

GEOCHEMISTRY

“Oxidation-Reduction potential”

Shekhar

Assistant Professor

Department of Geology

Patna Science College

Patna University

E-mail: sharan.srk@gmail.com

INTRODUCTION

“Oxidation” – loss of electron

“Reduction” – gain of electron

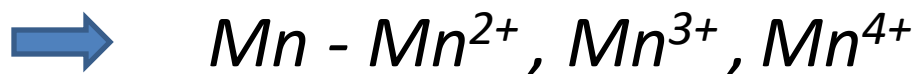
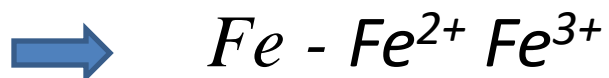
Thus oxidation - reduction reaction involve the *transfer of electron and the resultant change in valence.*

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

“Oxidation potential is a factor which provides the quantitative measure for this energy change.”

INTRODUCTION

- Many element exist in more than one valence state
e.g.,



- * *Metals in 0 valence are mostly electropositive*
- * *Non-metals with 0 valence usually electronegative*
- * *Some are both electron acceptor as well as electron donor.*

INTRODUCTION



- *The Fe^{2+} in magnetite oxidises by losing an electron*
- *conversely oxygen gains an electron and is thereby reduced.*

- A reduced system – availability of electrons is high.
 - *electron donor in excess than electron acceptor*
- An oxidised system – availability of electron is low
 - *electron acceptor in excess than electron donor*

REDOX IN NATURAL WATER

- Chemical reaction in aqueous media includes:



These reaction largely control the redox reaction during sedimentation

pH of natural water is variable - $\sim 4 - 9$

The oxidation potential of natural environment(pH 7.0) – $0.41 - 0.82 V$

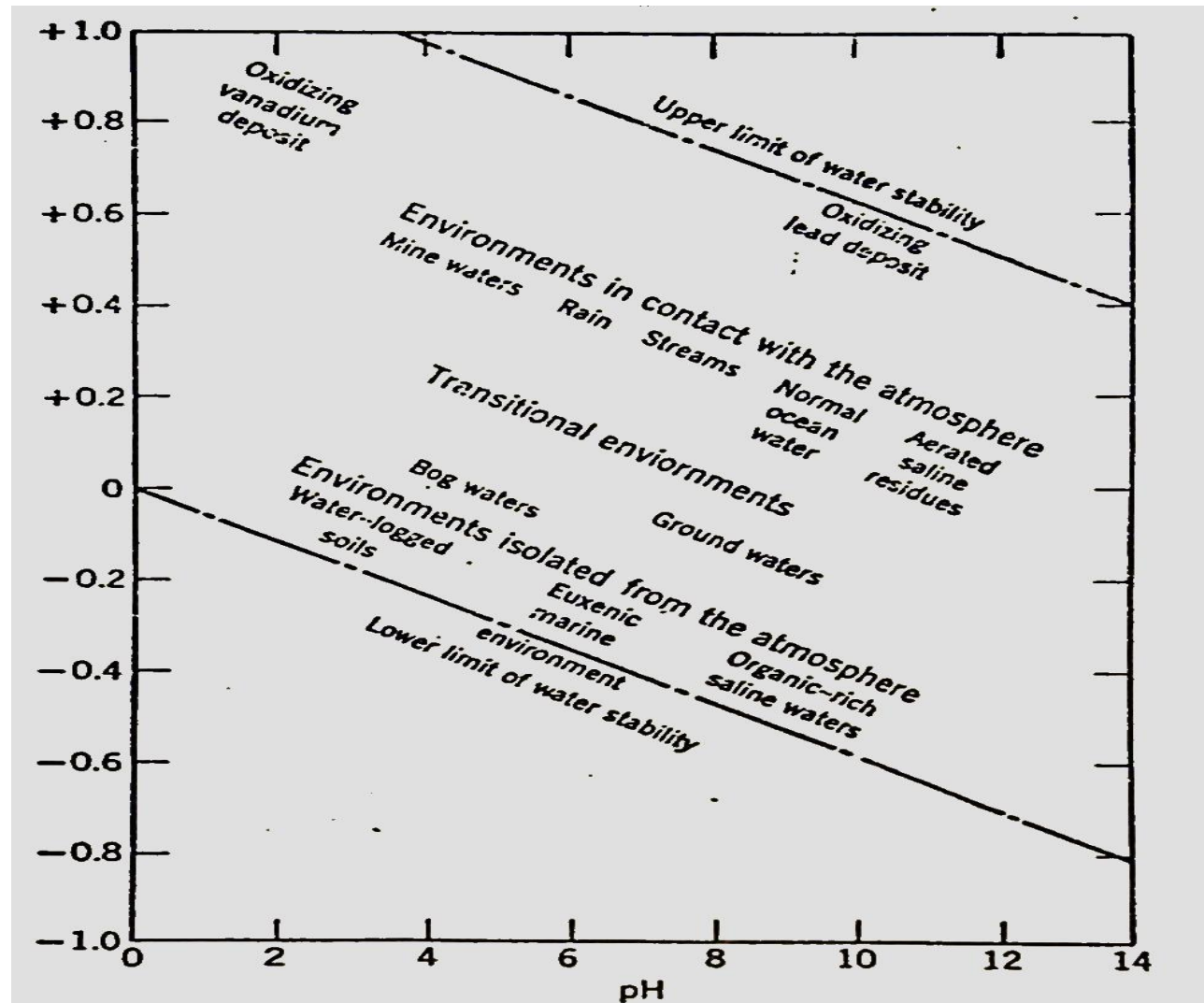
** The solution, transportation & deposition of elements that may occur in 2 or more oxidation state are directly and powerfully influenced by Oxidation potential of the environment*

Natural environments as characterised by Eh and pH

Oxidation potential $\propto 1/pH$

The sediments & soil predominate the Earth's surface resulting by the interaction of water with the pre existing rocks.

By comparing this diagram, can easily interpret the precipitation of metals in a specific environment.



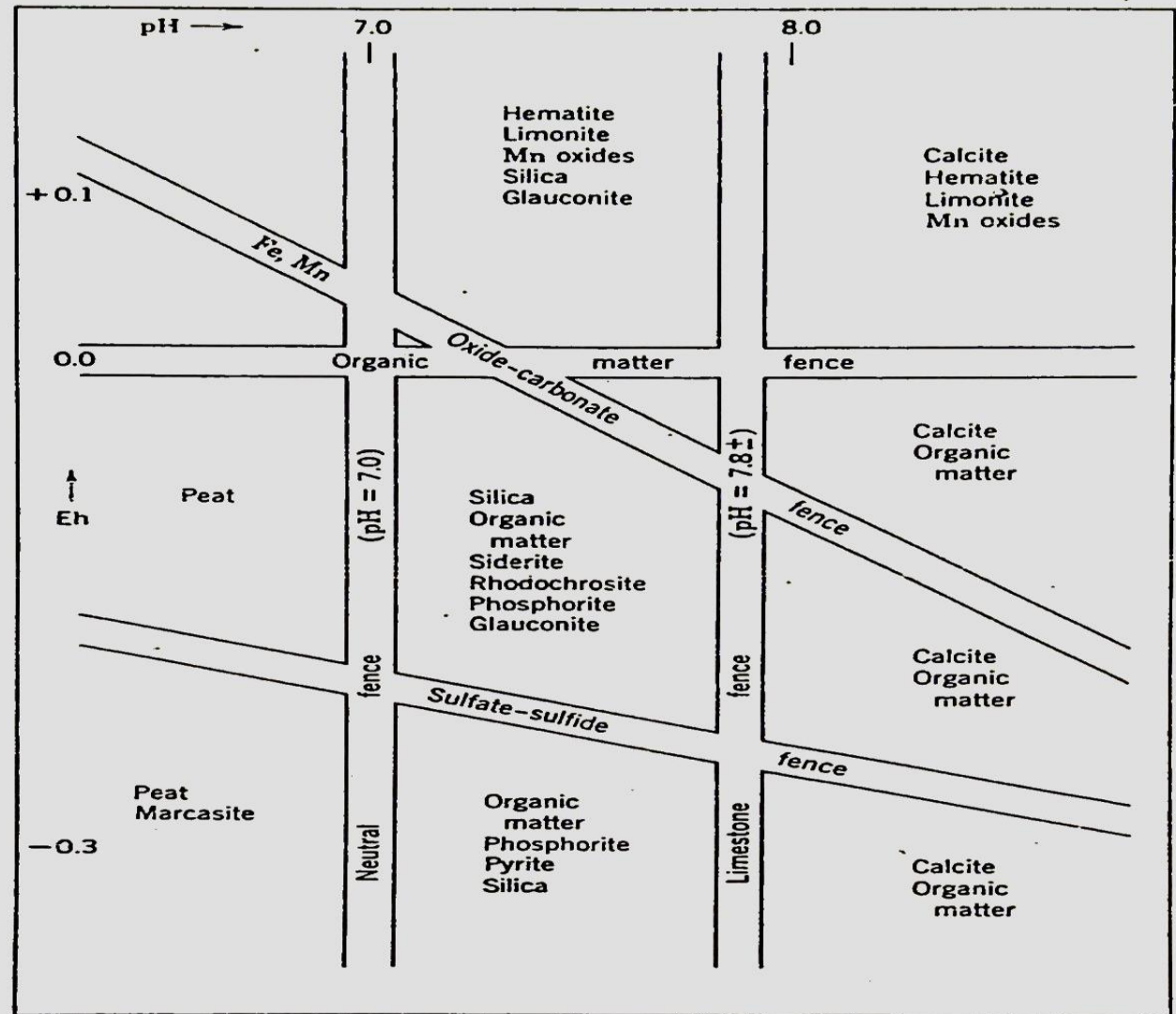
Source: Principle of Geochemistry, Brian Mason

Sedimentary associations in relation to environmental limitation imposed by Eh and pH

Given by Krumbein & Garrels (1952).

Oxidation potential & pH controls the nature of many sedimentary products.

Geochemical fence represents a combination of pH & Eh which acts as a boundary line.



TRANSITION METAL IN AQUEOUS SOLUTION

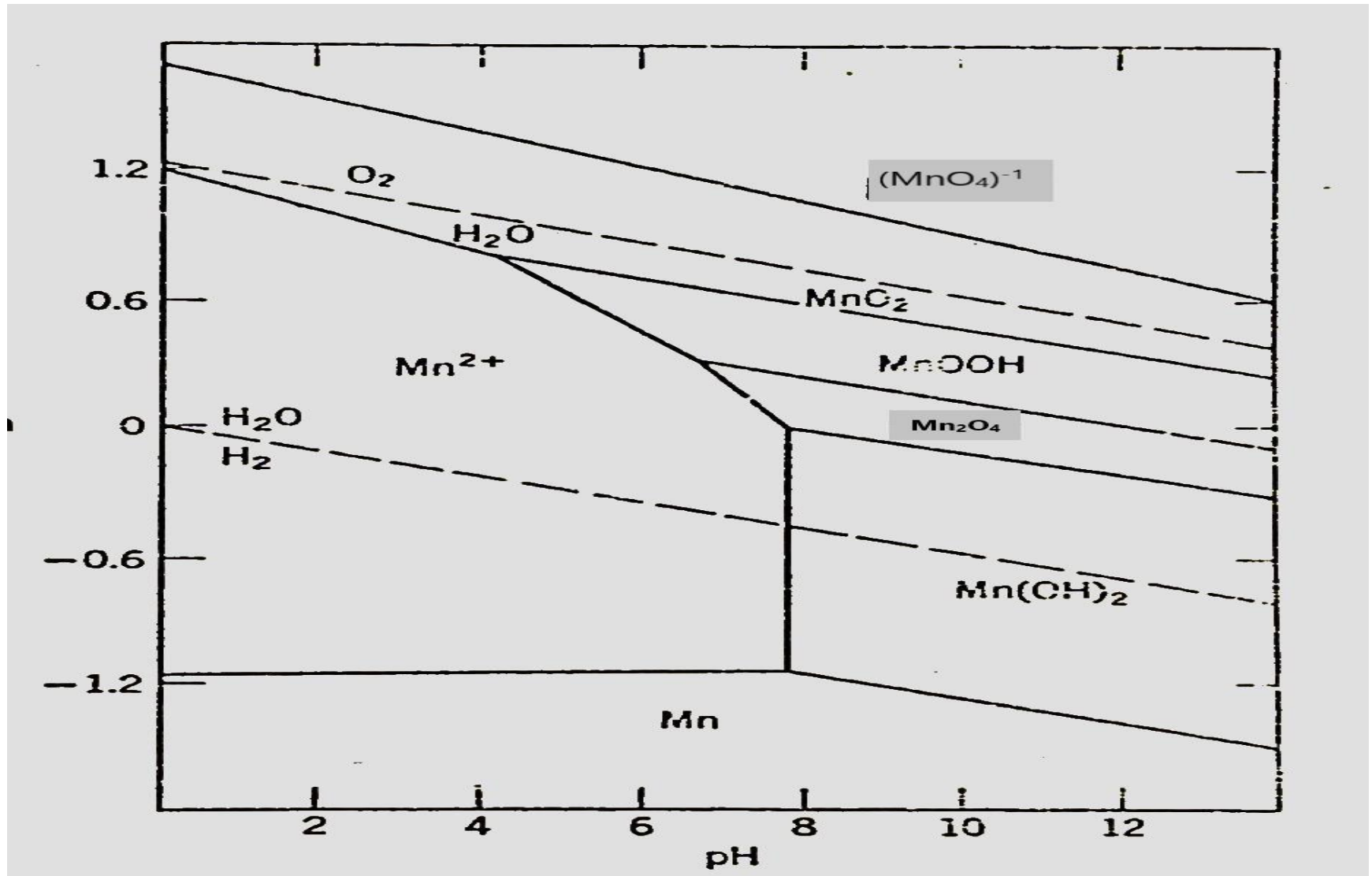
- Redox conditions influence a strong control on the concentration of these elements.
- Many transition metals have more than one valence state.
- The best examples of this behaviour are provided by *iron and manganese*.
- More soluble in their reduced form than in oxidized forms.

Mn-H₂O SYSTEM

- Under reducing environment:
 - *Low pH -- Occur as manganous compound*
 - *pH > 8 – precipitate as Mn(OH)₂*
- Low oxidising environment:
 - *Low pH: occur as manganous ion*
 - *pH > 8: Mn(OH)₂ \longrightarrow Mn₂O₄ \longrightarrow MnOOH \longrightarrow MnO₂*
- Under highly oxidising environment:
 - *MnO₂ is the stable phase at all pH.*

** Permanganate decomposes liberating O₂ & precipitating MnO₂*

Eh- pH diagram for the system Mn-H₂O



Source: *Principle of Geochemistry*, Brian Mason

Fe-H₂O SYSTEM

- The concentrations of Fe are quite low under high Eh and near neutral pH.

- At lower pH:

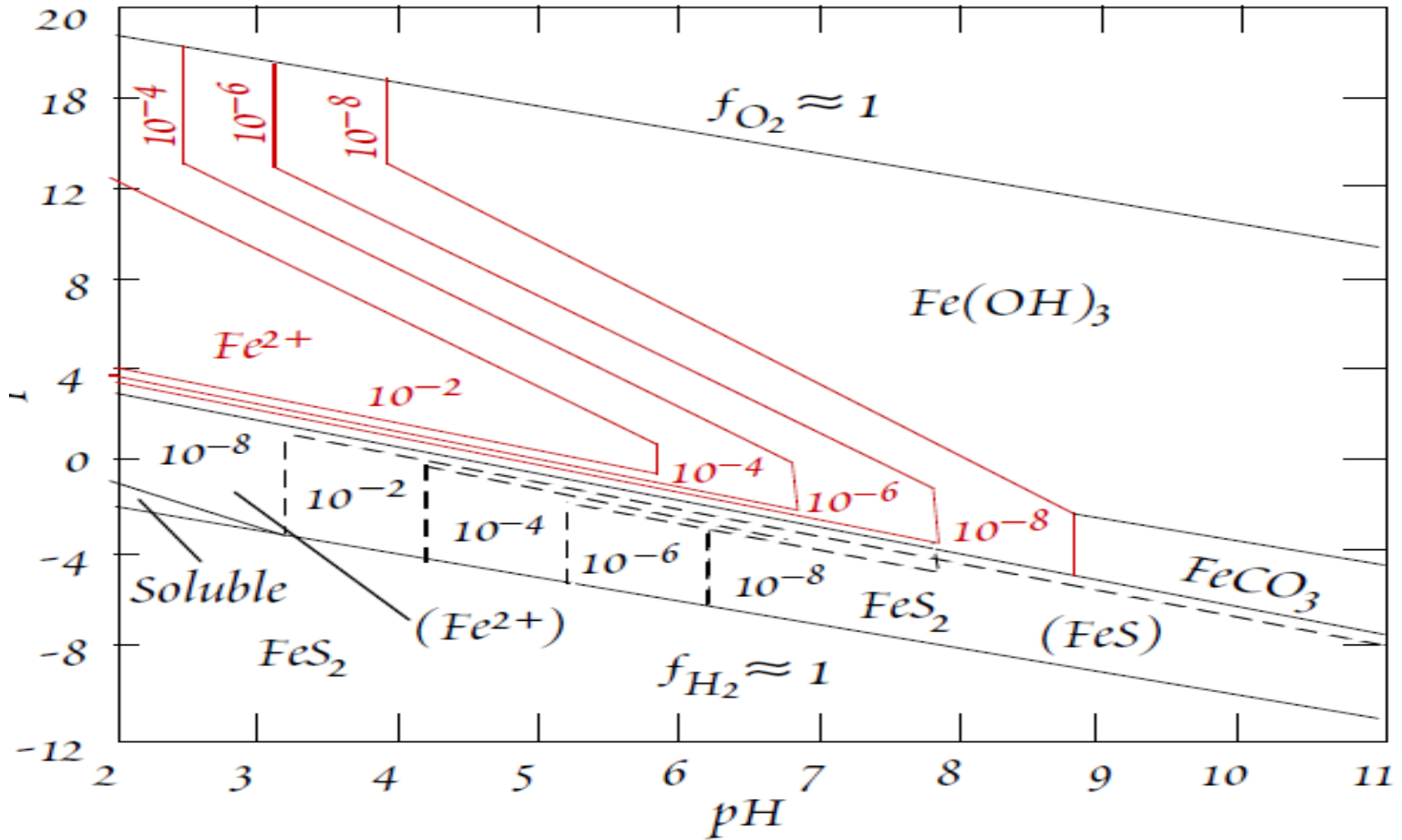


(sulfide ores gets oxidised to sulphate)

- Under anoxic condition:



Eh- pH diagram for the system Fe-H₂O



References & for further study

- *Mason, B., Moore, C. B., Principle of Geochemistry: John Wiley & sons*
- *White, W. M., Geochemistry: 2015 John Wiley & Sons, Ltd.*