component, the OH NMR resonance shifts toward lower field and broadens. This is highly indicative of the formation of a hydrogen bonded complex. To date, our investigation shows that the proton spectrum of a model phenol, *o*-phenylphenol, is shifted downfield on the addition of the basic component. We have also observed that the ^{14}N NMR signal of 5 percent pyridine in CS_2 solution broadens and is chemically shifted toward higher field with the addition of either the acidic component or the model phenol.

It is of interest to note that asphaltenes derived from petroleum also have an acid-base structure. By treating asphaltenes isolated from a California crude with HCl gas in toluene solution, as described for coal asphaltenes, we obtained acidic and basic components in a weight ratio of 44/56.

In the case of asphaltenes derived from petroleum, the NMR spectrum of the acidic component was not definitive for the presence of a hydroxyl resonance. This is probably due to the very high molecular weight range of petroleum-derived asphaltenes (~ 3000) (*11*) compared to that of coal asphaltenes (~ 500). It was, however, possible to confirm the presence of aromatic phenols in the acidic component of petroleum asphaltene by thin layer chromatography and use of visualization sprays.

HEINZ W. STERNBERG*
RAPHAEL RAYMOND
FRANK K. SCHWEIGHARDT

Pittsburgh Energy Research Center,
Energy Research and Development
Administration,
Pittsburgh, Pennsylvania 15213

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2. The fraction remaining in solution and referred to here as the acidic component contains some neutral material. Mass spectrometric analysis indicates the presence of perylene, 1,12-benzoperylene, coronene, and possibly dibenzopyrene. At present we know that the neutral material comprises less than 50 percent of the acidic component, since 50 percent of this fraction, which is now free of asphaltene bases, is soluble in hexane. A hexane-soluble, neutral material could not be present in the acidic component, since the asphaltenes were prepared by precipitation with excess hexane from toluene solution.
3. This conclusion is based on the following evidence. The acidic component, dissolved in toluene, was treated with metallic sodium at reflux temperature to replace acidic hydrogen. Decomposition of the resulting sodium compound with water and titration of the sodium hydroxide formed gave the amount of hydrogen that had been replaced by sodium. This amount of hydrogen was larger than could be accounted for by assuming that all of the oxygen in the acidic component was present as phenolic hydroxyl. The amount of acidic hydrogen could, however, be accounted for by assuming that all the nitrogen in the acidic component was present as acidic nitrogen, that is, as a nitrogen with an acidic (sodium replaceable) hydrogen such as pyrrole or indole. Since oxygen-carbon bonds of the ring or ether type are not cleaved by metallic sodium, we conclude that all oxygen in the acidic compound is OH oxygen.
4. A literature survey shows that benzene and other π-electron systems participate in hydrogen bonding. See, for example, Z. Yoshida and E. Csawa, *J. Am Chem. Soc.* **88**, 4019 (1966); R. Mathur, E. D. Becker, N. C. Li, *J. Phys. Chem.* **67**, 2190 (1963).
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8. The difference in molecular weights between the 415° and 450°C asphaltenes is due to the difference in the severity of thermal degradation at these temperatures. At 415°C, thermal degradation is less severe, that is, fewer bonds are broken than at 450°C. Consequently, the fragments produced at 415°C are larger and have a higher molecular weight than those produced at 450°C.
9. It is interesting to note that these fractions have a relatively low molecular weight. Evidently, the conversation of asphaltenes to oil is the result of considerable degradation. On the basis of the ultimate analyses, it is evident that there has been a considerable loss of oxygen, nitrogen, and sulfur, probably due to hydrogenolysis.
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* Present address: Lawrence Livermore Laboratory, University of California, P.O. Box 808, Livermore 94550.

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Ice-Rafted Sediments as a Cause of Some Thermokarst Lakes in the Noatak River Delta, Alaska

Abstract. *Irregular, barren polygonal sheets of mud scattered over the landscape of the western portion of the Noatak River Delta are derived from lake-bottom sediments, ice-rafted during flooding. The evidence suggests that the sheets of mud change the albedo and the thermal regime of the soil, induce the development of thermokarst, and lead to the formation of ponds and lakes. The angular perimeters, especially of the small ponds, support the suggested mode of formation.*

The western portion of the Noatak River Delta (67°03′N, 162°40′W), Alaska, covers about 7 km² and is punctuated by lakes constituting about three-fourths of the area. Many of the lakes have angular perimeters ranging from triangular to trapezoidal, or irregularly polygonal (Fig. 1). The unusual perimeters of the lakes are especially evident in the case of small ponds with well-defined sides (Fig. 2) and vertical edges. Rounded and cuspated shores occur mainly in large lakes (Fig. 1). I suggest here a mode of formation for these lakes that, to my knowledge, has not yet been described in the literature.

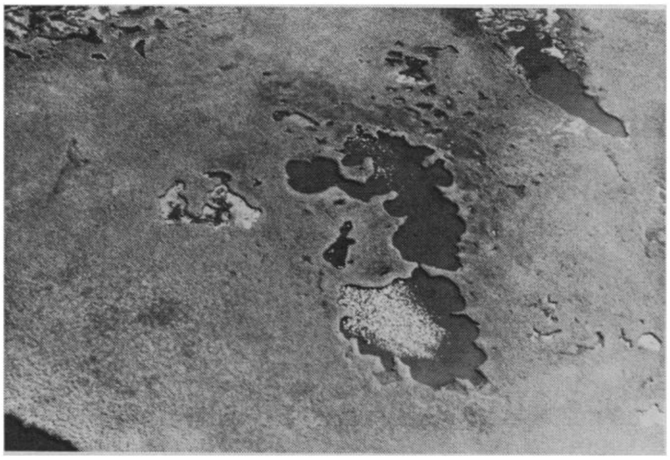
The mechanism invoked involves as a first step the complete freezing of existing shallow lakes, channels, and tidal flats. The lakes and other shallow bodies of water that freeze to the bottom incorporate, in the lower part of the ice, bottom sediments such as silt, algal mats, decomposed organic material, anoxic ooze, mosses, or, as observed in one case, sediments with aquatic plants. Subsequent river flooding in the spring and autumn, or storms from the sea, lift jagged ice floes with adhering sediments and float them over the delta. Once the flooding recedes, the ice floes are deposited on the landscape and, upon melting, leave silty sediments and the other material that was frozen to the ice. The suggested process does not necessarily explain all the lakes in the delta, some of which probably form as thaw lakes starting in thermal contraction cracks and others of which form in different ways from the one outlined here.

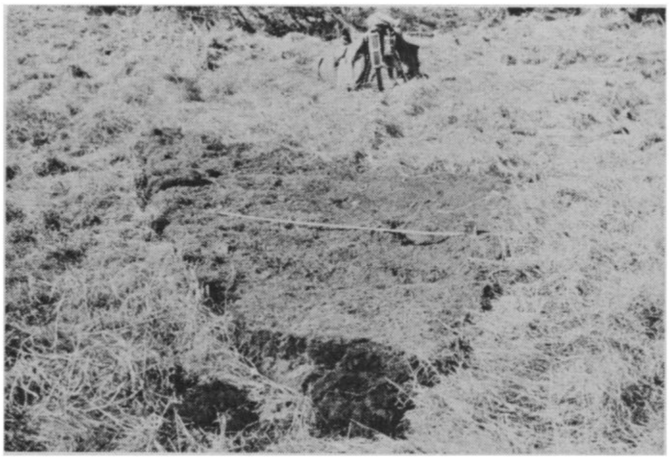
Dionne (*1*) proposed a mechanism for the formation of pitted schorre—shallow angular depressions filled with water in salt tidal marsh—in the St. Lawrence estuary. This mechanism involves the tearing and rafting of pieces of the marsh surface, including the vegetation and soil previously encased in ice, by ice floes driven ashore during spring flooding. Although there is an apparent resemblance between the geometry of the shallow ponds in the Noatak River Delta and of those in the St. Lawrence estuary, the mode of formation is different. In the case of Dionne's mechanism, the ice-rafted sediments are derived from the marsh surface, as evidenced by the presence of grass rafts and sod encased in ice blocks. In the case of the Noatak, the ice-rafted sediments are derived from the bottoms of the lakes as evidenced by the presence of gastropods, algal material, and black anoxic ooze. I would not, however, preclude, a priori, that Dionne's mode of formation is not operating in some places in the Noatak Delta.

Although the entire sequence of events has not actually been observed in the Noatak Delta, it can be inferred from the numerous barren sheets of mud, seen in the summer of 1973, scattered over the landscape and reflecting the distinctive shape of jagged ice floes (Fig. 3). The most commonly observed sediments are barren silt deposits, 3 to 4 cm thick, showing desiccation cracks and in some cases salty efflorescences. These geometric silt deposits change the albedo and the thermal regime of the soil, resulting in a lowering of the frost table, which in the vegetated delta flats was at a depth of 15 to 36 cm during the latter part of June 1973. The induced thaw is expected to reflect the size and shape of the ice-rafted sediments left by the melting of the ice floes. The resulting thermokarst (*2*) depressions are thought to develop into ponds. However, no ponds would be expected to develop in cases where the ice floes come to rest at sites not propitious for the formation of a pond. Obviously, the presence of ice lenses and the ice content of the permafrost are two factors that are very important in determining the evolution of the thermokarst lakes. Substrata containing ice-rich permafrost are the most susceptible to the formation of thermokarst lakes. In some places a collection of ice blocks has probably induced the formation of a number of small ponds that, once enlarged by the melting of the underlying frozen ground, coalesce to form larger bodies of water. The lakes thought to have formed by this process show irregular geometric shorelines that betray the suggested mode of formation as contrasted with the long, narrow, channel-like lakes that start in thermal contraction cracks.

In one particular instance a triangular sheet of barren mud with sides measuring 283, 230, and 400 cm (Fig. 3) exhibited dead, decomposed mosses mixed with mineral sediments near one edge and a barren surface over the remainder of the sheet. The thickness of the layer of dead moss mixed with the mineral sediments was 4 to 5 cm. Below this layer, numerous gastropods, like those found in nearby lakes, were present (*3*). The thickness of the mud deposit varied from 2.5 to 7.0 cm. Although no distinct horizonation or layering was noticeable, a cross section showed that the first 5 cm consisted of a dark yellowish gray (10Y4/1) (*4*) fine silt containing gastropods and characterized by a fine granular structure. Below this layer, 2 cm of black (10Y1/1), very fine, anoxic lake-bottom ooze gave off a strong H_2S odor. The sheet of mud rested uncomformably on depressed, brownish, tundra vegetation which was buried by the ice-rafted sediments.

Other sediment sheets were also measured and described, and transects were made across them and the adjacent landscape. These transects revealed that the depths to the frost table beneath the mud sheets exceeded the depths observed in the adjacent areas, except in a few cases where depressions had already developed. I tentatively interpret these results as indicating an incipient collapse of the region immediately under the mud cover as the result of the





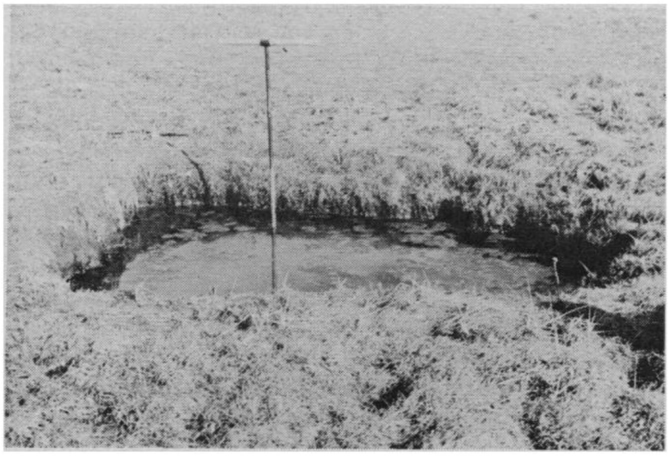


Fig. 1 (upper left). Aerial view of lakes displaying angular perimeters and cuspated shores, western portion of the Noatak River Delta, Alaska. Fig. 2 (lower left). Small pond in the Noatak River Delta, Alaska. The steep and angular shores are believed to be due to differential thawing. Fig. 3 (upper right). Mud patch derived from lake-bottom sediments believed to have been ice-rafted during flooding, Noatak River Delta, Alaska.

degradation of the underlying permafrost.

Two areas—one covered with ice-rafted sediments and one without—were instrumented with thermal probes placed at the surface, at 6 cm and at 13 cm; the temperature was recorded four times a day with a telethermometer (Yellow Springs). For five consecutive days of measurement, starting on 18 June and ending on 22 June 1973, the soil under the ice-rafted sediments was consistently warmer than the nearby vegetation-covered soil, probably because of the dark color of the ice-rafted sediments and their lack of insulating vegetation. On 19 June 1973, at 0840, the two sites showed maximum differences as follows: the temperature of the ice-rafted sediments exceeded the temperature at the corresponding depth for the vegetation-covered soil by 3.5°C at the surface, by 6.5°C at the 6-cm depth, and by 4.0°C at the 13-cm depth. Hence, the warmer soil would induce differential thawing that should lead to thermokarst development.

Once a pond has been initiated, repeated freezing of ice to the bottom and subsequent flooding would tend to lift the ice cover with its adhering sediments, further deepening the pond; indirect evidence in support of this process are the vertical and apparently sheared edges of ponds and lakes. This process stops when the lakes are too deep to freeze to the bottom. However, shallow portions of deep lakes and shallow channels of the Noatak Delta can still contribute ice-rafted sediments. As mentioned above, the process outlined depends on the occurrence of floods. Conversations with the local Eskimos and with Buck Maxson, a pilot from Kotzebue, established that a severe storm occurred during November 1972, a storm the likes of which had not been recorded for some 20 years, flooding the Noatak Delta, rafting numerous ice floes, and leaving them stranded after the waters had receded. This was further confirmed by ERTS-1 (Earth Resources Technology Satellite) mission images (70 1313-21585-7-01 and 1314-22043-07-01) taken on 1 and 2 June 1973, which documented these effects. Some floes stranded at this time were responsible for the sediment patches I observed during the summer of 1973 after the ice had melted. Numerous sediment patches of similar origin were also observed along the west coast of Alaska between Kotzebue and Point Hope (5). Since many lakes whose shorelines have the characteristic shape of ice floes were observed in the western part of the delta, it is conceivable that similar floods could have been the initiating cause of these lakes and that other deltas and tidal marshes of the Arctic also can be affected by the same process. Although this evolutionary process for the formation of deltaic lakes has not been observed in its entirety, it supports the view that landscapes are often formed by catastrophic events, in this case by storms rather than by slow, everyday processes.

F. C. UGOLINI
College of Forest Resources, University of Washington, Seattle 98195

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Polycyclic Aromatic Hydrocarbons in Soils and Recent Sediments

Abstract. *Soils and recent marine sediments contain a complex polycyclic aromatic hydrocarbon assemblage. There is a high degree of similarity in the molecular weight distribution of the many series of alkyl homologs of these aromatic hydrocarbons, and this distribution varies little over a wide range of depositional environments. The evidence suggests that these hydrocarbons are formed in natural fires, are dispersed and mixed by air transport, and are eventually deposited into surface sediments. The analytical, geochemical, and environmental implications of these findings are discussed.*

Polycyclic aromatic hydrocarbons (PAH) occur commonly in soils and young marine sediments (1). Until recently it had been thought that this sedimentary PAH fraction consisted of a limited number of unsubstituted hydrocarbons, but newer analyses with greater analytical resolution have now demonstrated a far greater compositional complexity and the presence of extended series of alkyl homologs (2, 3). Thus, the marine sediments of Buzzards Bay, Massachusetts, contain, in addition to the previously known parent hydrocarbons, homologs extending to at least C_{12} and extended series of naphthenologs and thienologs.

The discovery of these complex PAH assemblages in recent sediments has considerable geochemical and environmental significance. In order to study the regional variability of the PAH fraction and to obtain clues on its origin, we have analyzed samples that cover depositional and chemical environments ranging from continental and coastal soils to marsh and subtidal marine deposits, and from high to low oxidation-reduction potentials (4).

We used the method of Giger and Blumer (2) in the sampling and initial work-up; this involves solvent extraction, separation by adsorption and gel permeation chromatography, and charge transfer complexation. The purified aromatic concentrate is separated by chromatography on alumina. In order to determine the molecular weight distribution within several PAH series, we collect in a single fraction, after the elution of most dicyclic aromatics, all the tri- and tetracyclic compounds (anthracenes, phenanthrenes, pyrenes, fluoranthenes, chrysenes, triphenylenes, benzanthracenes, and others). To assure complete recovery of the most strongly retained four-ring compounds, elution is continued into the pentacyclic fraction.

This tri- and tetracyclic concentrate is then subjected to mass spectral probe distillation. While the probe warms up, first through indirect heating from the source and then through programming, spectra are collected at 12 ev until the sample is completely exhausted. The intensities of the molecular ions are integrated over the course of the distil-