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FINAL REPORT ON NASA NAG 54563 - PREBIOTIC EVOLUTION OF NITROGEN COMPOUNDS 1996 through 1999

G. Arrhenius

Support from this four year grant has funded our research on two general problems. One involves attempts to model the abiotic formation of simple source compounds for functional biomolecules, their concentration from dilute state in the hydrosphere and, in several cases, surface induced reactions to form precursor monomers for bioactive end products (refs. 1-5).

Because of the pervasiveness and antiquity of phosphate based biochemistry and the catalytic activity of RNA we have exploring the hypothesis of an RNA World as an early stage in the emergence of life. This concept is now rather generally considered, but has been questioned due to the earlier lack of an experimentally demonstrated successful scheme for the spontaneous formation of ribose phosphate, the key backbone molecule in RNA. That impediment has now been removed. This has been achieved by demonstrating probable sources of activated (condensed) highly soluble and strongly sorbed phosphates in nature (Refs. 1,2) and effective condensation of aldehyde phosphates to form ribose phosphate in high yield (ref.6), thereby placing the RNA World concept on a somewhat safer experimental footing.

Like all work in this field these experiments are oversimplifications that largely ignore competing side reactions with other compounds expected to be present. None the less our choice of experimental conditions aim at selective processes that eliminate interfering reactions. We have also sought to narrow the credibility gap by simulating geophysically and geochemically plausible conditions surrounding the putative prebiotic reactions.

Continued work on related problems during the past year have led to the demonstration of a facile phosphorylation of aldehydes with amidotriphosphate, both components in dilute solution, and in the presence of magnesium ion (ref.7). We have begun studies of further acceleration of this process by surface active, concentrating minerals, extending the efficiency of the reaction to the micromolar range of reactants.

The second area of our studies is a search for the earliest traces of life on Earth, and the early environments on Earth and Mars. We have as part of this been characterizing the graphitic residues, thought on the basis of their carbon isotope composition to represent the remains of microorganism in Earth's oldest known sedimentary rocks (ref.13). This investigation has most recently been extended to even older, highly metamorphosed rocks (granites and gneisses). In these the biogenic carbon isotope signature tends to be significantly affected by progressive equilibration with the unfractionated inorganic carbon reservoir. We have consequently been looking for supplemental biomarkers that are sufficiently conserved (ref.8). As a potential indicator of this kind we have begun exploring the content and isotopic composition of nitrogen in graphite, inherited from the biogenic source material. Much of the effort last year has been devoted to the construction of a vacuum line for high sensitivity massspectrometric measurement of nitrogen and carbon (ref.9). A concurrent effort has been made to clarify in detail the mineralogical and petrological features of the graphite bearing Archean banded iron formations and carbonaceous shales (ref.10).

In these studies we have also searched for any physical or chemical effects on Earth of the heavy bombardment observed on the Moon and decaying there until about 3.450 Ma. These impacts have conventionally been hypothesized to caused by an invasion into the inner solar system by a swarm of marauding objects, affecting all of the planets there. However, the expected impact effects have so far not been recognized in the coeval early Archean sediment sequences that we are studying, or in martian meteorites. This apparent absence points to the possibility that the lunar bombardment instead represents the final phase in the accretion of the Moon in its orbit with little effect on the planets (ref.11, 12). Analyses for enhanced platinum metal concentrations and for physical disturbances of the finely laminated banded iron sediments have provided our major tools in this search. Initial analyses, carried out by neutron activation, have failed to identify any strata with enhanced platinum elements and all indications at the present time thus point at a low average impact rate on Earth around 3.780-3,800 million years ago.

Our field campaigns investigating the 3.78 Ga Isua formation in southern West Greenland have been carried out during four consecutive years, involving the PI, one postdoctoral and two graduate students as participants. During the summer of 1999 additional brecciated rock sections were sampled which could possibly be surge deposits caused by major meteorite impacts - these samples are now being processed for analysis and for continued study of the environmental conditions in this early era during which life emerged on Earth.

Support from the present grant has been essential in demonstration of biogenic graphite (isotopically identifiable chemofossils) in these oldest sedimentary rocks currently known to be preserved on Earth. (ref. 13)The same source of support has made it possible to demonstrate the mineral catalyzed processes discussed above and in the references, leading to molecules of biological complexity, previously thought to be unattainable. The great value of this support is gratefully acknowledged.

OTHER SOURCES OF FUNDING

Limited funding support from NASA's NSCORT Exobiology Program in La Jolla has been utilized to further the research goals reported above. The 1/2 graduate student fellowship received from the same source has been of decisive importance in supporting Mark van Zuilen in his initial work toward analysis of nitrogen and noble gases in biogenic and abiogenic graphite in the Archean.

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