Abiogenically Formed Complex Organics and the Origin of Life on Earth-like Planets in Habitable Zones. Uma Gayathri Kamakolanu<sup>1</sup>, Friedemann T. Freund<sup>1,2</sup>, and Jeremy Tregloan-Reed<sup>3</sup>, <sup>1</sup> SETI Institute, Carl Sagan Center/NASA Ames Research Center, 189 Bernardo Ave, Mountain View, CA 94043 <u>k umagayathri@yahoo.com</u>, <sup>2</sup> NASA Ames Research Center, MS 245-4, Moffett Field CA 94035, <u>Friedemann.T.Freund@nasa.gov</u>, <sup>3</sup> NASA Ames Research Center, Moffett Field.

Introduction: Copious amounts of the gas/fluid phase components  $H_2/H_2O/CO/CO_2/NH_3/N_2/H_2S/SO_2$  become trapped during planet formation. As minerals crystallize out of magmas, the gas/fluid components become incorporated into the matrix of minerals such as olivine in form of oxyanion species such as  $OH^-$ . C, N and S also form oxyanions. Under equilibrium conditions the solutes exsolve. During cooling, after the onset of non-equilirium conditions, a redox reaction causes electrons to be transferred from the oxygens onto the low-z elements (which are electropositive relative to oxygen), oxidizing oxygen to the peroxy state (valence  $1^-$ ), while the low-elements H, C, N and S become chemically reduced. For instance, hydroxyl pairs:  $O_3Si-OH HO-SiO_3 \Leftrightarrow O_3Si-OO-SiO_3 + H_2$ .

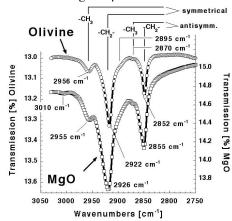
To the extent that the solute species are still diffusively mobile, the now reduced low-z "impurities" are being pushed into dislocations and other segregation sites inside the mineral matrix. The denser the mineral matrix, the stronger the segregation force. At the internal segregation sites such as dislocations or subgrain boundaries. There the chemically reduced solute C, N, and S precipitate within the 3-dimenionally structured lattice environment forming C-C-, C-N-, C-S and C-O bonds. The lattice-bound  $H_2$  will follow suite forming -C-H, -C-OH, -COOH and similar functional groups. We assign to the polyatomic CHONS segregates a formula  $[C_x H_v O_z N_i S_i]^{n-}$  and call them proto-organics.

This is confirmed by the appearance of the spectroscopic signature of "organic entities" suggestive of aliphatic hydrocarbons. Fig. 1 shows the C-H stretching bands recorded from upper mantle derived gem quality olivine and melt grown MgO single crystals [1, 2]. The organics associated with interstellar dust display a similar, through broadened aliphatic signature [3, 4].

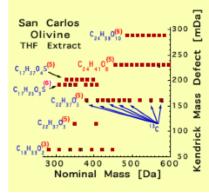
**Discussion**: If an exoplanet in the habitable zone possesses oceans and landmasses as early Earth surely did, weathering will free  $\left[C_xH_vO_zN_iS_i\right]^{n+}$  segregates from the tight embrace of their host minerals turning them into  $C_xH_vO_{(z+n)}N_iS_i$  molecules. This is a powerful source of stereochemically preformed, complex organic CHONS, O-rich, probably carboxylic-type.

Solvent extraction of crushed MgO single crystals have yielded carboxylic acids in sufficient quantities to grow mm-sized succinic acids crystals [1]. Recently THF extraction of crushed gem-quality, upper mantlederived olivine single crystals produced series of ho-

mologous, O-rich, sometimes S-bearing compounds with molecular weights up to 600 amu.



**Fig.1** C–H stretching bands at 3.4 μm recorded from a melt-grown high purity MgO and a gem-quality olivine crystal from the upper mantle.



**Fig. 2** Examples of complex organics, THF-extracted from crushed gem-quality olivine crystals

**Summary**: The redox conversion of traces of the fluid phase components  $CO/CO_2/H_2O/N_2/SH_2/SO_2$  to  $H_2$ , organic C, reduced N and S inside the matrix of minerals leads to the new concept of **Organic Chemistry in the Solid State**. We are exploring this concept to understand the Origin of Life on Earth and beyond.

References: [1] Freund, F., A. Gupta, and D. Kumar (1999), Origins Life Evol. Biosphere, 29, 489-509. [2] Freund, F., A. Staple, and J. Scoville (2001), Proc. Natl. Acad. Sci., 98, 2142-2147. [3] Freund, M. M., and F. T. Freund (2006), Astrophys. J., 639, 210-226. [4] F. T. Freund, and Freund, M. M., (2014), American Journal of Analytical Chemistry, (in print).