

the North Atlantic), ice-rafting will probably be due to icebergs, because they will melt later, and be transported further than coastal ice because of larger size and smaller ratio of volume to surface.

It is difficult to discriminate between material transported by icebergs, and coastal winter ice; both will be transported by the same systems of wind and current. The presence of many contemporaneous shallow-water organisms (foraminifera and molluscs) in ice-rafted deep-water sediments (4) may be an indication of transport by coastal ice, since the possibilities of picking up unconsolidated sediments with organisms in them is considerably higher in a normal littoral situation than in the calving front of a glacier.

An alternative model to that suggested by Herman and Hopkins (1) could be that their unit III was formed when the climate was cold enough for the formation of coastal winter ice, but that the real glaciation started only at the time of unit II.

During a period of general cooling, there may be a time lag between the stage when coastal winter ice is formed and the onset of a glaciation. The length of this time lag depends on the rate of temperature change, the topography on land, and the precipitation and wind systems. In those parts of the North Atlantic where the coastal areas were obliquely uplifted during the Neogene (5), the early accumulation of ice on land probably took place on the landward side of the water divide. It may have taken considerable time after the onset of the glaciation before appreciable amounts of glacial ice were drained into the ocean and could give ice-rafted sediments.

Generally speaking, the first occurrence of ice-rafting indicates cooling to a level where coastal winter ice is formed. The dating of the onset of glaciation is better made on the consequent eustatic drop in sea level.

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Observations in the nearshore zone of the Chukchi and Beaufort seas confirm that sand and gravel can be lifted from the beach by adfrozen sea ice [for example, see (1)], but gravel from beach sources can be readily recognized in cores and bottom samples by its high degree of rounding (2). Grounded pressure ridges are also known to lift coarse material from relict sand and gravel patches on the continental shelves of the Bering and Beaufort seas. An area of relict Pleistocene gravel on the floor of northern Bering Sea near Nome (3), for example, is surrounded by a halo about a kilometer wide in which bottom muds contain an outward-diminishing admixture of pebbles (2), evidently translocated by grounded pressure ridges. Near the stamukhi zone in Beaufort Sea (4), floating remnants of once-grounded pressure ridges have yielded mixtures of mud and erratic boulders with attached epifauna, material evidently scraped up from submerged outcrops of Flaxman Formation (5). Sand and gravel lifted by grounded pressure ridges, however, appears unlikely to be transported any great distance before melting returns it to the sea floor.

In contrast, ice islands derived from ice shelves off northern Ellesmere Island contain abundant coarse detritus on their upper surfaces and presumably in their interiors (6), and some of these ice islands reach and become grounded on the Beaufort Sea shelf. Striated glacial erratics of a different suite of lithologies are found in the late Pleistocene Flaxman Formation of the Beaufort Sea coast (5). The Flaxman Formation erratics consist partly of rock types that could reach the Arctic Ocean only by glacial transport from their inland outcrop areas in northern Canada and northern Greenland. Similar erratics are found at Skull Cliff (7) in beds that appear to be at least as

old as early Pleistocene and equivalent in age to unit II of Herman and Hopkins (8). Scanning microscope studies of surface textures of quartz grains confirm that some of the coarse debris of unit I (Pliocene) has also undergone glacial handling (9). These are the reasons why we are inclined to believe that glacial icebergs are the major source of coarse erratic material in all three of the zones recognized within Arctic Basin deep-sea cores.

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Interstellar Chemistry: Polycyanoacetylene Formation

We disagree with one of the conclusions reached by Hayatsu *et al.* (1) regarding the origin of interstellar carbynes and cyanopolyacetylenes. They found evidence for carbyne fragments in the Allende meteorite in the form $-(C\equiv C)_n$ and $-(C\equiv C)_n-CN$ and, in the laboratory, showed that such carbynes can form metastably at low temperatures from CO and H₂ by a catalytic reaction on chromite. They concluded that this process in the solar nebula formed carbynes on the

Allende meteorite. They went on to suggest, however, that the polycyanoacetylenes that have been detected in a few interstellar clouds are produced by fragmentation of polymerized cyanoacetylenes formed on grains, rather than built up stepwise by gas phase ion-molecule reactions.

To the contrary, it was shown by Langer *et al.* (2) that the simplest polycyanoacetylene, HC₃N, is produced by gas phase ion-molecule reactions, rather

than by catalysis on grain surfaces or the dissociation of even longer molecules formed in stellar atmospheres, in the richest source of polycyanoacetylenes, the Heiles cloud 2 region of the Taurus molecular cloud complex. The evidence is the detection of deuterated cyanoacetylene, DC₃N, in an interstellar cloud. Further observations of DC₃N are necessary to clarify the role of ion-molecule chemistry in the formation of HC₃N in sources other than the one position observed in Taurus.

As noted by Watson *et al.* (3), measurement of the relative abundances of the deuterated and protonated forms of a molecule in an interstellar cloud can discriminate between formation by gas phase reactions and by grain catalysis. The presence of large abundances of deuterated molecules can only be explained in terms of an ion-molecule gas phase model of the interstellar chemistry. In addition to DC₃N, the following molecules have been observed in interstellar clouds in their deuterated form and have been shown to derive from ion-molecule reactions: HCO⁺, HCN, N₂H⁺, and H₂CO (4).

Furthermore, Hayatsu *et al.* point out that Fischer-Tropsch reactions predict a decrease in relative abundance of successive homologs of the polycyanoacetylenes (HC_{2n+1}N/HC_{2n-1}N ~ 1/4), which they argue agrees with the observed ratios. Recent studies show that HC₅N/HC₃N ~ 1 (5) and so may rule out grain catalysis by this method entirely.

We would not assert that only gas phase ion-molecule reactions produce molecules in interstellar clouds. In fact, it is clear that there are places, such as the star IRC + 10216, where the long carbon chains are formed in the absence of ion-molecule chemistry. Yet unambiguous evidence for catalytic formation of molecules on grains in clouds exists only for the special case of H₂ and no other molecule.

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We fully agree with Langer *et al.* that the deuterium in interstellar cyanopolyacetylenes such as DC₃N was grafted on by ions such as H₂D⁺ or DCO⁺. But this was only the last embellishment of a long carbon chain; the crucial question is how this carbon chain formed in the first place.

We do not share the belief of Langer *et al.* that these chains formed by ion-molecule reactions in the gas phase. A telling clue is the relatively high abundance of heavier cyanopolyacetylenes; for example, in TMC-1, successive homologs from HC₃N to HC₉N decrease in abundance by a mean factor of 0.27 (1, 2). This means that the probability of chain growth by two carbon atoms is 0.27, whereas the probability of chain destruction is 0.73. In other words, conversion to the next homolog is one-third as likely as all other fates combined: hydrogenation, branching, dissociation, ionization, chain termination, and so on.

Several authors have proposed ingenious schemes for gas-phase buildup of cyanoacetylenes, using intermediates that themselves are rare, such as C₂H₂. However, it remains to be shown, by a truly comprehensive review of all relevant reactions, that so hydrogen-poor a series as H-(C≡C)_n-CN can be made and preserved, with a net growth probability of 0.27, in a gas phase where H outnumbered C by a factor of 1000.

On the other hand, grain surfaces have the proven ability to catalyze the growth of carbon chains, either by the well-known Fischer-Tropsch reaction (yielding hydrocarbons, alcohols, and so on) or by the disproportionation of CO [yielding free C, up to at least C₆ (3)]. The slope of the distribution depends on reaction conditions, but typically corresponds to a decline of 0.35 to 0.8 times for every two carbon atoms. This range

encompasses all astronomically observed ratios reported to date, including the HC₅N/HC₃N ratio of ~ 0.7 (4) that Langer *et al.* claim "rule[s] out grain catalysis . . . entirely."

A logarithmic distribution of similar slope can also arise by another process: fragmentation of larger molecules or polymers. We have suggested (2, 3) that the primary products of grain catalysis may first polymerize, and later break down to smaller fragments on some type of provocation.

A serious problem with grain catalysis is that it requires relatively high temperatures and densities. But there are possible solutions to this problem (2, 5).

We strongly agree with Langer *et al.* that the occurrence of cyanopolyacetylenes in the infrared star IRC +10216 (6) shows that nature knows how to make these compounds by a nonionic mechanism. But being disciples of William of Ockham, we would like to go a step further and note that this mechanism may well be the dominant one even in molecular clouds where ions are present. If ions are irrelevant for cyanoacetylenes in one place, perhaps they are irrelevant for them in all places, except for the final deuteration. Of course, we have no quarrel with the role of ions in building smaller molecules.

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