THE SEARCH FOR INDIGENOUS LUNAR ORGANIC MATTER

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Abstract. Early lunar conditions are not inconsistent with the production of large quantities of prebiological organic matter now sequestered in the lunar subsurface. The absence of substantial water and organic compounds from the superficial layers of the lunar surface may not be indicative of the composition of deeper regions.

The absence of abundant organic compounds in those lunar samples returned to Earth has been an evident source of disappointment to at least some workers in the field. From these initial negative or equivocal results some have concluded that there is nothing to be gained by further exploration for lunar organic chemistry. In the present paper I wish to argue that the absence of organic compounds from the returned lunar samples is expected even for a lunar history rich in primordial organics, that the sites most likely to yield lunar organic compounds have not been investigated, and that there is an area of investigation conceiveably critical to problems in prebiological chemistry and the early history of the solar system awaiting continued lunar exploration, manned or unmanned.

The fraction of reliably-determined simple organic compounds in the returned lunar fines, as detailed elsewhere in these Symposium Proceedings, is of the order of one part per million. The experiments particularly of Abell *et al.* (1970, 1971) have shown that these compounds – largely simple hydrocarbons – are not products of the extraction techniques in Earth-bound laboratories but are truly in the lunar fines. Thus the organics represent roughly 10^{-2} of the total lunar carbon, as determined, for example, by Kaplan *et al.* (1970). Hayes (1972) has argued that solar wind, and meteoritic and cometary implantation of carbon on the Moon may contribute only about one-half the observed carbon, leaving approximately one-half the carbon in the fines examined to date as indigenous. This is an interesting possibility, but as Hayes himself recognizes the uncertainties in these calculations – particularly of the solar wind carbon implantation rate – are too large to be given very much weight.

It is instructive to compare the fraction 10^{-6} of organics in the returned lunar fines with the comparable fractions for the two other kinds of objects available to us. The ratio of the biosphere mass to the mass of the Earth is of the order of 10^{-10} . But we know from the depletion of noble gases on the Earth relative to their cosmic abundances that during the formation of the Earth a very major fraction of the total volatiles in the atmosphere was lost to space (Suess, 1949; Brown, 1952). Of course, it is conceiveable that much larger quantities of organogenic elements exist in the interior of the Earth. The carbonaceous chondrites are $\sim 10^{-2}$ organics by mass; all known meteorites represent very roughly $\sim 10^{-4}$ organics by mass. Conditions on the asteroids, the presumed parent bodies of the meteorites, are certainly less conducive to synthesizing or retaining organic compounds than conditions on the Earth. In addition, the selection effects in the safe transit of carbonaceous meteorites to the Earth work in the direction of lowering the apparent organic content of meteorites. The lunar organic content $\sim 10^{-6}$ falls pleasingly between the amounts for the Earth and the meteorites. However, this agreement cannot be considered satisfactory until we understand the reasons for the discrepancy between the Earth and the meteorites. One reasonable explanation would appear to be that the Earth, being a large differentiated object, has been thoroughly outgassed and, moreover, has had virtually all its primary atmosphere lost to space. The meteorite parent bodies, being much less differentiated, have been degassed to a much smaller extent and therefore retain larger fractions of the organic compounds which must clearly date from their very early history. Yet the surfaces of the Earth and the asteroids (we assume that most meteorites do not come from the deep interiors of asteroids) are much richer both in organics and in other volatiles than the lunar surface, as evidenced by the returned fines. This circumstance needs explaining.

The survival of organic compounds under lunar conditions is obviously relevant to the problem. I here briefly summarize the results of a recent investigation to be reported in more detail elsewhere (Sagan et al., 1972). A mixture of amino acids was added to a finely pulverized olivine basalt with the approximate optical and thermal properties of lunar surface material. The mixture was then irradiated in high vacuum at about 400 K by a proton beam of approximately 2 keV energy for the equivalent of 1.5×10^4 yrs' exposure to the proton component of the solar wind. The recovery of amino acids was then compared by gas chromatographic techniques with recovery from unirradiated and unheated mixtures. The preliminary results indicate a roughly 10^4 yr half life for amino acids in the top few cm of lunar regolith. Such factors as possible reciprocity failure and the high (nonaqueous) initial amino acid concentration are not likely to change this result by more than an order of magnitude. We have not yet investigated the degradation products of amino acids under these simulated lunar conditions, which include temperatures comparable to those at lunar noon, but the results are very suggestive that even large quantities of moderately complex organic compounds entrained in the uppermost lunar regolith would not long survive the inclemencies of the present lunar environment. Many of the degradation products of more complex organics under lunar conditions must be simple molecules which readily escape from the present Moon.

The median depth of the lunar regolith seems to be very roughly 4 meters (Shoemaker, 1971); this is the depth of, on the average, 1 circulation due to micrometeoritic gardening or turnover during the characteristic age of the regolith of approximately 4×10^9 yr, corresponding to a gardening rate of about 1 mm (10^6 yr)⁻¹. Thus, the top few cm of the lunar regolith has very recently been exposed to the temperatures and proton fluxes of the lunar surface, and is the least likely place to search for lunar organic compounds of even moderate complexity. These results also tend to cast considerable doubt on claims of indigenous amino acids and other relatively labile organics in the returned fines.

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On the other hand, the surface of the Earth experiences somewhat lower temperatures, considerably lower vacuums and negligible proton irradiation. The asteroids experience considerably lower temperatures and proton fluxes; but, more important, the vast bulk of the meteorites do not arise from mobile powdery surficial layers of asteroids. Thus, if there is any reason to believe that organic matter may have been produced in the early history of the Moon, it may still be present, locked in cold storage, beneath the currently gardened lunar regolith – say at a depth of 10 m or more.

I proposed such models some years ago (Sagan, 1960a), and wish here to bring the ideas up to date. The differentiation of the Moon is a clear consequence of analysis of the returned lunar samples. Most models (see, e.g., Wood, 1972) invoke two melting events, the first at about 4.6×10^9 yr ago, due to the gravitational potential energy of accretion and perhaps now extinct radionuclides; and a subsequent melting event a few hundred million years later, due to the radioactive decay of those radionuclides concentrated to the lunar surface by the initial melting events. From the abundance of radioactive elements at the lunar surface and the requirement that the lunar interior not be molten today, estimates have been made (see, e.g., Ringwood, 1970) that at least the outermost 20% of the lunar volume melted at the time of formation. This corresponds to a depth of several hundred kms. As the radioactive elements were concentrated to the lunar surface it is inevitable that volatiles, and particularly volatile gases, would similarly be concentrated and contribute to a primitive lunar atmosphere. Let F be the fraction by mass of the Moon which was originally comprised of volatile gases. Then from the mass and radius of the Moon it follows that in the first few hundred million years of lunar history at least $5 \times 10^6 F \text{ gm cm}^{-2}$ of volatiles were outgassed. The most conservative estimate for F is surely the present surface value of around 10^{-6} . With such a value it follows that approximately 10 gm cm⁻² of atmosphere was outgassed. With a typical meteoritic value of $F \sim 10^{-4}$ we derive a loading density of atmosphere comparable to the present atmosphere of the Earth. Since most models show the initial condensation and melting processes to have been rapid and the melt to have been convective, on the geological time scale the atmosphere can be considered introduced instantaneously: a big burp model of the origin of the primordial lunar atmosphere.

In such an atmosphere, effects of ionization and solar wind streaming – dominant for the question of the lifetime of present lunar microatmospheres (see, e.g., Johnson, 1971) – are ineffective, and the principal escape process is the classical Jeans escape of the high velocity tail of the Maxwell-Boltzmann distribution from the very thin exosphere. Total time scales for the depletion of such gases as water, methane and ammonia or their heavy atoms from such an exosphere is very roughly 10–1000 yr. The principal uncertainty is the exospheric temperature. Assuming the primitive lunar atmosphere reflected cosmic composition, its exosphere would be chiefly hydrogen. Because of the high thermal conductivity of hydrogen and the radiation thermostating of reduced polyatomic molecules, the exosphere temperature on the early Moon should have been low, as it is, for example, in the atmospheres of the contemporary Jovian planets. But the amount of gas in a planetary exosphere is only of the order of 10^{-5} cm of air at normal temperature and pressure. Thus for the time scale for the entire primitive atmosphere to escape a correction factor B, devised by Spitzer (1952), is introduced. For the lunar atmospheres we are discussing here, we take values of B ranging from 10^4 to about 10^7 (see, e.g., Sagan, 1967). Thus, within the uncertainty of these crude calculations, the primitive lunar atmosphere could have lasted for as short a period as 10^5 yr (for $F \sim 10^{-6}$) or lasted so long that the present epoch is witnessing the escape of the last remnant of the primordial atmosphere. The most likely value for the lifetime of the primordial lunar atmosphere appears to me to be $\sim 10^8$ yr, although the uncertainty is of course considerable. In this case the interval between the first and second melting events on the Moon may have been a period in which the Moon was very different from its present form, and, in particular, possessed an extensive reducing atmosphere.

In such an atmosphere significant prebiological organic chemistry can be expected. Laboratory quantum yields for ultraviolet radiation alone are so high (Sagan and Khare, 1971) that all the atmospheric carbon must have been processed at least once through organic compounds. Such an atmosphere provides some protection to the surface against ultraviolet radiation, and considerable protection against solar protons and micrometeoritic pyrolysis. If the pressures were towards the higher end mentioned above, even some nearsurface liquid water would have been possible in the first few hundred million years of lunar history.

We thus envision significant outgassing of volatiles about 4.5×10^9 yr ago; a lunar reducing atmosphere gradually leaking away to space in the next few hundred million years; and having significantly departed by roughly the time of the remelting of the lunar surface. The yields of organic compounds from such an atmosphere may have been many tens of gm cm⁻² or more. It may be objected that the oldest lunar rocks do not exhibit any sign of such volatiles – yet when molten should have come to equilibrium with the atmosphere suggested here. However, there are no individual rocks dated closer than a few hundred million years to the model ages of the origin of the Moon. The rock evidence applies to later epochs. But it certainly must follow that by, say, 4.1×10^9 yr ago the bulk of the lunar atmosphere had escaped to space. The characterization of volatiles from significantly older rocks is, of course, the critical test of the ideas present here.

Note that the contribution from comets striking the primitive Moon may have been substantial. Such objects may have been more common then, and cometary masses $\sim 10^{19}$ gm are not uncommon today. The impact of one such comet on the Moon in its first 10^9 yr is comparable in effect to the entire hypothesized outgassing if F is $\sim 10^{-6}$; and even for larger values of F the possibility of significant cometary contributions cannot be discounted.

In this model the interior of the Moon below a depth of several hundred km may have a composition characterized by considerably larger volatile fractions than the lunar samples analyzed to date. Several lines of evidence support this possibility. Dark halo craters are indicative of the outgassing of some volatiles from depth, and carbon compounds are at least a good candidate (Urey, 1971). There is now a large literature on lunar transient events (see, e.g., Cameron, 1972) which seem correlated with maximum tidal stress on the Moon and seismic events, and are likely due to outgassing of unspecified volatiles. Kozyrev's (1962) visual and spectral observations of Alphonsus again are suggestive of an outgassing event, although his spectral identification of C_2 remains in some doubt. More recently intermittent bursts of species of high mass/charge ratio have been detected by the suprathermal ion detectors left on the lunar surface by the Apollo 12 and 14 astronauts (Freeman *et al.*, 1972); water is strongly suspected as a major constituent, and the authors propose that the observations represent venting from beneath the lunar surface. Subsequent observations, alluded to by Freeman *et al.* (1972), are more clearly indicative of water and seem to be well-correlated with lunar seismic events. Independent evidence of sporadic gas release on the lunar surface and probably unconnected with the Apollo spacecraft itself was discovered by the cold cathode ionization gauge left by Apollos 12 and 14 (see, e.g., Johnson, 1971).

On this model certain locales are indicated in the search for indigenous lunar organic matter. The upper layers of the lunar regolith are strongly counterindicated. In general samples should be taken from beneath the present regolith, that is at a depth of at least several meters. This is barely within the capability of the Apollo boring cores. Ideal locations to look for indigenous organic matter on the Moon include deep craters formed just after solidification of the underlying bedrock, or permanently shaded craters near the poles of the Moon, where both pyrolysis and photolysis of sequestered organics should be minimized. Examples of the former can be selected today. Searches for the latter must await development of versatile unmanned lunar rovers. The best strategy would be to acquire deep cores from such craters in a landing site otherwise suspected of outgassing events. The interior of the lunar crater Alphonsus – replete with dark halo craters and the locale of Kozyrev's observations – thus emerges as a prime candidate in the search for lunar organic matter.

The interval between the origin of the Earth and the epoch of the earliest identified fossils is sufficiently short to suggest that the origin of life occurred in the first few hundred million years of Earth history. It is therefore not entirely out of the question that the origin of life may have also occurred on the Moon under the conditions described in the present paper; although this is clearly one further speculative remove. Remains of such a lunar biota would also not be expected in the top few cms of lunar pulverized debris. Accordingly, if there ever was any justification for the quarantine of returned lunar samples such a quarantine should be continued each time samples are returned from novel lunar locales – particularly locales at depth, or associated with outgassing events. Likewise efforts should be maintained to avoid the introduction of terrestrial microorganisms into such locales (cf. Sagan, 1960b). Just as the absence of interesting organic chemistry from the first returned lunar samples is not an argument against searches for organic chemistry in other more plausible lunar environments, so also the absence of material of biological interest in the few samples studied to date does not imply that all concerns about forward and backward contamination have dwindled to zero, or that future returned samples have no biological interest. The Moon is a heterogenous body and its exploration is just beginning.

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