UNIVERSITÉ DE STRASBOURG

ChemPhys

Ferromagnesian silicates and iron(II) monosulfides rocks as sources of magnetite and hydrogen

(Bassez 2008, 2009, 2013, 2014, OLEB 2015, OLEB 2016 submitted)

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

Introduction

Serpentinization reaction: $(FeIIMg)_2SiO_4 + (FeIIMg)SiO_3 + H_2O + CO_2$

$$\rightarrow (FeIIMg)_3Si_2O_5(OH)_4 + (FeIIMg)_3Si_4O_{10}(OH)_2 + (FeIIMg)(OH)_2 +$$

$$Fe_3O_4 + SiO_2 + FeCO_3 + MgCO_3 + H_2$$

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2$$

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

Enthalpies and free enthalpies of hydrolysis and carbonation of olivine $(Fe_{0.5}Mg_{0.5})_2SiO_4$

| Hydrolysis and carbonation of olivine $(Fe_{0.5}Mg_{0.5})_2SiO_{4(s)}$	$\Delta_r H^0$ $=\sum_i \nu_i . \Delta_f H_i^0$ $kJ.mol^{-1}$	$\Delta_r G^0$ $=\sum_i \nu_i . \Delta_f G_i^0$ $kJ.mol^{-1}$	$\Delta_r G^0 =$ $\Delta_r H^0 - T.\Delta_r S^0$ $kJ.mol^{-1}$	
$1/4\ Fe_2SiO_{4(s)} + 1/6H_2O_{(l)} \rightarrow 1/6Fe_3O_{4(s)} + 1/4SiO_{2(s)} + 1/6H_{2(g)}$	+3.56	+1.43	+1.45	(1)
$1/4Fe_2SiO_{4(s)} + H_2O_{(l)} \rightarrow 1/2Fe(OH)_{3(s)} + 1/4SiO_{2(s)} + 1/4H_{2(g)}$	+3.47	+3.35	+3.34	(1)'
$1/4Fe_2SiO_{4(s)} + 1/4H_2O_{(l)} \rightarrow 1/4Fe_2O_{3(s)} + 1/4SiO_{2(s)} + 1/4H_{2(g)}$	+6.77	+3.87	+3.85	(1)''
$1/4Mg_2SiO_{4(s)} + 3/8H_2O_{(l)} \rightarrow 1/8Mg_3Si_2O_5(OH)_{4(s)} + 1/8Mg(OH)_{2(s)}$	-10.13	-5.92		(2)
$1/4Fe_2SiO_{4(s)} + 1/2CO_{2(g)} \rightarrow 1/2FeCO_{3(s)} + 1/4SiO_{2(s)}$	-39.32	-13.50		(3)
$1/4Mg_2SiO_{4(s)} + 1/2CO_{2(g)} \rightarrow 1/2MgCO_{3(s)} + 1/4SiO_{2(s)}$	-44.32	-18.22		(4)

Hydrolysis and carbonation of pyroxene $(Fe_{0.5}Mg_{0.5})_2SiO_{3(s)}$	$\Delta_rH^0 = \sum_i \nu_i.\Delta_fH_i^0$	$\Delta_rG^0 = \sum_i \nu_i.\Delta_fG_i^0$	$\Delta_rG^0 = \Delta_rH^0 - T.\Delta_rS^0$	
$1/4FeSiO_{3(s)} + 1/12H_2O_{(l)} \rightarrow 1/12Fe_3O_{4(s)} + 3/12SiO_{2(s)} + 1/12H_{2(g)}$	+1.97	+0.79	+0.80	(5)
$1/4FeSiO_{3(s)} + 1/2H_2O_{(l)} \rightarrow 1/4Fe(OH)_{3(s)} + 1/4SiO_{2(s)} + 1/8H_{2(g)}$	+1.92	+1.75	+1.74	(5)'
$1/4FeSiO_{3(s)} + 1/8H_2O_{(l)} \rightarrow 1/8Fe_2O_{3(s)} + 1/4SiO_{2(s)} + 1/8H_{2(g)}$	+3.57	+2.01	+2.02	(5)''
$1/4MgSiO_{3(s)} + 1/6H_2O_{(l)} \rightarrow 1/12Mg_3Si_2O_5(OH)_{4(s)} + 1/12SiO_{2(s)}$	-5.19	-3.30		(6)
$1/4FeSiO_{3(s)} + 1/4CO_{2(g)} \rightarrow 1/4FeCO_{3(s)} + 1/4SiO_{2(s)}$	-19.47	-6.67		(7)
$1/4MgSiO_{3(s)} + 1/4CO_{2(g)} \rightarrow 1/4MgCO_{3(s)} + 1/4SiO_{2(s)}$	-21.22	-8.27		(8)
Dehydration of chrysotile $Mg_3Si_2O_5(OH)_{4(s)}$				
$Mg_3Si_2O_5(OH)_{4(s)} + 2SiO_{2(s)} \rightarrow Mg_3Si_4O_{10}(OH)_{2(s)} + H_2O_{(l)}$	-4.40	-12.30		(9)

E-pH diagram for Fe-H₂O 350 °C, 250 bar (25Mpa)
(Cook & Olive 2012, with permission)
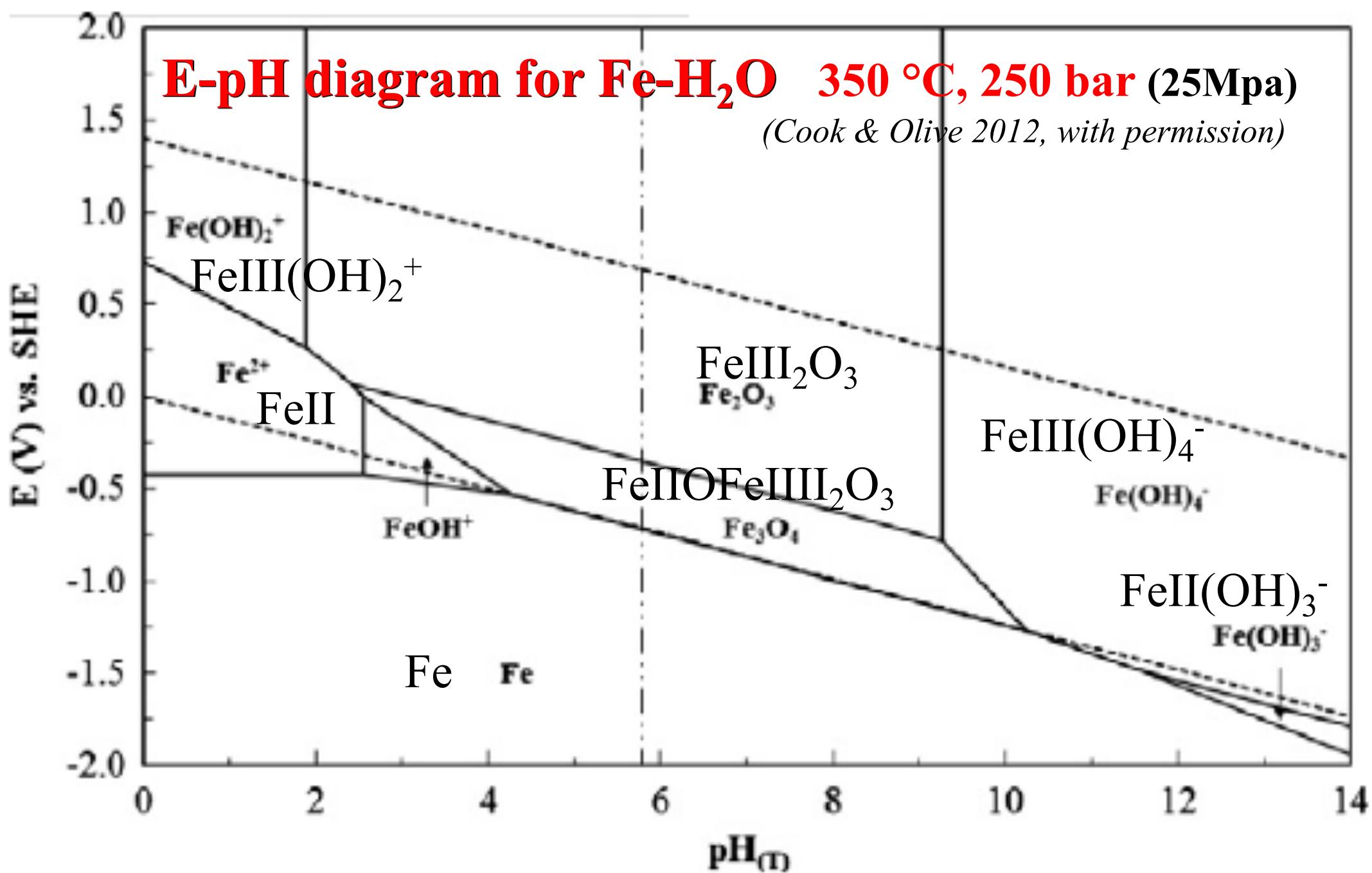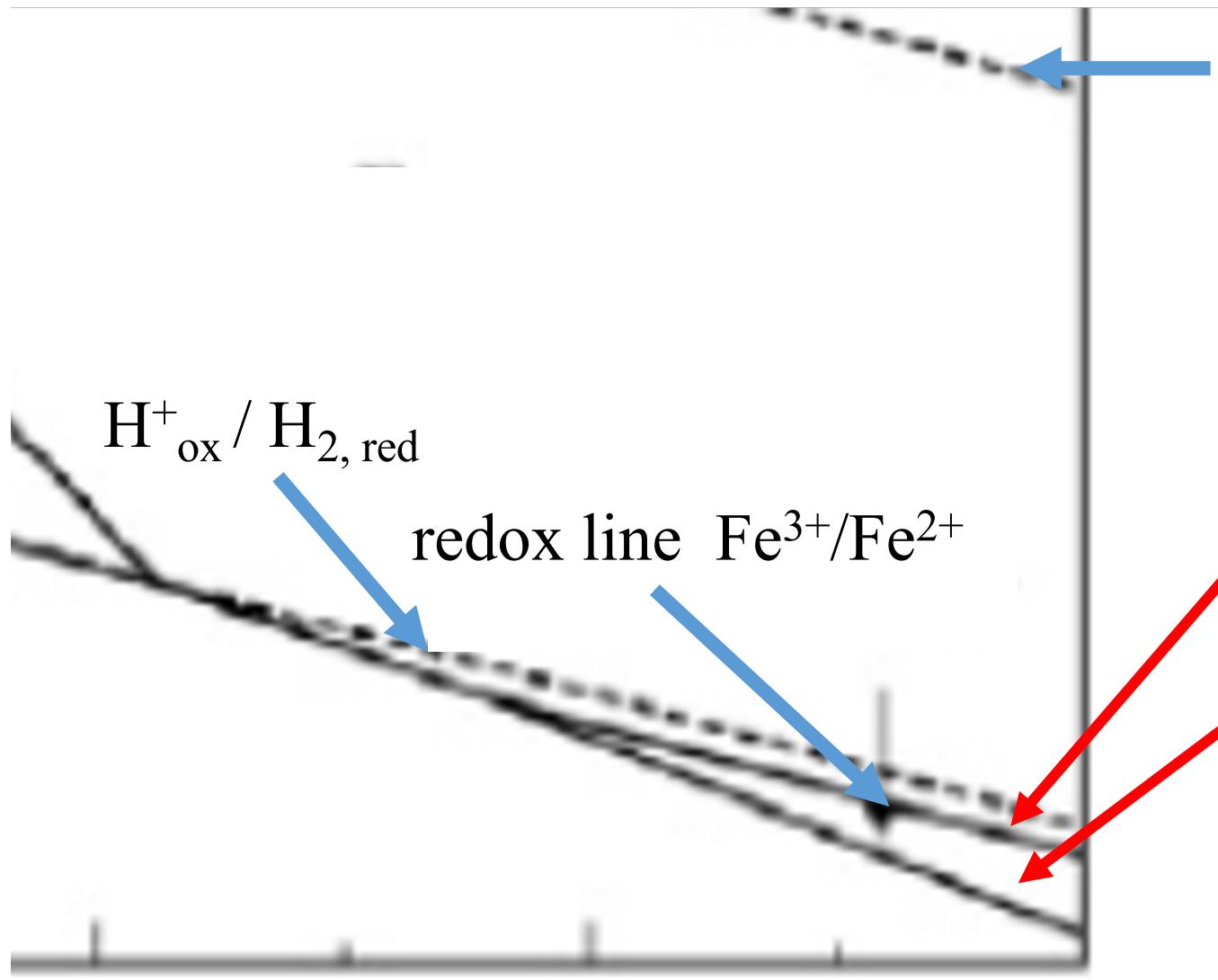
Equilibrium line of the redox system $O_2 ox / H_2O$ red, $\quad O_2 / O^{--}$

$H^+_{ox} / H_{2, red}$

redox line Fe^{3+}/Fe^{2+}

$Fe(III)(OH)_4^-$

$Fe(II)(OH)_3^-$

10   12   14

E-pH diagram for Fe-H₂O   25°C, 1atm   *(Marcel POURBAIX 1963)*

pH ~6.5- 7

$3Fe^{2+} + 6OH^-$

$\rightarrow$ **Fe_3O_4** $+ 2H_2O$ + **H_2**

$3Fe + 8\,OH^- = Fe_3O_4 + 4H_2O +$
$4H_2$ pH>7

Anoxic hydrolysis of silicates

$$2\ Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + H_2$$

350°C, pH = 11.5-14, $2Fe^{II}(OH)_3^- + 2H_2O \rightarrow 2Fe^{III}(OH)_4^- + H_2$

25°C, pH = 6.5-7, $3Fe^{2+} + 6OH^- \rightarrow Fe_3O_4 + 2H_2O + H_2$
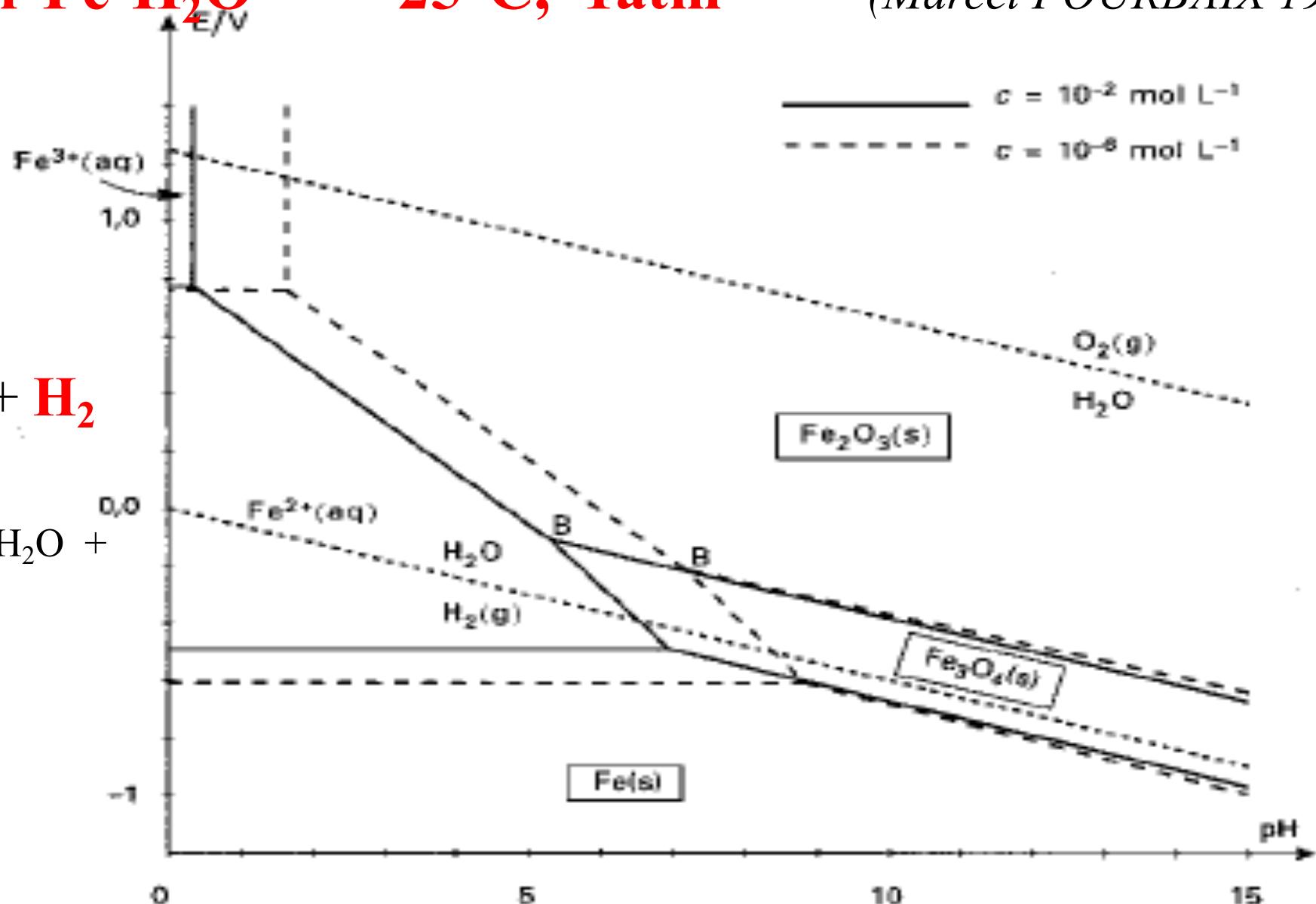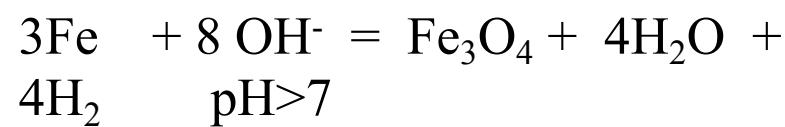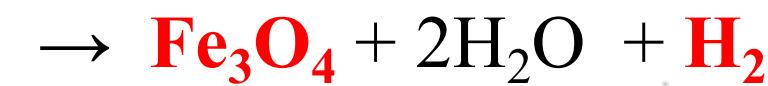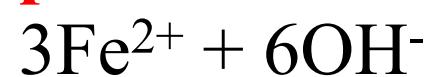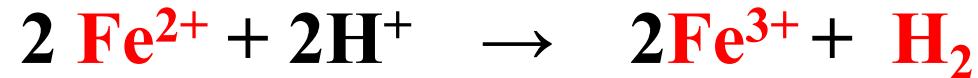
FeIII can be incorporated inside goethite

FeIII(OH)$_4$$^-$: the alkaline form of dissolved goethite
FeO(OH)H$_2$O(OH)$^-$ = the anion form of Fe(OH)$_3$

Goethite α-Fe(III)O(OH)
Natural goethite is **hydrated: FeO(OH)H$_2$O = Fe(OH)$_3$**

Ferric iron speciation is controlled by the species
Fe^{3+}, FeIII(OH)$_2$$^+$ and FeIII(OH)$_4$$^-$ depending on pH *(Albarède 2003)*

FeIII can be incorporated into the hydolysis products of the Mg-endmembers to form FeIII-phyllosilicates

- **T-O phyllosilicate lizardite/chrysotile $Mg_3Si_2O_5(OH)_4$**

$$[(3Mg)^{+6} (Si_2O_5)^{2-} (4OH)^{4-}]$$

can form as $(Mg^{II},Fe^{II})_3Si_2O_5(OH)_4$ or $(Al^{III},Fe^{III})_2Si_2O_5(OH)_4$

- **T-O-T phyllosilicate talc $Mg_3Si_4O_{10}(OH)_2$**

$$[(3Mg)^{+6} (Si_4O_{10})^{4-} (2OH)^{2-}]$$

can form as $(Mg^{II},Fe^{II})_3Si_4O_{10}(OH)_2$ or $(Al^{III},Fe^{III})_2Si_4O_{10}(OH)_2$

Exp: Magnetite associated with FeS, not with FeMg-silicates

* **lherzolite-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 H_2:** 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 H_2**

« pentlandite is found together with magnetite »
« when fluid accessed the sulfides, heazlewoodite and magnetite precipitated... »

Pn: $Ni_{4.9}Fe_{4.1}S_8$,   Py: ~FeS = troilite,   Hzl: Ni_3S_2

2. Anoxic hydrolysis of iron(II) monosulfide rocks

troilite : FeS = stoechiometric 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^+ / H_2 ⟶

FeS_2

Fe_3O_4

FeS

E-pH diagram for Fe-S-H$_2$O in high salinity brine **at 25°C**

(Digby Macdonald 1993 with permission)

Equilibrium line of redox system H$^+$ / H$_2$

Anoxic hydrolysis of sulfides

250°C: pH = 3.5 to 8   FeS + 4/3H$_2$O → 1/3Fe$_3$O$_4$ + H$_2$S + 1/3H$_2$

$\Delta_r H^0 = + 89.57$ **kJ/mol of FeS** $\Delta_r G^0 = + 46.47$ kJ/mol of FeS

25°C : pH 5.4 to 9.5   FeS + H$_2$S → **FeS$_2$ + H$_2$**

$\Delta_r H^0 = - 48.3$ kJ/mol of FeS $\Delta_r G^0 = - 23.8$ kJ/mol of FeS

O$_2$ not required for Fe$_3$O$_4$

Fe^{2+} → Fe^{3+} + e$^-$

H$^+$ + e$^-$ → ½ H$_2$ Fe(II)S(-II)   Fe(II)Fe(III)$_2$O$_4$ Fe(II)S(-I)$_2$

Enthalpy of serpentinization of $(Fe_{0.5}Mg_{0.5})_2SiO_4$ olivine

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

$\Delta_r H^0 =$ **-90.31 kJ/mole** of $(Fe_{0.5}Mg_{0.5})_2SiO_4$ olivine

$\Delta_r H^0 = -524.35$ kJ/kg of $(Fe_{0.5}Mg_{0.5})_2SiO_4$ olivine

$$(Fe_{0.5}Mg_{0.5})_2SiO_4 + 11/8H_2O + CO_2 \rightarrow 1/2Fe(OH)_3 + 1/8Mg_3Si_2O_5(OH)_{4(s)} + 1/8Mg(OH)_{2(s)} + 1/2FeCO_3 + 1/2MgCO_3 + 3/4SiO_2 + 1/4H_2$$

Enthalpy of serpentinization for $(Fe_{0.5}Mg_{0.5})SiO_3$ pyroxene

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

$\Delta_r H^0 =$ **-43.98 kJ/mole** of pyroxene $(Fe_{0.5}Mg_{0.5})SiO_3$

$\Delta_r H^0 = -378.61$ kJ/kg of pyroxene $(Fe_{0.5}Mg_{0.5})SiO_3$

$$(Fe_{0.5}Mg_{0.5})SiO_3 + 2/3H_2O + 1/2CO_2 \rightarrow 1/4Fe(OH)_3 + 1/12Mg_3Si_2O_5(OH)_{4(s)} + 1/4FeCO_3 + 1/4MgCO_3 + 5/6SiO_2 + 1/8H_2$$

Exp: Anoxic oxidation of FeS into Fe_3O_4 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) $\rightarrow$ greigite Fe_3S_4
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**

Exp: Anoxic oxidation of FeS into FeS$_2$ at 25°C

3. **FeS** + H$_2$S → **FeS$_2$** + H$_2$ between 25°C and 125°C

(Rickard 1997 and ref herein)

4.   FeS + deionized, distilled, sonicated H$_2$O → 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 O$_2$ is remaining

Summary
Anoxic oxidation of rocks

Type of rocks interacting with water	Minerals formed at 25°C	Minerals formed at 350°-250°C geobiotropic
Ferromagnesian silicate	1. Fe(II)-phyllosilicates A little Fe_3O_4	2. Fe(III)-phyllosilicates 350°C $Fe(OH)_3$, $FeO(OH)$, Fe_2O_3 Fe_3O_4 (traces), FeMg-carbonates
Iron(II) monosulfide	3. FeS_2	4. Fe_3O_4 ~100° -250°C

Geological terrain: Rainbow

* **365°C**, low **pH 3-4**, **H$_2$S** (1.3 mM/kg), high **H$_2$** (16 mM/kg)
CH$_4$ (2.5), N$_2$ (1.8), CO (5µM/kg) no SO$_4$, no Mg

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ *(Charlou et al 2002, 2010, Edmonds 2010)*

* Two types of chimneys with FeS or FeS$_2$,
$\qquad$ above layers of sulfides and **Fe$_3$O$_4$** $\qquad\qquad$ *(Marques et al 2006)*

* Strong positive magnetic anomaly, up to 35 A.m^{-1} *(Tivey & Dyment 2010)*

Hydrothermal percolation through iron sulfide rocks: hydrolysis of sulfides
$\quad$ **250°C pH=3.5 to 8**: **FeS** + 4/3H$_2$O → 1/3**Fe$_3$O$_4$** + **H$_2$S** + **1/3H$_2$**

Geological terrain: Mawrth Vallis on Mars

1. 100-200m lower layer : Fe(III)-smectite phyllosilicates and
ferric oxide/hydroxides species
2. 5-10 m intermediate layer : ferrous phase
3. 10-50 m upper layer: Al(III)-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)*

Hydrothermal hydrolysis of silicates
Goethite/hematite, $(Mg^{II},Fe^{II})_3Si_2O_5(OH)_4$ or $(Al^{III},Fe^{III})_2Si_2O_5(OH)_4$

Conclusion

- **Anoxic hydrolysis of ferromagnesian silicates rocks (serpentinization):**

$\rightarrow$ goethite/hematite, FeIII-phyllosilicates   **350°C   pH=11.5 to 14** and **H_2**

- **Anoxic hydrolysis of iron(II) monosulfides rocks:**

        $\rightarrow$ magnetite   **250°C   pH 3.5 to 8** and **H_2**

in an emergent equation?   pH=3.5 to 8:   **FeS + 4/3H_2O $\rightarrow$ 1/3Fe_3O_4 + H_2S + 1/3H_2**

250°C – 500°C : $CO_{2(g)}$+ **$H_{2(g)}$**$\rightarrow$**$CO_{(g)}$** + $H_2O_{(g)}$
                                            $\rightarrow$ **amino acids**

**A link between the world of rocks
and the world of life and astrobiology**

Acknowledgments

Rainbow 36°14N 33°54W
Ashadze, Logatchev, MARK, TAG, Broken Spur,
Lucky Strike (37°18N 32°16W),
Menez Gwen (37°50N, 31°30W, 280°C, pH4.2, H_2S<1.5)

H_2S (1.3 Rainbow) (8.5 to 11 at Broken Spur)

(Sao Miguel 37°50N   25°30W)

	Rainbow	Lucky Strike	Menez Gwen				(Charlou 2010, Seyfried 2015)
	ultramafic	volcanic	volcanic				
	36°14N	37°17	37°50				
T	365/360	170/364	275/284				
pH	2.8/3.0	3.5/3.7	4.2/4.3				
depth,m	2300	1700	850				
SO4 mM/kg	0		0	0			
H2S mM/kg	1.2/1.4	2.5/3.0	<1.5				
CH4 mM/kg	2.5/1.6		1.35/2.63				

	Ashadze1	Ashadze2	Logatchev2	Logatchev1	MARK1/2	TAG	Broken Spur	*Lost City*
	ultramafic	ultramafic	ultramafic	ultramafic	volcanic	volcanic	ultramafic	
	12°58'N	12°59'N	14°43'N	14°45'N	23°N	26°N	29°N	30°07'N
T	355	296	320	346/352	335/350	321/290	356/364	*94*
pH	3.1	4.1	4.2	3.3/3.9	3.9/3.7	3.1		*12.1*
Depth,m	4088	3263	2700	3000	3460	3670	3200/3400	*780*
SO4 mM/kg	0	0	0	0	0	0	0	1-6
H2S mM/kg	1	--	1.9	1.1/1.4	5.9	6.7	8.5/11.0	0-0.22 (Seyfried 2015)
CH4 mM/kg				2/2.6				1.11-1.36

Lost City: rocks highly serpentinized, chimneys in carbonates; water no sc (374°C, 22MPa)
hydrolysis of silicates, high pH.   H2S may come from some sulfide hydrolysis ; SO4 a radionuclide : U

Laboratory syntheses of macromolecules containing amino acids

- *1983, J Mol Evol : Gordon Schlesinger and Stanley Miller :*
$$\text{Figure 2 indicates :}$$
$$H_2 / CO_2 = 0 \quad \text{yield of amino acids} = \text{c.a. } 0.0008 \%$$
$$H_2 / CO = 0 \quad \text{yield of amino acids} = \text{c.a. } 0.04 \%$$

- *1990, OLEB : Kensei Kobayashi et al*
$$(CO + N_2 + H_2O)_g + \text{protons, He ions, e}^-, \text{ soft X-rays, } \gamma \text{ rays,}$$
$$\rightarrow \text{macromolecules} \rightarrow \textbf{amino acids} \quad (\text{UV requires } NH_3)$$
$$\textbf{CO not CO}_2$$

Laboratory production of CO

1. $CO_{2(g)} + H_{2(g)} \rightarrow CO_{(g)} + H_2O_{(g)}$ P_{atm}, H_2 flow - **500°C** / 5h

   (Chen et al 2000)

2. $CO_{2\ \textbf{hydroth (dis)}} + 4\ H_{2(dis)} \rightarrow CO_{(dis)} + CH_{4(dis)} + 2\ H_2O_{(sc)}$

   390°C   **400 bars**   *(Foustoukos & Seyfried 2004)*

   250°C-300°C   **250 bars**   **(***Fu & Seyfried 2009)*

   CO is produced through high-T hydrogenation of CO_2

   Question: Where H_2 is produced in hydrothermal conditions?

   $CO_{(g)} + H_{2(g)} \rightarrow CH_{4(g)} + hydrocarbons_{(g)}$ *(FTT, Anderson 1984)*

Fe(III)-phyllosilicates

Hydrothermal H$_2$, CO, amino-acids ?

Al(III)-phyllosilicates

Mawrth Vallis

Upon (Loizeau et al 2010)

10 km

Hypothesis

Lower layer: anoxic hydrolysis and carbonation of olivine and pyroxene
Hydrothermal H_2 release

Upper layer: $(Al^{III}, Fe^{III})_2 Si_2 O_5 (OH)_4$? proof of the hydrolysis of Mg-silicates
$(Al^{III}, Fe^{III})_2 Si_4 O_{10} (OH)_2$? proof of the dehydration of Mg-silicates
anoxic hydrolysis and carbonation of olivine and pyroxene,
Hydrothermal H_2 release
protected by the observed caprock
sulfate: oxic oxidation in radiolyzed water of FeS

Prebiotic synthesis:
350 torr CO, 350 torr N_2 and liquid water producing 20 torr
Cosmic radiation or radionuclides

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

*Lost City→94°C, rocks highly serpentinized, chimneys in carbonates
pH9-11,[H2]↑15mmol/kg, *(Kelley Sci.307, 2005, Proskurowski Sci. 319, 2008)*

calcium carbonate aragonite-brucite chimneys, 90°C, pH 9-12, *(Kelley et al 2005, Charlou et al 2010, Seyfried et al 2015)*

* Rainbow 365°C, 235 bar   pH=2.8   [H_2]=16 mmol/kg
(Charlou...2002)
Since FeS produces Fe_3O_4 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:
$$Fe_{24}S_{32}(s) + H_2O(l) \rightarrow Fe_{24}S_{31}O(s) + H_2S(aq)$$
Replacement of S (forming H_2S) by O (from H_2O)
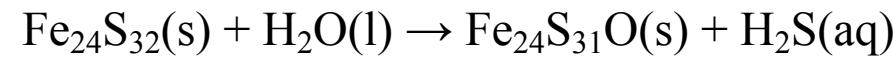
2. Conversion of natural goethite studied by differential scanning calorimetry
goethite converts to hematite from 260 to 685°C.
trace amounts of magnetite at 400 to 685°C;
FeII is proposed to arise from traces of organic matter or clay minerals
(Dekkers 1990)
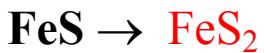
FeS → FeS$_2$
-     Troilite & pyrrhotite oxidized by distilled, deionized water, sonicated

→ 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 SiO$_2$ are those of quartz.

Entropy values are calculated considering $S^0(H_2)=130.45$ J.K^{-1}.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.