

Geobiotropy: the evolution of rocks as sign of components of life

Marie-Paule BASSEZ

<http://chemphys.u-strasbg.fr/mpb>

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Introduction

Which minerals produced by rocks may be signatures of components of life ?

(Marie Paule Bassez 2013, 2014, 2015 OLEB, 2016 OLEB submitted)

Experimental syntheses of peptide like molecules

(CO + N₂ + H₂O)_g + protons, He ions, e⁻, soft X-rays, γ rays,
→ peptide-like molecules → **amino acids** (UV requires NH₃)
CO not CO₂ (*Kensei KOBAYASHI...OLEB1990..2008....*)

1. Anoxic Hydr FeMgSilicate 2. Anoxic Hydr FeS 3. Oxic Hydr FeMgSilica & FeS
4. Conclusion: Geobiotropic Signs 5. A geological terrain: Mawrth Vallis

1. Anoxic hydrolysis of rocks containing the ferromagnesian silicates, olivine, pyroxene

Enthalpies and free enthalpies of hydrolysis and carbonation of olivine $(\text{Fe}_{0.5}\text{Mg}_{0.5})_2\text{SiO}_4$

| Hydrolysis and carbonation of olivine $(\text{Fe}_{0.5}\text{Mg}_{0.5})_2\text{SiO}_{4(s)}$ | $\Delta_r H^0$ $=\sum_i \nu_i \cdot \Delta_f H_i^0$ kJ.mol ⁻¹ | $\Delta_r G^0$ $=\sum_i \nu_i \cdot \Delta_f G_i^0$ kJ.mol ⁻¹ | $\Delta_r G^0 =$ $\Delta_r H^0 - T \cdot \Delta_r S^0$ kJ.mol ⁻¹ | |
|--|--|--|---|-------|
| $1/4 \text{Fe}_2\text{SiO}_{4(s)} + 1/6 \text{H}_2\text{O}_{(l)} \rightarrow 1/6 \text{Fe}_3\text{O}_{4(s)} + 1/4 \text{SiO}_{2(s)} + 1/6 \text{H}_2(g)$ | +3.56 | +1.43 | +1.45 | (1) |
| $1/4 \text{Fe}_2\text{SiO}_{4(s)} + \text{H}_2\text{O}_{(l)} \rightarrow 1/2 \text{Fe}(\text{OH})_{3(s)} + 1/4 \text{SiO}_{2(s)} + 1/4 \text{H}_2(g)$ | +3.47 | +3.35 | +3.34 | (1)' |
| $1/4 \text{Fe}_2\text{SiO}_{4(s)} + 1/4 \text{H}_2\text{O}_{(l)} \rightarrow 1/4 \text{Fe}_2\text{O}_{3(s)} + 1/4 \text{SiO}_{2(s)} + 1/4 \text{H}_2(g)$ | +6.77 | +3.87 | +3.85 | (1)'' |
| $1/4 \text{Mg}_2\text{SiO}_{4(s)} + 3/8 \text{H}_2\text{O}_{(l)} \rightarrow 1/8 \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_{4(s)} + 1/8 \text{Mg}(\text{OH})_{2(s)}$ | -10.13 | -5.92 | | (2) |
| $1/4 \text{Fe}_2\text{SiO}_{4(s)} + 1/2 \text{CO}_2(g) \rightarrow 1/2 \text{FeCO}_{3(s)} + 1/4 \text{SiO}_{2(s)}$ | -39.32 | -13.50 | | (3) |
| $1/4 \text{Mg}_2\text{SiO}_{4(s)} + 1/2 \text{CO}_2(g) \rightarrow 1/2 \text{MgCO}_{3(s)} + 1/4 \text{SiO}_{2(s)}$ | -44.32 | -18.22 | | (4) |

| Enthalpies and free enthalpies of hydrolysis and carbonation, of pyroxene (Fe_{0.5}Mg_{0.5})SiO₃ | | | | |
|--|---|---|---|-------|
| Hydrolysis and carbonation of pyroxene (Fe _{0.5} Mg _{0.5}) ₂ SiO _{3(s)} | $\Delta_r H^0$ = $\sum_i \nu_i \cdot \Delta_f H_i^0$ | $\Delta_r G^0$ = $\sum_i \nu_i \cdot \Delta_f G_i^0$ | $\Delta_r G^0 =$ $\Delta_r H^0 - T \cdot \Delta_r S^0$ | |
| $1/4\text{FeSiO}_{3(s)} + 1/12\text{H}_2\text{O}_{(l)} \rightarrow 1/12\text{Fe}_3\text{O}_{4(s)} + 3/12\text{SiO}_{2(s)} + 1/12\text{H}_{2(g)}$ | +1.97 | +0.79 | +0.80 | (5) |
| $1/4\text{FeSiO}_{3(s)} + 1/2\text{H}_2\text{O}_{(l)} \rightarrow 1/4\text{Fe}(\text{OH})_{3(s)} + 1/4\text{SiO}_{2(s)} + 1/8\text{H}_{2(g)}$ | +1.92 | +1.75 | +1.74 | (5)' |
| $1/4\text{FeSiO}_{3(s)} + 1/8\text{H}_2\text{O}_{(l)} \rightarrow 1/8\text{Fe}_2\text{O}_{3(s)} + 1/4\text{SiO}_{2(s)} + 1/8\text{H}_{2(g)}$ | +3.57 | +2.01 | +2.02 | (5)'' |
| $1/4\text{MgSiO}_{3(s)} + 1/6\text{H}_2\text{O}_{(l)} \rightarrow 1/12\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_{4(s)} + 1/12\text{SiO}_{2(s)}$ | -5.19 | -3.30 | | (6) |
| $1/4\text{FeSiO}_{3(s)} + 1/4\text{CO}_{2(g)} \rightarrow 1/4\text{FeCO}_{3(s)} + 1/4\text{SiO}_{2(s)}$ | -19.47 | -6.67 | | (7) |
| $1/4\text{MgSiO}_{3(s)} + 1/4\text{CO}_{2(g)} \rightarrow 1/4\text{MgCO}_{3(s)} + 1/4\text{SiO}_{2(s)}$ | -21.22 | -8.27 | | (8) |
| Dehydration of chrysotile Mg₃Si₂O₅(OH)_{4(s)} | | | | |
| $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_{4(s)} + 2\text{SiO}_{2(s)} \rightarrow \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_{2(s)} + \text{H}_2\text{O}_{(l)}$ | -4.40 | -12.30 | | (9) |

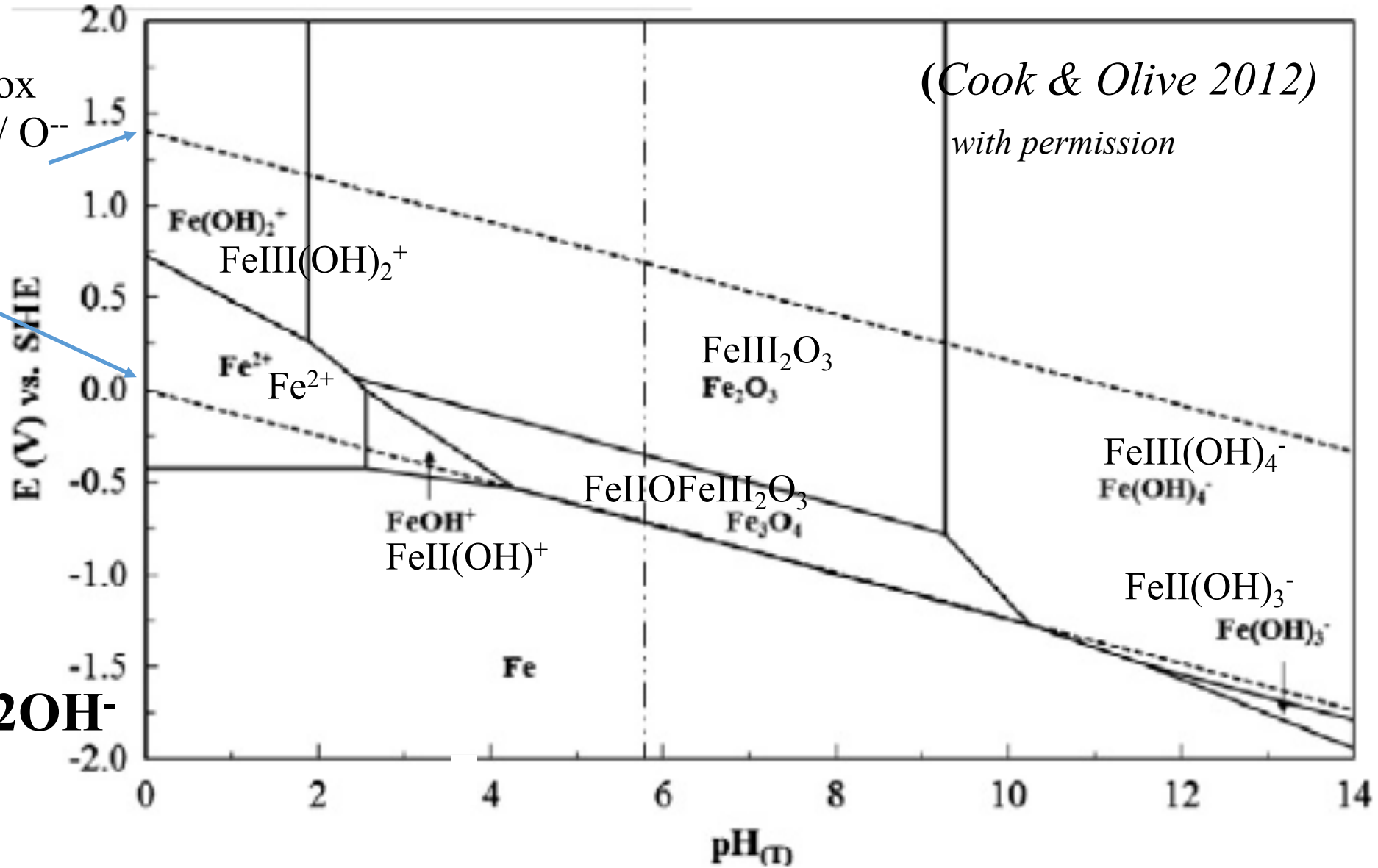
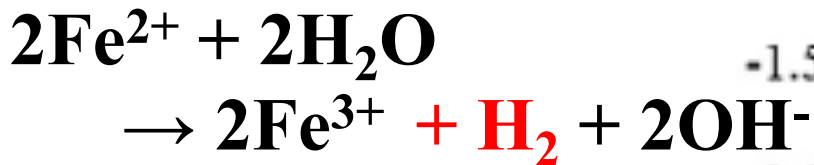
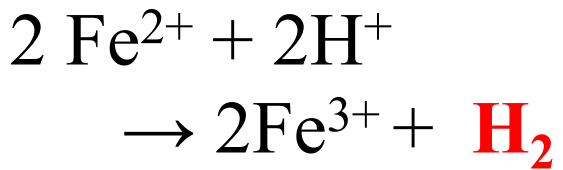
E-pH diagram for Fe-H₂O

350 °C, 250 bar (25 MPa)

Equilibrium line of the redox system O₂ox/H₂O red, O₂ / O²⁻

H₂Oox/ H₂red ; H⁺/ H₂

pH = 11.5 to 14:

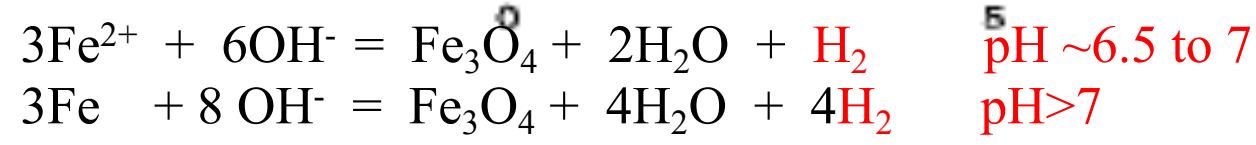
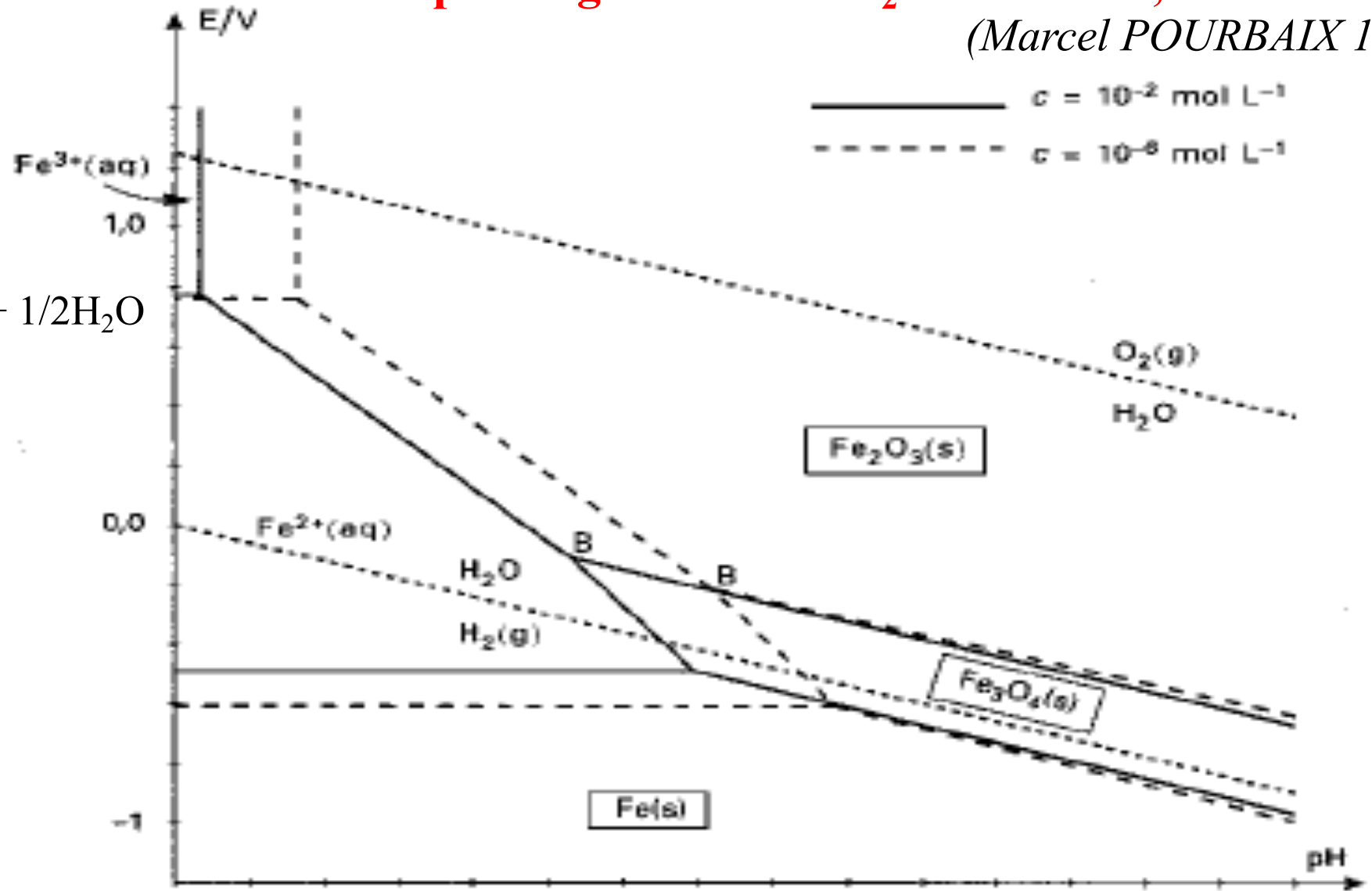


E-pH diagram for Fe-H₂O

25°C, 1atm

(Marcel POURBAIX 1963)

pH < 6.5 10⁻² mol.L⁻¹
 pH < 8.7 10⁻⁶ mol.L⁻¹
 $\text{Fe}^{2+} + 1/4\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + 1/2\text{H}_2\text{O}$



Magnetite is associated with FeS not with FeMg-silicates

* **herzolite-peridotite** : 62 vol% olivine (Seyfried, Foustoukos, Fu, 2007)
reacting on seawater at **200°C** and **50MPa**, during 3 to 7 months:
pH_(25°C) : from 6.2 to 12.2 ; high H₂ : up to 76 mmol.kg⁻¹
« trace amount of magnetite »

* **harzburgite-peridotite** : 70 wt% olivine, pentlandite, troilite (Klein et al 2015)
reacting on seawater at **300°C** and **35 MPa**, during 1.5 years:
pH_(25°C) from 6.3 to 9.0 ; production of H₂
« pentlandite is found together with magnetite »
« when fluid accessed the sulfides, heazlewoodite and magnetite precipitated... »

Pn: Ni_{4.9}Fe_{4.1}S₈, Py: ~FeS = troilite, Hzl: Ni₃S₂

FeIII(OH)₄⁻ : the alkaline form of dissolved goethite
FeO(OH)H₂O(OH)⁻ = the anion form of Fe(OH)₃

Goethite α-Fe(III)O(OH)

Natural goethite is hydrated: FeO(OH)H₂O = Fe(OH)₃

Ferric iron speciation is controlled by the species

Fe³⁺, FeIII(OH)₂⁺ and FeIII(OH)₄⁻ depending on pH (*Albarède 2003*)

Fe III can be incorporated into the hydrolysis products of the Mg-endmembers to form **FeIII-phyllsilicates**

- **T-O phyllosilicate lizardite/chrysotile** $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$
 $[(3\text{Mg})^{+6} (\text{Si}_2\text{O}_5)^{2-} (4\text{OH})^{4-}]$
 can form as $(\text{Mg}^{\text{II}},\text{Fe}^{\text{II}})_3\text{Si}_2\text{O}_5(\text{OH})_4$ or **$(\text{Al}^{\text{III}},\text{Fe}^{\text{III}})_2\text{Si}_2\text{O}_5(\text{OH})_4$**
- **T-O-T phyllosilicate talc** $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$
 $[(3\text{Mg})^{+6} (\text{Si}_4\text{O}_{10})^{4-} (2\text{OH})^{2-}]$
 can form as $(\text{Mg}^{\text{II}},\text{Fe}^{\text{II}})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ or **$(\text{Al}^{\text{III}},\text{Fe}^{\text{III}})_2\text{Si}_4\text{O}_{10}(\text{OH})_2$**

1. Anoxic Hydr FeMgSilicate **2. Anoxic Hydr FeS** 3. Oxic Hydr FeMgSilica & FeS
4. Conclusion: Geobiotropic Signs 5. A geological terrain: Mawrth Vallis

2. Anoxic hydrolysis of iron(II) monosulfide rocks

troilite : FeS = stoichiometric pyrrhotite hexagonal

pyrrhotite: Fe_{1-x}S $x < 0.13$ is Fe deficient
($x=0.10$: Fe_9S_{10} hexagonal $x=0.125$: Fe_7S_8 monoclinic)

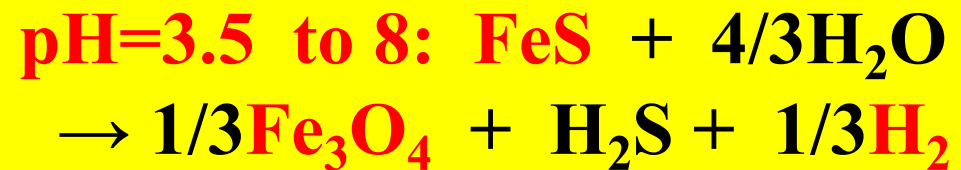
mackinawite = tetragonal FeS = Fe_{1+x}S

E-pH diagram for Fe-S-H₂O

in high-salinity brine at 250°C
(Digby Macdonald 1993, with permission)



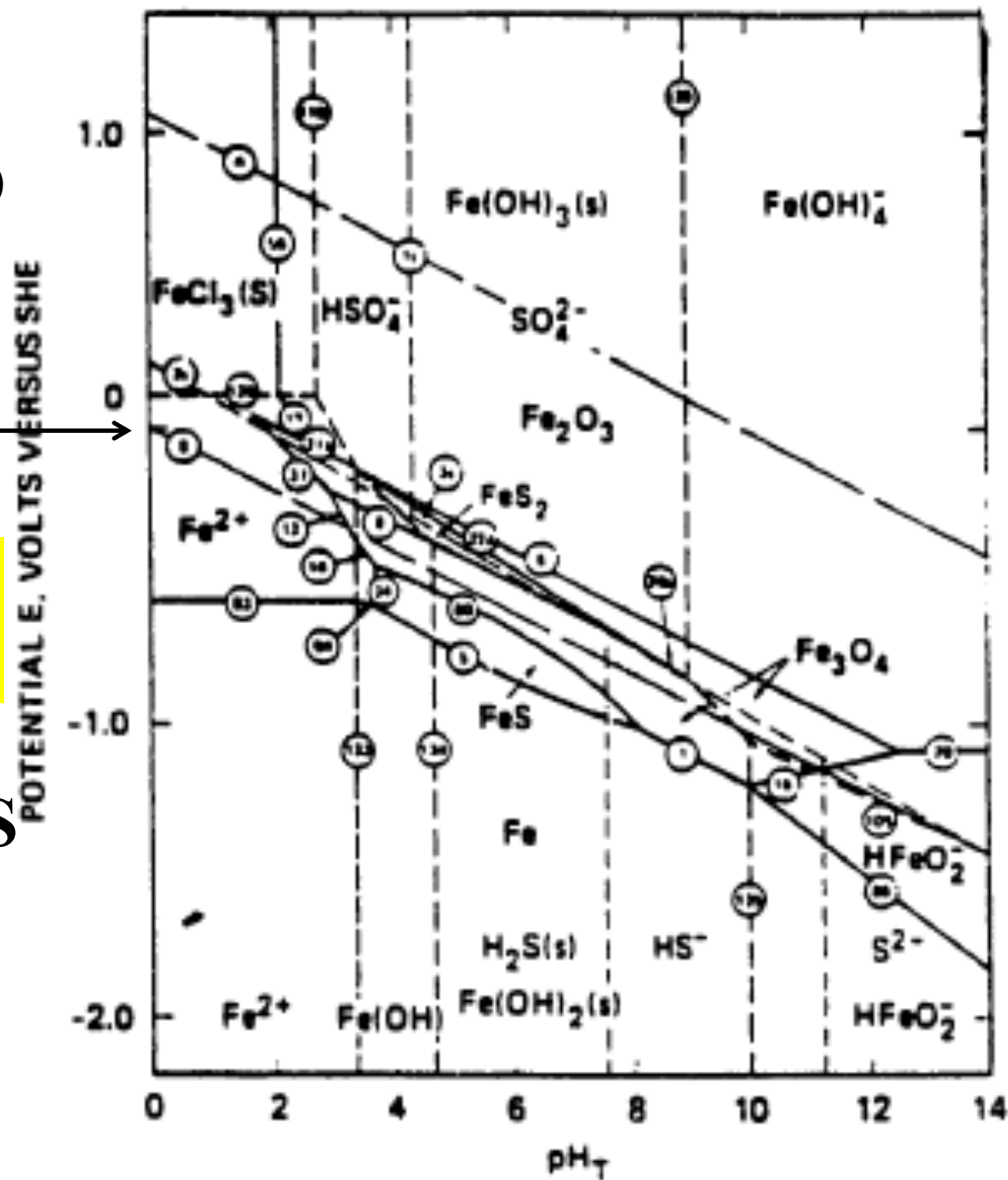
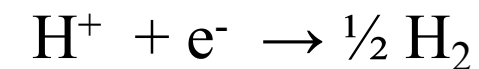
redox line H⁺ / H₂ →



$\Delta_r H^0 = + 89.57 \text{ kJ/mol of FeS}$

$\Delta_r G^0 = + 46.47 \text{ kJ/mol of FeS}$

O₂ not required for Fe₃O₄



E-pH diagram for Fe-S-H₂O

in high salinity brine at 25°C

(Digby Macdonald 1993, with permission)

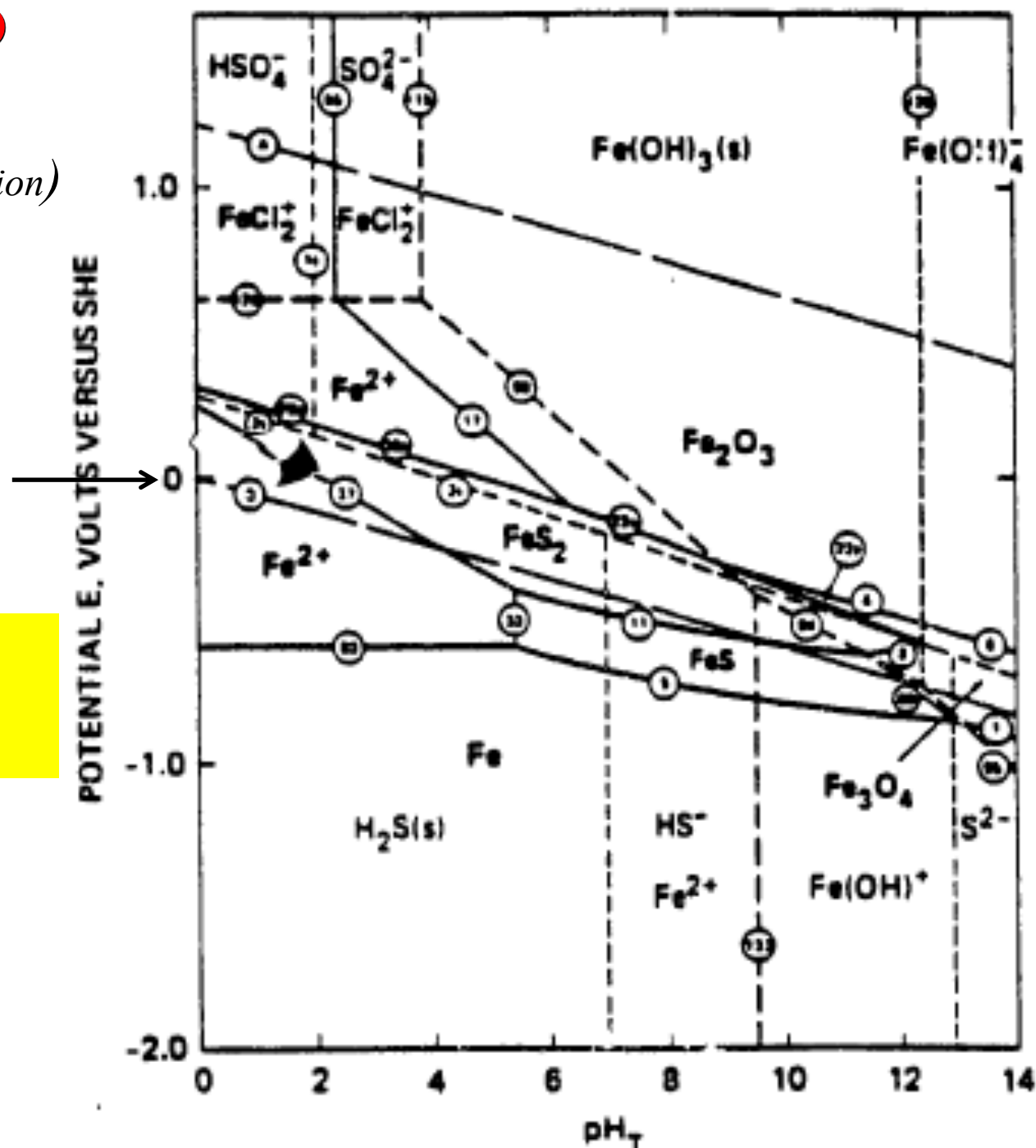
Equilibrium line of
redox system H⁺ / H₂

Fe(II)S(-I)₂

**pH 5.4 to 9.5: FeS + H₂S
→ FeS₂ + H₂**

$\Delta_r H^0 = -48.3$ kJ/mol of FeS

$\Delta_r G^0 = -23.8$ kJ/mol of FeS)

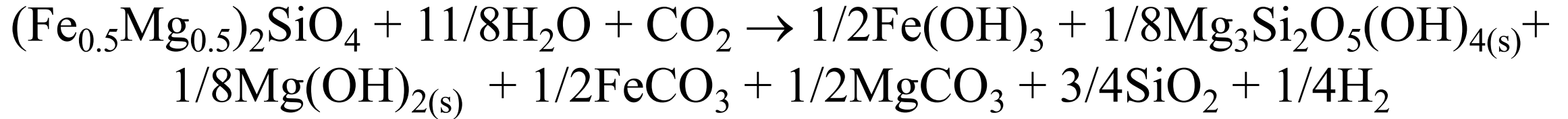


Enthalpy of serpentinization for $(\text{Fe}_{0.5}\text{Mg}_{0.5})_2\text{SiO}_4$ olivine

calculated by summation of enthalpies of the 4 equations 1', 2, 3 and 4:

$$\Delta_r H^0 = -90.31 \text{ kJ/mole of } (\text{Fe}_{0.5}\text{Mg}_{0.5})_2\text{SiO}_4 \text{ olivine}$$

$$\Delta_r H^0 = -524.35 \text{ kJ/kg of } (\text{Fe}_{0.5}\text{Mg}_{0.5})_2\text{SiO}_4 \text{ olivine}$$

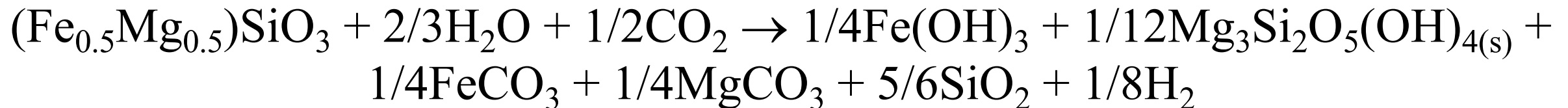


Enthalpy of serpentinization for $(\text{Fe}_{0.5}\text{Mg}_{0.5})\text{SiO}_3$ pyroxene

calculated by summation of enthalpies of equations 5', 6, 7 and 8:

$$\Delta_r H^0 = -43.98 \text{ kJ/mole of pyroxene } (\text{Fe}_{0.5}\text{Mg}_{0.5})\text{SiO}_3$$

$$\Delta_r H^0 = -378.61 \text{ kJ/kg of pyroxene } (\text{Fe}_{0.5}\text{Mg}_{0.5})\text{SiO}_3$$



Other related experiments

anoxic oxidation of FeS into Fe₃O₄ at 250°C

1. **Mackinawite** heated in sealed tubes *(Lennie et al. 1997)*

X-ray diffraction and **TEM**, transmission electron microscopy :

* 70°C (Sample1) and 100°C (S2) → greigite **Fe₃S₄**

transformation is complete at 200°C

* **above 245°C** : diffraction patterns of greigite disappear
pyrrhotite and **magnetite** appear

2. **Clays** in confined atmosphere *(Kars et al 2012, Aubourg & Pozzi 2010)*

Magnetization measurements

* < 85°C **pyrrhotite**

* **from 85 to 250°C** : magnetite

Other related experiments

anoxic oxidation of FeS into FeS₂ at 25°C

3. FeS + H₂S → FeS₂ + H₂ between 25°C and 125°C

(Rickard 1997 and ref herein)

4. FeS + deionized, distilled, sonicated H₂O → pH 5.5

35% FeOOH, 5.5 % S-rich sulfides (S-S bonds) and no sulfates *(Jones et al 1992)*

FeO(OH) difficult to understand with E-pH diagrams, unless some O₂ is remaining

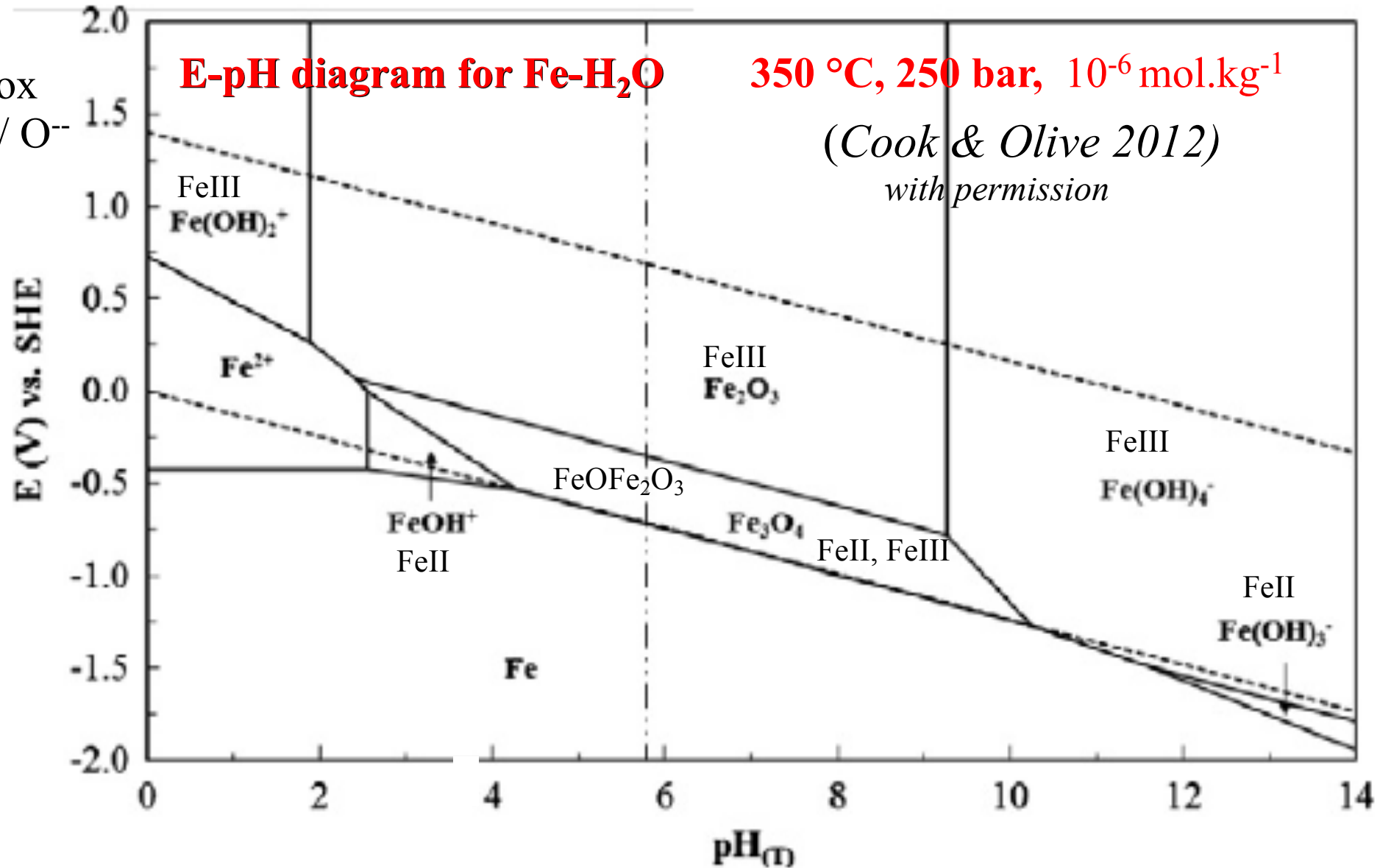
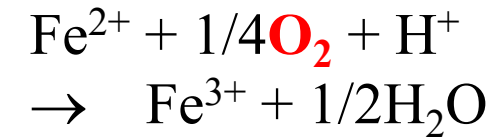
1. Anoxic Hydr FeMgSilicate 2. Anoxic Hydr FeS 3. **Oxic Hydr FeMgSilica & FeS**
4. Conclusion: Geobiotropic Signs 5. A geological terrain: Mawrth Vallis

3. Oxic hydrolyses of ferromagnesian silicates and iron(II) monosulfides rocks

Oxic hydrolysis of ferromagnesian silicate rocks

Equilibrium line of the redox system O_{2ox}/H_2O red, O_2 / O^{2-}

pH < 1.9, FeII \rightarrow Fe(OH) $_2^+$
 pH 1.9-2.5, FeII \rightarrow Fe $_2$ O $_3$
 pH 2.5-4.2, FeII \rightarrow Fe $_3$ O $_4$



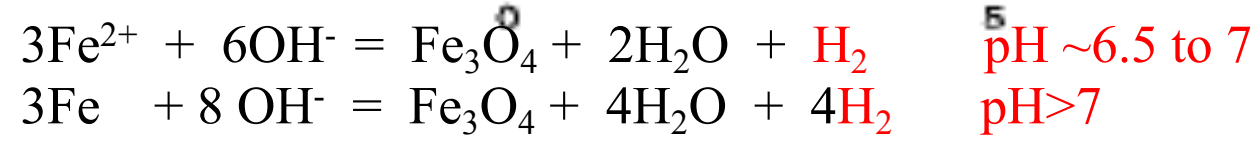
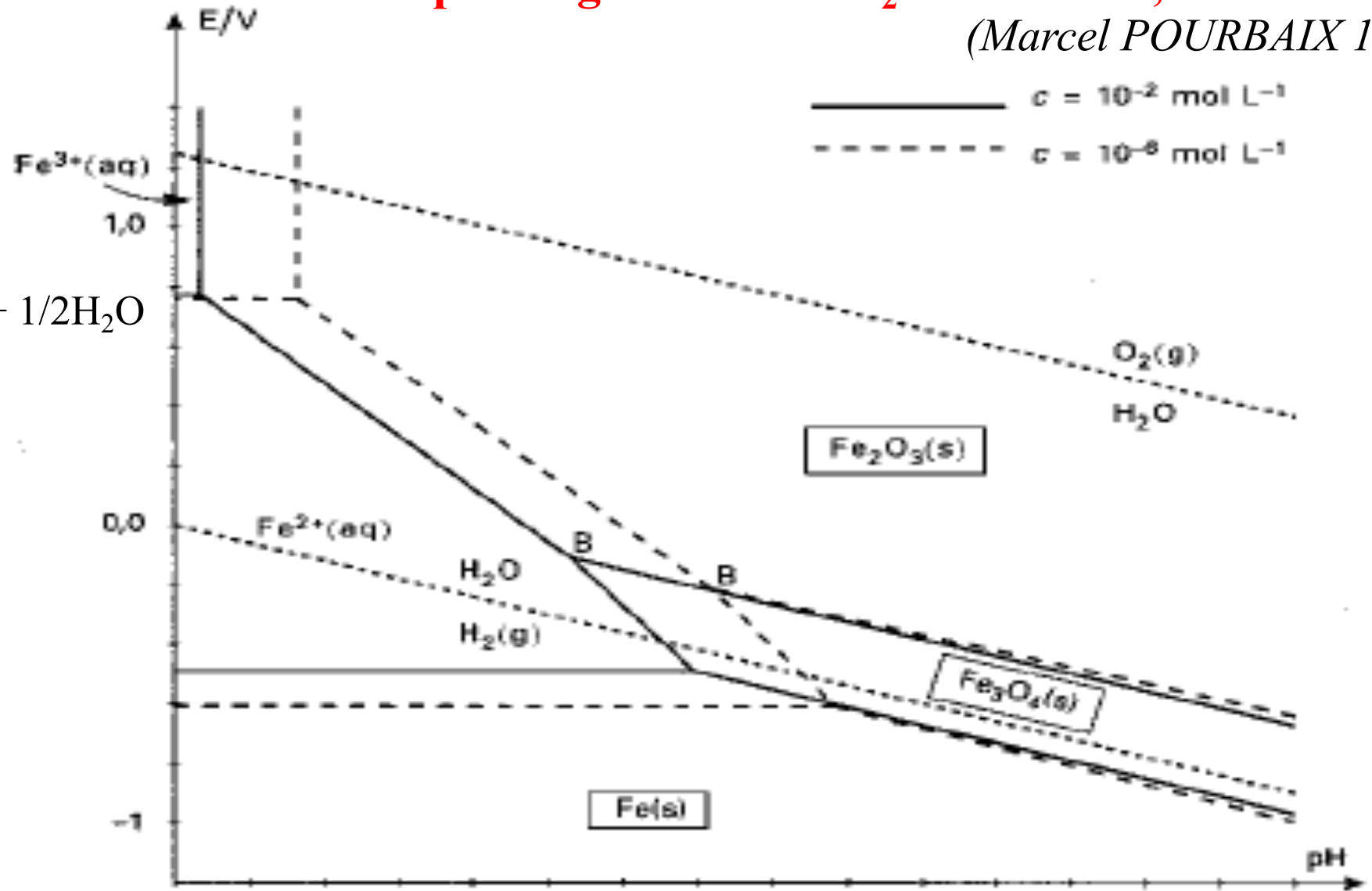
Fe(OH) $_2^+$ acidic species of FeO(OH)

E-pH diagram for Fe-H₂O

25°C, 1atm

(Marcel POURBAIX 1963)

pH < 6.5 10⁻² mol.L⁻¹
 pH < 8.7 10⁻⁶ mol.L⁻¹
 $\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \frac{1}{2}\text{H}_2\text{O}$



Related laboratory experiments

1. **Deprotonation** of synthetic **goethite** $\alpha\text{-FeO(OH)}$ by heating in air
from 25°C to 800°C \rightarrow **hematite** $\alpha\text{-Fe}_2\text{O}_3$

Removal of adsorbed H_2O : at $\sim 70^\circ\text{C}$

Protohematite $\text{Fe}_{2-x/3}(\text{OH})_x\text{O}_{3-x}$ at 270°C

Only hematite at 800°C (conversion complete)

Studied by synchrotron diffraction *(Gualtieri & Venturelli 1999)*

2. **Dehydration of synthetic goethite**, by heating in air
from 155°C to 610°C \rightarrow **hematite** $\alpha\text{-Fe}_2\text{O}_3$

$255\text{-}405^\circ\text{C}$, hematite, goethite and intermediate spinel: magnetite

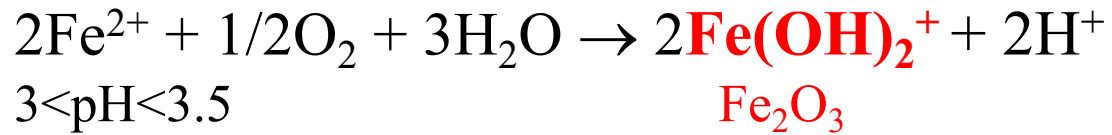
500 and 610°C : only hematite *(Özdemir 2000)*

Studied by induced magnetization and X-ray diffraction

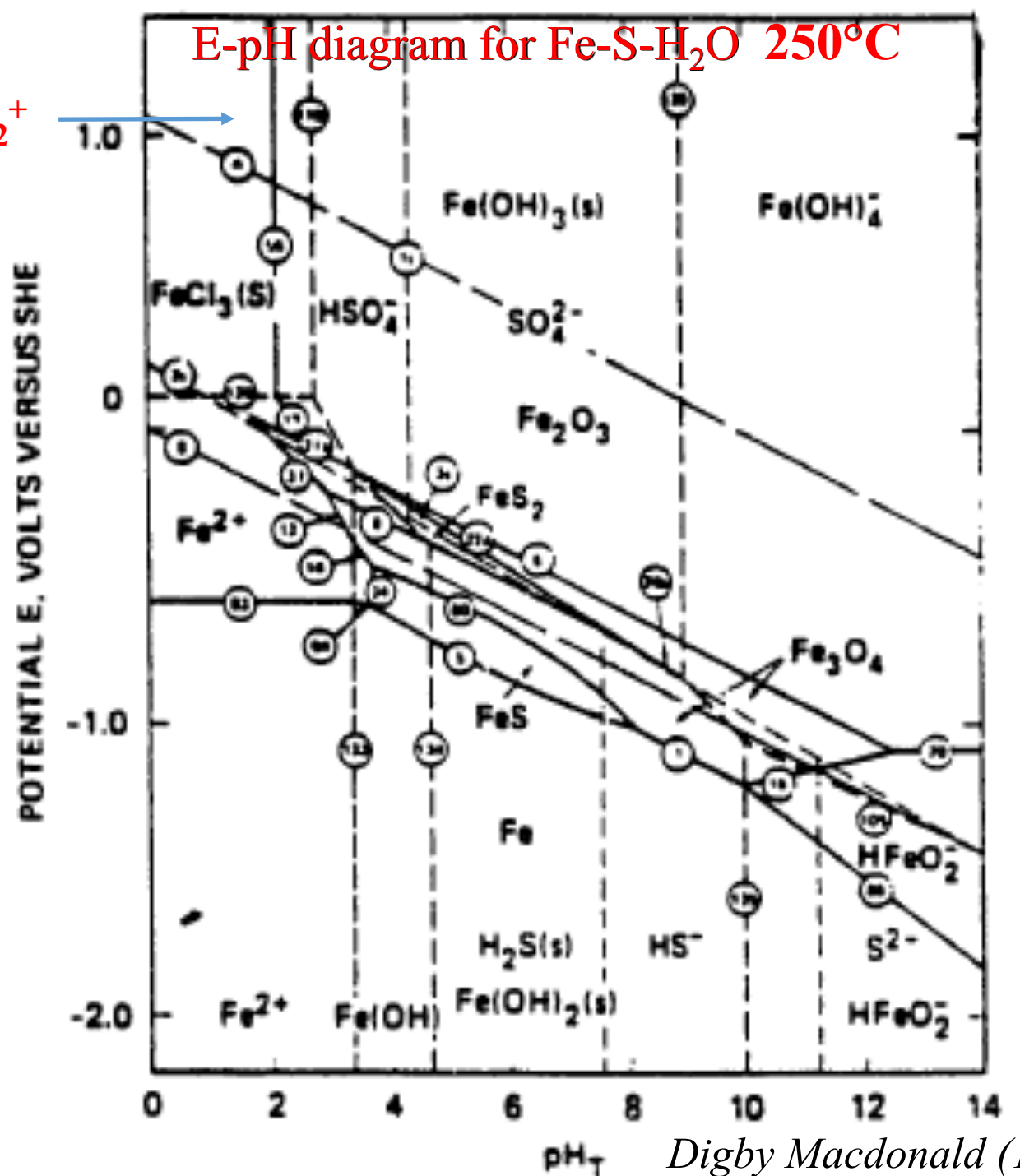
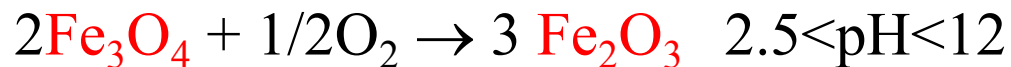
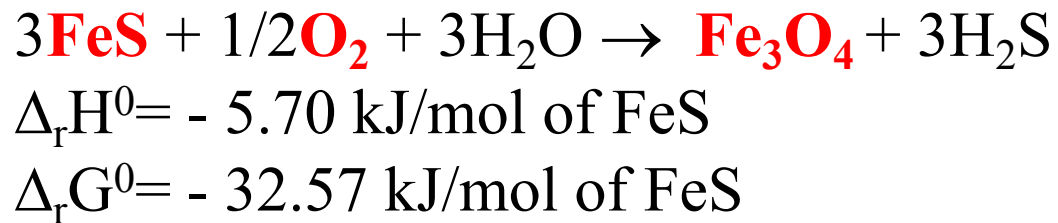
Oxic hydrolysis of iron(II) monosulfide rocks

(Digby Macdonald 1993, with permission)

pH < 3



3.7 < pH < 8



Digby Macdonald (1993)

Oxic hydrolysis of iron(II) monosulfide rocks 25°C

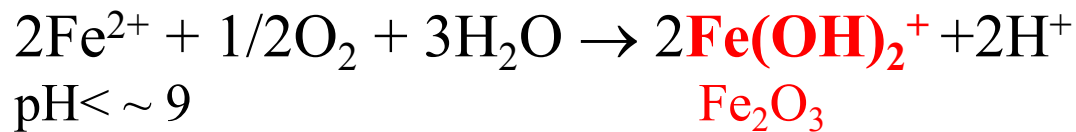
(Digby Macdonald 1993
with permission)

Equilibrium line of redox system H^+ / H_2

$5 < pH < 12$

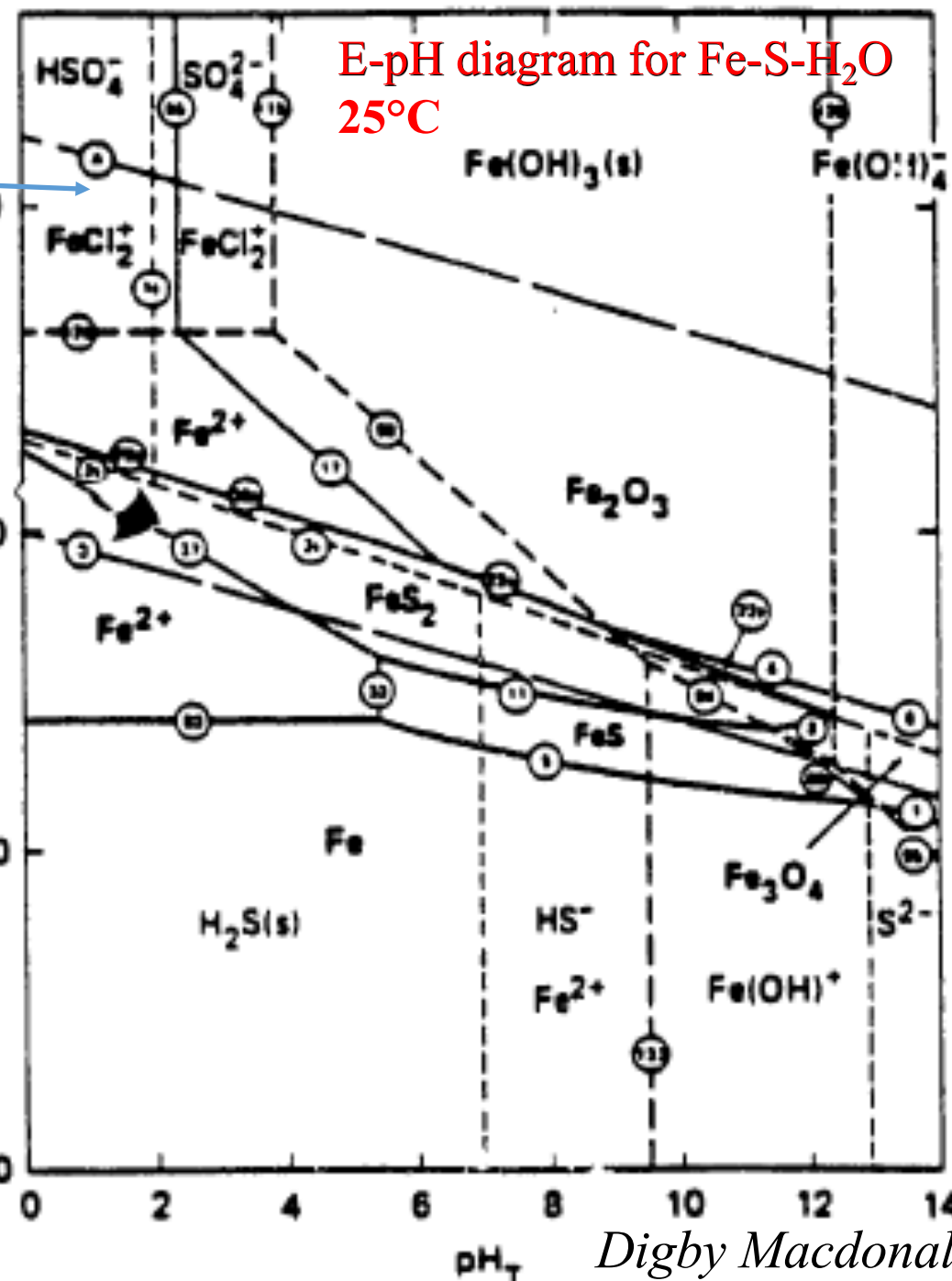


$pH < 4$



$Fe(OH)_2^+$

POTENTIAL E. VOLTS VERSUS SHE
1.0
0
-1.0
-2.0



E-pH diagram for Fe-S-H₂O 25°C

Digby Macdonald 1993

Related laboratory experiments

Oxic oxidation of FeS into Fe₃O₄ at high T

Magnetic dipole moments measurements during heating **in vacuum and air**

- of iron meteorites containing **troilite** and **pyrrhotite**

Curie T at **580°C** and X-rays → troilite, pyrrhotite, **magnetite** after heating.
(Lovering & Parry 1962)

Formation of magnetite is reported as difficult to explain without O₂

Our E-pH analysis shows anoxic production of magnetite with release of H₂

- of **pyrrhotite** rocks from Massif Central/France

→ production of **magnetite** at 400°C *(Bina et al. 1991)*

Related laboratory experiments

Oxic oxidation of FeS into FeS₂ at 25°C

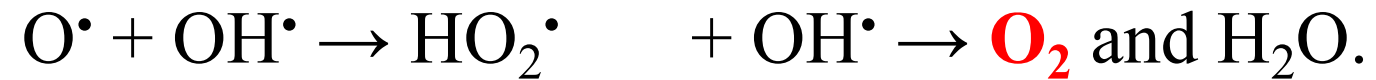
- **Troilite** oxidation in oxygen-bearing solutions at 35°C
→ **pH~5** , poorly ordered solid phases assigned to **polysulfide**,
amorphous ferric trihydroxide, goethite, lepidocrocite and **minor sulfate**
(Chirita et al 2008)

Radiolyzed water

When the energy absorbed is low



When the energy absorbed \uparrow radical density \uparrow



Production of O_2 dominates for $\text{LET} > 300 \text{ keV}\cdot\mu\text{m}^{-1}$ (*Gervais et al. 2005*)

Linear energy transfer = energy transferred per unit of penetration depth

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4. Conclusion

| Type of rocks interacting with water | Minerals formed at 25°C | Minerals formed at 250-350°C geobiotropic |
|--------------------------------------|---|---|
| | O₂ absent in water | |
| Ferromagnesian silicate | 1. | 2. Fe(III)-phyllosilicates Fe(OH) ₃ , FeO(OH), Fe ₂ O ₃ Fe ₃ O ₄ (traces), FeMg-carbonates |
| Iron(II) monosulfide | 3. FeS ₂ | 4. Fe ₃ O ₄ |
| | O₂ in radiolyzed water | |
| Ferromagnesian silicate | 5. Fe ₃ O ₄ Fe ₂ O ₃ , Fe(OH) ₃ , FeO(OH) | 6. Fe ₃ O ₄ Fe ₂ O ₃ , Fe(OH) ₃ , FeO(OH) |
| Iron(II) monosulfide | 7. FeS ₂ Fe ₂ O ₃ , Fe(OH) ₃ , FeO(OH) sulfates | 8. Fe ₃ O ₄ Fe ₂ O ₃ , Fe(OH) ₃ , FeO(OH) sulfates |

Geobiotropy ή τροπή

the physico-chemical evolution of rocks in association with
the formation of molecules of biological interest

1. Anoxic Hydr FeMgSilicate
2. Anoxic Hydr FeS
3. Oxic Hydr FeMgSilica & FeS
4. Conclusion: Geobiotropic Signs
5. **A geological terrain: Mawrth Vallis**

5. An example of geological terrain: Mawrth Vallis on Mars ??

1. 100-200m lower layer : **Fe^{III}/Mg-smectite phyllosilicates** and **ferric oxide/hydroxides** species
2. 5-10 m intermediate layer : ferrous phase
3. 10-50 m upper layer: **Al-smectite-phyllosilicates**
ferric oxide/hydroxides
sulfates such as jarosite ? gibbsite Al(OH)₃ ?
4. A few meters protecting **caprock** (*Loizeau et al 2010, Bishop et al 2013*)



10 km

**Fe, Mg-
phyllosilicates**

Mawrth Vallis

**Hydrothermal H₂, CO,
amino-acids ?**

Al-phyllosilicates

Upon (Loizeau et al 2010)

Acknowledgments

Michel Cassir and **Kevin Ogle**,
Ecole Nationale Supérieure de Chimie de Paris,

Richard Welter, Université de Strasbourg,

Hypothesis

Lower layer: **anoxic** hydrolysis and carbonation of olivine and pyroxene
Hydrothermal H₂ release

Upper layer: $(\text{Al}^{\text{III}}, \text{Fe}^{\text{III}})_2\text{Si}_2\text{O}_5(\text{OH})_4$? proof of the hydrolysis of Mg-silicates
 $(\text{Al}^{\text{III}}, \text{Fe}^{\text{III}})_2\text{Si}_4\text{O}_{10}(\text{OH})_2$? proof of the dehydration of Mg-silicates
anoxic hydrolysis and carbonation of olivine and pyroxene,
Hydrothermal H₂ release
protected by the observed caprock
sulfate: oxic oxidation in radiolyzed water of FeS

Prebiotic synthesis:

350 torr CO, 350 torr N₂ and liquid water producing 20 torr
Cosmic radiation or radionuclides

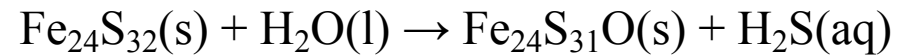
***Lost City**→90°C, rocks highly serpentized, chimneys in carbonates
pH9-11,[H₂]↑15mmol/kg, (*Kelley Sci.307, 2005, Proskurowski Sci. 319, 2008*)

* **Rainbow 365°C, 235 bar** pH=2.8 [H₂]=16 mmol/kg
(*Charlou...2002*)

Since FeS produces Fe₃O₄ only at very high pH ~13 at 25°C and at pH ~3.5 to 8 at 250°C, it is plausible to propose by extrapolation that pH of magnetite formation from ferrous sulfide decreases when temperature increases. That might explain the pH value ~3 at the Rainbow field which vent fluids at ~365°C and shows sulfide chimneys, and also at other low pH hydrothermal vents of the spreading ridges, as discussed in §3.2..

2. Action of water on greigite *(Santos et al march 2016)*

Computational methods:



Replacement of S (forming H₂S) by O (from H₂O)

2. Conversion of natural goethite studied by differential scanning calorimetry

goethite converts to hematite from 260 to 685°C.

trace amounts of magnetite at 400 to 685°C;

FeII is proposed to arise from traces of organic matter or clay minerals

(Dekkers 1990)

FeS → **FeS₂**

- Troilite & pyrrhotite oxidized by distilled, deionized water, sonicated
→ **pH 5.5**

35% FeO(OH), 5.5 % S-rich sulfides (S-S bonds), no sulfates (*Jones et al 1992*)

* Individual values from Robie and Hemingway's 1995 tables, at 298.15K and 1 bar.

Values for SiO₂ are those of quartz.

Entropy values are calculated considering $S^0(\text{H}_2)=130.45 \text{ J.K}^{-1}.\text{mol}^{-1}$.

The ferromagnesian silicates olivine and pyroxene may be written in this way, considering that the rock contain as much iron than magnesium. Considering also that equal quantities of endmembers react with water and with carbon dioxide, one elementary reaction must start with one fourth of the endmember silicate.

Thus the hydrolyses of fayalite and ferrosilite (Fe endmembers) in the absence of oxygen lead preferentially to ferric oxide hydroxides and ferric trihydroxide, following eq. (1)' and (5)' and after dehydration to hematite, instead of magnetite, following equations (1)" and (5)" which are precisely more endothermic than equations (1) and (5). Ferric ion is incorporated into hydroxides.