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KAOLINITE-CATALYZED AIR OXIDATION OF HYDRAZINE: CONSIDERATION OF SEVERAL COMPOSITIONAL, STRUCTURAL AND ENERGETIC FACTORS IN SURFACE ACTIVATION

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It appears from the fossil record that single-celled terrestrial life forms had proliferated by 0.7-0.9 b.y. after the formation of the earth. Since impact heating did not end until several hundred million years after the bulk accretion, a very narrow window has been established for the complex sequence of precursive chemical processes required to produce, collect and assemble the organic constituents of cellular life. It has long been recognized by biologists that surfaces, particularly those with special sites, i.e. phospholipid membranes with protein receptors and channels, have unique and varied functional properties, including the capacity to differentially recognize and act to alter or transport materials. It has been even longer accepted by chemists that solid surfaces have powerful catalytic properties that cannot be even approximately explained by their bulk chemical composition and structure. By contrast, the Origin of Life Community has been dishearteningly grudging in its acceptance even of the concept (much less the need for careful investigation) of the fact that terrestrially abundant mineral surfaces, particularly those with structural defects, have powerful informational and energetic properties. Natural surfaces show not only a potential, but a capacity to promote chemical reactions leading to the synthesis and oligomerization of biologically significant monomers under conditions that better represent those of early earth than do single phase models. Homogeneous, single-phase, artificial laboratory models for organic synthesis of biologically significant molecules still 'rain' supreme from the atmosphere to the soup. Leading scholars of organic material in comets and interstellar ices still pass off mineral grains as "inert silicaeous contaminants" with a straight face in the O. of L. and Space Sciences Communities with scholarly and funding impunity. For some minerals, their complexity is adequate to sustain membrane, even whole cell, molecular operations of types required to emulate the functional attributes of living systems. It can be postulated that the specific adsorption and catalytic powers of these special minerals may prove adequate to adequate to produce a translation mechanism between inorganic protolife systems and self-organizing assemblies of organic molecules capable of serving as organic protolife forms.

Clay minerals have been shown to have numerous,curious, energetic properties by virtue of ultra-violet light release which can be triggered by gentle environmental changes such as wetting and dewetting by a variety of liquids, unique among them water and hydrazine. Since both water and hydrazine play multiple key roles in the air-oxidation of hydrazine on kaolinite surfaces, this reaction would seem to have prime potential for studying interrelationships of energy storage, release and chemical reactivity of clay surfaces, capacities basic to either the Bernal or Cairns-Smith roles of minerals in the origin of life. Establishment of the capacity for stored electronic energy to significantly alter surface chemistry is important, regardless of the reaction chosen to demonstrate it. Hydrazine air oxidation is overawingly complex, given the possibilities for step-wise control and monitoring of parameters. In the light of recently extended characterization of the kaolinite and model sheet catalysts we used to study hydrazine oxidation, gamma-irradiated silica, previous studies of hydrazine air-oxidation on aluminosilicate surfaces have been reevaluated. Our former conclusion remains intact that, whereas trace structural and surface contaminants do play some role in the catalysis of oxidation, they are not the only, nor even the dominant, catalytic centers. Initial intermediates in the oxidation can now be proposed which are consistent with production via O^--centers as well as ferric iron centers. The greater than square dependence of the initial reaction rate on the weight of the clay is discussed in the light of these various mechanistic possibilities.