La Géobiotropie

ou l'eau dans l'état en dessous du point critique pour la formation des minéraux de fer ferrique et des molecules de la vie

extraits des articles :
Bassez MP, Orig Life Evol Biosph 47:453-480 (2017)
Bassez MP, Orig Life Evol Biosph (accès libre et en ligne le 8 August 2018)
Bassez MP, en preparation (2018)

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Rencontres de la Société Française d'Exobiologie, St Michel l'Observatoire, 15-18 Oct 2018

Four processes all occuring in high-subcritical water, hscw lead to the formation of ferric minerals and molecules of life

critical point of water: Tc=374°C, Pc=22.1MPa

hsc water: **300°-350°C, 10-25 MPa,**

pH ~9.5-14

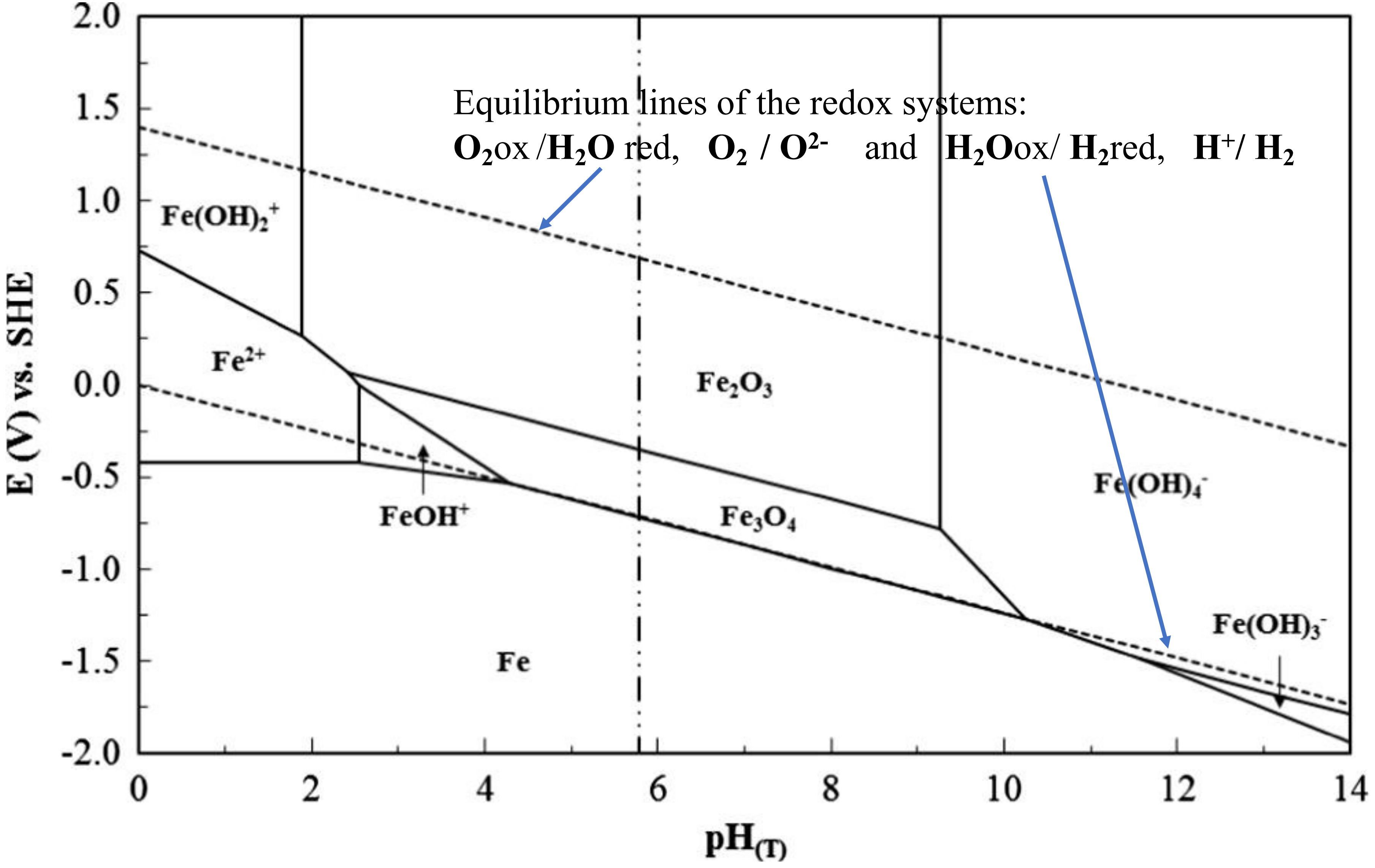
1. **Oxidation of Fe^{II}** into **Fe^{III}**
   concomitant to reduction of the H^+ of water to **produce H_2**

2. High **Solubility** of SiO_2, **quartz & amorphous silica**

3. **Interaction** between **Fe^{II}-silicates** and hscw undersaturated in silica
   for production of Fe^{III}-oxides & Fe^{III}-silicates (Banded Iron Formations) and H_2

4. **Hydrogenation** of **CO_2** by H_2 in hscw, to produce CO

1. Oxidation of Fe^{II} in anoxic conditions, at high pH, at 350°C, 25MPa



$Fe^{II}(OH)_3^- + H_2O_{hsc} \rightarrow Fe^{III}(OH)_4^- + ½ H_2$

Fig. Pourbaix diagram for iron and water at 350°C, 25 MPa, 10^{-6} mol/kg

Credit: ***William G. Cook & Robert P. Olive 2012****, with permission*
Pourbaix diagrams for the iron-water system extended to high & low-supercritical conditions. Corrosion Science 55: 326-331.

2. High Solubility of SiO_2 in high-subcritical water

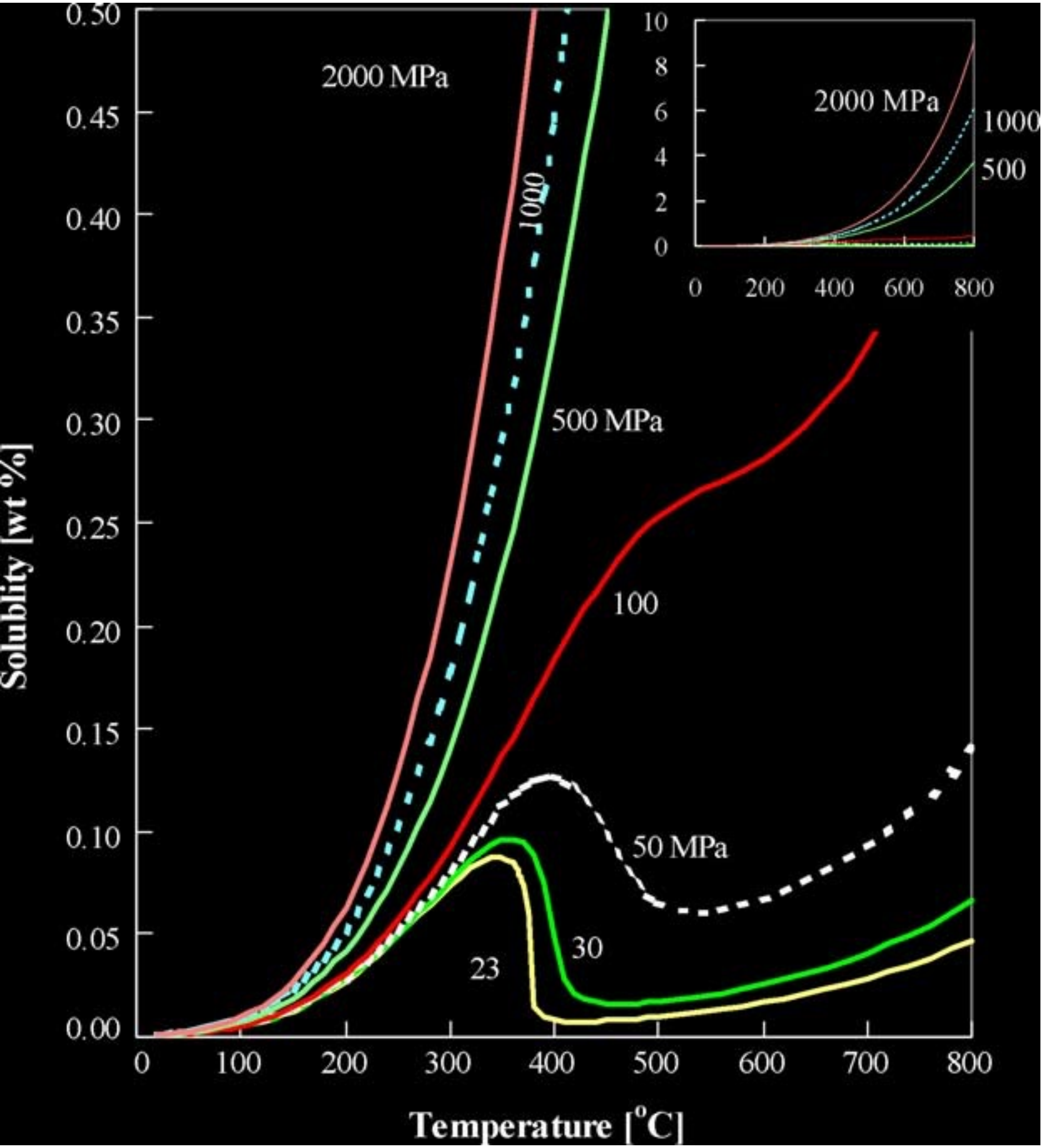


Fig. Solubility of quartz (SiO_2) as a function of T&P

Credit: ***Richard L. Smith Jr. & Zhen Fang (2011)*** *Properties and phase equilibria of fluid mixtures as the basis for developing green chemical processes.* Fluid Phase Equilibria 302: 65-73.

The solubility of quartz, SiO_2, in water is calculated up to 800°C and 2000 MPa.

« At a constant pressure of ***23 MPa****, the SiO_2 solubility increases to a value of 0.087 wt% at* ***350°C*** *and drastically decreases to 0.0081 wt% at 450°C »*

Everett Shock, Harold Helgeson, Dimitri Sverjensky (1989) *Geochim Cosmochim Acta* 53:2157-2183

Solubility of quartz: ***Kennedy (1950)***

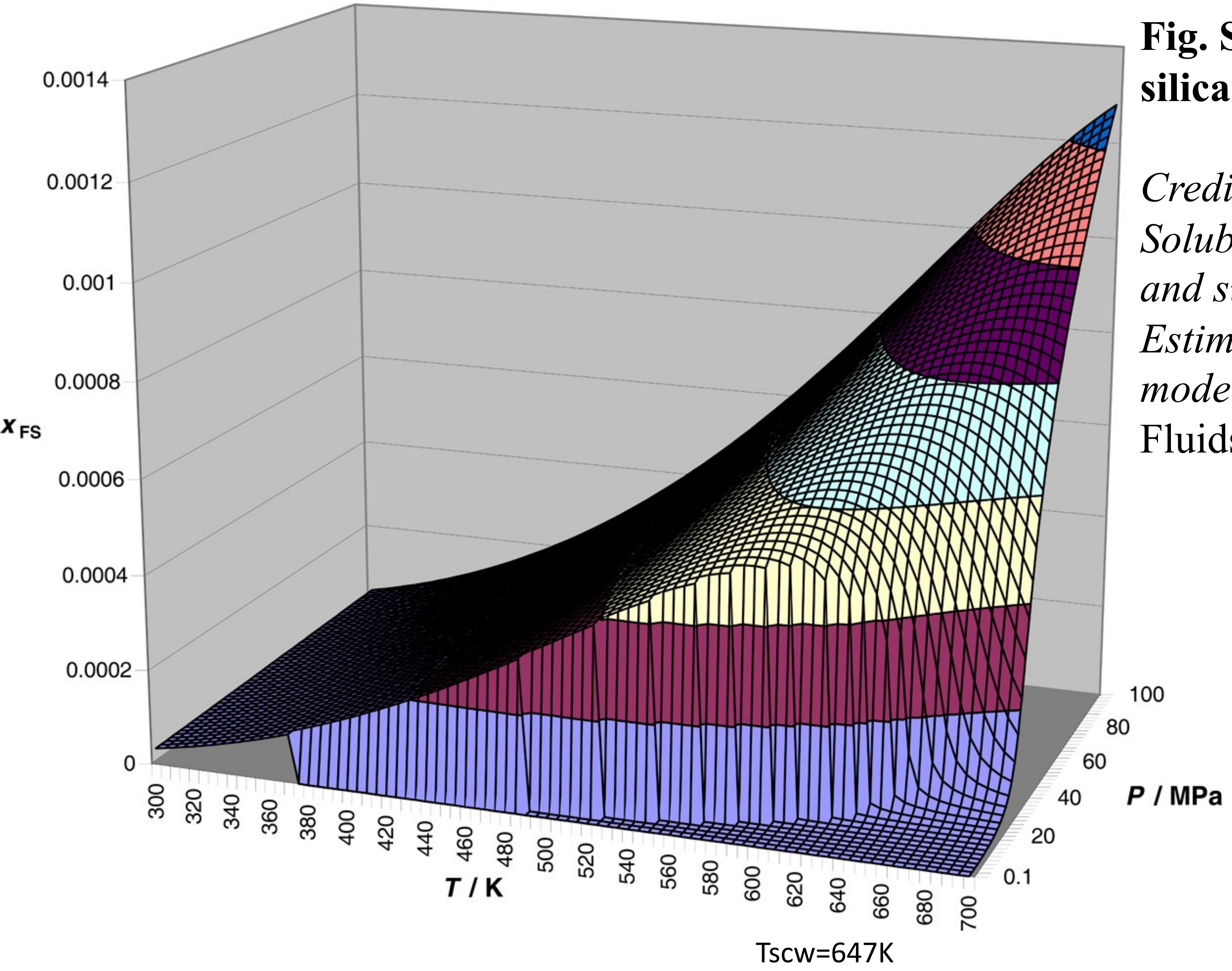


Fig. Solubility of amorphous silica as a function of T&P

Credit: ***Karasek*** *et al.* ***(2013)*** *Solubility of fused silica in sub- and supercritical water: Estimation from a thermodynamic model.* The J. of Supercritical Fluids 83: 72-77 *with permission*

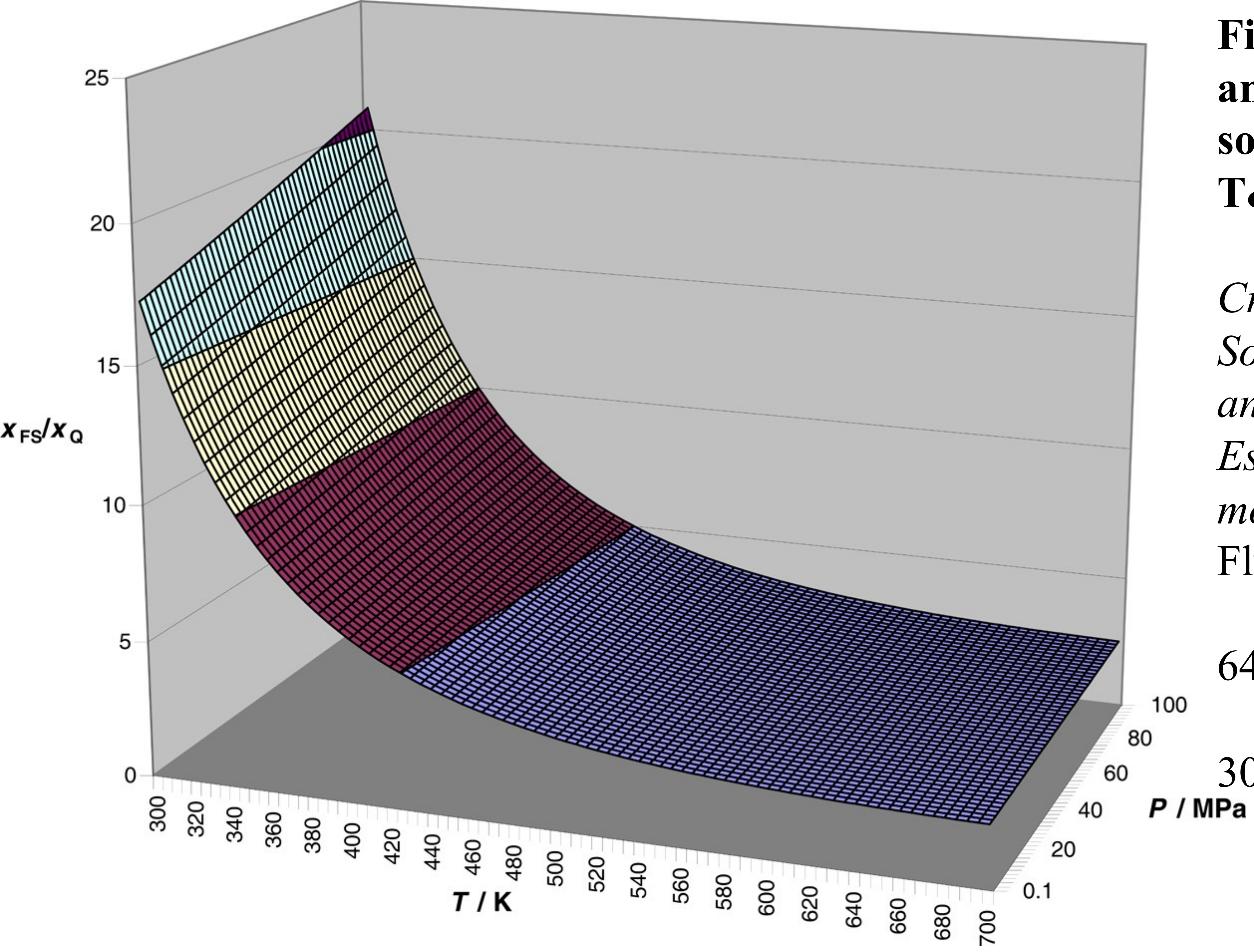


Fig. Ratio of the solubility of amorphous silica to the solubility of quartz at the same T&P

Credit: ***Karasek*** *et al.* ***(2013)*** *Solubility of fused silica in sub- and supercritical water: Estimation from a thermodynamic model.* The J. of Supercritical Fluids 83: 72-77 *with permission*

647K (374°C) & 22.1 MPa:
ratio= ca 2

300K(27°C) & 0.1 Mpa (1atm)
ratio= ca 17

3. Interaction between Fe^{II}-silicates with alkaline high-subcritical water for the production of Fe^{III}-oxides, Fe^{III}-silicates and H_2

Formation of ferric oxides

*** Dissolution of fayalite and formation of the ferric trihydroxide anion:**

$$Fe^{II}{}_2SiO_{4(s)} + H_2O_{high\text{-}subcritical} + OH^- \rightarrow Fe^{2+}{}_{(diss)} + SiO_{2(quartz,\ diss\ in\ hscw)} + SiO_{2(amorph,\ diss\ in\ hscw)}$$

$$\rightarrow Fe^{III}(OH)_4{}^-{}_{(diss)}\ (= Fe^{III}O(OH)H_2O\ OH^-) + H_{2(g\ diss\ in\ hscw)}$$

*** Dehydration of ferric trihydroxide into the ferric oxide hydroxides goethite & lepidocrocite**

$$Fe^{III}O(OH)H_2O_{(s)} \rightarrow Fe^{III}O(OH)_{(s)} + H_2O$$

*** Dehydration of the ferric oxide hydroxides into hematite, with possibly ferrihydrite Fe_5HO_8-$4H_2O$ as intermediate:** $2Fe^{III}O(OH)_{(s)} \rightarrow Fe^{III}{}_2O_{3(s)} + H_2O$

Formation of ferric silicates

Hydrolysis of fayalite to form Fe^{III}-greenalite

* $Fe^{2+}_{(diss)} + SiO_{2(diss)} + H_2O_{(anoxic,\ 25°C)} \rightarrow Fe^{II}$-silica gel $\rightarrow$ greenalite *Tosca et al (2016)*

In hscw:

$Fe^{2+}_{(diss)} + Fe^{3+}_{(diss)} + H_2O_{(hsc)} + SiO_{2(diss)} \rightarrow Fe^{II},Fe^{III}$-silica gel $\rightarrow$ **$(Fe^{II}_3, Fe^{III}_2)\ Si_2O_5(OH)_{4(am)}$**

Fe^{III}-greenalite

* The iron analog of the serpentine chrysotile is: **greenalite: $Fe^{II}_3Si_2O_5(OH)_{4(s)}$**

$$2Mg_2SiO_{4(s)} + 3H_2O \rightarrow Mg_3Si_2O_5(OH)_{4(s)} + Mg(OH)_{2(s)}$$

forsterite chrysotile

$$Mg_3Si_2O_5(OH)_{4(s)} + 2SiO_{2(diss)} \rightarrow Mg_3Si_4O_{10}(OH)_2 + H_2O$$

talc

* **Dehydration of Fe^{III}-greenalite into Fe^{III}-minnesotaite in a sol. supersaturated in silica**

$(Fe^{II}_3, Fe^{III}_2)\ Si_2O_5(OH)_{4(am)} + 2SiO_{2(diss)} \rightarrow$ **$(Fe^{II}_3, Fe^{III}_2)\ Si_4O_{10}(OH)_2$** $+ H_2O_{(hsc)}$

Fe^{III}-minnesotaite

4. Hydrogenation of CO_2 by H_2 in hscw for production of CO

$CO_{2(diss)} + H_{2(diss)} \rightarrow CO_{(diss)} + CH_{4(diss)}$ 250°C-300°C, 25 MPa *Fu & Seyfried (2009)*

$H_{2(g)}$ is injected in seawater containing dissolved CO_2 and Fe_3O_4 as catalyst

Prebiotic Chemistry

- $CO + H_2 + N_2 \rightarrow$ CH_3NH_2 $CH_3C{\equiv}N$ $CH_3N{=}CH_2$ **300°C** *(Hill & Nuth 2003)*
  precursors of amino acids
- $CO + H_2 + NH_3 \rightarrow$ amino acids **374°C** *Pizzarello (2012)*
- $CO + H_2O + N_2 \rightarrow$ amino acids, organic functions excitation by protons, gamma rays...
  Kobayashi (1989)…Bassez et al. (2012)

Geobiotropy inside fluid inclusions

The transformation of **rocks which contain Fe^{II}-silicates, in alkaline hscw,** in the presence of CO_2 & N_2, leads to the synthesis of macromolecules of **life**, at ca 300°-370°C, or 25°C & cosmic radiation

Geobiotropy

or Follow the water in its high-subcritical state

$Fe^{II}(OH)_3^-{}_{(diss)} + H_2O_{high\text{-}subcritical} \rightarrow Fe^{III}(OH)_4^-{}_{(diss\ in\ hscw)} + 1/2\ H_{2(g,\ diss\ in\ hscw)}$ **pH ~9.5-14**

$Fe_2SiO_{4(s)} + H_2O_{(hsc)}$ → **Ferric oxides** **goethite, hematite** $+ SiO_{2(quartz\ \&\ amorph, diss\ in\ hscw)} + H_{2g}$

secondary **magnetite**

Ferric silicates

Greenalite
$(Fe^{II}_3,Fe^{III}_2)Si_2O_5(OH)_4$

Minnesotaite
$(Fe^{II})_3Si_4O_{10}(OH)_2$
$(Fe^{II}_3,Fe^{III}_2)Si_4O_{10}(OH)_2$

Riebeckite
$Na_2(Fe^{II}_3,Fe^{III}_2)Si_8O_{22}(OH)_2$

Stilpnomelane
$K(Fe^{II},Mg,Fe^{III})_8(Si,Al)_{12}(O,OH)_{27}$

Aminoacids
Organic functions
inside fluid inclusions
enclosed in chert, hematite
& siderite

$(H_2 + CO_2)_{diss.\ in\ hscw} \rightarrow CO$

$CO + H_2/H_2O + N_2/NH_3$
Heat or microwave
or cosmic radiation
→ **molecules of life**

MP Bassez 2018

300°-350°C   10-25MPa

From the numbers emerges the form

1. **Fe^{II}** $(OH)_3^-{}_{diss}$ + **$H_2O_{high\text{-}subcritical}$** → **$Fe^{III}$** $(OH)_4^-{}_{diss\ in\ hscw}$ + 1/2**H_2 diss in hscw** **pH~9.5-14**
   no Fe^{III} above Tc (374°C, 22.1MPa) *(Bassez 2013)*
2. 3 SiO_2 quartz → SiO_2 **diss quartz** + ~ 2 SiO_2 **amorph** *(Shock et al.1989) (Smith&Fang 2011) (Karasek et al. 2013)*
   no $SiO_{2\ diss}$ above Tc
3. $CO_{2\ diss}$ + $H_{2\ diss}$ → CO_{diss} + $CH_{4\ diss}$ 250°-300°C, 25MPa, catalyst:Fe_3O_4 *(Fu & Seyfried 2009)*
4. **$Fe_2SiO_{4(s)}$** + **$H_2O_{(hsc)}$** → **SiO_2 diss Q** + **SiO_2 amorph silica**
   → **Ferric oxides**: goethite, hematite + **$H_{2(diss\ in\ hscw)}$**

   → **Ferric silicates**: greenalite $(Fe^{II}{}_3,Fe^{III}{}_2)Si_2O_5(OH)_4$
   minnesotaite $(Fe^{II}{}_3,Fe^{III}{}_2)Si_4O_{10}(OH)_2$

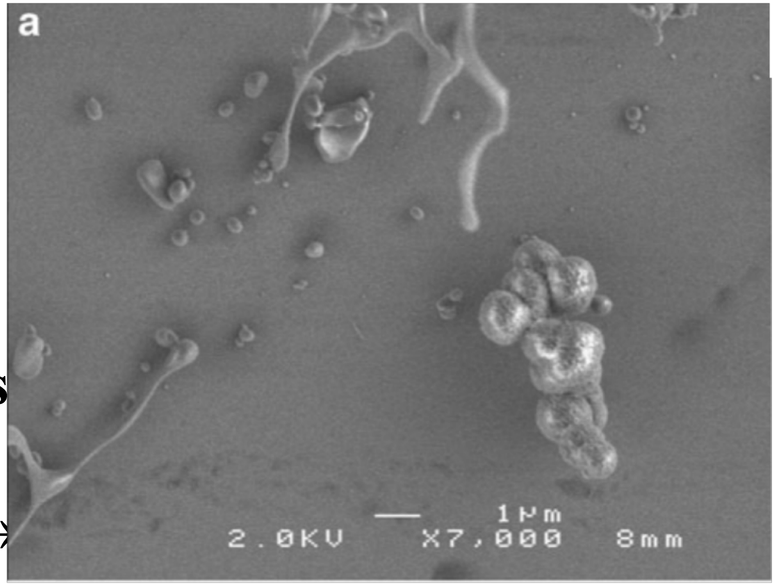
$(Fe^{II}{}_3,Fe^{III}{}_2)Si_2O_5(OH)_4 + SiO_{2(diss)} \rightarrow (Fe^{II}{}_3,Fe^{III}{}_2)Si_4O_{10}(OH)_2 + H_2O$

→ **H_2**

H_2+CO_2→CO; CO_g+H_2O_g+N_{2g} + γ, protons..→**organic functional groups**

(Kobayashi et al.1990, room T) *(Takano et al. 2004, 765°C,10s)*

(Kurihara et al. 2012, 300°C, 25MPa, 2min) *(Bassez, Takano, Kobayashi 2012)* →



References

Witzel T (1997-1998) Supervisor Bassez MP *Etude bibliographique de l'eau supercritique.* Rapport de stage de 1ère année, IUT-Chimie, Université Louis Pasteur, Strasbourg

Bassez MP (1999) *La structure de l'eau supercritique et l'origine de la vie*. In: Sciences et Technologies: regards croisés sciences pour l'ingénieur, informatique, mathématiques, biologie, biochimie, chimie. L'Harmattan ed., ISBN 2-7384-7367-9, p.583-591

Bassez MP (2003) *Is high-pressure water the cradle of life?* Journal of Physics: Condensed Matter 15: L353- L361

Bassez MP, Takano Y, Kobayashi K (2012) Prebiotic organic microstructures. Orig Life Evol Biosph 42:307–316 https://link.springer.com/article/10.1007/s11084-012-9290-5 open

Bassez MP (2013) *Geochemical origin of biological molecules*. EGU'2013:Vienna, Austria, Session: Planetary & Solar System Sciences/Origins and Astrobiology/Planetary Evolution and Life/PS8.1, Oral:Tues. April 9th/9h30, EGU2013-22. Geophysical Research Abstracts 15, EGU2013-22 http://meetingorganizer.copernicus.org/EGU2013/EGU2013-22.pdf open

Bassez MP (2015) *Water, air, earth and cosmic radiation*. Origins of Life and Evolution of Biospheres 45(1): 5-13

Bassez MP (2016) *Geobiotropy*. LPSC'2016, The Woodlands, US. Abstr #1853. http://www.hou.usra.edu/meetings/lpsc2016/pdf/1853.pdf open

Bassez MP (2017a) *Ferromagnesian silicate and ferrosulfide rocks as a source of magnetite and hydrogen*. WRI-15. Procedia Earth and Planetary Science 17, 492-495 open https://www.sciencedirect.com/science/article/pii/S1878522016301588

Bassez MP (2017b) *Anoxic and oxic oxidation of rocks containing Fe(II)Mg-silicates and Fe(II)-monosulfides as a source of Fe(III)-minerals and hydrogen; Geobiotropy*. OLEB 47:453-480

Bassez MP (2018) *Water near its supercritical point and at alkaline pH for the production of ferric oxides and silicates in anoxic conditions. A new hypothesis for the synthesis of minerals observed in Banded Iron Formations and for the related geobiotropic chemistry inside fluid inclusions*. Orig Life Evol Biosph DOI 10.1007/s11084-018-9560-y open on-line 8 August 2018 https://link.springer.com/article/10.1007%2Fs11084-018-9560-y

Cook GW & Olive PR (2012) *Pourbaix diagrams for the iron-water system extended to high & low supercritical conditions.* Corros Sci 55: 326–331 doi:10.1016/j.corsci.2011.10.034

Fu Q, Seyfried Jr WE (2009) *Experimental study of abiotic synthesis processes in a hydrothermal flow system*. LPSC'2009, 23 March 2009/10h45, The Woodlands, U.S., Astrobiology/Abstr #2504 https://www.lpi.usra.edu/meetings/lpsc2009/pdf/sess104.pdf open

Hill HGM & Nuth J (2003) *The catalytic potential of cosmic dust: implications for prebiotic chemistry in the solar nebula and other protoplanetary systems*. Astrobiology 3(2): 291–304

Karasek P, Stavikova L, Planeta J, Hohnova B, Roth M (2013) *Solubility of fused silica in sub- and supercritical water: estimation from a thermodynamic model.* J. Supercrit. Fluids 83: 72–77 http://dx.doi.org/10.1016/j.supflu.2013.08.012

Kennedy GC (1950) *A portion of the system silica-water.* Econ Geol *45: 629-653*

Kobayashi K, Oshima T, and Yanagawa H (1989) Chem Lett 1527.

Kobayashi K, Tsuchiya M, Oshima T, Yanagawa H (1990) *Abiotic synthesis of amino acids and imidazole by proton irradiation of simulated primitive earth atmospheres.* Orig Life Evol Biosph 20: 99–109

Kurihara H, Yabuta H, Kaneko T, Obayashi Y, Takano Y, Kobayashi K (2012) *Characterisation of organic aggregates formed by heating products of simulated primitive Earth atmosphere experiments*. *Chem Lett* **2**41: 441–443 doi:10.1246/cl.2012.441

Pizzarello S (2012) *Catalytic syntheses of amino acids and their significance for nebular and planetary chemistry.* Meteorit Planet Sci 47(8): 1291–1296 doi: 10.1111/j.1945-5100.2012.01390.x

Shock EL, Helgeson HC, Sverjensky DA (1989) *Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: standard partial molal properties of inorganic neutral species*. Geochim Cosmochim Acta 53: 2157–2183

Smith RL Jr & Fang Z (2011) *Properties and phase equilibria of fluid mixtures as the basis for developing green chemical processes*. Fluid Phase Equilib 302: 65–73 doi:10.1016/j.fluid.2010.09.030

Takano Y, Marumo K, Yabashi S, Kaneko T, Kobayashi K (2004) Pyrolysis of complex organics following high-energy proton irradiation of a simple inorganic gas mixture. Applied Physics Letters 85(9): 1633-1635 doi: 10.1063/1.1785858

Tosca NJ, Guggenheim S, Pufahl PK (2016) *An authigenic origin for Precambrian greenalite: Implications for iron formation and the chemistry of ancient seawater*. GSA Bull 128(3–4):511–530