Surface conditions from thermodynamics of phyllosilicates and implications for the presence of methane on early Mars

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Background and Objectives

- Several phases identified in Nili Fossae:
  - Smectites (nontronite, Mg-smectite, Poulet et al., 2005)
  - Carbonates (magnesite, Ehlmann *et al., 2008, Science*)
  - Chlorite
  - Serpentine (Ehlmann *et al.*, 2009, JGR)
  - Olivine
- Decipher complex geochemistry
- Special focus on temperature and CO_2
  - Implications for early atmosphere and methane

Fluid composition (Catling, 1999)

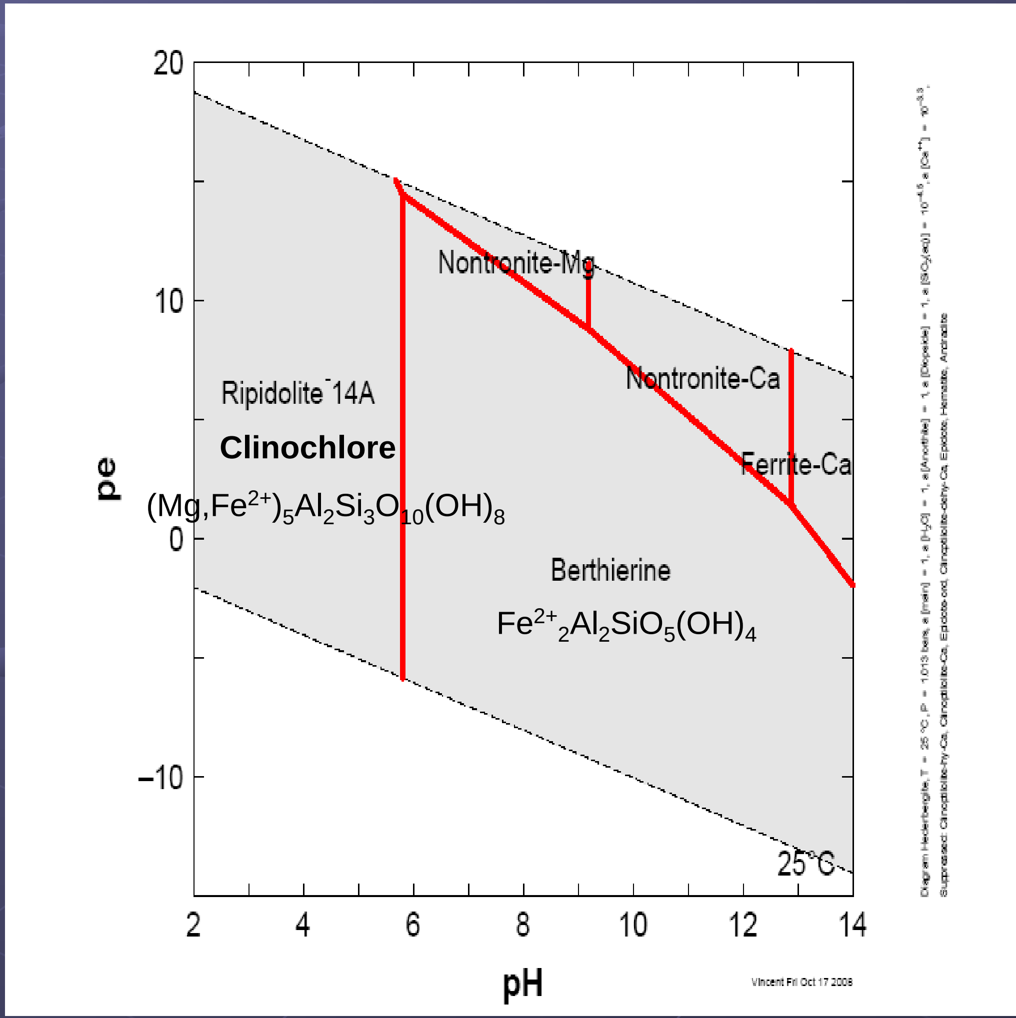
Specie	Conc. (mg L^{-1})	Log (activity)
SiO_2	60.1	-4.5
Al^{3+}	1	-4.4
$Fe^{2+/3+}$	44.7	-3.1
Mg^{2+}	24.3	-3.0
Ca^{2+}	20	-3.3
Na^{+}	18.4	-3.1
K^{+}	2.7	-4.2
Cl^{-}	23	-3.2
SO_4^{2-}	17.3	-3.7

Thermodynamic simulations

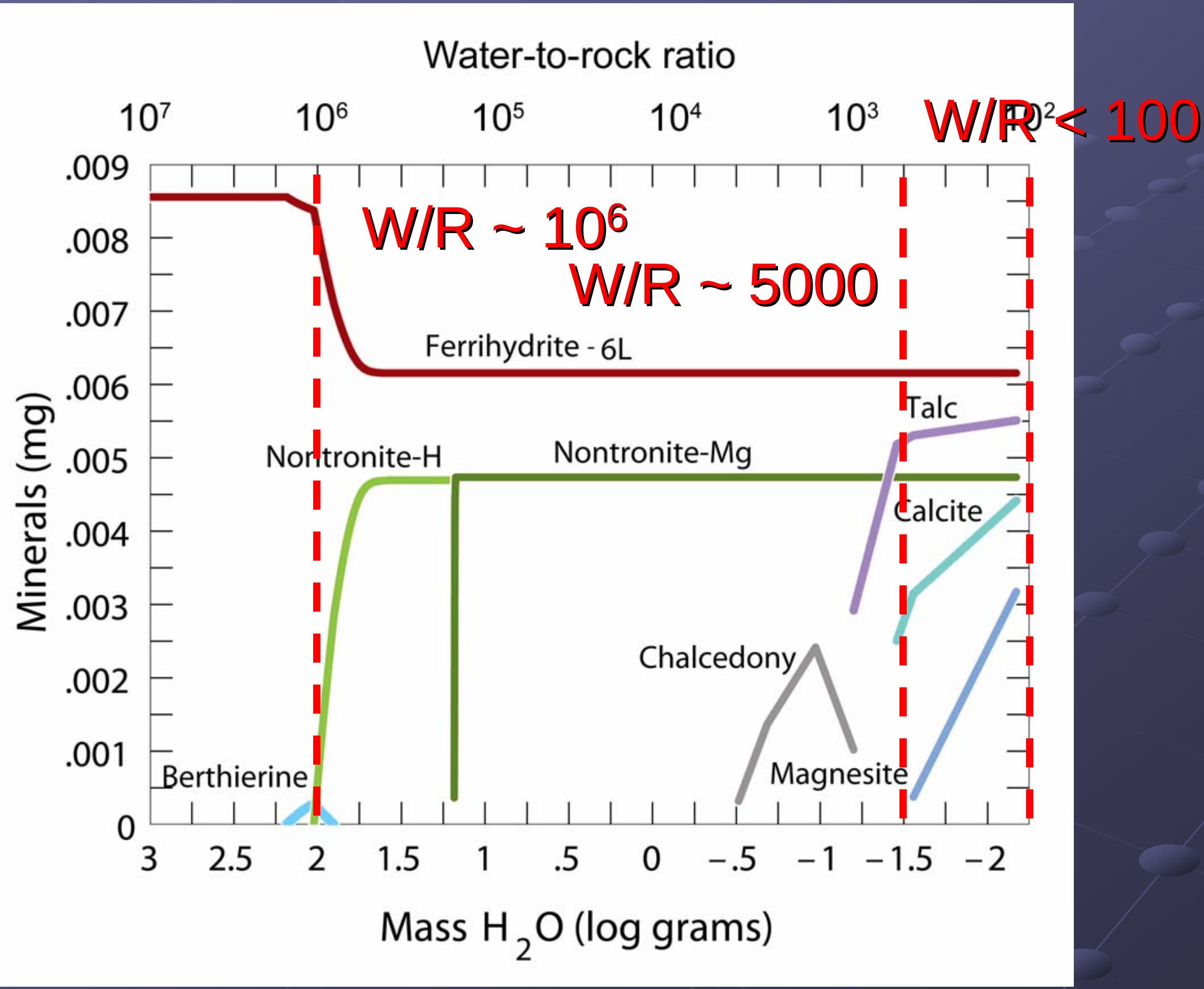
- Geochemical workbench software package
- *thermo.com.v8.r6*+ basic database
- Contains approx. 300 relevant silicate phases
- Ions and water activities calculated using the Debye-Huckel model
- Back reactions allowed
- Charge balance
  - H^+ in evaporation simulation
  - Cl^- in temperature simulations

Nontronite

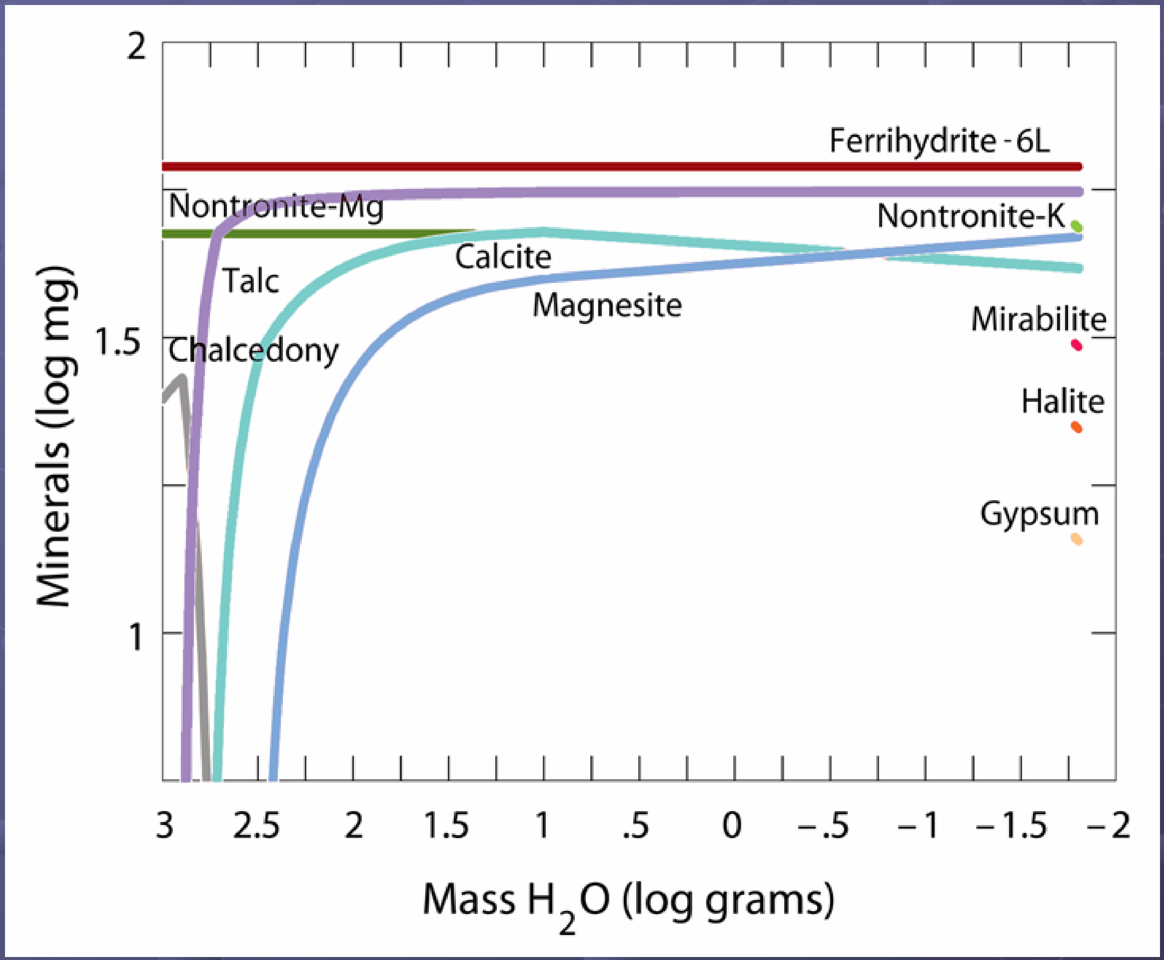
- Primary phases
  - Hedenbergite = Fe^{2+}
  - Diopside = Mg^{2+}
  - Anorthite = Al^{3+}
- Nontronite: 6 < pH < 12 (*Chevrier et al., 2007, Nature*)
- Formation of clinochlore at low pH



Concentrations divided by 10^4

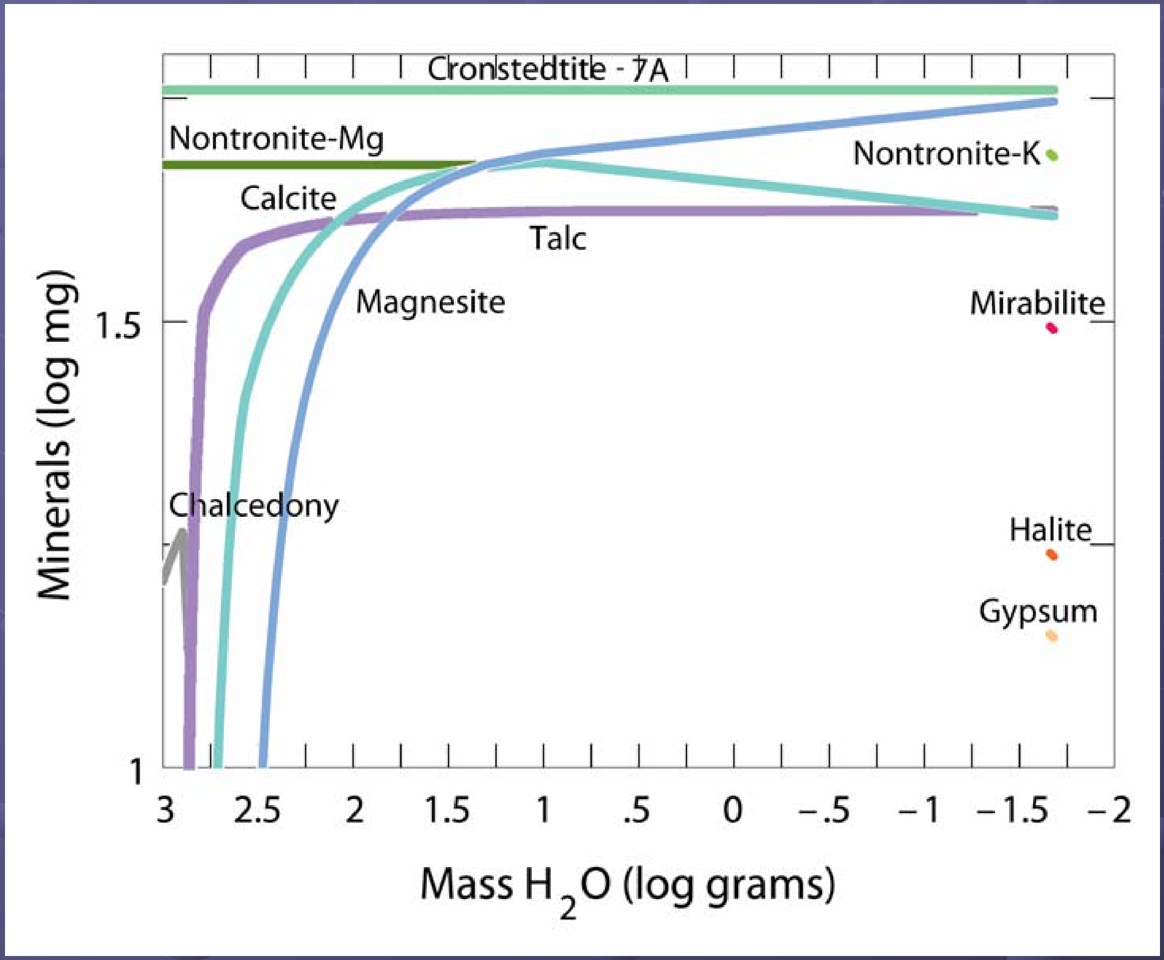


Evaporation simulations Low p_{CO2} – Oxidizing cond.



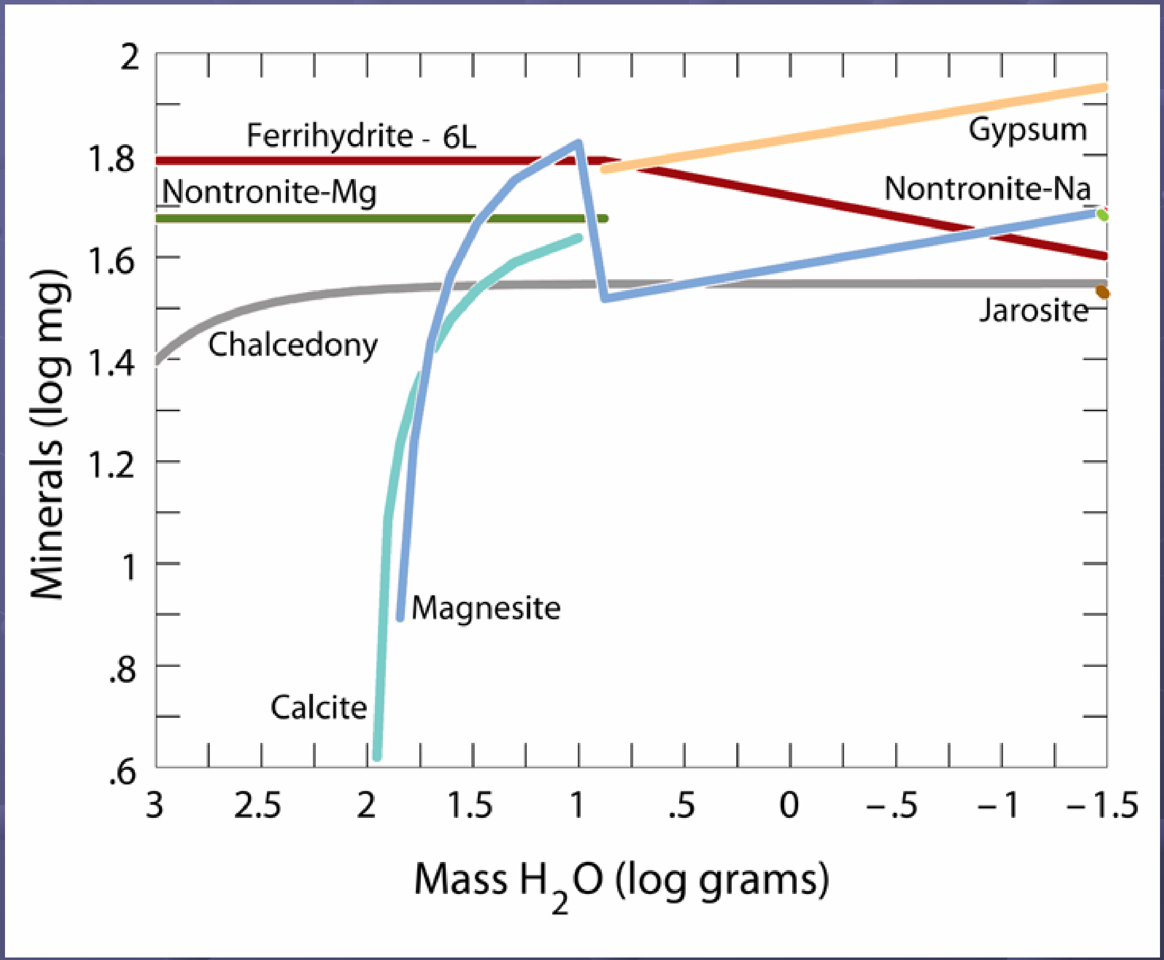
- p_{CO2} = 6 mbar
- pH ~ 6-7
- pe = 13.05 (Fe^{2+}/Fe^{3+})

Evaporation simulations Low p_{CO2} – Reducing cond.



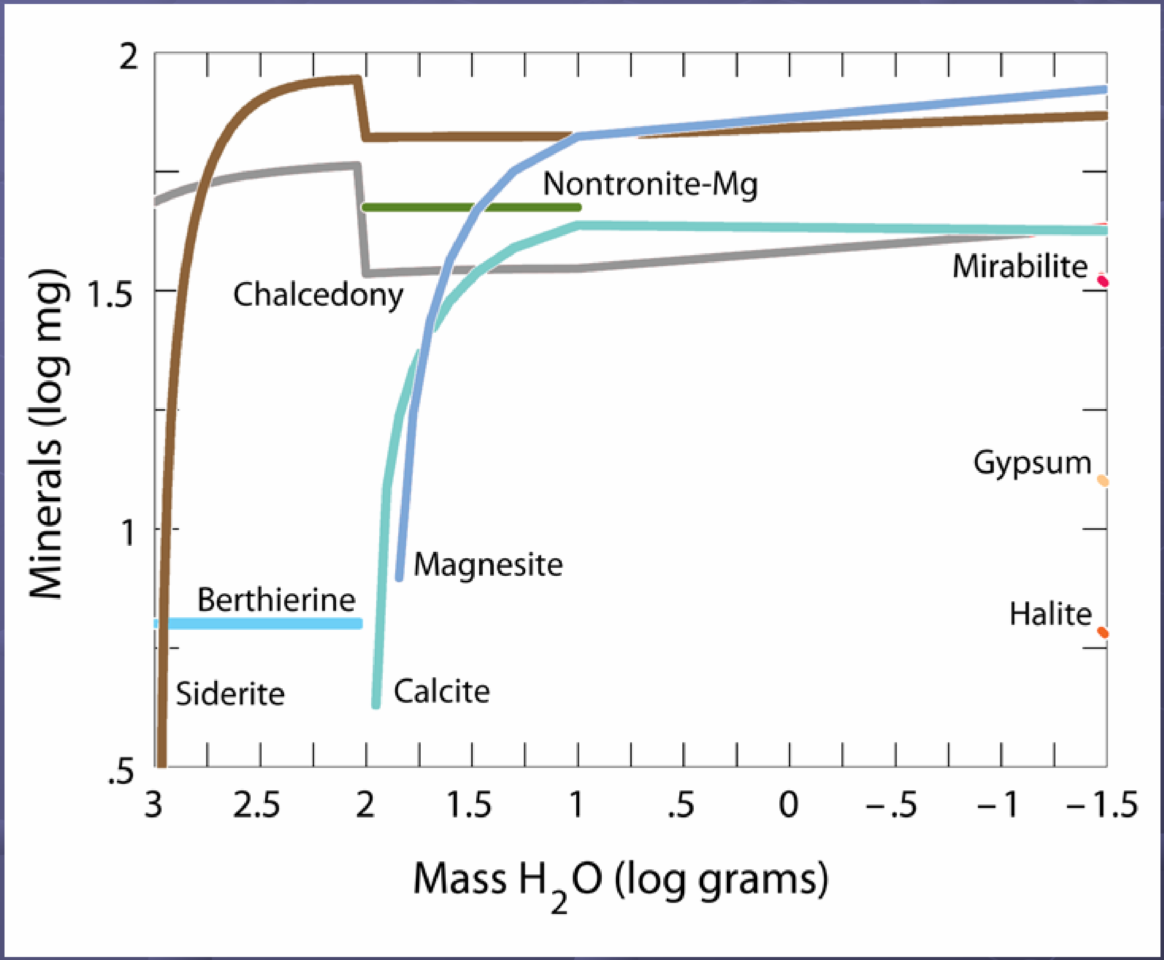
- p_{CO2} = 6 mbar
- pH ~ 6-7
- pe = 0

Evaporation simulations High p_{CO2} – Oxidizing cond.



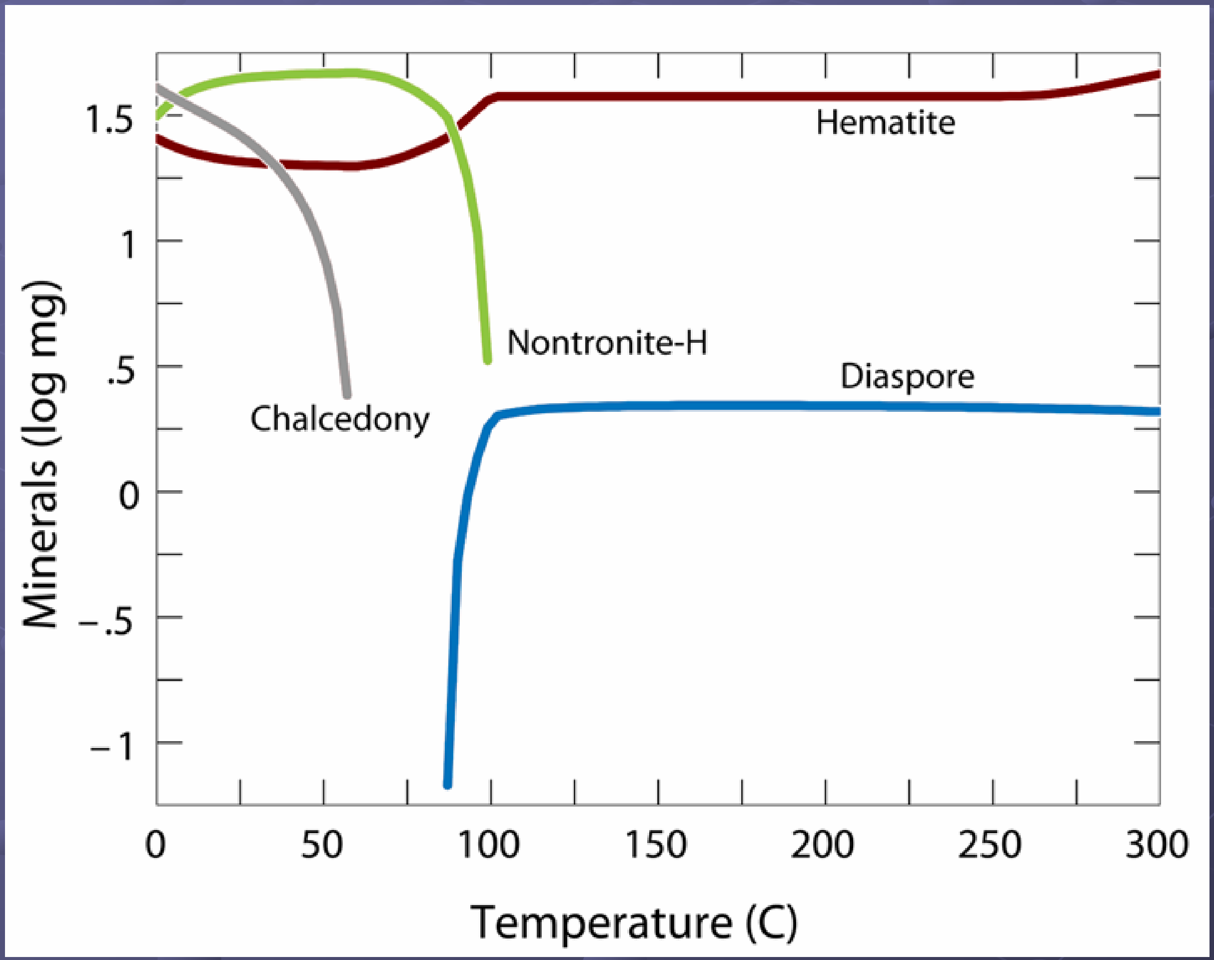
- p_{CO2} = 1 bar
- pH ~ 6-7
- pe = 13.05 (Fe^{2+}/Fe^{3+})

Evaporation simulations High p_{CO2} – Reducing cond.



- p_{CO2} = 1 bar
- pH ~ 6-7
- pe = 0

Temperature effect: Low p_{CO2} – Oxidizing cond.



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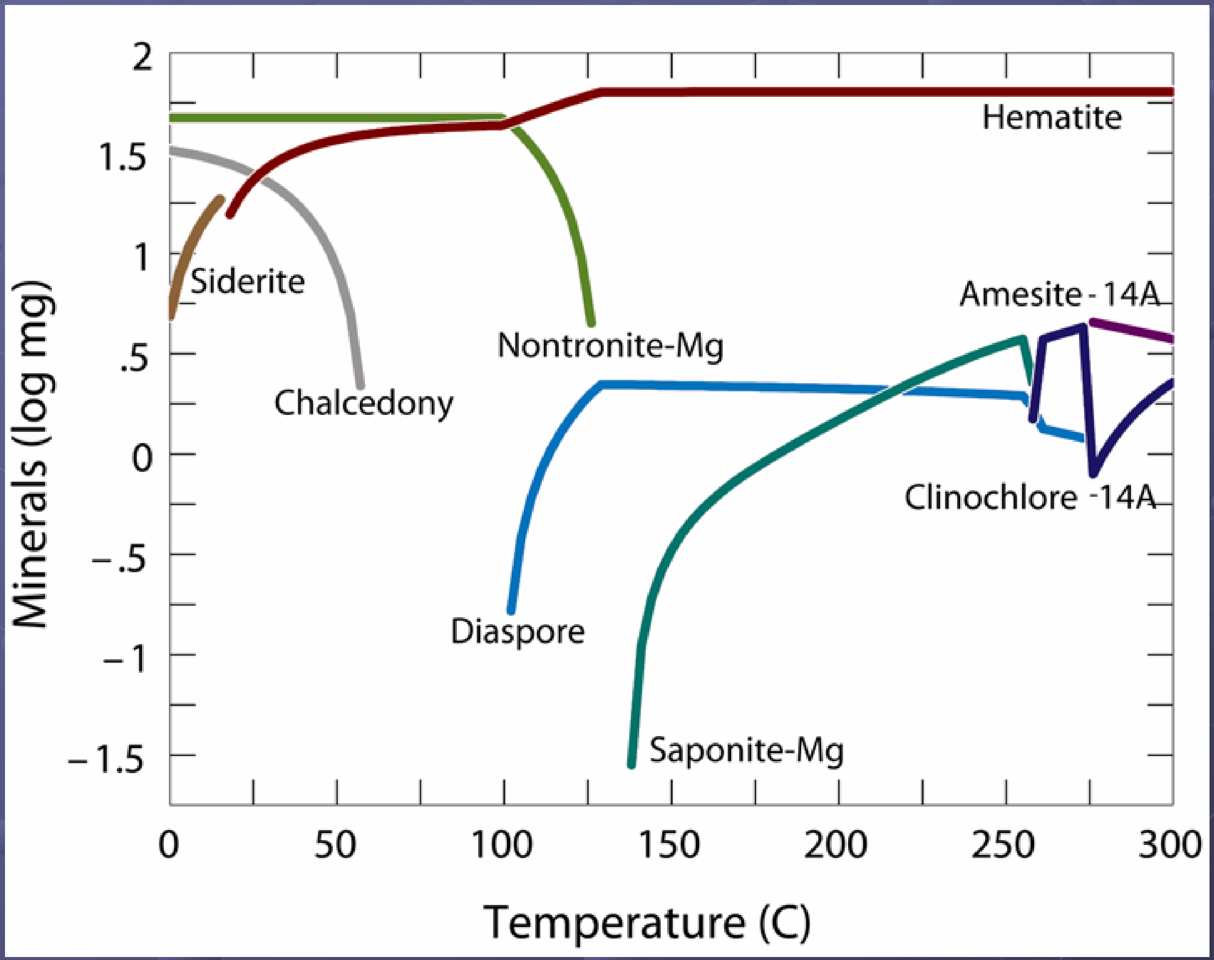

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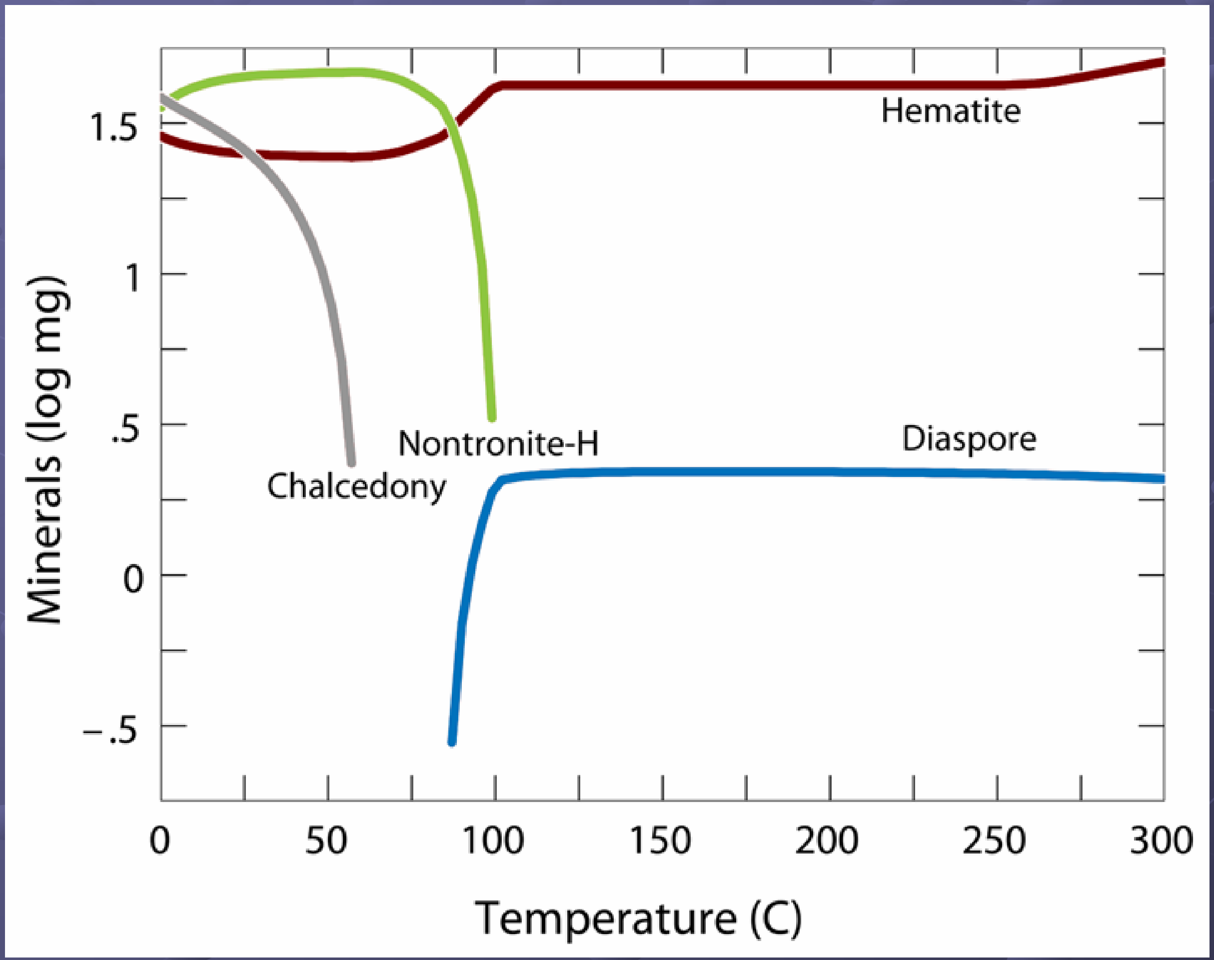

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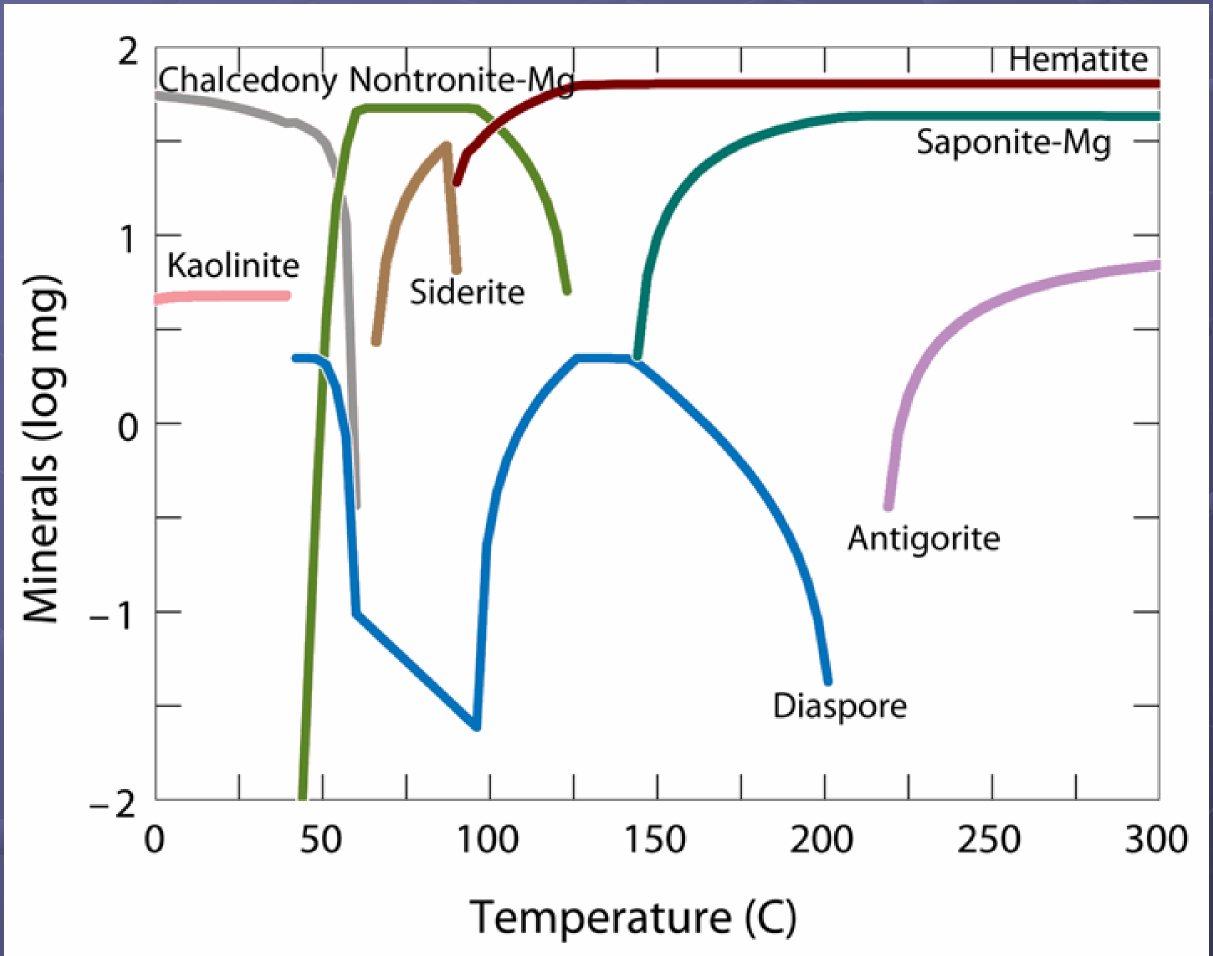
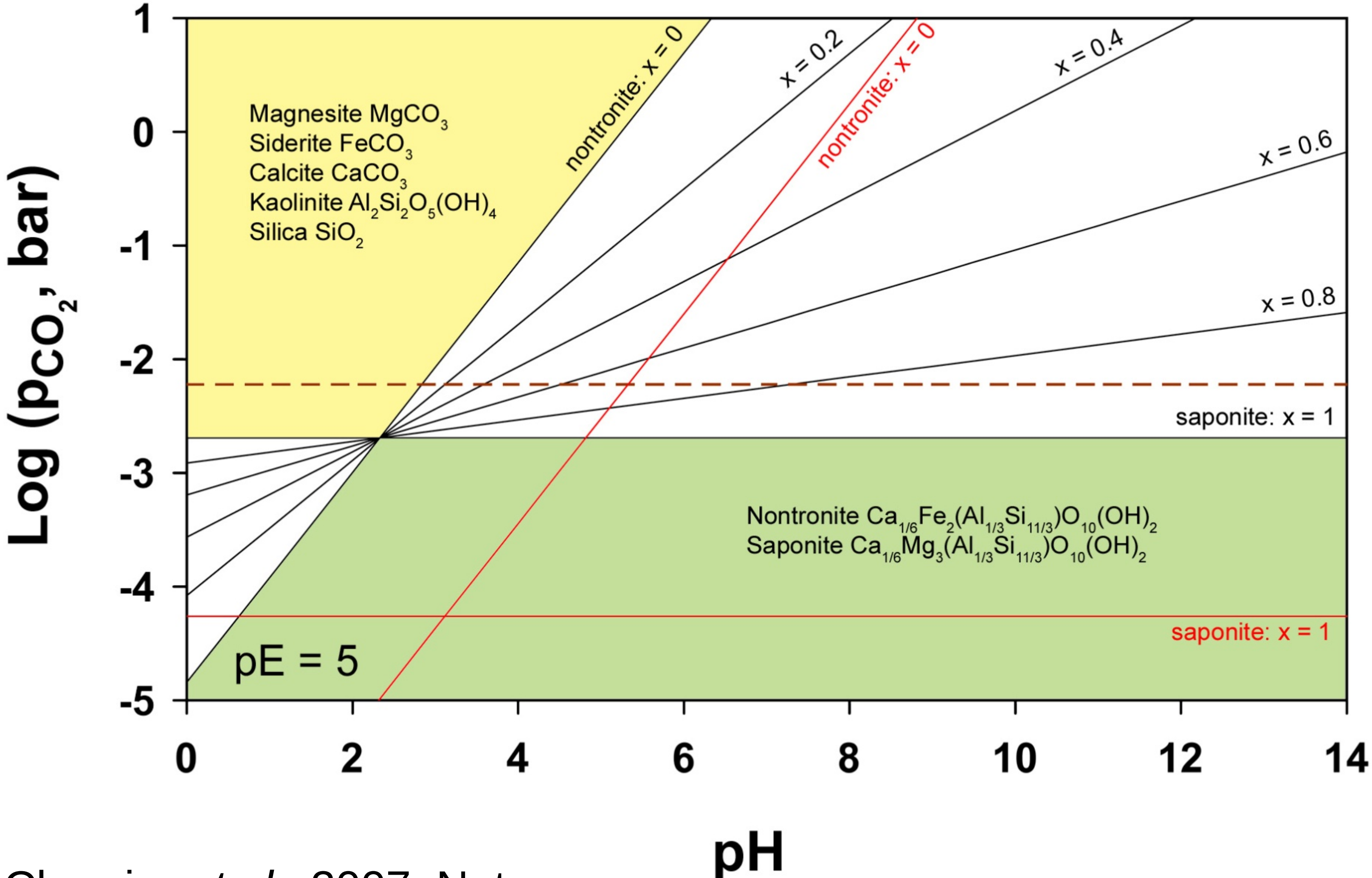


- p_{CO2} = 1 bar
- pe = 0

- Nontronite
  - Weathering conditions in the presence of (very) abundant water
  - Typical surface mineral (low T)
  - Indicate oxidizing conditions
- Magnesite
  - Lower water-to-rock ratio: Evolution of solutions
  - No requirement for high p_{CO2}
- Serpentine
  - Relatively high temperature
  - Presence of hematite
  - Probable more magnesian solutions (olivine)
  - “Quite” incompatible with magnesite

Early atmosphere



Chevrier *et al.*, 2007, Nature

Serpentinization reactions

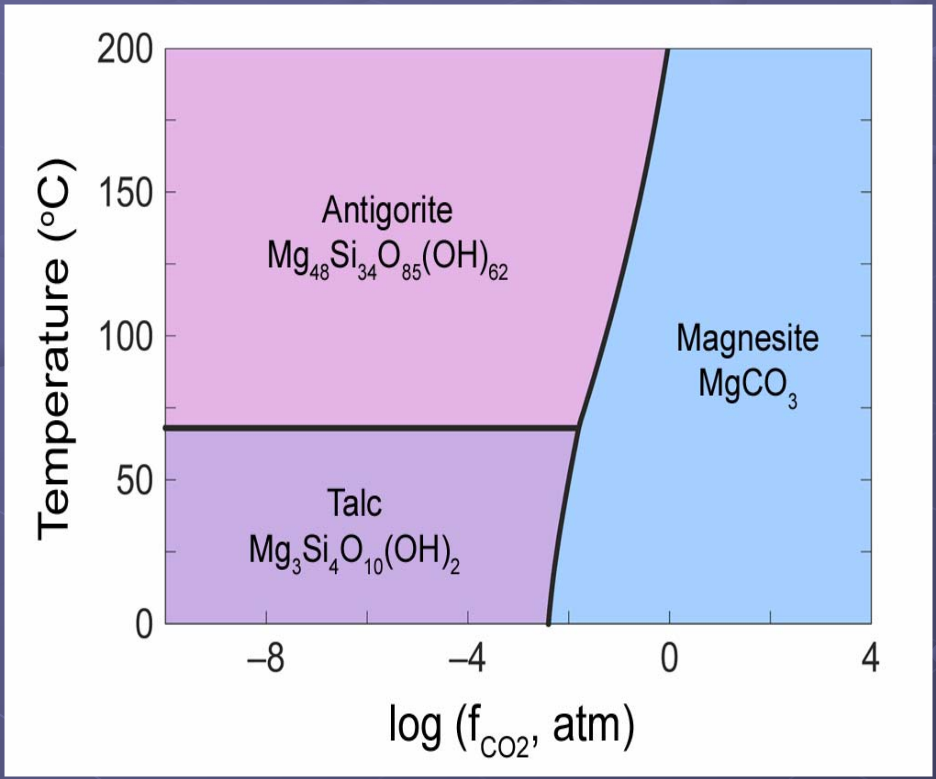
	Reactions
R1	$3Fe_2SiO_4 + 2H_2O = 3SiO_{2[quartz]} + 2Fe_3O_4 + 2H_{2(aq)}$
R2	$3Fe_2SiO_4 + 2H_2O = 3SiO_{2[Amorph\text{-}Silica]} + 2Fe_3O_4 + 2H_{2(aq)}$
R3	$3Fe_2SiO_4 + 2H_2O = 3SiO_{2(aq)} + 2Fe_3O_4 + 2H_{2(aq)}$
R4	$6Fe_2SiO_4 + 7H_2O = 3Fe_3Si_2O_5(OH)_4{}^a + Fe_3O_4 + H_{2(aq)}$
R5	$2Mg_2SiO_4 + 3H_2O = Mg(OH)_2 + Mg_3Si_2O_5(OH)_4$
R6	$6Fe_2SiO_4 + CO_{2(aq)} + 2H_2O = 6SiO_{2[Quartz]} + 4Fe_3O_4 + CH_4$
R7	$24Fe_2SiO_4 + 26H_2O + CO_{2(aq)} = 12Fe_3Si_2O_5(OH)_4{}^a + 4Fe_3O_4 + CH_4$
R8	$3FeSiO_3 + H_2O = Fe_3O_4 + H_{2(aq)} + 3SiO_{2(aq)}$
R9	$3FeSiO_3 + H_2O = Fe_3O_4 + H_{2(aq)} + 3SiO_{2[Amorph\text{-}Silica]}$
R10	$12FeSiO_3 + 2H_2O + CO_{2(aq)} = 4Fe_3O_4 + CH_4 + 12SiO_{2(aq)}$
R11	$12FeSiO_3 + 2H_2O + CO_{2(aq)} = 4Fe_3O_4 + CH_4 + 12SiO_{2[Amorph\text{-}Silica]}$
R12	$4H_2 + CO_2 = CH_4 + 2H_2O$
R13	$H_2 + SO_2 = H_2S + O_2$

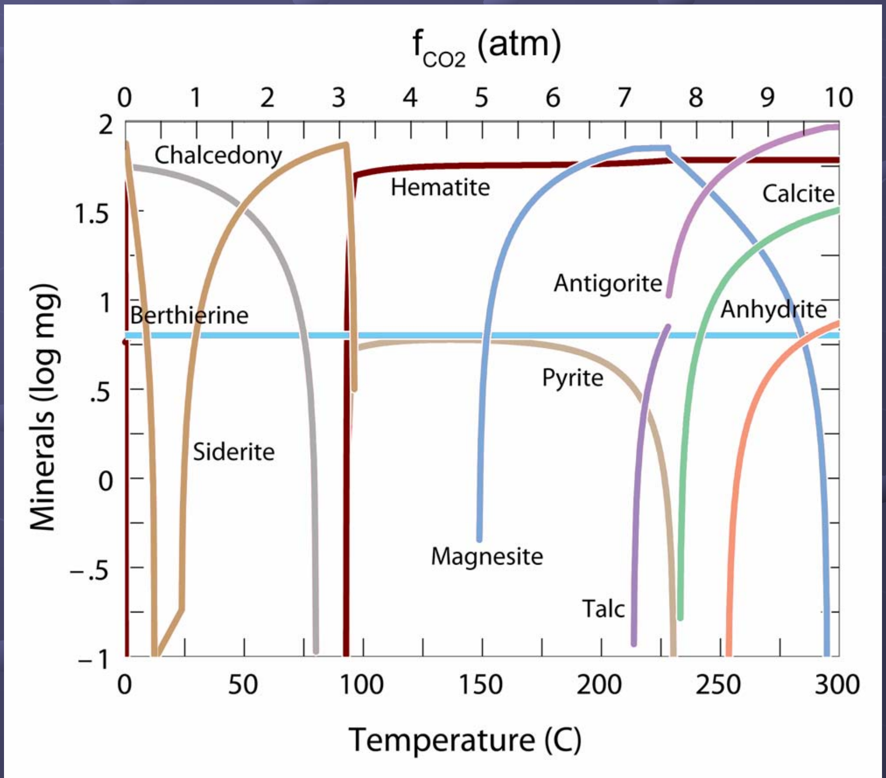
Oze and Sharma, 2005, GRL

Carbonation of Mg-silicates

$2\ Mg_3Si_2O_5(OH)_4 + 3\ CO_2 \Leftrightarrow Mg_3Si_4O_{10}(OH)_2 + 3\ MgCO_3 + 3\ H_2O$

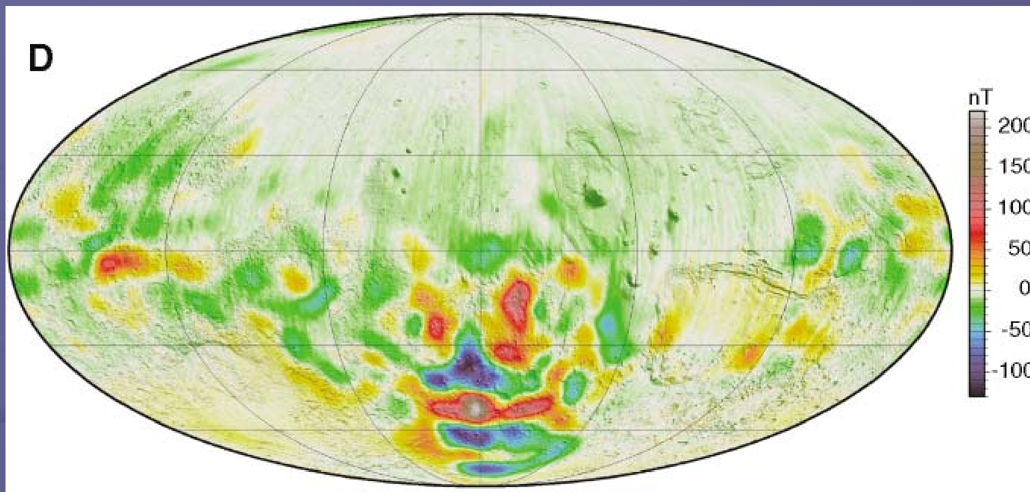
Serpentine + CO_2 ⇔ Talc + Magnesite + H_2O





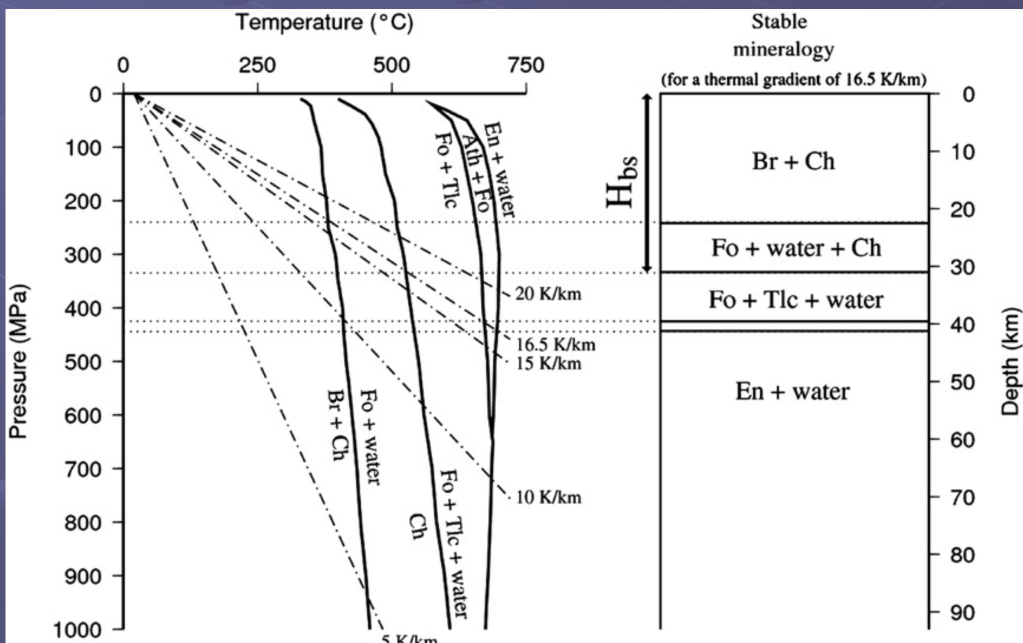
Siderite ($FeCO_3$ only) at low-T (<100°C)

Serpentinization on early Mars



Solomon *et al.*, 2005, Nature

- Early Mars (high thermal gradient)
- Formation of magnetite
  - Magnetization of early crust
- Formation of methane



Quesnel *et al.*, 2009, EPSL

Conclusions

Olivine $(Mg_{0.8}Fe_{0.2})_2SiO_4$ (ALH84001)

Mg pole

- Serpentine
- With CO_2
  - Magnesite
  - Talc (?)
- Observations from OMEGA and CRISM

Fe pole

- Oxidation by water
  - Formation of Fe^{3+}
  - Formation of H_2
  - Magnetite
- With CO_2
  - Methane
- Methane and magnetization

Conclusions (2)

- Serpentinization explains a lot of observations from magnetization to methane, i.e. deep crust to atmosphere in *the same region*
- Methane is actually the very last of the chain of serpentinization reactions
  - Serpentinization produces H_2
  - Methane could result from early life (methanogens)
- Problem: how do you transit from 3.8-4 byr to today
  - Process still active (hydrothermalism, deep life)
  - Passive process: buffer effect by deep clathrates (Chastain and Chevrier, 2006, PSS)