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Introduction: Prebiotic chemistry has been demonstrated to occur with primary molecules such as CO, N₂, H₂O, NH₃, CH₄, H₂CO. These molecules are present all over the universe. However the formation of molecules of biological interest requires first, concentration of the primary molecules in order for reactions to start [1,2]. Liquid and solid environments in the universe are consequently more appropriate.

A second requirement for synthesis of peptide like molecules seems to be the presence of CO instead of CO₂ [3]. Carbon monoxide is widely present in the gas phase. However its concentration might be higher inside veins of rocks or faults, niches and cavities [2]. Question is: how CO can be formed in a rocky world?

I call geobiotropy the process of physico-chemical evolution from the world of rocks towards the world of molecules of biological interest. Geobiotropy is a word constructed with the greek word ἡ τροπή, used by Platon and Aristote to mean evolution. This process is developed below.

Results and Discussion: CO has been experimentally formed through hydrogenation of CO₂ in a flow of H₂ at 500°C and atmospheric pressure [4]. It is also produced at 300°C and 350 bar [5] or in supercritical water [6]. It is consequently necessary to consider local heat and local physico-chemical conditions instead of global ones. Questions become: where in a rocky world are found high concentrations of H₂? and which elementary reactions could produce enough heat to transform CO₂ into CO?

Rocks such as peridotites, gabbros and basalts, which contain ferromagnesian minerals, can thermodynamically evolve in the presence of liquid H₂O and dissolved CO₂, towards the formation of prebiotic molecules [7-9]. Some elementary reactions are exothermic and produce serpentine and carbonates: such are hydrolyses of enstatite and forsterite and carbonations of both iron and magnesium olivine and pyroxene. Heat locally released from these exothermic reactions can induce the endothermic production of H₂ which in turn reacts with CO₂ in hydrothermal conditions to form CO. Excitation by gamma rays [10] or cosmic radiation would consecutively produce prebiotic molecules.

This process of H₂ production requires liquid water and a triggering process which allows to overcome activation energies of the exothermic reactions. Up to

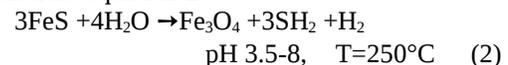
now, water in the universe was considered mostly in solid and gas phases. However local events [9] might induce physico-chemical conditions where water is in liquid or supercritical states and that produce sufficient heat to overcome activation energies. A recent experiment on forsterite exposed to water and carbon dioxide shows deposits of magnesite crystals and quartz particles, at 120°C and 80 bar of CO₂. [11]. Consequently local heating processes around 120°C, 80 bar are sufficient to trigger the exothermic carbonation reactions. In this local context, ferromagnesian rocks can evolve towards the formation of CO. Signatures of such geological origin of biomolecules might consequently be, serpentine and or talc, associated with iron and magnesium carbonates [7-9].

I analyze [7-9] the thermodynamic equilibrium E-pH diagrams constructed for iron, water and dissolved carbon dioxide at different temperatures and pressures and I deduce equation 1:

$$2\text{FeII} + 2\text{H}^+ \rightarrow 2\text{FeIII} + \text{H}_2 \quad T=350^\circ\text{C} \quad \text{pH } 11.5-14 \quad (1)$$

H₂ seems released for T and P values near the critical point of water and for high pH values, 11.5-14. This observation might explain the laboratory values of pH, 9.7-12.2 and [H₂] up to 76 mmol.kg⁻¹ obtained when peridotite reacts with water at 200°C and 500bar during 3-7 months [12]. It might contribute to the explanation of the high pH, 9-11, of the Lost City hydrothermal vent located at 800m depth, where rocks are highly serpentinized, chimneys are in carbonates, temperature are reported to attain 90°C, and [H₂] increases up to 15mmol.kg⁻¹ [13,14]. Elevated production of H₂ seems to occur in ultrabasic environments, for HTHP water up to the supercritical point. Such areas might be around the heating processes cited above [9], either on Earth or Mars and extraterrestrial objects.

I analyze [7-9] also the E-pH diagrams constructed at 250°C for ternary systems Fe-S-H₂O and I construct equation 2:



I discuss these equations here. SH₂ release occurs at lower pH as a consequence of the evolution of FeS. This observation might explain the Rainbow

hydrothermal site where pH 4.97 and T 370°C are measured at Auberger vent [15].

Equation 2 might also explain the effects produced by the fall of the asteroid near Chelyabinsk in February 2013 [16]. In the recovered meteorites, olivine and pyroxene seem to be not serpentinized, troilite grains FeS are abundant and a great amount of CHNO and CHOS organic molecules have been discovered. Sulfur smells and heat are witnessed and anomalies in magnetization are described. Reaction 2 would contribute to explain not only the sulfur smell, but also the anomalies in magnetization which might be introduced by the synthesis and deposit of Fe₃O₄. And also the H₂ produced might induce formation of organic molecules as described above.

Another application of equation 2 is the belt of sulfates discovered on Mars [17]. By superposition of this belt on the USGS geological map of Mars, we see that it follows exactly Valles Marineris until Meridiani Planum. In Meridiani Planum haematite and magnetite have been detected in association with olivine and pyroxene and no serpentine [18]. The belt continues into Terra Sirenum and, to some extent, seems to follow the banded structure of the magnetic field [19].

Equation 2 predicts that hydrolysis of troilite would lead to the formation of H₂S, magnetite and H₂. Magnetization anomalies might be contributed by the synthesized FeIII ions, and sulfates deposits by the radiolytic sulfur cycle showing the action of cosmic radiation on water and sulfur grains, sulfur ions and H₂S. It would consequently be appropriate to search for some remaining troilite in Terra Sirenum and along Valles Marineris until Meridiani Planum.

In the context of geobiotropy, evolution from the Rainbow floor, the Chelyabinsk asteroid and the the path Meridiani Planum, Valles Marineris, up to Terra Sirenum on Mars, start not with ferrosilicates but with ferrosulfide. Another signature for synthesis of molecules of biological interest might consequently be the presence of troilite associated with magnetite or FeIII ions.

A third signature of the rocky world to predict a possibility of geobiotropy is the presence of radioactive rocks at the origin of water radiolysis. It is discussed [20,10,21,9] that whenever radionuclides such as U, Th, or K, are present, there is enough H₂ available through water radiolysis to produce CO from

CO₂ in a locally warm environment, which in turn, will produce biological molecules after excitation by gamma rays. It seems appropriate to search for short-lived now-extinct radionuclides and also long-lived ones .

Conclusion: The described thermodynamics of elementary chemical evolution of ferromagnesian, ferrosulfide and radioactive rocks, associated to the analyses of oxydo-reduction diagrams, allow the determination of three kinds of signatures for geobiotropy on Earth or extraterrestrial objects. Such signatures might be iron and magnesium carbonates in association with serpentine and/or talc, or troilite located in ancient water areas and associated with magnetite or FeIII ions, or long-lived and now extinct radionuclides.

References: [1] Bassez M. P. (1999) *Sci. Technol. Regards Croises, proceed. CNRIUT'1999-Aix-en-Provence, Oral*, 583-591. [2] Bassez M. P. (2003) *J. Phys.: Cond. Matter* 15 L353-L361. [3] Kobayashi K. et al. (2008) *Electr. Comm. Jpn* 91 (3), 15–21. [4] Chen C.S. et al. (2000) *Catalysis. Lett.* 68, 45-48. [5] Seewald S. J. et al. (2006) *Geochim. Cosmochim. Acta* 70, 446-460. [6] Foustoukos D. I., Seyfried W. E. (2004) *Science* 304:1002-1005. [7] Bassez M. P. (2013) *EGU'2013, Oral PS8.1, Geophys. Res. Abstracts 2013, 15*, EGU2013-22. [8] Bassez M. P. (2014) *EANA'2014 Edinburgh, Oral-Oct13th*. [9] Bassez M. P. (2015) *OLEB 45*: 5-13. [10] Bassez M. P. (2009) *OLEB 39 (3-4)*, 223–225; *proc. ISSOL'2008-Firenze*. [11] Aaberg I. et al. (2013) *Goldschmidt Conf. Abstracts*. [12] Seyfried W. E. Jr., Foustoukos D.I., Qi Fu (2007) *Geochim. Cosmochim. Acta* 71, 3872. [13] Kelley S. D. et al. (2005) *Science* 307 (5714) 1428-1434. [14] Proskurowski, G. et al. (2008) *Science* 319, 604-607. [15] Seyfried W. E. Jr. et al. (2011) *Geochim. Cosmochim. Acta* 75, 1574-1593. [16] Popova P. O. (2013) *Science* 342, 1069-1073. [17] Ehlmann L. B., Edwards S. C. (2014) *Annu. Rev. Earth Planet. Sci.* 42: 291–315. [18] Arvidson E. R. et al. (2006) *J. Geophysical Res.* 111, E12S08, 1-19. [19] Lillis J. R. et al. (2008) *Icarus* 194, 575-596. [20] Bassez M. P. (2008) *CNRIUT'2008-Lyon, actes-29 Mai, 1C:1-8*. [21] Bassez M. P. (2009) *C. R. Chimie, Acad. Sci. Paris, 12 (6-7)* 801-807.