High Subcritical Water for the syn-Formation of Ferric Minerals and Molecules of Life

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Abstract

Considering the theme for AbSciCon 2019: "Understanding and Enabling the Search for Life on Worlds Near and Far", it is worth to set the emphasis on ferric minerals and show that their formation in the absence of oxygen does not require the necessary presence of microorganisms but can occur during the alkaline interaction of ferrous silicates rocks with water in conditions of temperature and pressure near the critical point. The results show that molecules of life can form in a path which is concomitant to this specific water-rock interaction and that organic matter of biological interest can form inside inclusions in the produced minerals. The knowledge about the formation of ferric iron in anoxic alkaline conditions may be important for the understanding of the Earth oxygenation and of extraterrestrial objects such as Enceladus. It is concluded that the search for the molecules of life may be connected to the search of amorphous silica, quartz, ferric oxides, amorphous and crystalline ferric silicates, in association with siderite. The observation of ferric minerals on early Earth and extraterrestrial objects does not mean that life had already emerged at the time of formation of the minerals.

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Architecture of the Research

The research started in 1997 with the study of the structure of water under pressure and the dissolution of apolar molecules in supercritical water. Since 2013, results show that **anoxic, alkaline pH ~9.5-14, high subcritical, hsubc, water, ~300-350 °C, ~10-25 MPa, ~700-600 kg/m^3**, constructs the continuity from rock to life in the process conceptualized with the term **geobiotropy**. When this peculiar water interacts with rocks containing Fe-silicates, crystalline and amorphous silica, and ferric minerals can form. The minerals that are observed in Banded Iron Formations of the Archean to early Paleoproterozoic Earth can be explained by this action *(Bassez 2018)*. On the Saturn's moon Enceladus, the interaction with Fe,Mg-silicates rocks can be at the origin of the Cassini observations.

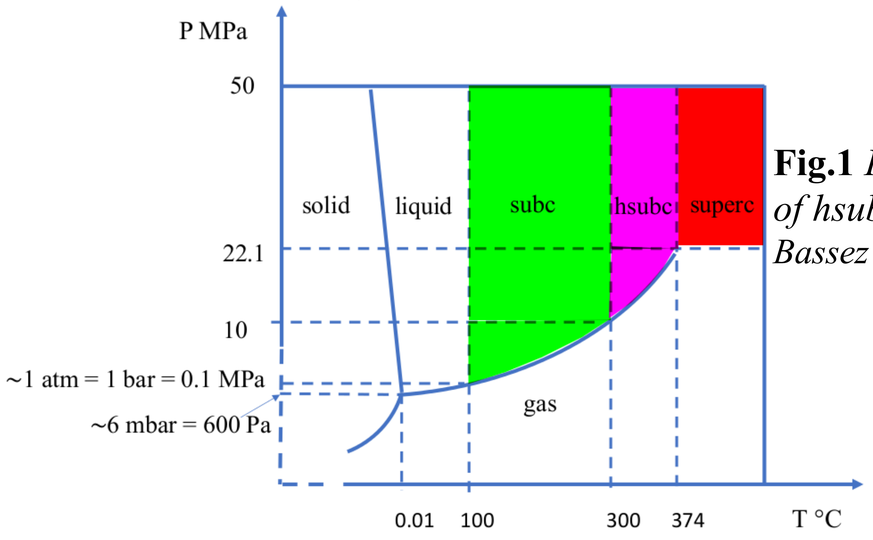


Fig.1 *P,T domain of hsubc water Bassez 2019*

Results

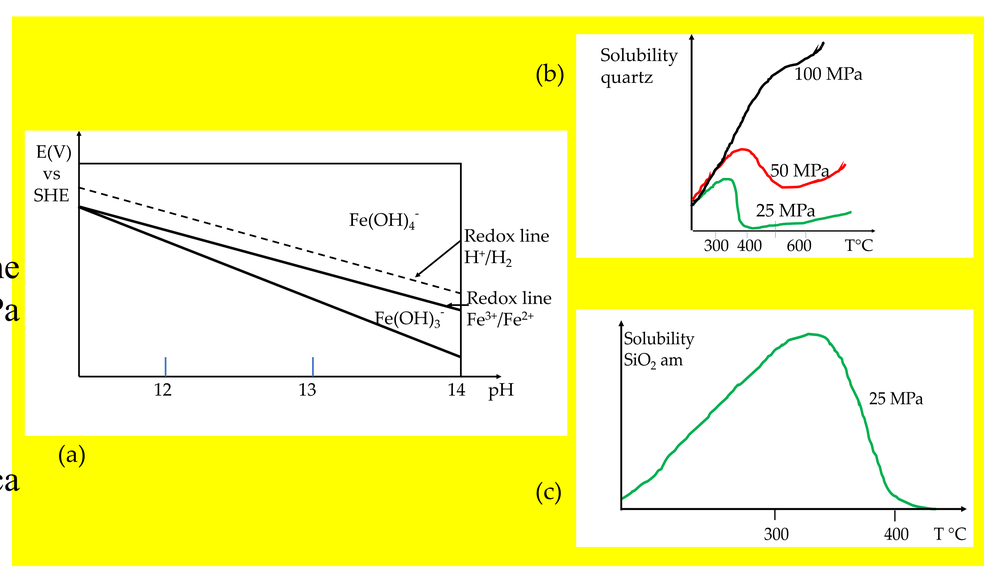


Fig.2 ***a)*** **E-pH** diagram for the Fe-H_2O system at 350°C, 25 MPa *Cook, Olive 2012*
b) **Solubility** of quartz in water *Smith, Fang 2011*
c) **Solubility** of amorphous silica *Karasek et al. 2013*

Processes in hsubc water for the formation of H_2, SiO_2, Fe^{3+}, CO, basic pH

1. ***Fe^{3+} and H_2 form in anoxic hsubc water at alkaline pH ~9.5-14***

$Fe^{II}(OH)_3^-{}_{diss} + \mathbf{H_2O_{hsubc}} \rightarrow \mathbf{Fe^{III}}(OH)_4^-{}_{diss} + 1/2\mathbf{H_2}_{\ diss}$ (no Fe^{3+} in H_2O_{supc}) *(Bassez 2013)*

2. ***The solubility of silica is higher in hsubc water***

$3SiO_{2\ diss\ in\ hsubcw} = SiO_{2\ \mathbf{Q,\ diss}} + \sim 2SiO_{2\ \mathbf{amorph,\ diss}}$ (no $SiO_{2\ diss}$ in H_2O_{supc})
(Shock et al.1989) (Smith&Fang 2011) (Karasek et al. 2013)

3. ***Dissolution of fayalite in hsubc water***

$Fe_2SiO_{4(s)} + \mathbf{H_2O_{hsubc}} \rightarrow \mathbf{SiO_{2\ Q,\ diss}}, \mathbf{SiO_{2\ am,\ diss}}, (\mathbf{Fe^{2+}}, \mathbf{Fe^{3+}}, \mathbf{H_2})_{diss}, \mathbf{Fe^{III}}$-oxides&silicates

4. ***Hydrolysis of siderite in hsubc water***

$3FeCO_3 + H_2O_{hsubc} \rightarrow Fe_3O_4 + 3CO_{2\ diss} + \mathbf{H_2}_{\ diss}$ *(educed from Milesi et al.2015 experiment)*

5. ***Formation of the reactive CO in hsubc water***

$CO_{2\ diss\ in\ hsubcw} + H_{2\ \mathbf{diss}} \rightarrow \mathbf{CO_{diss}}$ & $CH_{4\ diss}$ *(detected with catal. Fe_3O_4, Fu, Seyfried 2009)*

Rem: $NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$ at 270 °C in chem labs

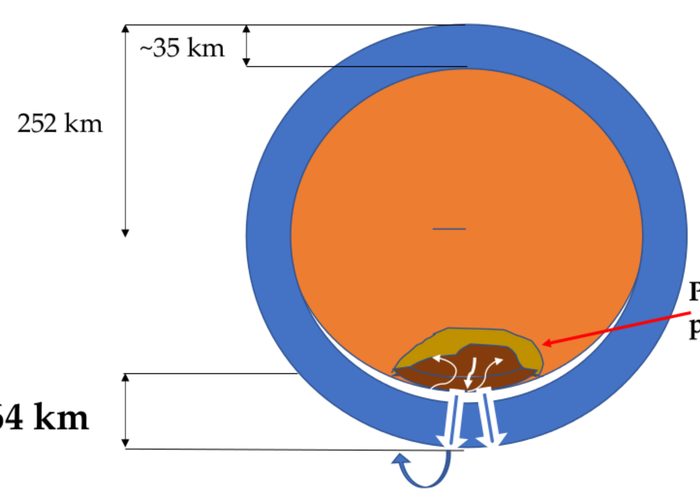
$CO + H_2 \rightarrow$ **organic molecules of life** in irradiated gas mixtures of H_2/H_2O, CO, N_2/NH_3 at low T, or in Sabatier-Fisher-Haber reactions (FTT) with H_2/H_2O, CO/CO_2, N_2/NH_3 .

Heat on Enceladus

Radioactive decay to set water in the liquid state
Exothermic carbonations of Fe,Mg-silicates:
$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + \mathbf{SiO_2}$; $Fe_2SiO_4 + 2CO_2 \rightarrow 2FeCO_3 + \mathbf{SiO_2}$
Exothermic hydrolysis of Mg-silicates & endothermic hydrolysis of Fe-silicates
$\Delta_rH° = -524.35$ kJ/kg of $(Fe_{0.5}Mg_{0.5})_2SiO_4$ olivine,
$\Delta_rH° = -378.61$ kJ/kg of $(Fe_{0.5}Mg_{0.5})SiO_3$ pyroxene *Bassez OLEB2017*
Exothermic Sabatier Fischer Haber reactions + ***Exothermic react. of CaC_2*** calcium carbide on Mg + ***Exothermic hydrolysis of CaC_2 to form C_2H_2*** *Bassez Geosciences2019*

Enceladus data: Mean density 1608.3 kg/m^3 *Porco 2006*; Acceleration of gravity 0.113 m/s^2 *Travis 2015*; Thickness of the ice crust 30-40 km *Iess 2014*; Ice crust density 900 kg/m^3 *chosen for the calculation*; hsubc water density at 10MPa and 300°C: 700 kg/m^3 *Bassez 2019, educed from Fig.2 in Cook & Olive 2012*; pH 11-12 *Glein 2015*, CO_2, CH_4, C_2H_2, NH_3, H_2CO, CH_3CHO, HCN, C_3H_6, C_4H_2, C_4H_4, C_4H_8, C_6H_6, probably ^{40}Ar, mass 28 (N_2 or CO), H_2, NaCl, $NaHCO_3$, Na_2CO_3, K^+, SiO_2.

A hypothesized water cycle in Enceladus



Peridotite-like rock with olivine, pyroxene and thickness > ~27 km

Results: *Bassez 2019*
* Core density: 2000 kg/m^3
* With a layer of liquid water ~1 km thick, percolating water at 300°C is « hsubc » at 10 MPa, at a depth of ~28 km inside the core and ~64 km below the surface.

H_2, SiO_2 are produced and ejected with alkaline H_2O (pH ~9.5-14) through the conduits. They return to the surface and also fill the E-ring. The bottom of the ice crust melts, percolates and replaces the ejected water.

Conclusion

The observed heat, H_2, pH, silica, Na salts & organic molecules can be explained by the **interaction of alkaline high subcritical water with Fe,Mg-silicates located at a depth of ~64 km and higher** below Enceladus surface. The hydrothermal conditions that are near the supercritical state have the values **pH ~9.5-14, ~10-25 MPa, ~300-350 °C, densities ~700-600 kg/m^3**. ***Future models on Enceladus need to specify the term «hydrothermal» with the values of water in the high subcritical domain.***

References: *M.-P. Bassez Geophys. Res. Abstr. 15 EGU2013-22 (**2013**); OLEB 45:5-13 (**2015**); LPSC**2016** Abtrs.1853, OLEB 47:453-480 (**2017**); 48:289-320 (**2018**) open; Geosciences 9(6)249 (**2019**) open.*

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