Icarus 212 (2011) 885–895

Contents lists available at ScienceDirect

Icarus

journal homepage: www.elsevier.com/locate/icarus

UV photolysis, organic molecules in young disks, and the origin of meteoritic amino acids

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ARTICLE INFO

Article history:
Received 14 June 2010
Revised 13 December 2010
Accepted 4 January 2011
Available online 14 January 2011

Keywords:
Organic chemistry
Origin, Solar System
Solar nebula
Meteorites

ABSTRACT

The origin of complex organic molecules such as amino acids and their precursors found in meteorites and comets is unknown. Previous studies have accounted for the complex organic inventory of the Solar System by aqueous chemistry on warm meteoritic parent bodies, or by accretion of organics formed in the interstellar medium. This paper proposes a third possibility: that complex organics were created *in situ* by ultraviolet light from nearby O/B stars irradiating ices already in the Sun's protoplanetary disk. If the Sun was born in a dense cluster near UV-bright stars, the flux hitting the disk from external stars could be many orders of magnitude higher than that from the Sun alone. Such photolysis of ices in the laboratory can rapidly produce amino acid precursors and other complex organic molecules. I present a simple model coupling grain growth and UV exposure in a young circumstellar disk. It is shown that the production may be sufficient to create the Solar System's entire complex organic inventory within 10^6 yr. Subsequent aqueous alteration on meteoritic parent bodies is not ruled out.

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1. Introduction

The early Solar System was replete with complex organic molecules, which can be seen today in preserved ancient bodies such as meteorites and comets. Upwards of 100 different amino acids have been detected on chondritic meteorites such as Murchison, Allende and Orguiel. Many of these have no known natural terrestrial occurrence (Ehrenfreund et al., 2001b), and are believed to be of extra-terrestrial origin. Comets and the interstellar medium (ISM) are also rich inventories of complex organic molecules, including amino acid precursors (Snyder, 2006). Amino acids and other complex organics have implications for the origins of life on Earth, so understanding their formation and history is an area of great interest. If these molecules are formed and distributed easily in a variety of disks and conditions, then pre-biotic compounds may be common throughout distant planetary systems.

Of the complex organics in the Solar System, amino acids are particularly interesting to study. These compounds are necessary for life, and may have been biotic precursors on Earth. Carbonaceous chondrites are typically 5% or more carbon by mass, most of which is in aromatic polymers and thousands of other pre-biotic organic compounds (Schmitt-Kopplin et al., 2010; Hayatsu and Anders, 1981). Laboratory studies have found Murchison to have some 10–30 ppm by mass in identified amino acids (Shock and Schulte, 1990). The simplest amino acid (glycine, NH_2CH_2COOH) has recently been detected in comets, but so far has eluded detection in the ISM (Elsila et al., 2009; Snyder, 2006; Kuan et al., 2003). Potential amino precursors such as formic acid (HCOOH) have been detected in comets but not the interstellar medium (Hollis et al., 2003; Bockelee-Morvan et al., 2000). However, amino acids in ice form in the interstellar medium (ISM) would be more stable but harder to detect than their corresponding gas forms in comets (Ehrenfreund et al., 2001a; Chyba et al., 1990), so it is likely that they exist in the ISM but have not yet been detected.

The origin of these molecules is unknown. Two broad explanations exist for the amino acids in our Solar System. First, they may be produced *endogenically*, by chemical synthesis within the Solar System itself. A variety of energy sources for this exist, including infall heating, radiogenic heating, lightning, and shocks. For the amino acids present on meteoritic parent bodies, the best-studied endogenic process is Strecker synthesis. This is a method by which amino acids are formed in aqueous environments, such as the warm sub-surface aquifers that could have been present on asteroids as they were heated by ^{26}Al and other radionuclides during their first few Myr (Ehrenfreund et al., 2001b). Amino acids are produced in the laboratory by this process, and sufficient ^{26}Al existed to heat parent bodies to liquid water temperatures (McSween et al., 2002). However, a serious problem exists with this model. Isotopic measurements of the chondritic amino acids consistently show deuterium *enhancements* of $\delta D = 600–2000‰$, while measurements of the water in these same bodies show deuterium *depletions* of roughly 100‰. *In situ* synthesis of aminos does not preferentially change the D/H ratio, so this argues that the water and organics come from distinct sources (Lerner, 1997).

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doi:10.1016/j.icarus.2011.01.002

Second, the molecules may have been inherited *exogenically* from the interstellar medium which formed the solar nebula. The ISM is known to be rich in complex chemistry, with over 150 different gas-phase species detected to date in molecular clouds (Herbst and van Dishoeck, 2009). Amino acids have not been detected in the ISM, but sugars, alcohols, polycyclic aromatic hydrocarbons (PAHs), and other complex molecules have been. The formation of these compounds in the ISM is thought to be due to a combination of processes, including gas phase, gas-grain, and UV-grain reactions. Once molecules are formed, stable compounds can be incorporated into young disks as new YSOs condense out of the ISM. This pathway is supported by measurements showing the organic composition of comets and the ISM to be quite similar (Bockelee-Morvan et al., 2000; Irvine et al., 2000).

Laboratory results have shown that simple ices can be turned into a zoo of amino acids and other complex organics simply by the presence of UV flux followed by a warming stage (Nuevo et al., 2008, 2007; Bernstein et al., 2002; Munoz Caro et al., 2002). Though these studies are performed at fluxes higher than the ISM, their total photon dosages are comparable to the current problem. Amino acids similar to those seen in meteorites are created. Moreover, chemical reactions (including photolysis) which occur at cold temperatures <70 K can preferentially increase D/H because deuterium's higher mass allows it to bond more readily than H at low temperatures. D/H enrichments are seen throughout the ISM, and the D/H enrichments in amino acids suggests that they too have a low-temperature origin compared with the water in meteorite parent bodies (Sandford et al., 2001). Continued UV exposure may sometimes destroy the same large molecules the UV created earlier, but for a proper range of timescales and fluxes, cold-temperature photolysis of ices may be a more plausible pathway to forming the meteoritic amino acids than warm aqueous synthesis.

The ISM formation model is not without problems. First, the high optical depth within dense molecular clouds blocks nearly all external UV light. The only source of UV within the clouds is that caused by cosmic rays interacting with gas in the clouds, resulting in a UV flux of 10^{-4}–10^{-5} G_0, where G_0 is the interstellar flux at the Sun today (Prasad and Tarafdar, 1983). Second, some organic molecules, such as the CHON particles in comets like Halley, may be easily destroyed by shocks during infall, although some debate exists on this point (Visser et al., 2009; Mumma et al., 1993; Zahnle and Grinspoon, 1990). Finally, some of the common meteoritic amino acids, such as α-aminoisobutyric acid (AIB) and isovaline, have not yet been produced by irradiation in the laboratory (Hudson et al., 2008), and it is not known whether this is due to these species only being formed during Strecker synthesis (as hypothesized by Ehrenfreund et al. (2001b)), or simply the ice experiments not using the proper initial mixtures. Nevertheless, overall the ISM formation model paints a plausible picture and may well play a role in the Solar System's organic history.

This paper proposes a third pathway for the formation of these complex organic molecules, which has not been examined previously. In our model, the solar nebula forms within a large molecular cloud similar to those in Orion. The Sun and its disk form completely, and condense and begin to grow. Within the next 1 Myr, nearby O and B stars turn on, bathing the young disk in UV light. These UV photons photo-evaporate gas from the disk (Throop and Bally, 2005; Johnstone et al., 1998), but also irradiate small ice grains exposed in the disk's outer skin layer. The simple ices grains, such as H_2O, CO_2 and NH_3, are exposed to the UV and begin to photolyze into more complex species. Each individual grain is exposed only briefly to UV light; they spend most of their time in the disk's dark, turbulent interior. Grains continue to grow, gas which has not formed planets is lost due to photo-evaporation and viscous loss, and within 5 Myr a gas-free debris disk is left with its ices enriched in complex organics. These organics can then be incorporated into comets, asteroids, and the planets. Organics produced in this way could complement, and perhaps greatly exceed, those produced by the other two pathways. This method is similar to the exogenic ISM production in that it relies on UV photochemistry, but at far high flux (10^6 G_0 vs. 10^{-5} G_0), at warmer temperatures, for a much shorter time. The model allows for subsequent aqueous alteration as seen in the meteoritic record.

Work by Robert (2002) proposed that the organic material was created by X-ray irradiation of the disk by the Sun during its T Tauri phase. They did not present a disk model, but used high-precision D/H measurements of organic and non-organic material to show that D/H fractionation varied with heliocentric distance, as would irradiation. Remusat et al. (2006) compared the meteoritic and interstellar D/H values, along with their C–H bond dissociation energies, and concluded that the Solar System's D/H enrichment was created *in situ*, rather than inherited from the ISM. They proposed that the young Sun might provide the necessary UV source; their model did not study the timescales or fluxes involved.

The source of the Earth's organic inventory (as opposed to the Solar nebula's) is a parallel question which has received some attention. It is believed that although some organics were probably synthesized on the young Earth *in situ* by lightning or spark discharges (Miller and Urey, 1959), shock heating in the terrestrial atmosphere (Chyba and Sagan, 1992), warm ocean vents (Corliss, 1990), or any number of other terrestrial processes, far more were probably delivered from external sources such as comets, asteroids, and interplanetary dust particles (Chyba and Sagan, 1992). This paper does not further address the origin of life or the Earth's inventory, except to acknowledge that increasing global abundance of organics in the solar nebula probably results in increased delivery to the Earth as well.

This paper uses a simple model to describe the production of complex organics in UV-illuminated disks in a variety of cases. The results are necessarily general, and do not explain the abundances or species in one particular sample or disk, but provides an initial assessment of the problem. External UV photolysis has been ignored in almost all previous models, yet it may be one of the most important sources of energy in both the young Solar System and other proto-planetary disks. The problem is set up in Section 2, and the model described in Section 3. Section 4 contains results, which are discussed in Section 5. Conclusions are in Section 6, and Appendix A contains a derivation of the simple grain growth model used here.

2. Background

2.1. Energy sources in the early solar nebula

Various surveys have shown that the majority of stars are born in dense clusters of 300–10^4 stars, where massive O and/or B stars can form (Adams et al., 2006; Lada and Lada, 2003). Due to the presence of decay products from short-live radionuclides such as ^{60}Fe that are only produced in supernovae, our Sun is thought to have formed in such an environment (Hester et al., 2004; Tachibana and Huss, 2003). The effects of such an environment can be enormous, compared with the classical 'closed box' view of Solar System formation where any environmental effects are easily ignored. Photo-evaporation by external stars can remove the disks on Myr timescales or shorter (Throop and Bally, 2005; Matsuyama et al., 2003; Johnstone et al., 1998). Close approaches between stars may be important, especially in the outer disk (Duncan et al., 2008; Adams et al., 2006). The high gas densities in such clusters can cause late infall of molecular cloud material onto disks after planetesimals have begun to form (Throop and Bally, 2008). And,

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