

ORGANIC SYNTHESIS IN THE SOLID STATE – IN THE SEEMINGLY FORBIDDING, HARD, DENSE MATRIX OF OLIVINE AND SIMILAR MINERALS Friedemann T. Freund, SETI Institute, Carl Sagan Center, 189 Bernardo Ave, Suite 200, Mountain View, CA 94043, USA friedemann.t.freund@nasa.gov

Introduction: Over that past decades, research into the abiotic synthesis of organic compounds has focused reactions that can occur in gas or fluid phases, at gas-solid and gas-liquid interfaces [1-3], and during intercalation into the soft solid matrix such clays [4]. It is widely – but wrongly – assumed that the dense, hard matrix of minerals is a medium, in which organic synthesis just cannot take place.

The reason for this misconception is that the behavior of the low-z elements C-H-O-N-S, present in magmatic systems as gas/fluid phase components, is not understood. Specifically: How do $H_2O/CO/CO_2/N_2/SH_2$ dissolve in the solid state? How do the solute C-H-O-N-S species interact chemically in the solid matrix?

Thermodynamics mandates that, whenever a mineral crystallizes from a fluid-laden magma, the fluid components enter as “impurities” into solid solution. The most common solute is hydroxyl such as Si-OH, introduced through dissolution of H_2O . However, all other components $H_2O/CO/CO_2/N_2$ also form solutes in the mineral matrix. During cooling, the solutes exsolve. At the same time a widely ignored redox conversion takes place [5], best known from the reaction $Si-OH-HO-Si \rightleftharpoons Si-OO-Si + H_2$, where H reduces from H^+ to H^0 while O oxidizes from O^{2-} to O^- [6]. All low-z solutes are subject to the redox conversion leading to chemically reduced C, N and S in solid matrix [7].

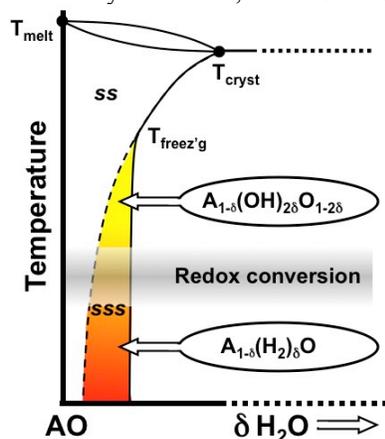


Figure 1: Binary AO- H_2O phase diagram: ss stands for “solid solution”, sss for “super-saturated solid solution”. In the sss state, under metastable conditions, the redox conversion transfers electron density from O^{2-} pnto the low-z’s.

Thus chemically reduced H, C and N bonded to O^- exist in the O^{2-} matrix. Supersaturation means that these low-z elements H, C and N continue to be driven to exsolve to the extent possible by their diffusive mobility. Dislocations are preferred sites for exsolution, offering “extra room” to accommodate the [-C-C-C-] entities, which assemble in the 3-D constrained space available in dislocations with C bonding to H, O^- , N and S [8]. It

has been proposed that C atoms diffuse in dense matrix by coupling to O^- [9].

The outcome is an assembly of low-z elements precipitating in the core of dislocations in compliance with the 3-D environment of the host matrix. As generic formula we write $[C_nH_xO_mN_yS_z]^{m-}$. The complexity of the heteroatomic, predominantly aliphatic proto-molecular entities is controlled by the geometry of the dislocations and by how many [-C-]_n can precipitate.

There is clear spectroscopic evidence for proto-molecular entities in solid matrix. Figure 2 shows the aliphatic ν_{C-H} stretching bands seen in the IR absorption spectrum of a laboratory-grown MgO and a mantle-derived olivine single crystal.

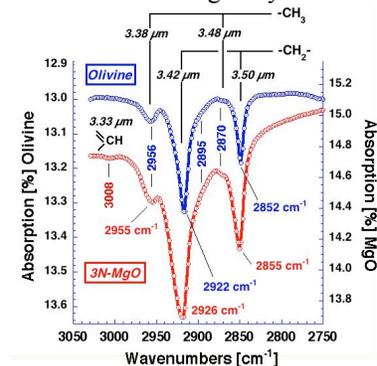


Figure 2a: ν_{C-H} IR stretching bands of a melt-grown MgO and a magma-grown olivine single crystal indicating the presence of aliphatic organics in the matrix of these crystals,

The C-H bonds can be pyrolyzed by heating the MgO crystal. Upon annealing at RT the aliphatic signature returns within short time, a few weeks, rebuilding the original diagnostically distinct IR spectrum. This observation implies (i) that the $-C_n-$ backbone was not destroyed by the pyrolysis and that (ii) the H atoms were able to return to build the [-CH], [-CH₂-] and [-CH₃] bonds with an amazingly short time.

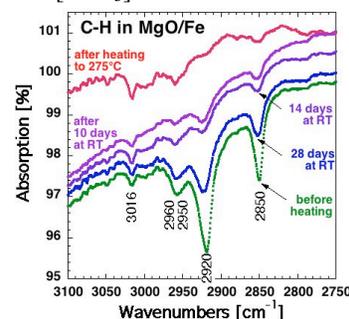


Figure 2b: Rapid return of the ν_{C-H} stretching bands during RT annealing, indicating that the broken C-H bonds are reconstituted in the structurally very dense MgO matrix.

Solvent extraction of crushed MgO crystals leads to carboxylic and dicarboxylic acids, $H_3C-(CH_2)_n-COOH$, $HOOC-(CH_2)_n-COOH$, to urea and glycolamide $(NH_2)CO$ and $H_2COH-CO-NH_2$, and to homologous families of higher molecular weight CHONS with up 40 C atoms.

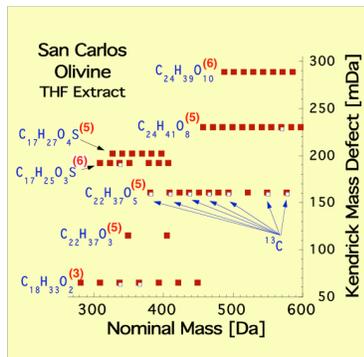


Figure 3: Families of O-rich high molecular weight aliphatic hydrocarbons solvent-extracted from crushed gem-quality olivine crystals, indicative of assembly of $[C_nH_xO_mN_yS_z]^{m-}$ entities inside the dense olivine structure.

Discussion: The observations reported here provide very strong support for a hitherto overlooked synthesis mechanism by which abiogenically complex organic compounds, O-rich, N-bearing and S-bearing with molecular weights of at least up to 600 amu can be assembled, namely in the seemingly forbidding, hard, dense matrix of olivine, the most abundant mineral in the universe. In fact, the dense matrix provides the strongest driving force for the segregation of relatively large atoms such as carbon [9]. An additional feature of this abiotic synthesis is that the 3-D matrix of the host mineral structure will obviously control the stereochemistry of the $[C_nH_xO_mN_yS_z]^{m-}$ that are assembled.

This is a universal synthesis pathway. In all likelihood it will be operational in any structurally dense mineral matrix, in particular in olivine crystals that have incorporated finite concentration of the low- z elements C, H, N and S by crystallizing from fluid-laden magmas or recrystallizing in other high temperature, fluid-laden environments. The same synthesis pathway may also apply to situations where nano-sized olivine grains condense out of the gas phase in the gas-rich outflows of dying stars. This mechanism has been proposed to account for the presence of complex organic matter associated with interstellar dust [9]. It probably also applies to organic molecules associated with comets [10].

In the experiments described here we used crushing of gem-quality, melt-grown MgO and upper mantle-derived olivine single crystals as the method of choice to expose some $[C_nH_xO_mN_yS_z]^{m-}$ on fracture surfaces and make them accessible for solvent extraction.

In nature weathering would be the dominant mechanism by which the organic compounds are released from the matrix encasement. In order to convert the $[C_nH_xO_mN_yS_z]^{m-}$ into free $C_nH_xO_mN_yS_z$ molecules during aqueous weathering, additional reactive steps will be required – steps that may change the C:H ratio while maintaining the integrity of the $-C_n-$ backbone.

The solid encasement, i.e. the assembly of polyatomic $[C_nH_xO_mN_yS_z]^{m-}$ precipitates along dislocations and other extended defects in a host mineral structure, provides for a highly unusual mechanism to assemble large CHONS with interesting properties: (i) they can

be O rich with one or more functional groups such as $-COOH$ and other reactive sites, (ii) they are stereochemically selected because the structured 3-D environment provided by dislocations restricts the ways how the $-C_n-$ chains can assemble either in a linear fashion or with sidechains.

No chemical reaction pathway in the unconfined gas or liquid phase, nor on solid-gas or solid-liquid interfaces, can provide such preselection of the organic molecules to be synthesized, neither with respect to the number of atoms forming the $-C_n-$ backbone nor with respect to the shape of the CHONS.

The questions raised here are very important in the context of setting the stage for achieving higher orders of complexity through the assembly of CHONS into larger, secondary structures. We may even speculate that, in order to build structures that could self-assemble and achieve replication, hence, a first form of life, it would be good to start from a selection of relatively few, but functionally diverse CHONS available in relatively high concentrations in the environment. This is better than having a greater diversity, but less functionality in the smaller molecules that can be assembled under prebiotic conditions through chemical reactions in the gas or liquid phase or at gas-solid and liquid-solid interfaces. Even the intercalation of small molecules into the soft matrix of clays [4] does not come even close to the efficacy of synthesizing stereochemically pre-selected macromolecular CHONS in the structurally dense mineral matrices.

Organic synthesis in the solid state, drawing on the solutes of the common gas/fluid phase components, may have been the best way, possibly the only way, to produce the complex CHONS necessary to give Life a chance here on Earth more than 3 GYrs ago, on other solid bodies in the solar system, and in suitable exoplanetary environments.

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