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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 incorporated during planetary accretion. As minerals crystallize out of magmas, gas/fluid components dissolve in the matrix of minerals such as olivine forming a solid solution. Solute species are OH^- as well as carboxy, nitroxy and sulfoxy anions. Under non-equilibrium conditions the solutes exsolve. During cooling, a redox reaction causes electrons to be transferred from the oxygens onto the low-z elements (which are electro-positive relative to oxygen), oxidizing oxygen to the peroxy state (valence 1^-), while the low-Z-elements become chemically reduced. For instance, hydroxyl pairs: O_3Si-OH $HO-SiO_3$ $O_3Si-OO-SiO_3 + H_2$.

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-dimensionally 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 $[C_xH_yO_zN_iS_j]^{n-}$ and call them proto-organics.

This is confirmed by the appearance of the spectroscopic signature of “organic entities” suggestive of mostly 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

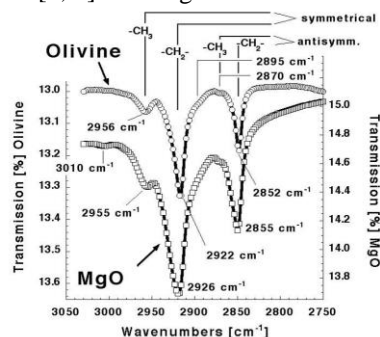


Fig.1 C–H stretching bands at $3.4 \mu m$ recorded from a melt-grown high purity MgO and a gem-quality olivine crystal from the upper mantle.

display a similar, through broadened aliphatic signature [3, 4]. **Figure 3** shows a model of a densely packed

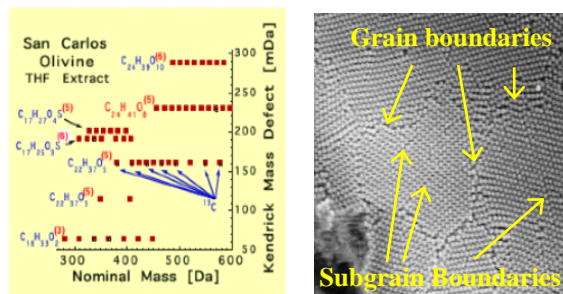


Fig. 2 Examples of complex organics, THF-extracted from crushed gem-quality olivine crystals, **Fig. 3:** Model of grain and subgrain boundaries as sites for C–H assembly.

polycrystalline material consisting of single crystals with grain boundaries between them and subgrain boundaries within them. These act as “dumping places” for solute C which probably diffuse via a mechanism that can be described as a coupled diffusion of a C atom bonded to O^- and the diffusion of the holes associated with the oxygen (O^- state) [3]. When H_2 join, they tie C–H bonds forming aliphatic groups.

Discussion: If an exoplanet in the habitable zone possesses oceans and landmasses as early Earth surely did, weathering will free $[C_xH_yO_zN_iS_j]^{n+}$ segregates from the tight embrace of their host minerals turning them into $C_xH_yO_{(z+n)}N_iS_j$ molecules. This is a powerful source of matrix embedded, 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 mantle-derived olivine single crystals produced series of homologous, O-rich, sometimes S-bearing compounds with molecular weights up to 600 amu.

Summary: The redox conversion of traces of the fluid phase components $CO/CO_2/H_2O/N_2/S_2/SO_2$ 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 biosignatures and precursors of possible Life on Mars 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., (2015), *American Journal of Analytical Chemistry*, 6, 342-349.