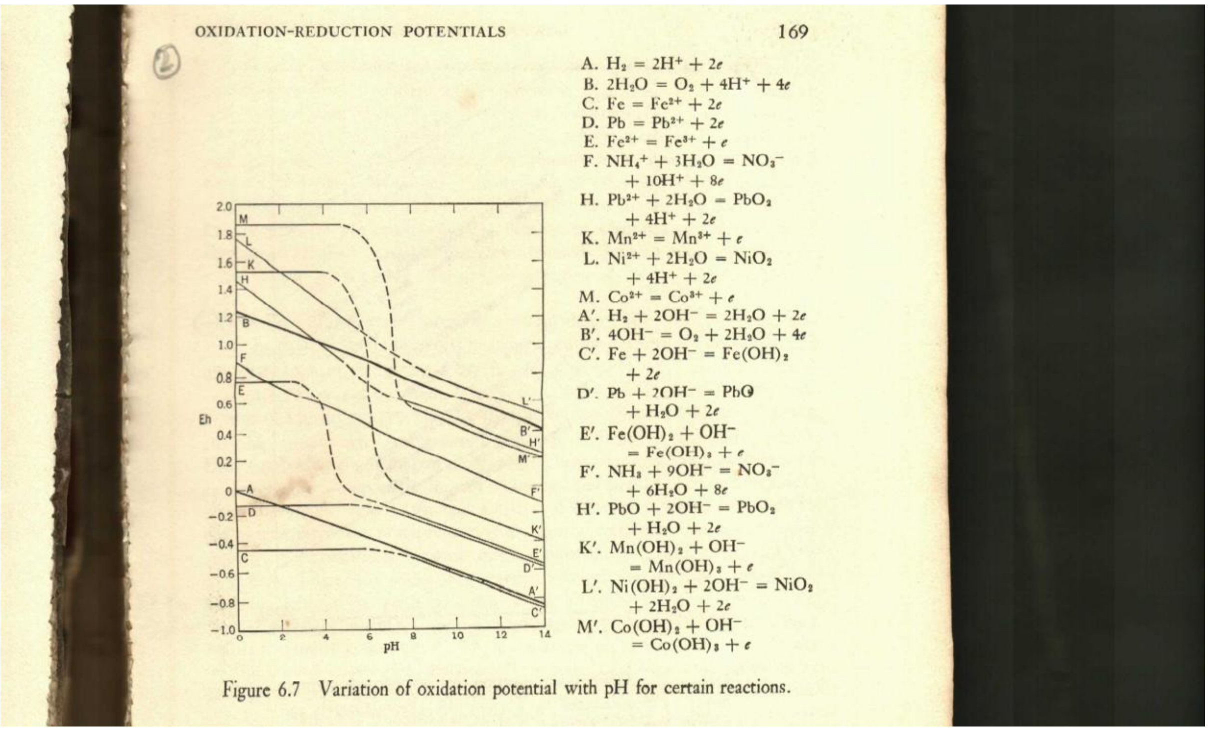
The solution, transportation and deposition of elements that may occur in two or more oxidation states are directly and powerfully influenced by the oxidation potential of the environment.

For example,the high potentials required to convert Bivalent Cobalt to Trivalent Co and Bivalent Pb to PbO_2 in acid solution indicate that the minerals Stanierite (CoOOH) and Plattenerite (PbO_2) are deposited from alkaline solutions for which the oxidation potentials are much less.

For many reactions Oxidation Potentials decrease rapidly with the increase of P^H. Therefore, **Oxidation proceeds more readily the more alkaline the solution.**

For example, CaCO3 precipitates in alkaline medium.

Fig 1: Variation of Oxidation Potential with P^H for certain reactions.



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②

A. $H_2 = 2H^+ + 2e$
B. $2H_2O = O_2 + 4H^+ + 4e$
C. $Fe = Fe^{2+} + 2e$
D. $Pb = Pb^{2+} + 2e$
E. $Fe^{2+} = Fe^{3+} + e$
F. $NH_4^+ + 3H_2O = NO_3^- + 10H^+ + 8e$
H. $Pb^{2+} + 2H_2O = PbO_2 + 4H^+ + 2e$
K. $Mn^{2+} = Mn^{3+} + e$
L. $Ni^{2+} + 2H_2O = NiO_2 + 4H^+ + 2e$
M. $Co^{2+} = Co^{3+} + e$
A′. $H_2 + 2OH^- = 2H_2O + 2e$
B′. $4OH^- = O_2 + 2H_2O + 4e$
C′. $Fe + 2OH^- = Fe(OH)_2 + 2e$
D′. $Pb + 2OH^- = PbO + H_2O + 2e$
E′. $Fe(OH)_2 + OH^- = Fe(OH)_3 + e$
F′. $NH_3 + 9OH^- = NO_3^- + 6H_2O + 8e$
H′. $PbO + 2OH^- = PbO_2 + H_2O + 2e$
K′. $Mn(OH)_2 + OH^- = Mn(OH)_3 + e$
L′. $Ni(OH)_2 + 2OH^- = NiO_2 + 2H_2O + 2e$
M′. $Co(OH)_2 + OH^- = Co(OH)_3 + e$

Figure 6.7 Variation of oxidation potential with pH for certain reactions.

3. DIFFERENT GEOCHEMICAL FENCES

The E_h – P^H diagrams provide a useful device for illustrating the stability fields of different minerals in an aqueous environment. The figure below shows the approximate position of some natural environments.

In this diagram Krumbein and garrel develop the concept of the “Geological Fence”, a boundary defined by the presence of a particular material on one side and its absence on the other, by the effect of certain chemical reaction.

A particular “Geochemical Fence” may represent a specific P^H value or a specific Oxidation Potential or a combination of both factors.

Many “Geochemical Fences “ can be defined.The most generally useful ones in considering sedimentary processes are the –

a) “Neutral Fence” at $P^H = 7$

b) “Limestone Fence” at $P^H = 7.8$

(at higher P^H Calcite is readily deposited, at lower P^H it tends to dissolve)

c) “Sulphate –Sulphide Fence” – determined by the sulphate sulphide oxidation potential

d) “Fe, Mn Oxide – Carbonate Fence” – determined by the oxidation potential at which ferrous and manganous compounds (mainly carbonates in the sedimentary environment) oxidised to the higher oxides.

e) “Organic Matter Fence” – below which organic matter is stable it and above which it oxidises to CO_2.

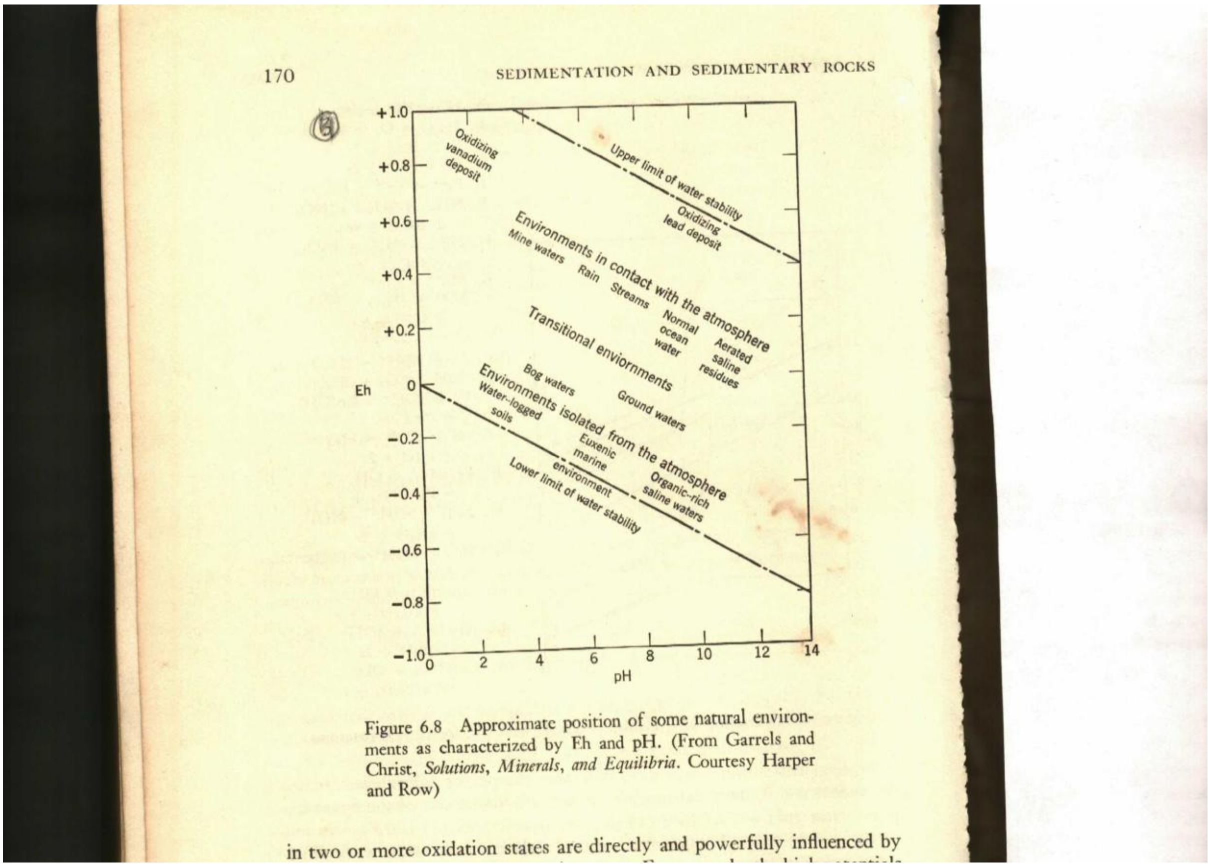

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Figure 6.8 Approximate position of some natural environments as characterized by Eh and pH. (From Garrels and Christ, *Solutions, Minerals, and Equilibria*. Courtesy Harper and Row)

in two or more oxidation states are directly and powerfully influenced by

4. SEPARATION OF Mn OF DIFFERENT VALENCY STATES BY E_h AND P^H

The system Mn – H_2O under varying conditionsof E_h and P^H provides an illustrative

Mn has not been found as naive metal as it only stable below E_h value of -1 for both acid and alkaline medium.

Under reducing conditions in the geological environment Mn occur as manganous compounds in acid solutions and precipitates as $Mn(OH)_2$ when the P^H exceeds 8.

In more oxidising conditions , the field of Mn ions shrinks towards more acid conditions.

On the alkaline side of the diagram $Mn(OH)_2$ (Pyrochroite) is successfully replaced by Mn_3O_4(Hausmanite),MnOOH (Manganite) and MnO_2 (Pyrolusite).

Under highly Oxidising Conditions MnO_2 (Pyrolusite) is the only stable phase over the whole range of P^H .

Permanganates do not occur under geological conditions – because aqueous solution of Permanganates are unstable and slowly decompose liberating Oxygen and precipitating MnO_2(Pyrolusite).

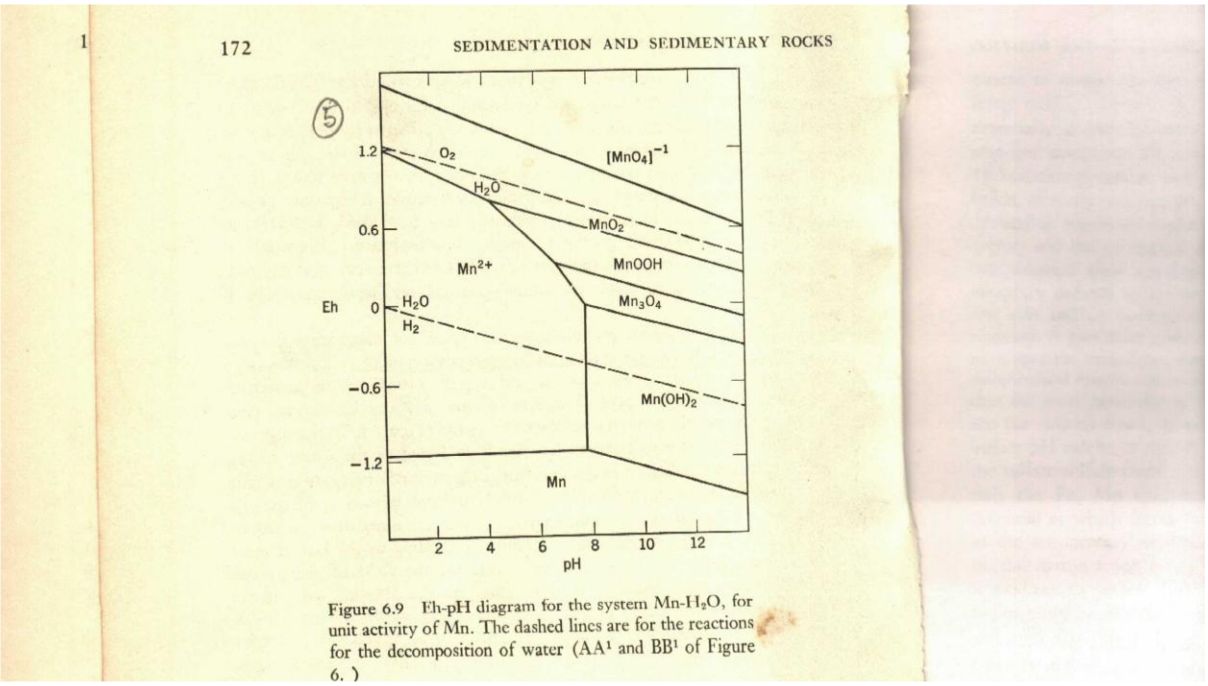

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Figure 6.9 Eh-pH diagram for the system Mn-H_2O, for unit activity of Mn. The dashed lines are for the reactions for the decomposition of water (AA^1 and BB^1 of Figure 6.)

5. **Fe PRECIPITATION**

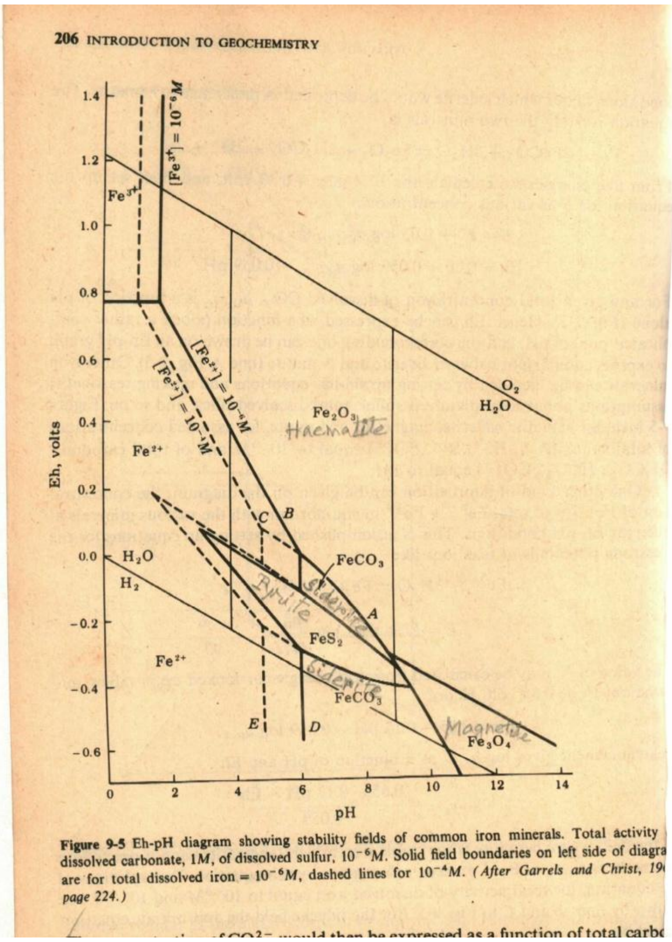
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Figure 9-5 Eh-pH diagram showing stability fields of common iron minerals. Total activity dissolved carbonate, $1M$, of dissolved sulfur, $10^{-6}M$. Solid field boundaries on left side of diagra are for total dissolved iron = $10^{-6}M$, dashed lines for $10^{-4}M$. *(After Garrels and Christ, 19 page 224.)*

would then be expressed as a function of total carb

Heamatite is the most common mineral in all moderately and strongly oxidising environment.

In reducing environment the stable minerals may be Pyrite(FeS_2), Siderite ($FeCO_3$), or Magnetite(Fe_3O_4), depending on the concentrations of Sulfur and Carbonate in the solution.

Siderite has two fields of stability separated by the field of Pyrite and Magnetite is stable only in contact with Strongly Basic Solution.

If dissolved Carbonate is smaller and dissolved Sulfur is higher, the field of Pyrite expands until it fills nearly the lower part of the diagram.

A small field of Pyrrhotite(FeS) is stable and may appear at the extreme lower edge of the natural E_h range.

If both Carbonate and sulphur are very low, the field of Magnetite extends into near-neutral environments.

Haematite may form from Siderite with increase in either P^H or $E_{h.}$

Within narrow range of E_h and P^H most pairs of Fe minerals are stable together – Magnetite – Haematite, Haematite – Siderite, Magnetite –Siderite, Siderite – Pyrite.

The occurrence of Siderite is practically restricted to neutral and basic solutions. It can precipitate from weakly acid solutions if the concentration of dissolved Fe is abnormally high.

6. SEPARATION OF Fe, Ni AND Co

The separation of closely related elements in the upper zone of the lithosphere by processes involving solution and redeposition is often brought about by their distinctive properties with respect to oxidation and reduction.

Thus the three elements Fe, Ni and Co often occur together in primary deposits, yet Supergene Processes result in their separation.

These three elements differ greatly in the potentials required to oxidise them beyond the bivalent state:

a) Fe is readily oxidised to the Trivalent state in alkaline and mildly acid environment.

b) Co requires a high potential even in alkaline solution and in acid solutions, and in acid solutions the potential required lies high above that for the release of Oxygen from water.

c) Ni does not form a Trivalent compound but a Dioxide is known, the formation of which even in alkaline solutions requires potentials somewhat higher than that for the release of O_2 from water.

These are reflected in Natural Occurrences:

1. The common form of Fe in Supergene Deposits is Hydrated Ferric Oxide ,i.e. Goethite($Fe_2O_3.H_2O$), Lepidocrocite($Fe_2O_3.H_2O$), Limonite($2Fe_2O_3.3H_2O$)
2. Hydrated Cobalt Oxide (Stainierite)is found only where conditions are Strongly Oxidising.
3. Higher Oxides of Nickel is not known as a mineral.

Thus separation of these three elements by supergene processes is well illustrated where intense weathering of Ultrabasic rocks give rise to Lateritic material rich in Fe_2O_3 , concentration of Ni as Garnierite $H_2(Ni,Mg)SiO_4.nH_2O$, and of the Co as Hydrated Co-Oxide or as Cobaltian Wad. .

7. SEPARATION OF Mn FROM Fe

Oxidation processesalso separateMn from Fe. Mn is often present in Solid Solution in primary minerals containing Fe,and the Ferrous and the Manganousions are mutually replaceable. Supergene Processes generally lead to fairly complete separation of Fe from Mn, because **the potential required to convert Fe to Ferric state is much lower than that required to convert Mn to MnO_2**.

Fe readily precipitates as Hydrated Ferric Oxide, whereas the Mn remains in solution longer and is eventually deposited under more Oxidising conditions as comparatively Fe-free MnO_2.

8. OXIDATION POTENTIALS &pH CONTROL ON THE NATURE OF SEDIMENTARY PRODUCTS

Krumbein and Garrels (1952) have devised an ingenious diagram which illustrates the relation between these factors and the sedimentary materials on which they act in the Figure below.

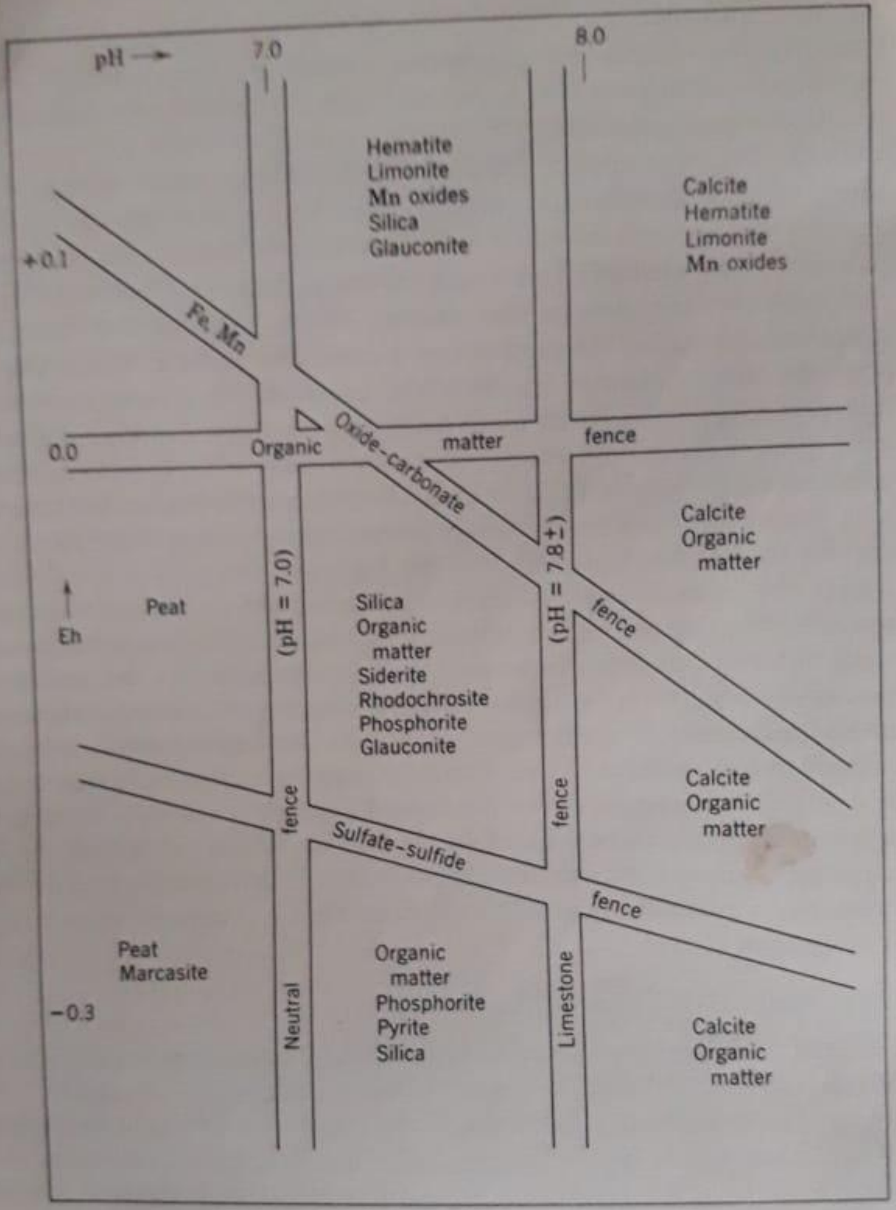

Figure 6.10 Sedimentary associations in relation to environmental limitations imposed by oxidation potential and pH. (After Krumbein and Garrels, *J. Geol.* **60,** 26, 1952)

In the above diagram they develop the concept of “Geological Fence”, a boundary defined by the presence of a particular mineral or material on one side and its absence on the other, in effect, by a certain chemical reaction. A particular geological fence may represent a specific pH value or a specific oxidation potential or a combination of both factors. In sedimentary domain many geochemical fences can be defined, but Krumbein and Garrels have shown that the most useful fences in sedimentary processes are the Natural Fences, at

i)pH = 7, acid-alkali fence

ii) pH = 7.8, the limestone fence, at higher pH calcite is readily deposited, at lower pH it tends to dissolve

iii) The sulfate-sulfide fence, determined by sulphate-sulfide oxidation potential

iv) The Fe-Mn oxide-carbonate fence, determined by the oxidation potential at which the ferrous and manganous compounds oxidise to the higher oxides

v) The organic matter fence, below which organic matter is stable and above which it oxidises to carbon dioxide.

As a result we obtain a classification of sedimentary environments based on the two significant parameters of pH and oxidation potential, and the careful study of a sedimentary deposit will elucidate the physicochemical conditions under which it developed.