isolated manganese or iron atoms stabilized in the 3+ oxidation state by the MgO lattice. Hydrocarbon could interact with the surface to form a stabilized carbanion, and then electron transfer could occur with subsequent release of a hydrocarbon free radical into the gas phase. The active catalytic site could then be regenerated by means of hydrogen atom recombination at the surface and abstraction of the surface-bound hydrogen by gas-phase radicals.

Several aspects of the proposed mechanism are critical to explaining the experimental data. Initial formation of carbanions at the surface would direct activation of the hydrocarbon to the primary position as a result of the inherent carbanion stabilities (primary > secondary > tertiary). Steric hindrance could also direct activation to the primary position; the ability of pure MgO to form carbanions at the surface has been reported (*8*). Electron transfer and subsequent desorption of hydrocarbon radicals would result in the directed formation of primary radicals. Gas-phase radical decomposition by means of accepted pathways of carbon-carbon bond scission would then produce the observed changes in product selectivities. The anomalously high selectivity to ethane observed during *n*-butane cracking could be attributed to abstraction of hydrogen from the catalyst surface by ethyl radicals. Alternative explanations, such as gas-phase hydrogen atom abstraction or catalytic hydrogenation of ethylene, are not likely. If most of the ethane were formed by gas-phase abstraction processes, the ratio of ethane to ethylene would be near that observed for thermal conversions under comparable reaction conditions. Experiments in which ethylene and hydrogen were passed over the Mn-MgO catalyst showed it had virtually no hydrogenation activity.

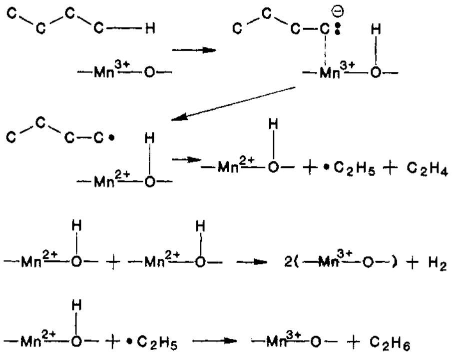

Fig. 3. Proposed mechanism for the selective cracking of *n*-butane over the Mn-MgO catalyst.

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Inorganic and Organic Sulfur Cycling in Salt-Marsh Pore Waters

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Sulfur species in pore waters of the Great Marsh, Delaware, were analyzed seasonally by polarographic methods. The species determined (and their concentrations in micromoles per liter) included inorganic sulfides (≤3360), polysulfides (≤326), thiosulfate (≤104), tetrathionate (≤302), organic thiols (≤2411), and organic disulfides (≤139). Anticipated were bisulfide increases with depth due to sulfate reduction and subsurface sulfate excesses and *p*H minima, the result of a seasonal redox cycle. Unanticipated was the pervasive presence of thiols (for example, glutathione), particularly during periods of biological production. Salt marshes appear to be unique among marine systems in producing high concentrations of thiols. Polysulfides, thiosulfate, and tetrathionate also exhibited seasonal subsurface maxima. These results suggest a dynamic seasonal cycling of sulfur in salt marshes involving abiological and biological reactions and dissolved and solid sulfur species. The chemosynthetic turnover of pyrite to organic sulfur is a likely pathway for this sulfur cycling. Thus, material, chemical, and energy cycles in wetlands appear to be optimally synergistic.

THE BIOGEOCHEMICAL ROLE OF SULfur in tidal wetlands is an area of intense research. Because sulfur is an important redox element under natural aquatic conditions, it is responsible for a number of important biogeochemical processes, such as sulfate reduction (*1, 2*), pyrite formation (*2, 3*), metal cycling (*4–6*), salt-marsh ecosystem energetics (*7, 8*), and atmospheric sulfur emissions (*9, 10*). Each of these processes depends upon the formation of one or more sulfur intermediates, which may have any oxidation state between +6 and −2. The intermediate oxidation states of sulfur may be organic or inorganic (*11*). For example, pyrite, FeS_2, forms readily when polysulfides (S_x^{2-}) are present (*12*). Pyrite can store reduced sulfur compounds, and its oxidation is believed to support salt-marsh food webs (*7, 8*). Once buried, pyrite appears geologically stable and is a primary reservoir of iron and sulfur in salt-marsh sediments (*2, 3*).

At present, our knowledge of the modes of formation and concentrations of organic sulfur compounds in natural aquatic systems is limited (*11*). In salt-marsh pore waters and sediments, such compounds may be precursors of organic sulfur in fossil fuels such as coal. The emission of organic sulfur compounds from tidal wetlands to the atmosphere may be an important remote source of stable, reduced sulfur compounds (*9*), which, when oxidized, act as remote acid rain precursors (*13*). The role of organic sulfur compounds in other biogeochemical processes in estuaries is not clear, although active participation in trace metal cycling appears likely (*4*).

Adequate methods for the determination of sulfur species in natural waters have only recently become available. Several species of sulfur in pore waters from Great Marsh, Delaware, were found at three depths during the summer period as a result of investigations with electrochemical titration methods and ultraviolet-visible spectroscopy (*4*);

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thiols and polysulfides were detected. Other researchers, using gas chromatography, have found trace quantitites of dissolved organic sulfur gases (dimethylsulfide, dimethyldisulfide, COS, and CS_2) emanating from salt marshes (*9, 10*) or in salt-marsh pore waters (*14*). We have developed a polarographic technique (*15*) that can be used to determine a variety of dissolved sulfur species in sediment pore waters, including sulfite (SO_3^{2-}), thiosulfate ($S_2O_3^{2-}$), inorganic S(−2) as bisulfide (SH^-) and polysulfides, inorganic S(0) as polysulfides, inorganic polythionates, thiols, and organic disulfides.

We used polarographic methods to analyze the sediment pore waters of Great Marsh for dissolved sulfur species. The pore water was obtained by hermetic extraction and squeezing of cored sediments (*16, 17*). Other diagenetic parameters such as pH, SO_4^{2-} concentration, and Cl^- concentration were also measured (*2*). Three samplings were performed in 1984 in Great Marsh, Delaware (75°11′W, 38°47′N), when productivity of marsh grass was beginning (15 March), high (28 June), and nearly at an end (2 November). As expected from earlier work, we found S(−2), $S_2O_3^{2-}$, and S_x^{2-} (Figs. 1 through 3).

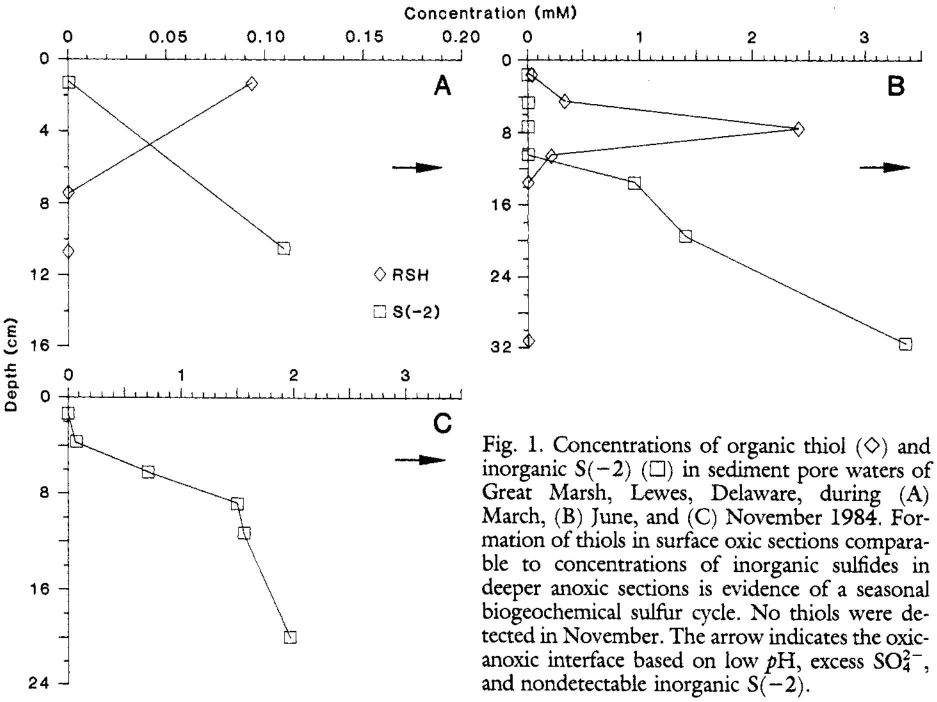


Fig. 1. Concentrations of organic thiol (◇) and inorganic S(−2) (□) in sediment pore waters of Great Marsh, Lewes, Delaware, during (A) March, (B) June, and (C) November 1984. Formation of thiols in surface oxic sections comparable to concentrations of inorganic sulfides in deeper anoxic sections is evidence of a seasonal biogeochemical sulfur cycle. No thiols were detected in November. The arrow indicates the oxic-anoxic interface based on low pH, excess SO_4^{2-}, and nondetectable inorganic S(−2).

An unknown thiol was the major dissolved organic sulfur species found from the surface to a depth of 3 cm in March and from the surface to 12 cm in June, when this species reached a peak concentration of 2.41 m*M* at 6 to 9 cm. The compound may be glutathione or some other small peptide (*15*). The thiol concentrations in this zone were as high as the corresponding inorganic S(−2) concentrations in the reduced zone. We also observed disulfides at depths of 0 to 3 cm (5 μ*M*) and 3 to 6 cm (139 μ*M*) in the summer. For March and June, thiol presence paralleled (i) increases in SO_4^{2-} in excess of normal seawater SO_4^{2-}/Cl^- ratios (Fig. 3A) and (ii) pH decreases (Fig. 3B).

These results are indicative of a sulfide oxidation process in the salt marsh that may result in the formation of organic sulfur compounds. Accordingly, no organic sulfur compounds including thiols were detected during the fall [only SO_4^{2-} depletion (reduction) and neutral pH values were observed]. Instead, large concentrations of tetrathionate were present between the surface and 5 cm (*18*). To our knowledge, this is the first reported observation of tetrathionate in salt-marsh wetlands. It suggests nearly quantitative loss or consumption of dissolved organic compounds during periods of greater reduction and grass dieback in the marsh. Such losses may occur by conversion to volatile forms, condensation to solid deposited phases, or metabolic use in chemosynthetic pathways. These results suggest a dynamic sulfur cycle in which sulfur is transformed from inorganic to organic species between the surface and a depth of 12 cm during warmer, more productive seasons and from organic to inorganic forms during cooler, less productive seasons. Part of the cycling may include the formation of solid phases of inorganic and organic sulfides as well.

Thiols could form by at least five pathways. We believe four of these may be minor in this system because they require basic conditions for thiol formation, and our observations indicate that thiols are formed under acidic conditions. These pathways are (i) nucleophilic displacement of SH^- with labile organic compounds (alcohols, methoxy, or halide compounds) (*19*), (ii) addition across double bonds by SH^- (*20*), (iii) direct formation through SO_4^{2-} reduction, and (iv) reaction of polysulfides with abundant lignins in reactions analogous to the Kraft process in pulp mills (*21*). Pulp mill reactions like reactions (i) and (ii) usually

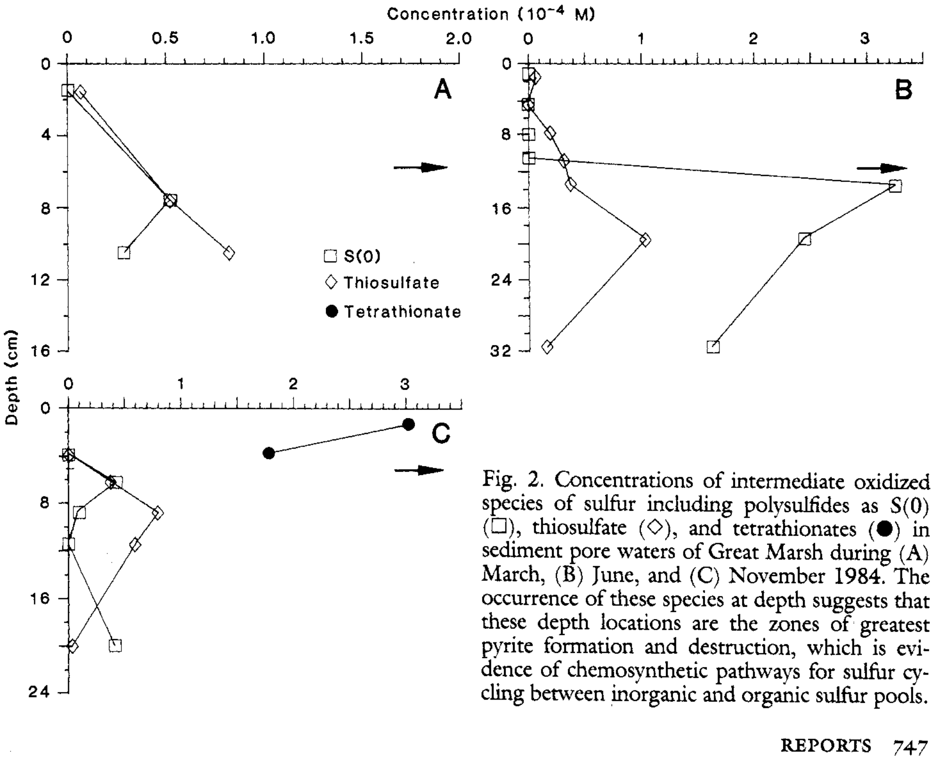


Fig. 2. Concentrations of intermediate oxidized species of sulfur including polysulfides as S(0) (□), thiosulfate (◇), and tetrathionates (●) in sediment pore waters of Great Marsh during (A) March, (B) June, and (C) November 1984. The occurrence of these species at depth suggests that these depth locations are the zones of greatest pyrite formation and destruction, which is evidence of chemosynthetic pathways for sulfur cycling between inorganic and organic sulfur pools.

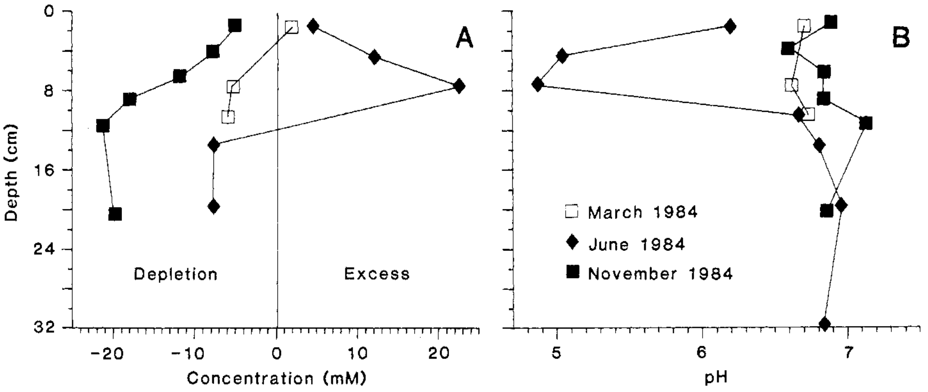


Fig. 3. (A) Excess SO_4^{2-} (normalized to seawater Cl^-) and (B) *p*H in sediment pore waters of Great Marsh during March (□), June (◆), and November (■) 1984. The excesses of SO_4^{2-} relative to seawater and the corresponding minima in *p*H are evidence of extensive seasonal sulfide oxidation including chemosynthesis of pyrite.

require basic and sulfide-rich conditions; however, the surface zones where thiols are formed are acidic and free of sulfide and have excess SO_4^{2-}. Selective vertical migration of reactants may be responsible for this effect, whereby organic sulfur compounds formed at greater depths under more basic sulfide conditions (for example, at the base of the root zone) migrate upward. The upward migration may be due to either volatilization of gaseous sulfide products, detected as a pervasive flux in this marsh (*9*), or evapotranspirative advection (*22*) that results in desiccation and increased salinities below ground (*2*). Supporting these physical phenomena that contribute to upward migration is the peak in thiols overlying a peak in thiosulfate and polysulfides during the summer.

A fifth and more likely pathway of thiol formation in the salt-marsh system is the reaction of organic compounds with sulfur anions such as $S_2O_3^{2-}$, which are generally present in the pore waters (*23*) or with partially oxidized sulfur solid phases such as pyrite, which are always present in the salt-marsh sediment (*2*). All five processes may occur to some extent, depending on season or sediment depth, but we believe the last mechanism is the most likely in the salt marsh because it allows all necessary ingredients to react or form with the observed zonation.

According to this mechanism, $S_2O_3^{2-}$, which formally contains both S(−2) and S(+6) sulfur, can act as a nucleophile to displace hydroxyl groups as in Eq. 1 (*24*):

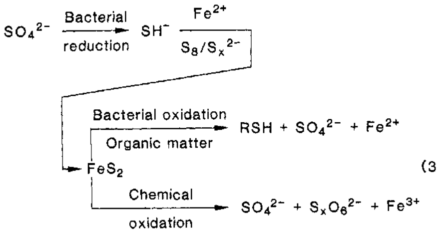
$$ROH + S_2O_3^{2-} \rightarrow RS^- + HSO_4^- \quad (1)$$

This reaction produces excess SO_4^{2-} and increased acidity, persistent features in this salt marsh, particularly in summer (*2*). The question then becomes how is $S_2O_3^{2-}$ produced, and how fast can it react with labile organic substrates? Thiosulfate could be produced via SO_4^{2-} reduction in which a series of two-electron transfers occur. Before $S_2O_3^{2-}$ can be reduced to S^{2-}, it reacts with labile substrates. This process seems unlikely because it would not lead to an excess of SO_4^{2-} in the pore waters. The $S_2O_3^{2-}$ could also be produced from the oxidation of H_2S, sulfide minerals, or volatile methyl sulfides. In the summer, the upper root zone of Great Marsh (0 to 12 cm) is an oxidizing zone in which SO_4^{2-} is regenerated. When diagenetically modeled (*2*), the rate of reoxidation of sulfides is greater than or equal to the SO_4^{2-} reduction rate. Hence, $S_2O_3^{2-}$ production via SH^- oxidation could occur when either inorganic or methyl sulfides diffuse upward for reaction in the oxidized zone where thiols are found.

Likewise, the zone of greatest thiol production occurs at 6 to 9 cm, the interval of optimal pyrite formation. Pyrite formation and destruction appear rapid in most salt-marsh sediments (*4*), including this zone of the Great Marsh (*2*). Thus, pyrite is a possible starting material for thiol production. As such, pyrite [which formally contains both S(0) and S(−2)] may be used directly by organisms in chemosynthesis in salt-marsh ecosystems (*25*). In this case, one sulfur atom from pyrite is eventually converted to a thiol such as glutathione, and the other sulfur atom is completely oxidized to SO_4^{2-} for its source of energy (Eq. 2):

$$FeS_2 \rightarrow RSH + SO_4^{2-} + Fe^{2+} \quad (2)$$

This process would not necessarily require molecular oxygen to effect the oxidation (*26*), as is the case for the chemical oxidation of pyrite (*27*). Such chemosynthetic oxidation of pyrite to $S_2O_3^{2-}$ and SO_4^{2-} by microbial catalysis could help explain the apparent speed and ease of pyrite recycling in salt-marsh sediments (*2, 3*). It could also account for the maxima in dissolved iron at depths near zones of pyrite formation and destruction (*4, 5*). The formation of glutathione or other simple peptides as the dominant component of the organic sulfur pool in salt-marsh sediments furnishes strong support for the idea of biogenic formation of organic sulfur compounds. For example, it has been proposed (*24*) that glutathione is the true enzymatic intermediate for sulfide and elemental sulfur oxidations to SO_4^{2-}. The thiol thus serves to link the inorganic sulfide (as SH^-) with elemental sulfur pools. Our data suggest that a thiol may be an important enzymatic intermediate for, or a by-product of, microbial pyrite oxidation. As such, pyrite formation and its chemosynthetic recycling via thiols (such as glutathione) may be an important biogeochemical process (Eq. 3):



(3)

Such a process would be the link, via pyrite, between the organic and inorganic sulfur pools in salt marshes and would have profound consequences for the cycling of energy and material in wetlands.

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16. Although the cores are cut and squeezed, this does not alter the inorganic species (*14*). We do not believe that the organic sulfur species of interest are affected by this processing since they are not detected at other positions of the rhizosphere or in other seasons in this salt marsh.
17. Cores were taken no closer to the creek bank than 2 m and within a 10-m lineal distance along the creek

bank. The March and June cores were cut into 3-cm sections, and the November core was cut into 2.5-cm sections. During the last 10 years, pore-water and solid-phase species (*2*), including sulfur species, have remained consistent at this site and agree to better than ±10% (frequently ±5%) for samples at the same depth and for the same season. This consistency is borne out in successful diagenetic modeling for sediments and their pore waters at this salt marsh site (*2*).

18. Tetrathionate reduces to thiosulfate at the mercury electrode at $E_{1/2} = -0.32$ V in seawater matrices. Cyclic voltammetry on the November sample (surface to 2.5 cm) confirmed the formation of thiosulfate from tetrathionate.
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23. Although $S_2O_3^{2-}$ concentrations are in some instances smaller than thiol concentrations, $S_2O_3^{2-}$ levels may not build up and may only approach a steady-state level. This has been noted in a Massachusetts salt marsh (*15*).
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28. This research was supported by grants to G.W.L. from the National Science Foundation, Division of Biotic Systems and Resources (DEB82-16376), and the Marine Chemistry Program (OCE85-17138), and the Petroleum Research Foundation; and grants to T.M.C. from the Marine Chemistry Program of the National Science Foundation (OCE84-11064 and OCE85-41757). We thank L. Cifuentes, G. Cutter, A. Giblin, R. Howarth, C. Lord, and J. Morse for comments on earlier drafts.

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New Dates on Northern Yukon Artifacts: Holocene Not Upper Pleistocene

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New radiocarbon dates on four artifacts that were thought to provide evidence for human occupation of the Yukon Territory during the upper Pleistocene indicate that all four are of late Holocene age. The original radiocarbon age obtained for one artifact (the so-called "Old Crow flesher") was in error by almost 26,000 years.

THE STUDY OF THE TIME AND CIRcumstances of the human colonization of the New World has preoccupied archeologists for more than a century. The earliest universally acknowledged North American sites are those that were occupied by people who made distinctive fluted stone projectile points approximately 11,500 years ago and who are usually given the name Clovis, after a locality in New Mexico. Although many sites and study areas have been presented as providing evidence for pre-Clovis human occupation in both North and South America (*1*), the validity of this evidence is not accepted by all investigators (*2*). Reexamination of one such body of evidence shows that four artifacts from the Old Crow locality in the northern Yukon Territory, Canada, which were previously thought to be of late Pleistocene age, were in fact from the late Holocene.

These artifacts were originally obtained from localities scattered along the Old Crow River (*3*, *4*), which meanders across the intermontane Old Crow Basin. In late Wisconsinan time, the river dissected the basin, exposing more than 30 m of Pleistocene sediment (*5*). This action exhumed hundreds of thousands of fossil bones from the Pleistocene deposits, and these were subsequently redeposited in and on the terraces and gravel bars that developed during the Holocene (*6*).

In 1966, a caribou (*Rangifer tarandus*) tibia that had been fashioned into a fleshing tool was found in one of these Holocene terrace deposits at locality 14N. This artifact is similar in form and material to tools made in late prehistoric and historic time for removing the flesh from skins used for clothing, shelter, and other purposes. In addition to this flesher, mammoth limb bones were found that had been fractured and flaked, presumably by humans, in a manner reminiscent of the production of stone tools. The man-made flesher and the flaked mammoth bone were immediately radiocarbon dated (*3*) to determine whether they were of the same age. If so, there would be strong evidence for a human culture of considerable antiquity that used mammoth bone for tools.

Carbon extracted from the inorganic, or apatite fraction (*7*) of the flesher and two of the fractured mammoth bones gave radiocarbon ages of 27,000 years before present (BP), 25,750 BP, and 29,100 BP, respectively (*3*). These dates were in general agreement with dates on carbon from the organic, or collagen fraction (*7*) of a mammoth femur (22,600 BP) and a bison humerus (33,800 BP) (*3*). The rather broad time range represented by the dates was explained by the observation that locality 14N is a Holocene terrace deposit into which the Pleistocene fossils had been transported by fluvial processes. The concordance between the early date for the flesher and those for the flaked mammoth bones suggested that an early North American culture existed in the Yukon in Pleistocene times and that the flesher represented a tool type that had been in use for a long time.

These dates, and in particular the one on the flesher, helped launch intensive multidisciplinary research in Old Crow Basin that continues to this day, and the flesher date is often cited as a cornerstone of arguments that favor pre-Clovis human occupation of the New World. Various arguments have also been advanced against these interpretations. It was suggested that the flesher could have been made recently on a bone that had already been fossilized, or that had been preserved by freezing (*8*). A much more serious possibility is that the age of the flesher is suspect as it was obtained on carbon extracted from the inorganic portion of the bone. Since the flesher was originally dated, research has shown that the inorganic bone fraction is susceptible to diagenetic exchange of carbon, and that the organic, proteinaceous carbon is preferable (*9*).

To test the original assumptions and conclusions about the Old Crow material, we took a new series of radiocarbon dates. The mammoth and bison bones from locality 14N had been entirely sacrificed for the original dates, but the man-modified working tip of the flesher (~21 g) was preserved so that it could be displayed. Only a small amount of this tip could be removed. The method of accelerator mass spectrometry (AMS) made it possible to obtain dates on bone samples of much less than 1 g.

The 36 bones chosen for dating formed three categories: (i) six bones were from known stratigraphic contexts, and three of these may have been modified by man when fresh; (ii) 26 of the bones (of which 24

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