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# IRON-CEMENTED GLACIAL DRIFT IN LOGAN COUNTY, NORTH DAKOTA

*John W. Bonneville*
*Department of Geology*
*University of North Dakota*

## INTRODUCTION

A number of deposits of iron-cemented glacial drift were found by the writer while mapping the surficial geology of southern Logan County, North Dakota, during the summer of 1960. An interpretation as to the origin and significance of these deposits was thought important because of their lithology, induration, alteration, and stratigraphic position below early Wisconsinan drift, and because of the significant occurrence of datable peat underlying one outcrop.

### Location and Physiography

The iron-cemented glacial drift was found in seven outcrops in three locations as shown on Fig. 1. All exposures of this drift were found in areas of bedrock controlled erosional topography with local relief of over 150 feet. The underlying Cretaceous Fox Hills formation consists largely of weakly-consolidated iron-rich sands. The well-indurated iron-cemented drift forms resistant caps on bedrock highs, and is overlain by thin early Wisconsinan till in most outcrops.

## METHODS AND RESULTS

Field studies.—A thorough field examination of Logan County revealed only seven outcrops of the iron-cemented drift. Tracing of these deposits under younger drift in two localities was possible, but drill holes in adjacent areas of thicker drift have not been made. Lithologic descriptions and stratigraphic relations were noted in the field, and 100 pounds of samples were brought back to the laboratory for examination.

Laboratory studies.—Twelve thin sections were made from different samples for a microscopic study of the sediment. Stannous chloride and HCl were used to dissolve the iron-cement from the drift for residue analysis.

Description of samples.—The iron-cemented drift is a clastic sediment, probably glacial gravels, with a heavy chemically or biochemically precipitated limonite-goethite cement hydrous iron oxides). All deposits are massive to weakly stratified, with numerous molds left where the more soluble pebbles have been completely leached out. (See Fig. 2.) The texture is rudaceous to arenaceous with a poor degree of sorting. The entire deposit has been stained and impregnated with precipitated limonite-goethite which then cemented the gravels into a resistant mass.

Laboratory tests showed up to 40% by volume and 55% by weight of the sediment consisted of iron oxides. Permeability and porosity

are moderate to high, and mineral composition is variable. Hand samples and thin sections show various altered and decomposed metamorphic and igneous rock fragments, chert, quartz, and Fox Hills sandstone pebbles. All carbonates have been completely leached out unlike any younger deposits in Logan County.

The thin sections made from this deposit were very similar to those described by Moore (9) in his studies of bog-ores in Ontario. He found in his examination of thin sections that the limonite was in the form of an opaque, reddish-brown mass, heterogeneous, and had no distinguishing features beyond a porous condition. His slides showed numerous angular to rounded quartz fragments, feldspars and some rock fragments with no preferred orientation in the limonite groundmass.

Angular silt-sized grains of quartz similar to those noted by Moore were observed in thin sections "floating" in the iron cement of the Logan County deposits. These were probably carried by local streams or aeolean action blowing sand and silt into the open bog during iron deposition.

### Stratigraphic Position and Topographic Expression

The generalized cross-section on Fig. 3 shows the relationship of the iron-cemented drift to the over and underlying sediments in the outcrop areas.

The iron-cemented drift forms a thin, resistant cap on bedrock highs where post-glacial erosion has dissected the area. In one locality the deposit is underlain by 0 to 3 feet of gray to black peaty silt. This silt has numerous carbonized plant remains which were collected and sent to the U. S. Geological Survey in Washington, D. C., for radiocarbon dating. Other $C^{14}$ material was collected from the overlying early Wisconsinan drift in northern Logan County. These samples together with $C^{14}$ material collected from younger drift sheets in Logan County will help decipher the glacial history and correlation of deposits in North Dakota.

### Age of the Iron-cemented Drift

The age of the surficial drift west of the Altamont-Max morainal complex in North Dakota has long been in controversy. To avoid confusion this drift is herein informally referred to as the Napoleon drift in Logan County. Numerous exposures are found in northwestern Logan County, North Dakota. Todd (10), Leonard (7), Leverett (8), Alden (1) and others have studied parts of this drift sheet and all have offered possible ages for it. Flint (2), has done the most comprehensive work in correlation of these outlying glacial deposits. Flint states that in South Dakota this drift is Iowan with some possible Tazewell drift included, based on tracing around the west side of the James Lobe from the type area in northeastern Iowa.

Continued tracing on aerial photos north from the South Dakota

border through McIntosh County into Logan County (24 miles) shows the same drift. Lemke and Colton (6) assigned a Tazewell (?) age to the drift, but this assignment is not supported by field evidence in the present writer's opinion.

Field examinations show that the lithologic and topographic expression of this drift in Logan County, and that described by Kay (5), and others, from the type Iowan in Iowa are strikingly similar. The well developed integrated drainage pattern, thin unleached drift, common gravelly knolls, stratigraphic position, and nearly continuous tracing from type area are all factors suggesting Iowan rather than Tazewell deposits. It is the writer's opinion that the Napoleon drift in Logan County is very probably Iowan in age, with erosional remnants of sub-Napoleon drift found in a few locations underlying it. The iron-cemented drift is such a deposit. The radiocarbon datings now in progress should help prove or disprove this tentative age assignment. If the Iowan age is supported by these $C^{14}$ dates, the iron cemented drift will then be the first proven pre-Iowan (pre-Wisconsinan) glacial deposit from North Dakota.

The deposition of the iron and the leaching of the carbonates probably took place during a major interglacial age.

**Possible Origin of Iron-cemented Deposits**

The limonite-goethite cementing material in the iron-cemented drift is most characteristic of bog-iron ores. Bog ore is composed principally of these minerals and has been described from northern and eastern Canada, northwestern and northeastern United States, Sweden, and northern Asia. In these areas percolating waters dissolve iron from the glacial drift and bedrock with the aid of carbonic and organic acids. The iron is carried in solution as soluble carbonate, sulphate, or combined with complex organic acids. The iron may then be precipitated chemically or biochemically in marshes, peat bogs, or other shallow surface depressions. (3).

Chemical precipitation takes place either by removal of the solvents by reaction with other materials in solution or by oxidation. It is generally agreed that plants and bacteria are the chief agents in producing the chemical action in the formation of bog-iron (4). The iron complex collects as a thin film on the surface of the water and then sinks or collects along the shore. When the iron becomes oxidized at or near the surface, insoluble limonite forms.

Forms of bog ore deposits.—The common form of bog ore deposits found are horizontally tabular bodies a few feet thick, and red to yellow in color. They are found as both soft or hard-bedded masses, concretions, or as a cement in gravels and sands which the iron-rich solutions have impregnated. The deposits studied by the writer are thought to have been such a porous gravel which has been impregnated by iron rich waters, from which the iron was precipitated.

Iron source.—The iron which was deposited must have been derived either from the existing glacial drift, or from the bedrock Fox Hills sandstone. Most of the iron probably came from the Fox Hills formation which contains many iron-bearing minerals, and is, in many near-by places, hydrostatically higher than the local depressions in which the iron was precipitated. This provided groundwaters an opportunity to remove iron from the Cretaceous sands and drift, and to carry it to depressions where it was precipitated as bog ore. Leonard (7) described a similar deposit he called an iron-cemented "boulder bed" in McKenzie, County, North Dakota, which he attributed to ground water precipitation of iron.

## SUMMARY AND CONCLUSIONS

The similarities in mineralogy, topography, structure, and probable origin between the iron-cemented material in Logan County and bog-ore deposits reported throughout glaciated areas of North American and other parts of the world, lead this writer to believe that the iron-cementing material was of the same origin. Thin sections of bog ore and the iron-cemented drift support this similarity further.

The tentative age assignment of Iowan for the Napoleon drift in Logan County is presently based on: 1. nearly continuous tracing of this drift from type Iowan in Iowa; 2. stratigraphic position below late Wisconsinan deposits, and above probable highly-weathered iron-cemented sub-Wisconsinan deposits; 3. thickness and lithologic similarities to type Iowan; 4. topographic expression; 5. integrated drainage pattern showing this surface is much older than late-Wisconsinan surfaces to the east in Logan County, but not showing the high degree of weathering that pre-Wisconsinan deposits have.

The significance of the iron-cemented drift located stratigraphically below a drift of probable Iowan age (subject to $C^{14}$ results) is important in the unravelling and regional correlation of the Pleistocene geology of North Dakota. If the age of the Napoleon drift is then Iowan, the underlying iron-cemented drift is pre-Wisconsinan, and is the first proven evidence that North Dakota was glaciated in pre-Wisconsinan time.

### Sequence of Events

One possible sequence of events in the formation of the iron-cemented drift deposits in Logan County can be divided into three stages. During the first stage meltwater run-off or increased local precipitation ahead of the first ice advance over this area formed swampy areas on the rough surface of the eroded Cretaceous rocks. Fine silts, clays, and plant debris were deposited in the depressions; this is the peaty basal material found today.

During the second stage the advancing ice overrode the area and deposited thin patchy gravelly drift. When this ice sheet retreated, swampy conditions and a high water table returned. The

rugged pre-glacial topography was little modified by the thin drift deposited. Iron began being dissolved by ground waters from the near-by drift and bedrock sands at higher elevations, and was carried to the lower areas where it was precipitated as bog-iron. The deposition of iron was halted when headward erosion of near-by streams with lower base levels drained the bogs. This increased the downward movement of groundwaters and the ultimate complete leaching of carbonate minerals in the iron-cemented gravels. Molds of these pebbles in the cemented drift are common; these voids are not filled with iron-cement which shows the leaching occurred **after** cementation ceased (due to draining of bogs).

During the third stage of development the early Wisconsinan (Iowan?) glacier advanced over the area and deposited a thin mantle of fresh drift over the leached iron-cemented patches of drift. This is the Napoleon drift sheet. Extensive erosion since that

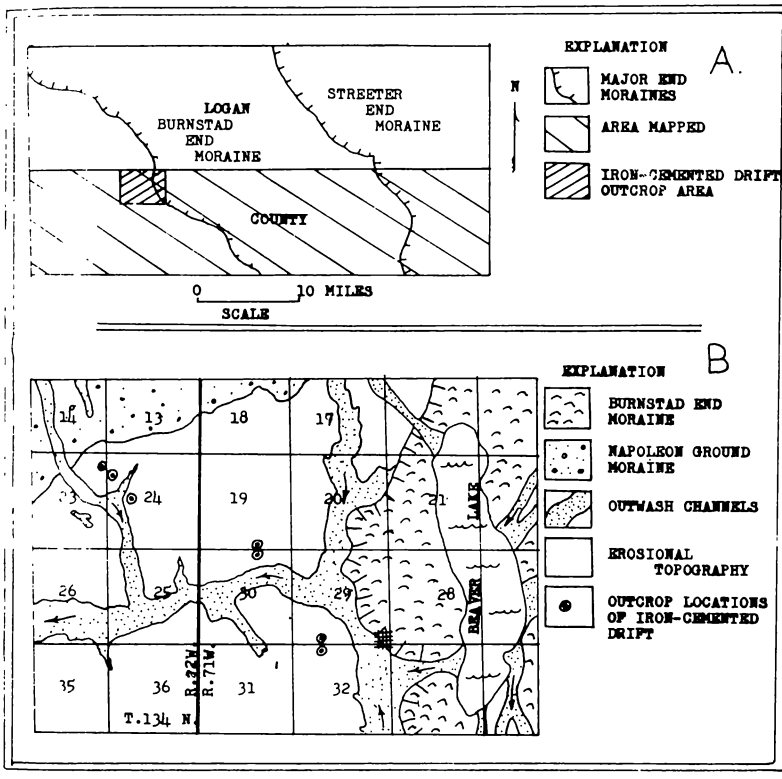


FIGURE 1. (A) Index map of Logan County showing the area where iron-cemented drift crops out. (B) Outcrop area expanded to show glacial geology and outcrop locations.

time has left the more resistant indurated iron-cemented drift capping bedrock highs. Where erosion has not yet progressed as far in adjacent areas to the north and west, any iron-cemented drift patches are still covered. No drill holes are available in near-by areas to prove the existence of additional and more extensive deposits of iron-cemented drift.

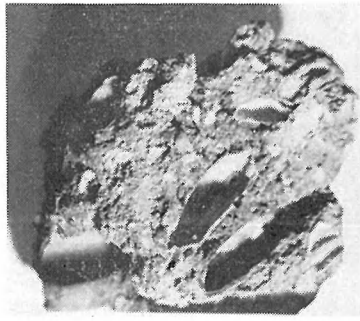

FIGURE 2. Photograph of iron-cemented drift sample showing large solution voids due to extensive leaching of carbonates.

## ACKNOWLEDGMENTS

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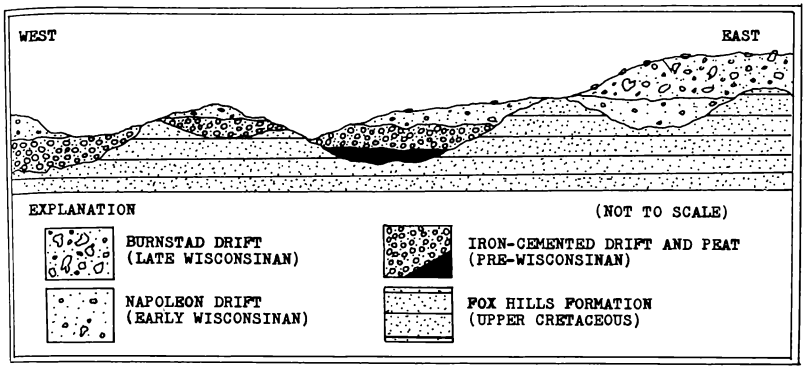


FIGURE 3. Generalized cross-section of iron-cemented drift outcrop area showing its relationship to older and younger sediments.

# LATE WISCONSIN MOLLUSCA FROM ICE-CONTACT DEPOSITS IN LOGAN COUNTY, NORTH DAKOTA

*Lee Clayton*
*Geology Department*
*University of North Dakota, Grand Forks*

## INTRODUCTION

During the summer of 1960, while mapping the glacial geology of northern Logan County, North Dakota, I collected samples of fossil Pleistocene fresh-water mollusk shells from four different localities. These shells were found in deposits of ice-contact stratified drift that was deposited from dead glacial ice during the last part of the Wisconsinan Age, probably during the last part of the Woodfordian Subage of Frye and Willman (5, p. 2).

## COLLECTION AND IDENTIFICATION

No attempt was made to make an extensive collection of the Pleistocene fossils of Logan County; the samples were merely collected during the course of field mapping. Samples from two localities consist of the more conspicuous shells that were picked off a fresh surface of the exposure. At two other localities a few quarts

of the most fossiliferous sediment were collected, and a few hundred shells were wet sieved from part of each of these samples, using a 16-mesh screen.

Identifications were based largely on the works of Baker (1, 2), Leonard (8, 9), and Taylor (13); they were also the authority for most of the environmental ranges. Because original descriptions or type specimens of most of the species were not examined, some of the identifications are tentative.

All of the specimens have been placed in the paleontology collection of the University of North Dakota Department of Geology.

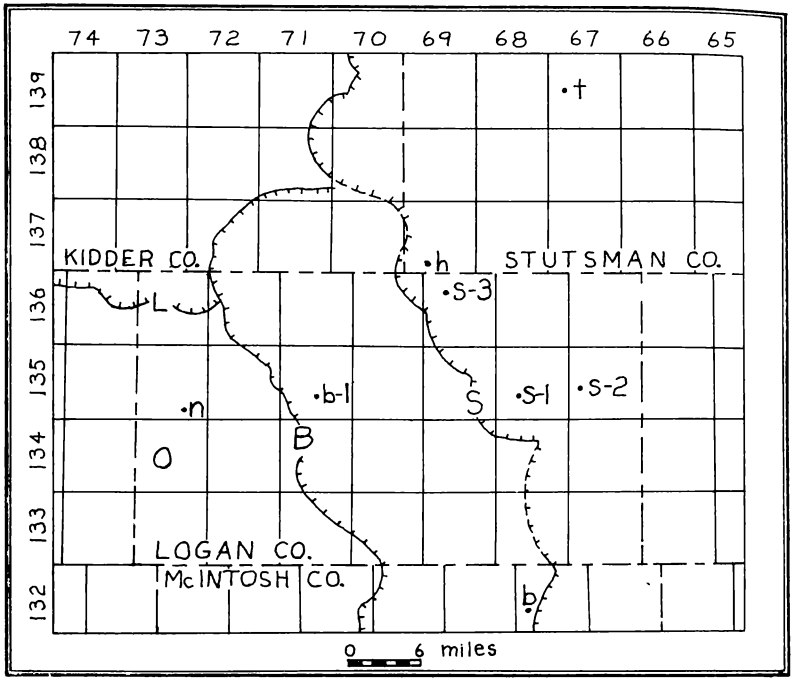


FIGURE 1. Localities of late Wisconsinan molluscan faunas and the limits of major ice advances in south-central North Dakota. O = older drift; L = outer limit of Long Lake advance; B = outer limit of Burnstad advance; S = outer limit of Street advance; b-1 = fauna from Burnstad drift; s-1, s-2, s-3 = faunas from Streeter drift; t, h, b, n = other mollusk localities.

## DESCRIPTION OF FAUNAS

### Fauna from Burnstad drift

Fossils were collected from the Burnstad drift (7, p. 58) at locality b-1, (see Fig. 1), 0.3 mile south of the northwest corner of sec. 27, T. 135 N., R. 71 W., 4½ miles north of Beaver Lake. The

sample was taken with a hand auger from a 4 foot bed of marl, which overlies an undetermined thickness of dark grey lake clay. The marl and clay were deposited in an irregular partly ice-walled lake that was associated with the dead Burnstad ice; the deposit probably belongs to the upper part of the Woodfordian Substage (see Fig. 2).

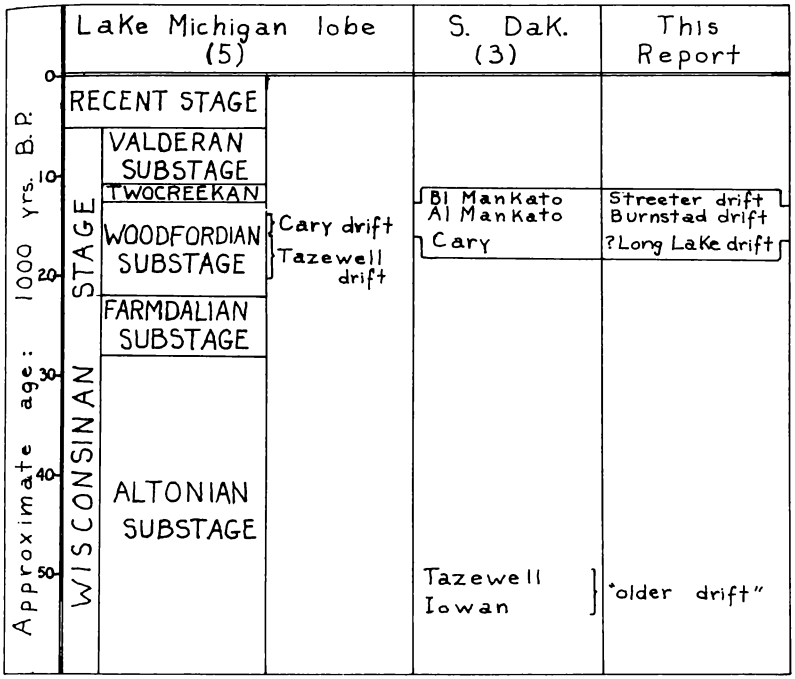


FIGURE 2. Suggested correlation of drifts in Fig. 1 of this report.

Two quarts of the marl were collected from an auger hole, and a few hundred mollusk shells were sieved from part of the sample. The following mollusks were identified:

| | UND No. |
|---|---|
| *Amnicola leightoni* Baker | 1777 |
| *Armiger crista* (Linnaeus) | 1785 |
| *Gyraulus parvus* (Say) | 1778 |
| *Helisoma trivolvis* (Say) | 1779 |
| Unidentified Lymnaeidae | 1780 |
| *Pisidium* sp. | 1781 |
| *Promenetus exacuous* (Say) | 1782 |
| *Valvata tricarinata* (Say) | 1783 |
| *Valvata* sp. | 1784 |

The most abundant species are *Gyraulus parvus, Promenetus exacuous,* and *Valvata tricarinata.* Ostracodes are also abundant.

All of the identified mollusks, except *Amnicola leightoni*, which is believed to be extinct, are found today in the Upper Midwest in a wide range of quiet fresh-water environments. However, *Valvata tricarinata* is found in bodies of water that do not dry up from year to year (13, p. 48). Most of the mollusks live only where there is submerged vegetation. It is assumed that environmental preferences of these mollusks were the same in late Wisconsinan time as they are today. Therefore the environment is thought to have been a fairly warm, quiet, and relatively permanent body of water with submerged vegetation.

**Fauna from Streeter drift**

Mollusk shells were collected from deposits of ice-contact drift at three different localities (see Fig. 1) in the Streeter dead-ice moraine (7, p. 55). The Streeter drift is slightly younger than the Burnstad drift but probably also belongs to the upper part of the Woodfordian Substage (see Fig. 2).

**Locality s-1.**—Locality s-1 is a roadcut at the northwest corner of sec. 28, T. 135 N., R. 68 W., 11 miles south-southwest of the town of Gackle. Fossils were taken from a small deposit of ice-contact lake silt capping a 50-foot high hill in dead-ice moraine behind the Streeter end moraine.

Three quarts of the fossiliferous silt were collected, and a few hundred shells were sieved from part of the sample. The following mollusks were identified:

| | UND No. |
|---|---|
| *Amincola leightoni* Baker | 1759 |
| *Armiger crista* (Linnaeus) | 1760 |
| *Fossaria* sp. | 1766 |
| *Gyraulus parvus* (Say) | 1762 |
| *Helisoma campanulata* (Say) | 1763 |
| *Physa* sp. | 1764 |
| *Pisidium* sp. | 1765 |
| *Promenetus exacuous* (Say) | 1794 |
| *Valvata tricarinata* (Say) | 1767 |
| *Valvata* sp. | 1768 |

*Amnicola leightoni, Gyraulus parvus,* and *Valvata tricarinata* are the most abundant species. Also present are Charcacaea oogonia and abundant ostracode carapaces.

This fauna is similar to that found in the Burnstad drift, indicating a rather warm, shallow, and quiet body of fresh water with submerged vegetation.

**Locality s-2.**—Locality s-2 is a roadcut 0.4 miles south of the northwest corner of sec. 20, T. 135 N., R. 67 W., 9 miles south of Gackle. Shells were taken from the base of a 1½ foot layer of silty and pebbly outwash sand lying on an undetermined thickness of lake clay. The exposure is in the middle of a 1½ mile wide ice-

contact lake plain that is elevated slightly above the surrounding dead-ice moraine. This lake was bounded on at least three sides be dead ice of the Streeter advance; the deposit is approximately the same age as that at locality s-1.

Only the most conspicuous shells were picked out of the sand. Articulated shells of at least two large thick-shelled species of the pelecypod family Unionidae (UND no. 1961) are quite common. Because the shells were so close to the surface, they are badly weathered and could not be identified. One shell each of *Sphaerium* sp. (UND no. 1770) and *Helisoma campanulata* (Say) (UND no. 1769) were also collected from the sand.

The presence of the abundant unionid shells and sorted outwash sand indicates that the environment was rather warm, moving meltwater.

**Locality s-3.**—Locality s-3 is a roadcut 0.4 mile north of the southwest corner of sec. 9, T. 136 N., R. 69 W., 4 miles south of Streeter. The deposit is a small body of ice-contact lake clay at the south edge of a 1½-mile wide ice-contact outwash plain. The clay and outwash was deposited by meltwater from the dead Streeter ice mass and is approxiamtely the same age as the ice-contact deposits at localities c-1 and s-2.

Nearly 100 of the more conspicuous shells were picked from a fresh surface of the roadcut. The following mollusks were identified:

| | UND No. |
|---|---|
| *Amnicola leightoni* Baker | 1771 |
| *Gyraulus parvus* (Say) | 1772 |
| *Gyraulus* sp. | 1773 |
| *Helisoma anceps* (Menke) | 1774 |
| *Helisoma campanulata* (Say) | 1795 |
| *Succenea avara* (Say) | 1795 |
| *Valvata tricarinata* (Say) | 1775 |
| Unidentified unionid fragments | |

This fauna is simiar to those found in the Burnstad drift and in the Streeter drift at locality s-1, except that it has a few shells transported from environments other than quiet water. *Succinea* is terrestrial and members of the Unionidae often live in moving water.

### Other occurrences

Shells of one or more large species of Unionidae have recently been found in south-central North Dakota in three other (see Fig. 1) ice-contact deposits that are thought to be approximately the same age as those described above. They are found at locality b, 0.5 mile south of the northwest corner of sec. 20, T. 132 N., R. 68 W., McIntosh County (John W. Bonneville, personal communication); locality t, SE¼SW¼ sec. 17, T. 139 N., R. 67 W., Stutsman County (14); and locality h, SE¼SE¼SE¼ sec. 29, T. 137 N., R. 69 W., Stutsman County (Charles J. Huxel, Jr., personal communication).

Gastropod shells were also collected from a roadcut in a small marl deposit at locality n (Fig. 1), 0.4 mile south of the northwest corner of sec. 35, T. 135 N., R. 73 W., in western Logan County. However, this is probably not an ice-contact deposit, and its stratigraphic position is not definitely known.

Gastropod shells are also abundant in post-glacial deposits in closed depressions on the Streeter and Burnstad drifts.

## CONCLUSIONS

**Water temperature.**—Such a varied and widely distributed fresh-water molluscan fauna in ice-contact stratified drift, to my knowledge, has never been described before. It is surprising that any life existed in meltwater so closely associated with glacial ice. It is believed that because the mollusks probably required temperatures similar to those of present-day North Dakota (14), the "ice-contact" bodies of water in which they lived were well insulated from the dead glacial ice by thick ablation drift. (The presence of this ablation drift is of considerable importance in the controversy over the origin of dead-ice moraine; in Alberta, Stalker (12, p. 32) believes that super-glacial drift is insignificant and "ice-pressing" of sub-glacal drift is a more important factor in the formation of dead-ice features.)

It is also evident that the ice that formed the dead-ice moraine melted slowly; it is thought that large amounts of cold meltwater would have kept the bodies of water too cold for the existance of the faunas described above.

**Water siltiness.**—Another evidence that the drift-covered dead ice melted slowly is the presence of *Valvata* and *Amnicola* in the ice-contact deposits. These prosobranch snails have gills and according to Frye and Leonard (4, p. 160) require relatively silt-free water. Meltwater was evidently formed slowly enough for the silt to settle out and for the water to be warmed by the sun.

**Dispersal.**—The presence of numerous species of gastropods in these relatively short lived ice-contact bodies of water suggests that they could migrate rapidly from nonglacial environments. Many of the ice-walled lakes probably had no direct connection with the proglacial drainage system; the fresh-water gastropods and *Pisidium* may have been carried into these lakes in mud on legs and feathers of water birds. Baker (2, p. 39-40), Yen (15, p. 294), and Pennek (10, p. 682) agree that water birds are an important means of geographic dispersal of fresh-water gastropods and small pelecypods. Because rapid disperal is indicated here, it is surprising that La Rocque (in 6, p. 291) thinks that the absence of *Sphaerium, Valvata,* and *Amnicola* from the deposits of a large late Wisconsinan proglacial lake (300 miles from the supposed location of the ice front) in Saskatchewan indicates a young undeveloped fauna and an environment that was reached with difficulty by mollusks. The

rapidity with which snails can be dispersed may not be generally recognized.

The presence of shells of the members of the Unionidae in the Streeter drift at localities s-2 and s-3 may indicate that the water in which these clams lived was connected with the proglacial drainage system. In their larval stages, Unionidae are parasitic on fish; therefore fish must have been present in the meltwater at these two localities. To get there, the fish probably had to swim up several miles of superglacial meltwater streams. Studies of the distribution of pelecypods in ice-contact deposits may help determine the pattern of superglacial drainage systems. This would show the general shape of the dead ice mass, and this in turn would be of considerable help in solving the problems of formation of dead-ice moraine and its various dead-ice features.

**Stratigraphic value.**—It thus seems that the study of late Wisconsinan fresh-water mollusks in south-central North Dakota will help solve many of the problems of local glacial geologic history. However, the regional stratigraphic value (that is, dating of deposits) of these mollusks is in doubt. In Kansas, mollusks have been found by Frye and Leonard (4, p. 147) to be the most useful fossil for Pleistocene stratigraphic correlations. The Pleistocene problems there, however, are considerably different from those of North Dakota. First, the Pleistocene subdivisions of Kansas consist mainly of loess and alluvium that contain a large proportion of land gastropods. Because of the works of Pilsbry (11), land gastropods can be fairly easily and confidently indentified, whereas fresh-water gastropods are still imperfectly known. Secondly, the Pleistocene deposits of Kansas have been divided into several stratigraphic units, each representing several thousand years, whereas the surface drift over much of North Dakota consists of till believed to have been deposited in only a few thousand years. So, at the present time, it seems that fresh-water mollusks will have little stratigraphic value in the northeastern two-thirds of North Dakota.

However, in southwestern North Dakota, where geomorphic correlation of older deposits is difficult, land gastropods, if found abundantly in loess or alluvium, may prove to be of considerable help in unraveling Pleistocene history.

## SUMMARY

In summary, the Pleistocene mollusks that have found in south-central North Dakota are apparently useful environmental indicators but are of little stratigraphic value. However, conclusions presented in this report are tentative and much more extensive studies need to be made on North Dakota Pleistocene molluscan faunas.

## ACKNOWLEDGMENTS

I wish to sincerely thank Dr. F. D. Holland, Jr. for his many suggestions and for his critical reading of the manuscript and S. J. Tuthill for our numerous conversations in which many of the ideas presented here were developed.

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# A MOLLUSCAN FAUNA AND LATE PLEISTOCENE CLIMATE IN SOUTHEASTERN NORTH DAKOTA

*Samuel J. Tuthill*

*Department of Geology*

*University of North Dakota, Grand Forks, North Dakota*

## INTRODUCTION

In August, 1959, Dr. Mark Rich, while conducting investigations for the North Dakota Geological Survey in Stutsman County, North Dakota, discovered an abundant freshwater molluscan fauna in a sand and gravel pit approximately two miles southwest of the village of Cleveland. The site (hereafter referred to as the Cleveland site) is in the SW¼, Sec. 17, T. 139 N., R. 67 W., Cleveland SW quadrangle. The surrounding topography and stratigraphic relationships unquestionably established the sediments of the pit as late Wisconsinan in age and as being ice-contact deposits, *i. e.*, as having been deposited in a body of water which depended upon blockage by glacial ice for its existence. Realizing the implications of such a fauna, Dr. Rich collected some of the larger mollusks and later brought his discovery to the attention of Drs. Wilson M. Laird, North Dakota State Geologist and Professor of Geology and F. D. Holland, Jr., Associate Professor of Geology at the University of North Dakota. In subsequent conferences, it was decided that further studies of this fauna should be made to determine the possible value of studies of Pleistocene molluscan faunas in connection with glacial geology of the state.

In the summer of 1960, while mapping glacial geology in Logan, McIntosh, and Kidder Counties, North Dakota, Messrs. Lee Clayton and John W. Bonneville, graduate students in the Department of Geology at the University of North Dakota, discovered six other exposures of fossiliferous ice-contact deposits. Independently, Mr. Charles Huxell of the United States Geological Survey discovered yet another exposure of fossiliferous ice-contact deposits in Stutsman County. To the writer's knowledge these comprise the entire number of ice-contact deposits known to contain Pleistocene freshwater mollusks in North America (Clayton, 1961, Fig. 1). Baker (1, 2, 3, 4), Shimek (17), Leonard (13), 14, 15), Leonard and Frye (16), Dall (7), Taylor (18, 19) and Winkler (20) have described many Pleistocene faunas, but these have all been from proglacial deposits or from areas remote from the ice sheet.

On October 14, 1960, the writer with the assistance of Mr. Kent A. Madenwald, both graduate students in the Department of Geology at the University of North Dakota, visited the Cleveland site and systematically sampled both the fauna and the sediments. These samples were later studied by the writer in the laboratory at the

University of North Dakota, and provided the basis for the conclusions here presented.

## METHODS

A series of fifteen samples was taken from the north face of the sand and gravel pit at the Cleveland site and placed in properly labeled, individual plastic bags. Samples were taken at eight-inch vertical intervals and each contained approximately two kilograms of sediments. Fossils of sufficient size to be recognized in the outcrop were collected and their orientation *in situ* noted. The various layers of sand and gravel were both photographed and sketched and the dip of the beds measured with a Brunton compass.

Each sample was examined under the binocular microscope (at magnifications of 54X and 108X,) the organic material removed and stored for later examination, and the sediments analyzed mechanically be sieving. The median grain size of each sample was plotted logarithmically against that percentage of the total number of specimens which it contained (see Fig. 1).

The fossils were identified, using the works listed above and those of Jones (12) and Berry (5). The preferred habitats, as given in the literature, of the still extant species was tabulated for comparison (see Fig. 2). The present range of two mollusks which have restricted present ranges were plotted on an outline map of North America (see Fig. 3).

## RESULTS

The following is a systematic list of the fossils taken from the Cleveland site:

Phylum MOLLUSCA
- Class GASTROPODA
  - Subclass PROSOBRANCHIA
    - Order MESOGASTROPODA
      - Family VALATIDAE
        - *Valvata tricarinata* (Say)
        - *V. bicarinata* Lea
        - *Amnicola leightoni* Baker
      - Family LIMNAEIDAE
        - *Fossaria obrussa* (Say)
      - Family PLANORBIDAE
        - *Gyraulus parvus* (Say)
        - *Gyraulus* sp.
        - *Helisoma anceps* (Menke)
        - *Helisoma* sp.
- Class PELECYPODA
  - Order PRIONODESMACEA
    - Family UNIONIDAE
      - *Andonta grandis* Say
      - *Anodontoides ferussicainus* (Lea)

Order TELEODESMACEA
Family SPHAERIDAE
*Sphaerium simile* (Say)
*Pisidium* sp. A
*Pisidium* sp. B
*Pisidium* sp. C
Phylum ARTHROPODA
Subphylum CRUSTACEA
Class OSTRACODA
Family CYPRIDAE
*Eucypris* sp. A
*Eucypris* sp. B
Phylum CHORADATA
Subphylum VERTEBRATA
Class AVES?*

*Several calcareous particles having a regular curvature and thickness were found at two horizons in the outcrop. After comparison under the microscope with chicken egg shells, these fragments were tentatively assigned to this class.

Kingdom PROTISTA
Phylum CHLOROPHYCEAE
Class CHAREAE
Family CHARACEAE
*Chara* sp.

The mechanical analysis yielded the following data:

| Level below the surface in inches | Median grain size in millimeters | Size Grade |
|---|---|---|
| 15 | ½ - 1 | Coarse sand |
| 21 | 8 - 16 | Medium pebbles |
| 29 | 8 - 16 | Medium pebbles |
| 37 | 2 - 4 | Very fine pebbles |
| 45 | 2 - 4 | Very fine pebbles |
| 53 | 1 - 2 | Very coarse sand |
| 61 | .25 - .125 | Fine sand |
| 69 | .125 - .0625 | Very fine sand |
| 77 | .125 - .0625 | Very fine sand |
| 85 | .125 - .0625 | Very fine sand |
| 93 | .25 - .125 | Very coarse sand |
| 101 | 2 - 4 | Very fine pebbles |
| 109 | 1 - 2 | Very coarse sand |
| 117 | 1 - 2 | Very coarse sand |
| 125 | .25 - .125 | Fine sand |

These data indicate that the flow of water depositing the sand layers experienced two interruptions, when faster water deposited the two gravel beds. The grain size of most of the samples containing mollusks was in the fine sand (½ to ¼ mm) range and is indicative of relatively slowly moving water. *Anodonta* and *Anodon-*

*toides* shells were found in the fine sand and very fine sand in positions indicative of a biocoenose. At both of the contacts of fine sand with overlying gravel, specimens were found to be rotated, crushed and filled with larger sediment. This was taken as evidence that these pelecypods lived in the fine sand environment and were killed by rapid burial by gravel, and that the aquatic environment thus underwent two cycles of deposition unfavorable to the pelecypods.

## DISCUSSION

The fauna unquestionably lived in close proximity to the glacier which occupied southwestern North Dakota during the late Wisconsinan Age of Frye and Wilman (10). Thus any climatic conditions inferred from the fauna will better illustrate the conditions at the glacial front than faunas from more distant locations. This is of special significance in that this fauna and those described by Clayton (6) are apparently the first from ice-contact deposits.

Being aquatic, this fauna and those of Clayton (6) form a better basis for inferring climatic conditions than do those containing primarily terrestral organisms which are subject to both humidity and temperature factors in the climate. No unquestionable technique for separating the effect of these two factors has yet been suggested. Thus most of the work based upon botanical and non-aquatic biological evidence remains in question, Shimek (17), and Eiseley (8).

The lithologic, topographic, and biologic information derived from this study are in complete accord. The grain size of most of the sediments indicates a slowly moving body of water, and the dip of the beds suggests that this might have been at the inlet of a stream in a small lake. The high elevation of these lake sediments above the surrounding terrain and the presence of nearby "stagnation moraine" features proves the intimacy of these deposits with the glacier. The fauna is a comingled northern and middle latitude assemblage. The Pleistocene range of *Valvata tricarinata* and *V. bicarinata* experienced a marked southern shift into Oklahoma and Texas during the Yarmouthian Age according to Taylor (19) and Taylor and Hibbard (18). No corresponding shift of the middle latitude clam, *Anodonta,* has been reported. *Anodonta* is found in the lowest beds sampled at the Cleveland site, thus it was not forced to retreat any great distance from the glacial front by adverse climatic conditions.

This picture of freshwater mollusks living in lakes on the Pleistocene ice sheet may at first appear anomalous. Glaciers today are found primarily in the higher latitudes and have become so associated in thought with Arctic climate that we assume the climatic conditions during Pleistocene glaciation must have been rigorous. However, it is unlikely that the climate was very warm. The mechanical analysis and environmental preferences of the extant species supports this idea. It is highly unlikely that the amount of detritus which would be carried in water from rapidly melting glacial ice would

permit successful occupation by mollusks. Thus it may be assumed that the aquatic environment was much like that which is mutually included in the present ranges (see Fig. 3) of *Valvata* and *Anodonta*, i.e. the Great Lakes, the upper Mississippi River, and the upper Ohio River drainages.

## SUMMARY

It is concluded that the climate during the late Wisconsinan Age during which this fauna lived was not rigorously cold, nor excessively warm, and probably approximated that which now exists in the Great Lakes region of the United States. The glacial ice melted slowly and was insulated by drift. The bodies of water on the ice were warmed sufficiently by the sun to permit the development of extensive molluscan faunas. Waters in front of the glacier were not greatly depressed in temperature, as indicated by the presence of still extant species of pelecypods, which do not have a range more northern than the Winnipeg Lakes, in the lowest layers of sediments sampled.

Further studies of Pleistocene mollusks are strongly urged as an aid to our better understanding of the glacial history of North Dakota.

## ACKNOWLEDGMENTS

The writer is greatly indebted to Dr. Mark Rich for suggesting the subject and permitting him to conduct the present investigation. His suggestions and encouragement throughout the study are gratefully recognized. Dr. F. D. Holland, Jr. rendered valuable assistance in matters of taxonomy, philosophy, and in the actual preparation of the manuscript. Mr. Lee Clayton was the source of much encouragement and discussions with him during the course of the study were of great help. Mr. E. A. Michel of Cleveland, North Dakota, owner of the Cleveland site, very graciously permitted the excavations necessary to the study and exhibited an exemplary enthusiasm for research. Mr. Kent A. Madenwald was of great assistance during the actual field work and his efforts are appreciated.

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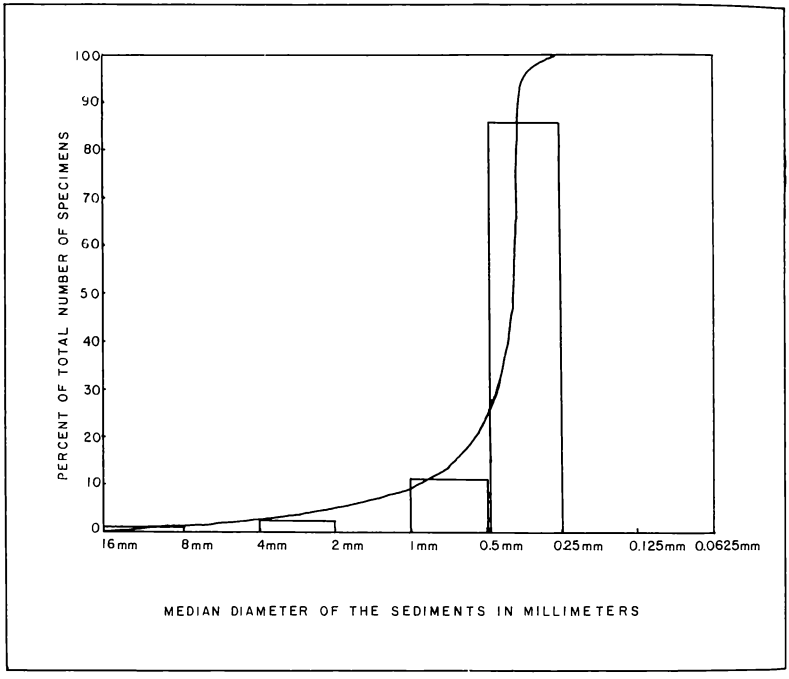


FIGURE 1. Histogram and cumulative curve showing the relationship between the median grain size of the sediment samples and their fossil content. Those samples having a median grain size in the medium sand range (½ to ¼ mm) contain approximately 85% of the organic material.

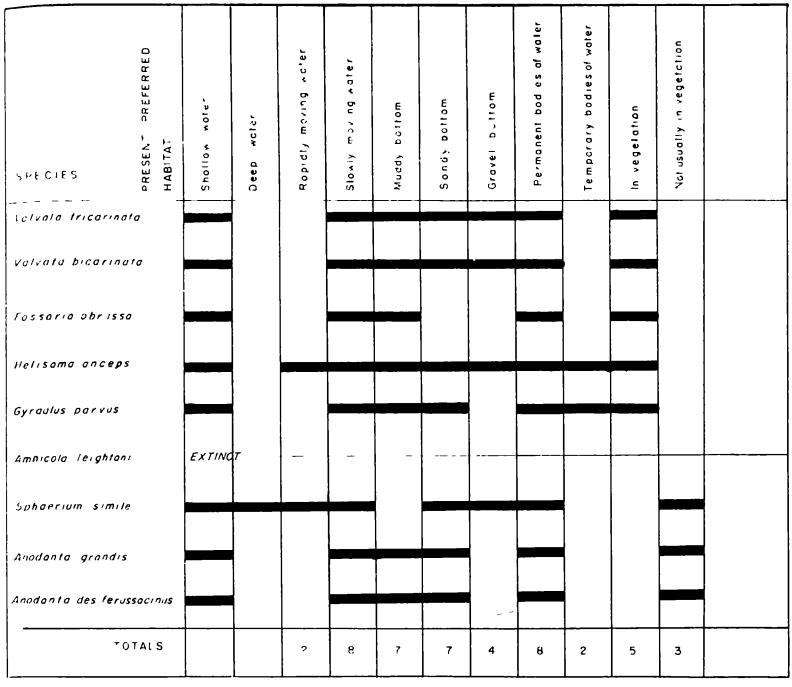


FIGURE 2. Chart representing the preferred habitats of selected extant species from the fauna at the Cleveland site. The fauna probably lived in a shallow, permanent, slowly moving body of water on a muddy or sandy bottom which had some vegetation.

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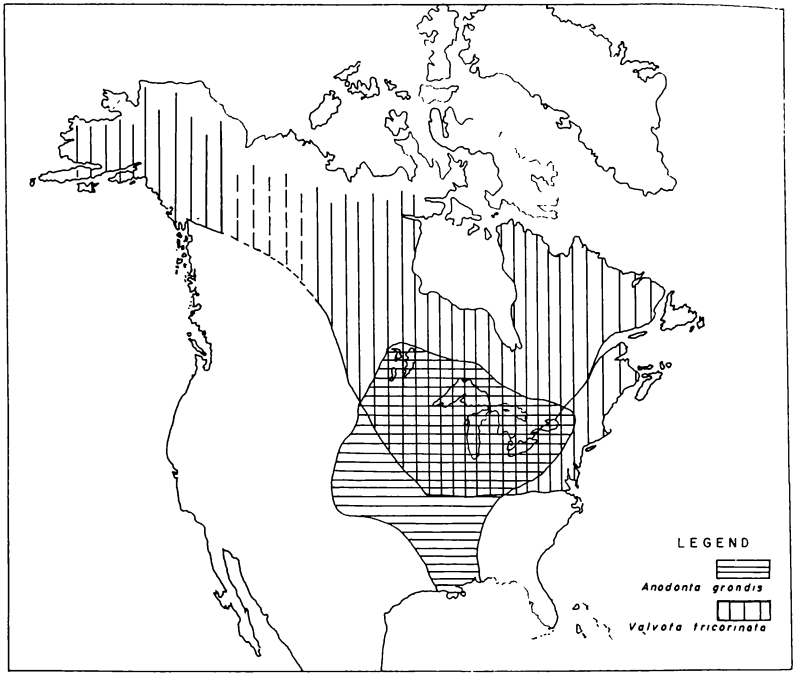



FIGURE 3. Sketch map of North America showing the modern ranges of *Anodonta grandis* and *Valvata tricarinata.* The overlapping portions of their ranges provide a reasonable basis for reconstructing the environment in which the fossil fauna from Cleveland, North Dakota, lived.

## THE MECHANISMS AND THE REACTIONS OF THE CHLORINATION OF BENZALDOXIMES

*Richard Klimpel, Franz H. Rathmann, and Gene R. Sparrow*
*School of Chemical Technology*
*North Dakota State University, Fargo, North Dakota*

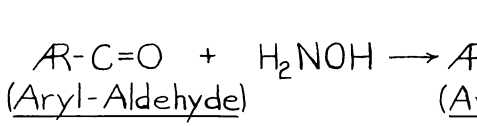
The formation of isoxazole ring compounds from various benzaldehydes has been subject to quite detailed study. The mechanisms

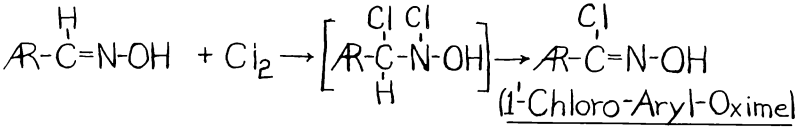
proposed by Adolfo Quilico and Raffaello Fusco in the Institute Chimica Generale della Reale Universita, Firenze, Italy, for the preparation of isoxazoles as indicated below, initiated further investigation (1).

**Reactions**

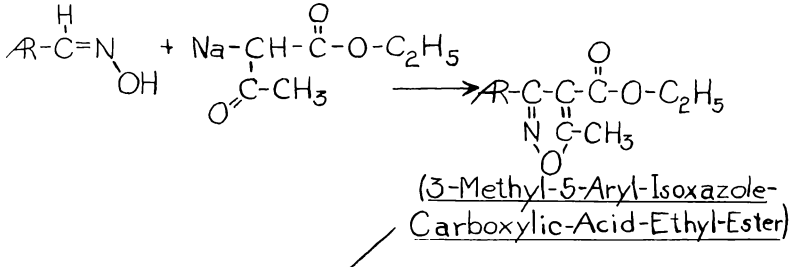
General Reactions

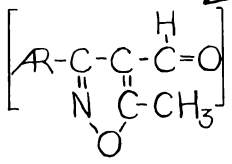
(Ar = Aryl Group)




General Reactions (Cont.)




Several isoxazole aldehydes were prepared by this procedure, as well as many intermediate benzaldoximes (2, 3). Most of the work reported here was concerned with the investigation of the chlorination of the benzaldoximes as an intermediate step in the preparation of the isoxazoles.

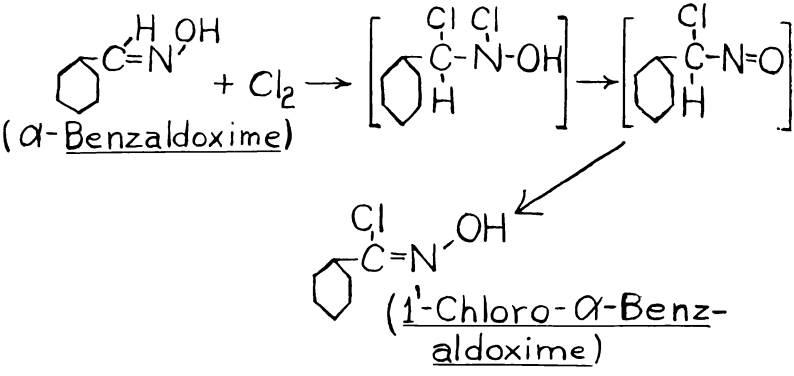
**$\alpha$- and $\beta$-Benzaldoximes.**

The preparation of the simplest of these 1'-chloro-aryl oximes, the 1'-chloro-benzaldoxime, has been under investigation for some time.

Earlier, a mechanism for this reaction was proposed by Piloti and Steinbock, and also by Werner and Buss (4, 5), involving the unstable intermediate dichloro-addition product and the 1'-nitroso-chloro-benzaldoxime.

General Mechanism

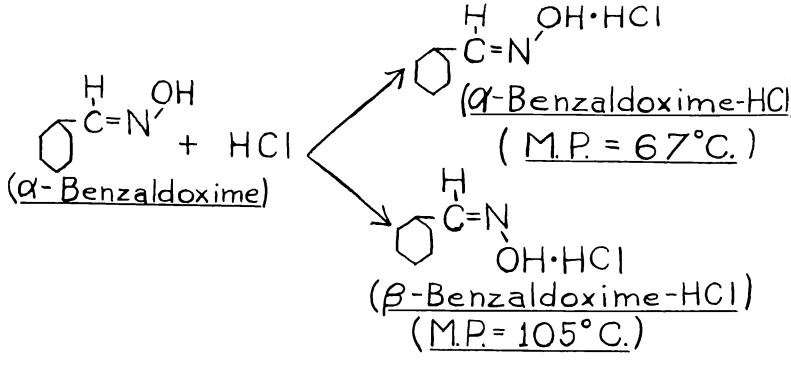
(⬡ = Benzene Ring)




(α-benzaldoxime) (1'-chloro-α-benzaldoxime)

Typical of such chlorination reactions was the color change from colorless to yellow to green to blue to green to yellow, and the appearance of a white precipitate. These color changes are characteristic of nitroso compounds, although the exact mechanism concerned was yet undetermined. Identification of this light, white precipitate indicated it to be a mixture of α- and β-benzaldoxime hydrochlorides

Hydrochloride Salts



with the β-form being favored at higher temperatures. (Melting range 60-95°C, N%-8.83. Theor. for $C_7H_7ONCl_2$ -8.89%.) This was further verified from the literature.(6).

These results indicated that the HCl formed in the chlorination reaction then reacted with some of the benzaldoxime initially present, to form the HCl salts. (6).

(β-HCl-salt) M.P.-105° (α-HCl-salt) M.P.-67°

Also reported, by Luxmoore, was a hydrate of the β-HCl salt melting at 57°C (7). This was also found in our work when slight amounts of water were present during the reaction. This hydrate, upon storing over concentrated $H_2SO_4$ and HCl, melted at 100°C. The pure β-HCl salt melts at 103°C.

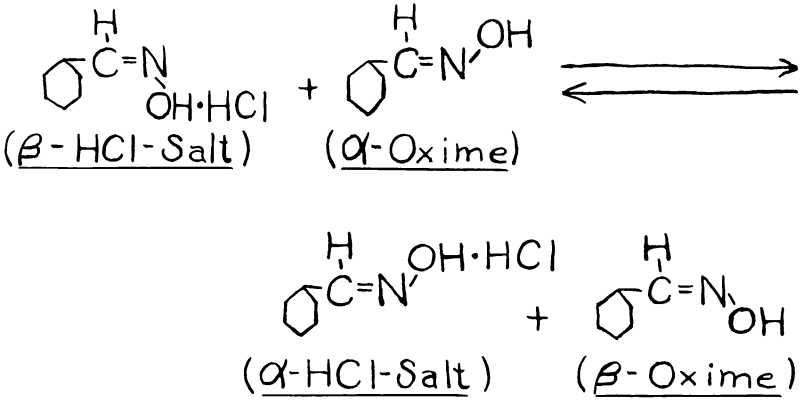
Throughout the chlorinations of the α-benzaldoxime at -10°, 0°, and 28°, the only HCl salt identified was the β-HCl salt. This was quite unstable, and decomposed within a short time to the α-benzaldoxime and the α-HCl salt. Quantitatively, approximately 40% of the initial benzaldoxime reacted to form the HCl salt, and 40-50% to form the 1'-chloro-α-benzaldoxime. Unaccounted for was 10-15% of the original benzaldoxime. This suggested the possible equilibrium;

oxime-HCl salt ⇆ oxime + HCl

thus preventing the complete reaction of the oxime.

Another possible explanation for this unaccounted for conversion involves the action of α-benzaldoxime as a base to form an equilibrium with β-benzaldoxime hydrochloride and α-HCl-salt. For this explanation the $K_b$ for α-benzaldoxime was calculated to be $1 \times 10^{-12}$, using the $K_a = 2.1 \times 10^{-11}$ reported in the literature (8).

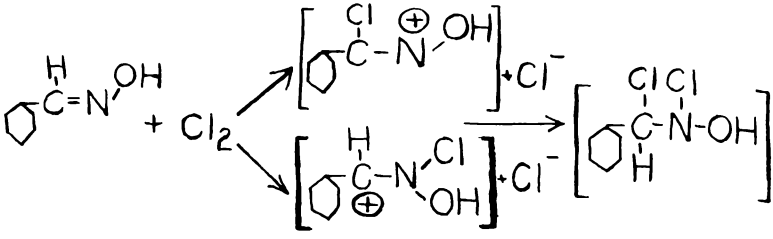
## Isomerism

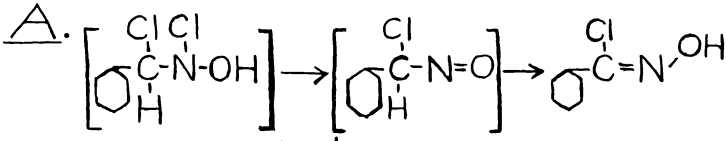



1'-chloro-α-benzaldoxime had been identified as a product of the reaction earlier as verified in this work, but the presence of a 1'-chloro-β-benzaldoxime has been doubtful. The 1'-chloro-α-oxime is

identified by its reaction with ethyl alcohol to produce the ethyl ester of $\alpha$-hydroximic acid. (M.P. 67-68°). (9).

Proposed Mechanisms:



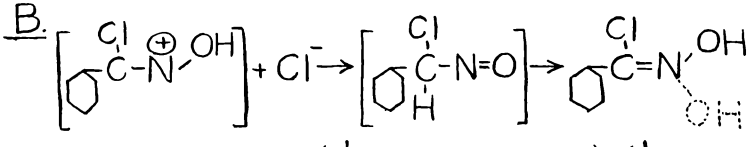


(Dichloro-Product) (1'-Nitroso-Cl-Benzaldoxime)

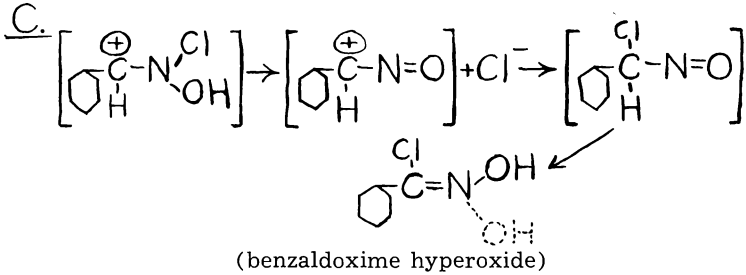
(benzhydroximic acid ethyl ester)

Prior to this work no attempt has been indicated by the literature to prepare the 1'-chloro-$\beta$-oxime separately, although its presence has been proposed.

Mechanisms (Cont.)



(1'-Nitroso-Oxime) (1'-Cl-Oxime)



(benzaldoxime hyperoxide)

In one method used to accomplish this, the $\beta$-benzaldoxime hydrochloride was converted into the $\beta$-benzaldoxime by rapidly

neutralizing with just sufficient $NH_4OH$ and then extracting with $CCl_4$. This was chlorinated at once so as to keep low the amount of its conversion into the $\alpha$-oxime. Upon analysis of the products, hydroxyl amine hydrochloride was discovered along with some 1-chloro-$\alpha$-oxime as well as also a compound of M. P. 110°, N-9.17% (Theor. 9.00%). This latter compound was probably the 1 $\beta$-Cl-benzaldoxime. At first it was believed to be the benzaldoxime peroxide as reported earlier by Werner and Buss. (5).

**Para-chloro-benzaldoxime.**

Upon chlorination of p-$\alpha$-chloro-benzaldoxime, similar color changes occurred at a slower rate. A white precipitate (M.P. 104-106°, and 105-108° out of alcohol) was formed. These reactions were carried out in a benzene solution at a temperature of 0° and 20°C. with a yield of 45% of the quite stable hydrochloride salt. Kjeldahl nitrogen determinations showed N-6.8% and 6.7% respectively. (Theor.-7.29%). Mohr titrations for available chlorine gave Cl%-16.5 and 17.0% (Theor.-18.5%). This indicated that a para-chloro-benzaldoxime HCl, most likely the $\beta$, was formed as a precipitate.

The long rectangular crystals formed out of the remaining solution were believed to be a 1-chloro-$\alpha$-para-chloro-zenzaldoxime, although they sublimed up to a temperature of 243°C before melting. This indicates that some HCl was bound by the 1'-Cl oxime. This product was earlier reported as melting at 75-76° (2).

**Ortho-chloro-benzaldoxime.**

The action of chlorine on the o-Cl-$\alpha$-benzaldoxime at 0°C formed a white precipitate of M. P. -67-68°. At first this was thought to be the $\beta$-HCl salt. However a high nitrogen content, N-8.41% (Theor. 17.29%) and no significant ionic chlorine excluded this compound and indicated the possibility of a mixture of the original oxime and one of the 1'-Cl-o-Cl-oximes, although these would be expected to have a higher M.P. The clear white crystals formed upon removal of the $CCl_4$ indicated that the 1'-Cl-$\alpha$-o-Cl-oxime was formed. (M.P.-138-139°).

The results thus obtained suggested the general mechanism shown on the following page with the position of the substituted group on the benzene ring influencing, to some extent, the final products obtained.

**Kinetics of the chlorination.**

The rate of reaction for these chlorinations appeared, at first by close observations of color changes, to be benzaldoxime, o-chloro-benzaldoxime, and p-chlorobenzaldoxime in decreasing order for the rate of reaction in equal concentrations of $CCl_4$ solution. Furthermore the reactions were found to be greatly accelerated by using a larger concentration of the oxime or by using benzene as a solvent.

By adding a solution of $Cl_2$ in $CCl_4$ to a solution of the oxime, and recording the transmittance of light at various time intervals, fairly smooth curves were obtained for the plot of light transmittance against time. Also by the slow addition of a solution of $Cl_2$ in $CCl_4$

to a solution of the oxime, and recording the ml added, time and color, further curves were obtained. Analysis of these curves together with the time of initial appearance of the HCl salt or precipitate led to some interesting results. Attempts were made to record data for reactions at -20°C, but the solubility of the HCl salts was greatly decreased at this temperature, resulting in interfering precipitates.

The complexity of such reaction kinetics is easily seen by considering the second order equation:

$$\frac{dx}{dt} = k\,(a - x)\,(b - x)$$

where the change in the amount of x formed is directly proportional to the rate constant and the concentrations of the remaining reagents left after a time, t.

$$\underset{(a)}{\text{Oxime}} + \underset{(b)}{Cl_2} \xrightarrow{k_1} \underset{(x)}{\text{Nitroso}} + \underset{(x)}{HCl}, \quad \frac{dx}{dt} = k_1(a-x)\,(b-x)$$

But this is not the final product, and thus a consecutive reaction involving another rate constant, $k_2$, also occurs. This appears to be mainly a first order reaction of a simple keto-enol tautomeric shift.

$$\underset{(a)}{\text{Oxime}} + \underset{(b)}{Cl_2} \xrightarrow{k_1} \underset{(x)}{\text{Nitroso}} \xrightarrow{k_2} \underset{(y)}{\text{Cl-Oxime}} + \underset{(y)}{HCl}$$

To further complicate the reaction, some of the final product formed, HCl, reacts in another second order reaction to form the oxime hydrochlorides.

$$\underset{(a)}{\text{Oxime}} + \underset{(z)}{HCl} \xrightarrow{k_3} \underset{(w)}{\text{Oxime - HCl}}$$

From the equations then:

$$k_1 = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)} = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

$$k_2 = \frac{1}{t} \ln \frac{a}{(a-x)} = \frac{2{,}303}{t} \log \frac{a}{(a-x)}$$

$$k_3 = \frac{1}{t(a-z)} \ln \frac{z(a-w)}{a(z-w)} = \frac{2.303}{t(a-z)} \log \frac{z(a-w)}{a(z-w)}$$

An indication of the reaction rates and their complexity is shown in Figure I on the following page.

Figure I is a plot of the log-absorption versus the time, as indicated in Table I. With the exception of the first portion of the graph, this represents the conversion of the blue nitroso compound to the 1'-Cl-o-Cl-oxime. The linearity of this portion of the graph strongly indicates that this reaction is of the first order.

It is hoped that a slower reacting system can be found or that more precise methods can be developed, to enable the exact determination of the order of the second stage reaction as well as that of the exceedingly rapid first reaction.

**TABLE I**

Chlorination of o-Cl-benzaldoxime
3ml of a 0.354N Cl in $CCl_4$ solution was added to
2ml of a 0.29N o-Cl-benzaldoxime solution of $CCl_4$
Temperature—0°C, wave length—530$\mu$

| % Transmission | Time | % Absorption |
|---|---|---|
| 100% | 0sec. | 0% |
| 30 | 10 | 70 |
| 26 | 15 | 74 |
| 40 | 25 | 60 |
| 46 | 35 | 54 |
| 49 | 50 | 51 |
| 52 | 60 | 48 |
| 57 | 75 | 43 |
| 61 | 90 | 39 |
| 68 | 110 | 32 |
| 71 | 120 | 29 |
| 52* | 240 | 48 |
| 73 | 300 | 27 |
| 75 | 360 | 25 |
| 82 | 390 | 18 |
| 87 | 600 | 13 |

*Precipitate formation began; system cloudy. Subsequent data not shown on graph.

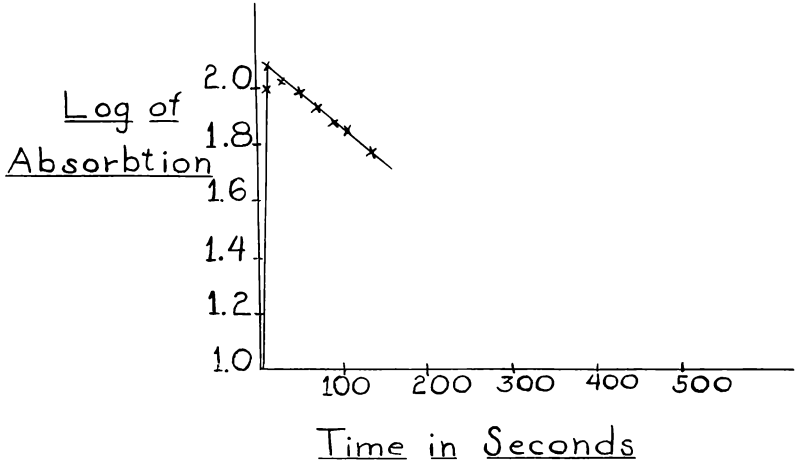



FIGURE 1. Graphic Analysis

The third reaction, $k_3$, is an interfering reaction quite dependent upon the nature of solvent used. It is essentially irreversible if the products are insoluble in the system; however it is an equilibrium reaction if the products are sufficiently soluble. This latter case has been indicated throughout reactions with water present.

At present it has been possible to make only a very rough approximation of $k_1$ using certain assumptions, hence these data are not reported here. It is hoped that in the very near future these kinetics can be evaluated, and further progress made in the preparation and studies of chloro-oximes.

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# THE PARTICLE SIZE DISTRIBUTION OF FLOUR OBTAINED FROM TWO VARIETIES OF NORTH DAKOTA HARD RED SPRING WHEAT

*Loren W. Hill, Leonard D. Sibbitt, K. A. Gilles*

*Department of Cereal Technology*

*North Dakota State University, Fargo, North Dakota*

## INTRODUCTION

The particle size range for similarly milled flours is nearly the same, regardless of the class or variety of wheat. The distribution of particles according to size within this range, however, varies greatly (1). Thus a hard spring wheat flour can easily be distinguished from a soft wheat flour by analysis of particle size distribu-

tion. Although varietal differences in distribution within a class are not as great as differences between classes, they are still sufficiently significant to determine the most practical use of a flour obtained from a certain variety. Even slight differences are important; for instance, the best pastry flour contains high percentages of particles with diameters ranging from 18 to 23 microns, while the best cake flour is composed of high percentages of particles having 21 to 27 micron diameter range (2). The significance of particle size distribution is not limited to soft wheat products such as cake and pastry flours, however. Beginning in 1959, some low quality winter wheat flour streams have been air classified to remove fractions which are suitable for blending into bread flours. A fraction suitable for cake flour has also been obtained from the same class of flour in this mmanner (3).

The object of this study was to determine the distribution of particle size in North Dakota hard red spring wheat varieties for the first time and to investigate varietal differences within this class. Four determinations of the distribution of particle size were performed on a blended flour of known characteristics to test the replicability of the method. Two varieties, having marked differences in milling and baking properties were also analyzed. Willet, a variety of extremely low flour yield, was compared with Selkirk, an acceptable variety. All the wheats were milled in an Allis-Chalmers experimental flour mill under the same conditions.

## MATERIALS AND METHODS

A simple sedimentation method based on Stoke's Law was used in the determination of particle size. This law, solved for the radius of the falling particle, is in the form:

$$r = \frac{9VN}{2g(d_1 - d_2)}$$

in which:

r = radius of particle in cm.
V = velocity of falling particle in cm./sec.
g = acceleration of gravity
$d_1$ = density of particle
$d_2$ = density of media
N = viscosity of media in poise

All values, except velocity of the falling particle, are constant at constant temperature. To determine the velocity, the length of fall of the particle was divided by the time of fall (4).

The apparatus used in determining length of fall is indicated in Figure 1. The buret was mounted exactly vertical and filled to the 50.0 ml. mark with mercury. The side arm on the buret was used to adjust the mercury level. Absolute methanol, a liquid which has little solvent action on flour, was added to the 17.5 ml. mark. Fifteen ml. of methanol was added to a 5 g. flour sample in an

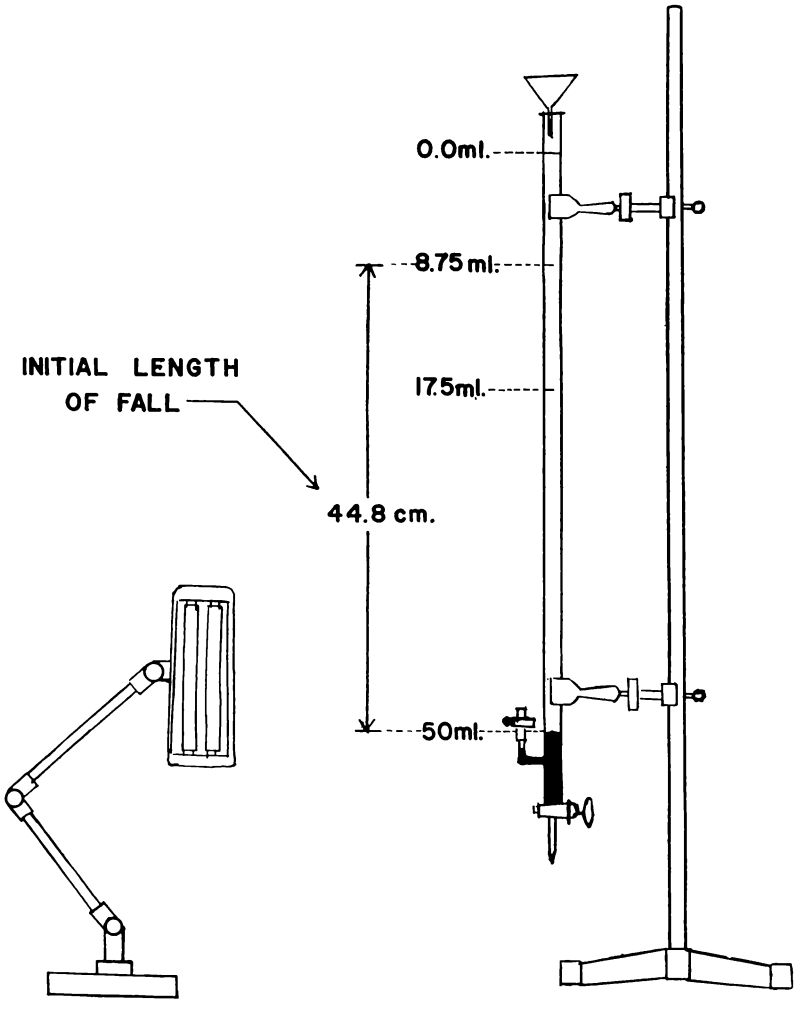


FIGURE 1. Apparatus for determining particle size and distribution of particle size.

Erlenmeyer flask fitted with a ground glass stopper. The flask was shaken vigorously for 30 seconds to form a suspension. The suspension was immediately poured into the buret and simultaneously a timer was started. The flour suspension filled the buret to the 0.0 ml. mark. Volume readings of sedimented flour were taken every minute for 15 minutes, and a final reading was taken after 25 minutes. The average length of particle fall during the first minute

**TABLE I**

**Replication of Particle Diameter**

| Time (minutes) | Run 1 Particle Size in Microns | Run 2 Particle Size in Microns | Run 3 Particle Size in Microns | Run 4 Particle Size in Microns |
|---|---|---|---|---|
| 1 | 111.7 | 111.7 | 111.7 | 111.7 |
| 2 | 78.6 | 78.5 | 78.5 | 78.6 |
| 3 | 62.5 | 62.3 | 62.1 | 62.7 |
| 4 | 52.4 | 52.1 | 52.2 | 52.6 |
| 5 | 45.4 | 45.0 | 45.1 | 45.4 |
| 6 | 40.4 | 40.3 | 40.3 | 40.5 |
| 7. | 36.9 | 36.8 | 36.8 | 37.0 |
| 8 | 34.2 | 34.2 | 34.1 | 34.3 |
| 9 | 32.1 | 32.0 | 32.0 | 32.1 |
| 10 | 30.3 | 30.3 | 30.2 | 30.4 |
| 11 | 28.8 | 28.8 | 28.8 | 29.0 |
| 12 | 27.5 | 27.5 | 27.5 | 27.8 |
| 13 | 26.4 | 26.4 | 26.4 | 26.5 |
| 14 | 25.4 | 25.4 | 25.4 | 25.6 |
| 15 | 24.6 | 24.6 | 24.5 | 24.6 |

## TABLE II

### Replication of Particle Size Distribution

| Time (minutes) | Average Diameter of Particles in Microns | Run 1 % of Total Flour | Run 2 % of Total Flour | Run 3 % of Total Flour | Run 4 % of Total Flour | Average % of Total Flour |
|---|---|---|---|---|---|---|
| 1 | 111.7 | 3.4 | 4.3 | 4.3 | 3.0 | 3.8 |
| 2 | 78.6 | 18.0 | 19.8 | 18.3 | 15.3 | 17.9 |
| 3 | 62.4 | 21.5 | 22.4 | 21.7 | 21.8 | 21.9 |
| 4 | 52.3 | 18.9 | 20.3 | 20.0 | 21.8 | 20.3 |
| 5 | 45.2 | 14.6 | 11.6 | 12.3 | 13.1 | 12.9 |
| 6 | 40.4 | 7.7 | 6.9 | 7.2 | 7.9 | 7.4 |
| 7 | 36.9 | 3.9 | 3.9 | 4.3 | 4.4 | 4.1 |
| 8 | 34.2 | 3.0 | 3.0 | 3.0 | 3.5 | 3.1 |
| 9 | 32.0 | 2.6 | 1.7 | 2.1 | 1.8 | 2.0 |
| 10 | 30.3 | 1.7 | 1.3 | 0.9 | 0.9 | 1.2 |
| 11 | 28.8 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 |
| 12 | 27.6 | 0.7 | 0.9 | 0.4 | 0.9 | 0.7 |
| 13 | 26.4 | 0.4 | 0.4 | 0.4 | 0.9 | 0.5 |
| 14 | 25.4 | 0.3 | 0.4 | 0.4 | 0.4 | 0.4 |
| 15 | 24.6 | 0.3 | 0.0 | 0.4 | 0.0 | 0.2 |

is equal to the distance between the 8.75 ml. mark and the 50.0 ml. mark. This distance is expressed in centimeters for use in Stoke's Law. The length of fall during each successive interval is then decreased by an amount equal to the height of flour sedimented in the preceding interval. The distribution of particle size was determined by calculating the percentage of total sedimented flour collected in each one minute interval.

The fluorescent lamp in Figure 1 is used to facilitate reading the volume of sedimented flour. This type lamp is superior to a microscopic lamp, as suggested by Evans (4), because it generates less heat which causes convection currents and changes in density of the methanol. Even with a fluorescent lamp, convection currents will interfere with sedimentation unless the lamp is swung away from the buret between readings.

Although flour particles are irregular rather than spherical, the expression of the size as a diameter is not a misnomer when the definition of diameter with respect to irregular particles is used. The diameter of an irregular particle is any one-dimensional distance passing throught the geometric center of the particle. Flour particles generally do not vary greatly from spherical symmetry; the ratio of longest to shortest diameter seldom exceeds four. It has been shown that settling velocity of flour particles is within 6% of the settling velocity of a sphere of equal volume (5).

## RESULTS

The greatest deviation in particle diameter in four runs on the same flour was 0.6 microns as indicated in Table I. It is evident that deviations in the determination of particle diameter are insignificant compared to the deviation in the distribution of particle size as shown in Table II. Since the over-all range in particle size varies little between classes and varieties, the distribution of the particles within the range is a more valuable measurement. The most pronounced deviations in the distribution of particle size occur in the fractions having a diameter of 75 to 111 microns. The amount of these larger particles may be effectively controlled by the use of woven sieves during milling and therefore, the inaccuracy in sedimentation in the 75 to 111 micron range is not a serious limitation to the practicality of the method. In the crucial 25 to 75 micron range, it can be seen that the deviation in successive runs is less than the deviation above 75 microns. Electroformed micro-mesh sieves, which are still in the experimental stage, must be used to determine particle size below 75 microns (5). One limitation of the method is caused by particles of small diameter remaining in suspension. Table II shows that those particles having a diameter less than 25 microns cannot be analyzed for particle size distribution by this simple sedimentation method. However, only 2.4% of the total flour volume is composed of particles which are too small to settle out.

The variation in particle size distribution of the two varieties analyzed far exceeds the deviations found in successive runs on the same flour in the replicability test. An examination of the particle size distribution curve (Figure 2) shows that in Selkirk more than

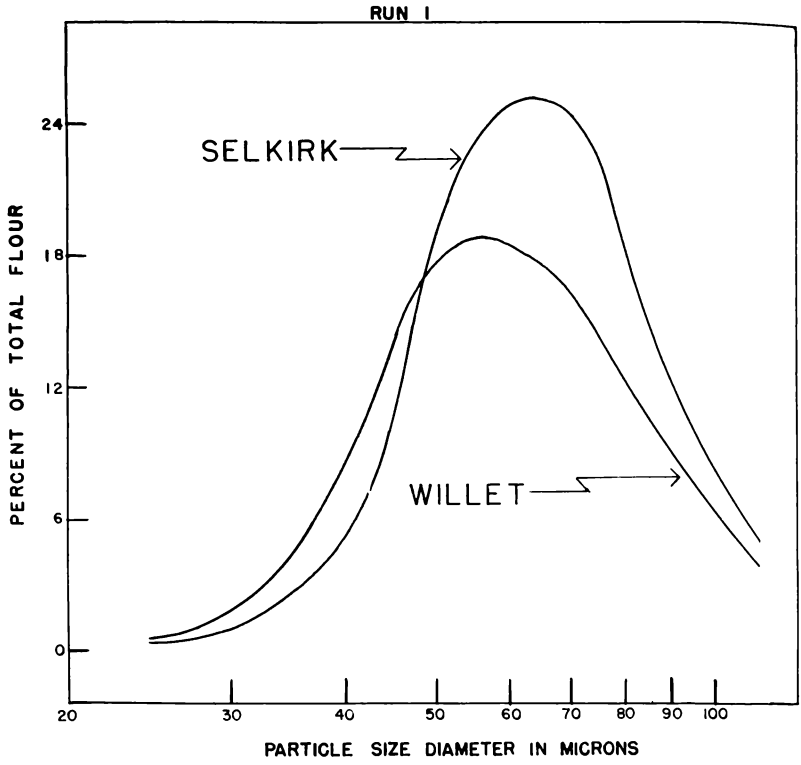


FIGURE 2. Vertical variation in particle size distribution.

25% of the particles are of one diameter as determined by this method, whereas in Willet, no single particle size contributed more than 20% to the total. The curve also shows that there are more smaller particles in Willet than in Selkirk. The greatest percentage of total flour in Selkirk had a particle size diameter of 62.2 microns, while the maximum percentage in Willet occurred at 52.8 microns. Moreover, the percentages of Willet below 45 microns in diameter, are significantly greater than the percentages of Selkirk in this range.

## DISCUSSION

The variation in distribution of flour particle size of Selkirk and Willet has definite practical significance. The quality of the two varieties for use in bread flour is very different. Flour made

## TABLE III

### Characteristics of Varieties Tested

| Variety | Wheat Protein | Flour Yield | | | Ash | Mixing Time | Loaf Volume | Farinogram Pattern | |
|---|---|---|---|---|---|---|---|---|---|
| | | Long Patent | Low Grade | Total Flour | | | | | |
| | % | % | % | % | % | | cc. | | |
| Selkirk | 14.9 | 64.5 | 3.6 | 68.1 | 0.42 | Medium | 868 | M. Strong | 6 |
| Willet | 15.8 | 60.5* | 3.2 | 63.7 | 0.37 | V. Short | 814 | Weak | 3 |

*Abnormal milling characteristics: Flour soft and fluffy; bran difficult to clean.

from Selkirk has characteristics which are commercially acceptable as shown in Table III. Willet, however, is considered unacceptable for bread flour because of its low flour yield, low loaf volume, and short mixing time. It has been shown that the correlation between particle size distribution and flour volume is high (1). It is probable that valuable information could be gained by distribution tests of experimental varieties of North Dakota hard red spring wheat. The extremely important task of quality testing of new varieties would be facilitated by distribution analysis.

The high protein and low ash in Willet flour are desirable characteristics. However, the extremely low flour yield makes Willet commercially unacceptable. If air classification on a commercial basis becomes practical, it is conceivable that a use could be found for Willet flour. Although soft winter wheats are generally used in cake flour, hard winter wheats have produced fractions acceptable for cake flour after air classification. Similar classification of Willet and other varieties which are unacceptable for producing bread flour may lead to new markets. If air classification leads to "tailor made" flour in industry, the superiority of hard red spring wheat for making bread may be threatened. Therefore, it is very important that the particle size distribution and physical characteristics of flours milled from North Dakota varieties be known and that the possibilities of air classification of hard red spring wheats be investigated.

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# WOODY PLANT COMMUNITIES IN THE BADLANDS OF WESTERN NORTH DAKOTA[1]

*Jack R. Nelson*

*Department of Botany*

*North Dakota State University, Fargo, North Dakota*

**Abstract**

The climax vegetation in the North Dakota Badlands is considered to be mixed-grass prairie. However, the broken nature of this region encourages the development of woody plant communities. The woody plant types are of small extent compared to the grassland, but they are of considerable importance as a source

of food and cover for the big game population of the region. The vegetative composition and structure of the four principal woody plant community types in this area were studied during the summers of 1959 and 1960. These types include the green ash, the juniper-slope, the cottonwood, and the silver sagebrush community types. Each of these types is characterized by a single dominant species in their superior stratum.

Ten stands of each of the four principal woody vegetation types were studied in detail. The mature tree stratum and the shrub and sapling stratum were sampled separately in each stand using a modification of the line-strip method (Woodin and Lindsey, 1954). Density, cover, basal area, frequency, height, and crown diameter estimates were obtained from 10 line-strips in each stand. One hundred 1-sq. meter and 100 1-sq. ft. quadrat samples were employed in each stand to obtain additional herb and shrub information.

The green ash type, dominated by *Fraxinus pennsylvanica,* is the most common woodland community type in the Badlands region. Ash forms moderately closed communities along the bottoms and sides of most of the ravines, on moderately steep north and east-facing slopes, and, to a lesser extent, in the bottomlands along the Little Missouri River and its larger tributaries. American elm (*Ulmus americana*) is the next most important tree in this type. Mature trees in this type attain only 20 to 30 feet in height and 5 to 6 inches dbh. Chokecherry (*Prunus virginiana*), western rose (*Rosa woodsii*), wolfberry (*Symphoricarpos occidentalis*), Juneberry (*Amelanchier alnifolia*), and wild plum (*Prunus americana*) produce a moderately dense undercover with saplings of ash and elm. Herbage cover is comprised largely of long-beaked sedge (*Carex sprengelii*) and Kentucky bluegrass (*Poa pratensis*). This community type is believed to be a westward post-climax extension of the maple-basswood forest of Minnesota. The green ash type is commonly used for shade by cattle and is an important source of winter browse for deer.

The juniper-slope type is a very dense tree type that characterizes the steep, northwest to northeast-facing slopes in the rougher breaks close to the Little Missouri River and along its major tributaries. The Rocky Mountain juniper (*Juniperus scopulorum*), the principal tree in this type, is the smallest tree in the region, attaining heights of only 10 to 15 feet and 4 to 6 inches dbh. Shrubs form a relatively open undercover in this type and include chokecherry, dwarf juniper (*Juniper communis*), skunkbush (*Rhus trilobata*), and wolfberry. A wiry midgrass, little ricegrass (*Oryzopsis micrantha*), produced considerably more cover than any other herb in this type. The juniper-slope type is believed to be a northeastward postclimax extension of the pinyon-juniper woodland from Wyoming and Montana. Because of its situation on steep slopes, the juniper-

slope type is little used by cattle. However, it appears to be important for summer cover and forage for mule deer.

The cottonwood type, characterized by *Populus deltoides*, is largely restricted to the Little Missouri floodplain. The cottonwood is the largest tree species in the Badlands, attaining 45 to 55 feet in height and 17 to 18 inches dbh. Green ash and American elm often form a secondary tree canopy in favorable sites. Wolfberry, western rose, and red dogwood (*Cornus stolonifera*) usually form a moderate to dense shrub cover, while poison ivy (*Rhus radicans*), and sweet clover (*Melilotus* spp.) are the principal herbs in this type. This normally open woodland type is relatively short-lived and appears to be replaced by the green ash and silver sagebrush types after about 50 to 150 years. This type is not a major forage source for livestock. However, large populations of whitetail deer utilize it the year-round.

The silver sagebrush type has previously been described from a limited number of stands by Hanson and Whitman (1938). This type, probably the most extensive shrub type in the region, generally occurs on the flood plains and lower terraces of the Little Missouri River and its larger tributaries. *Artemisia cana* is the principal shrub while wolfberry is an important associate. Grasses are important constituents of the type and include western wheatgrass (*Agropyron smithii*), green needlegrass (*Stipa virdula*), and bluegrama (*Bouteloua gracilis*). The silver sagebrush type is common in stream valleys throughout the Northern Great Plains. This is an important winter range type for cattle, as well as for deer and antelope.

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[1]Report of cooperative research sponsored by North Dakota Agricultural Experiment Station, North Dakota Institute for Regional Studies, and North Dakota Game and Fish Department.

# SOME ASPECTS OF GRASSLAND MICROCLIMATE IN SOUTHWESTERN NORTH DAKOTA

*Harold Goetz[1] and Warren C. Whitman*

*Agricultural Experiment Station*

*North Dakota State University, Fargo, North Dakota*

**Abstract**

Records of temperature, relative humidity, evaporation, and wind movement at heights of 5 inches and 5 feet over native-grass

sod were made at the Dickinson Experiment Station in part of the 1959 growing season and during the period from June 1 to August 29 in the 1960 season. Continuous records of temperature and relative humidity at the two heights were obtained with recording hygrothermographs. Miles of wind were measured with standard 3-cup anemometers, and evaporation losses from Livingston porous bulbs were obtained at both heights.

The data thus far obtained indicate substantial microclimatic effects in this type of grassland even though the average height of the grass cover is less than 10 inches. Average temperatures at the 5-foot level were slightly lower than at the 5-inch level from 7:00 p.m. to midnight, but were slightly higher from 2:00 a.m. to 6:00 p.m. Relative humidity was appreciably higher at the 5-inch level than at the 5-foot level during the daylight hours, but was lower at the 5-inch level at night.

The most significant differences in climate at the 5-inch and the 5-foot levels were in wind movement and evaporation. Wind movement at 5 feet was over twice that at 5 inches and evaporation averaged about 20 percent more at 5 feet than at 5 inches.

More refined instrumentation and continuous observation of additional factors such as soil temperatures, soil moisture, and solar radiation are needed before the general pattern of grassland microclimate can be established, and the relations between microclimate and grass growth can be evaluated.

[1]National Science Foundation Undergraduate Research Participant.

# THE STATUS OF PALEONTOLOGY IN NORTH DAKOTA

*F. D. Holland, Jr.*

*Associate Professor of Geology*

*University of North Dakota, Grand Forks, North Dakota*

*Invited Paper for the 53rd Annual Meeting of the North Dakota Academy of Science, at Grand Forks, North Dakota, May 5-6, 1961.*

## Introduction

Every once in a great while it behooves those working in a science to stop, examine their position, look backward and see where they have been and where they are going. I propose to do this in this paper. Aristotle has said, "He who sees things grow from the beginning will have the best view of them", and so I might have entitled this paper, "The History of Paleontology in North Dakota"; however, it is hoped that more can be accomplished than just reviewing the history. Perhaps I can, indeed, chart some of the roads which must be traveled in the future.

Recently a colleague of mine from our history department

pointed out that geologists would certainly not want historians running geological surveys and that, in like manner, scientists do not do the best job of writing history. Even with this admonition, I feel constrained to plunge ahead.

To accomplish the end outlined above, I have divided the paper into three parts—a survey of the past history of paleontology in North Dakota, a partial review of the status of the science today, and a glance into the future.

## A Backward Look

The fascinating field that is paleontology, the study of plants and animals of past geologic ages, has intrigued Man since he first developed imagination and curiosity.

Apparently this was equally true in North Dakota, for excavation of an Early Mandan Indian site, eight miles down river from the town of Fort Yates, Sioux County, has yielded (letter dated 2 November 1960, from W. Raymond Wood to Wilson M. Laird) an assemblage of fossil shells from the Fox Hills and Tongue River formations, or beds more than 60 million years old. The Fox Hills sandstone crops out not far from this site; but it must be nearly 40 miles to the nearest exposure of the Tongue River formation; and so the Indians must have carefully assembled these shells, some of which are commonly rather delicate and fragile. Were these Indians, then, the first fossil collectors in North Dakota? Surely they were!

Although not germane to the subject at hand it is intriguing to speculate on the use made of this cache of shells. Were these mystic objects used in an ancient rite? Were they trinkets brought home to the children? Or could the intellect have been stirred to puzzle the origin of these shells entombed in rock and to compare them with present-day shells found along the river bank?

Although numerous explorers, trappers, traders, and various entrepreneurs traversed parts of what is now North Dakota in the eighteenth centuy (La Verendrye in 1738, and his sons crossing through North Dakota in 1742 on their way to and from the Black Hills or the Big Horn Mountains; Jonathan Carver exploring the Red River valley in 1768 for the provincial government; James Mackay in 1795 penetrating as far north as the Mandan villages in the vicinity of present-day Bismarck; Charles Chaboillez establishing the first fur trading post within the boundary of North Dakota for the Northwest Company at Pembina in 1797; Alexander Henry establishing the Northwest Company post on the Red River at the mouth of the Park River and depots at the "Grandes Fourches" in 1800, and the establishment of Hudson Bay and XY Company posts at Pembina in 1801), none of these hardy souls—illustrious and lusty, romantic and daring, pioneering and roving though they were —apparently made significant scientific observations or collected

fossils to document for their more sedentary contemporaries the nature of this otherwise unexplored country.

One of them, the outstanding geographer and surveyor, David Thompson, was equipped and instructed in 1797 by the Northwest Company to determine the location of the 49th parallel and the company trading posts and the trails between them, to visit the Mandan Indians, and also to search for the fossil bones of large animals (Sheldon, 1961, p. 3). Thompson did an excellent job of surveying, especially in the vicinity of the Mouse River west of the Turtle Mountains and spent an unusually cold winter (1797-1798) with the Mandans, but I can find no record that he was successful in his search for fossils. It remained for the Lewis and Clark expedition to return with the first fossils collected by white men from North Dakota.

As you all know, perhaps one of the most significant events in early North Dakota history was the remarkable voyage of Meriwether Lewis and William Clark. Though rough and hardy men, little lettered by the standards of today, the excellence of their observations in the pursuit of their primary task, to explore the newly acquired Louisiana Purchase, in the face of grave obstacles, marks theirs as one of the truly great, scientific expeditions.

They entered (Reid, 1948) the state October 13, 1804, mapped the course of the Missouri River (Thwaites, 1959) through the state (as they had all along their route), noted the wildlife present in the area, and made what were apparently the first geological and paleontological observations. After their stay in a fort they erected near the present site of Stanton during the winter of 1804-05, they left what is now North Dakota on their westward trip on April 27, 1805, returned to North Dakota August 3, 1806, and took their final departure from the state on their way to St. Louis on August 20, 1806. Although it is a digression, perhaps, from the history of paleontology in North Dakota, their geological observations are so intriguing that they are worth recording here.

On 18 October 1804 at the Cannonball River, Lewis records,

> ". . . above the mouth of the river Great numbers of Stone perfectly round with fine Grit are in the Bluff and on the Shore, the river takes its name from those Stones which resemble Cannon Balls."[1]

". . . above the mouth of the river Great numbers of Stone perfectly round with fine Grit are in the Bluff and on the Shore, the river takes its name from those Stones which resemble Cannon Balls."[1]

Some of the more imporant observations were those of the baked or melted and fused red shale and sandstone locally called

[1]It should be mentioned that these "cannonballs" are sandstone concretions in the Fox Hills formation of Cretaceous age not in the Cannonball formation of Paleocene age.

today "scoria" or "clinker" and so commonly employed today for road metal in the western part of the State. On March 21, 1805, as they made preparations to leave their winter camp, Clark reports:

> "Saw an emence quantity of Pumice Stone on the Sides & foot of the hills and emence beds of Pumice Stone near the Tops of the[m], with evident marks of the Hills having once been on fire. I Collected Some [of] the different [sorts] i. e. Stone Pumice Stone & a hard earth, and put them into a furnace, the hard earth melted and glazed the others two and the hard Clay became a pumice Stone Glazed."

Shortly after they left Fort Mandan (April 7) Lewis discusses the geology near the present town of Riverdale (April 9) saying,

> "the Bluffs of the river which we passed today were upwards of a hundred feet high, formed of a mixture of yellow clay and sand many horizontal stratas of carbonated wood, having every appearance of pitcoal at a distance; were seen in the face of these bluffs. these stratas are of unequal thicknesses from 1 to 5 feet, and appear at different elevations above the water some of them as much as eighty feet. the hills of the river are very broken, and many of them have the appearance of having been on fire at some former period. considerable quantities of pumice stone and lava appear in many parts of these hills where they are broken and washed Down by the rain and melting snow."

On the following day (April 10) just south of the site of Old Fort Berthold they noticed a bluff which Lewis records, ". . . is now on fire and throws out considerable quantities of smoke which has a strong sulphurious smell." This is probably the first record of a burning coal bed in North Dakota.

The voyagers continued their observation of the "clinker"-capped hills until exposures seen near the present Mountrail-McKenzie county line on 16 April led Lewis (Reid, 1948, p. 241-242) to speculate on the origin of this so-called "scoria".

> "I believe it to be the stratas of coal seen in those hills which causes the fire and birnt appearances frequently met with in this quarter. where those birnt appearances are to be seen in the face of the river bluffs, the coal is seldom seen, and when you meet with it in the neighbourhood of the stratas of birnt earth, the coal appears to be presisely at the same hight, and is nearly of the same thickness, togeter with the sand and a sulphurious substance which usually accompanys it."

The experiments of Clark, and these ideas of Lewis, antedate

the theories of George Catlin and John James Audubon by approximately 30 and 40 years respectively, and yet the interpretation is far more modern than the erroneous ideas held by the latter two. The words "pumice", "lava", and "scoria" used by early explorers were simply unfortunate choices and it is to be regretted that these technical terms connoting igneous activity have become entrenched in local modern usage for the sedimentary rock formed in the baking and fusing of shale and sandstone by burning of the underlying lignite.

Yet another significant observation was made on 16 April for Lewis (Reid, 1948, p. 241) writes,

> "I met with several stones today that had the appearance of wood first carbonated and then petrefyed by the water of the river, which I have discovered has that effect on many vegitable substances when exposed to it's influence for a length of time."

In these terms Lewis writes what is presumed to be the first record of fossils from North Dakota!

Lewis and Clark made other geological observations including "alkali" and glacial drift (without regarding it as such) and experimented with the combustion of lignite. It is interesting to note, however, that they mistook the Killdeer Mountains for the "turtle mountains". The return trip of the travelers through the state in 1806, made wih relative haste, required only 17 days, and no geological observations were recorded.

The famous botanist Thomas Nuttall visited North Dakota in 1811 as did the naturalists John Bradbury in 1811 and William Price Hunt in 1812, but they seem not to have recorded geological or paleontological observations in the state.

Many other voyageurs, trappers, and hunters crisscrossed North Dakota and plied her waterways, but the next significant records were those left by the artist George Catlin who, in 1832, was on the first steamboat to reach the Yellowstone River. Catlin wrote like the artist he was and misinterpreted the origin of "clinker" although his word pictures of the Badlands[2] are as beautiful as his brightly colored paintings. On his voyage downstream from the post at the mouth of the Yellowstone he recorded his observations of the country and the rock strata. In discussing buttes along the way he wrote (Catlin, 1913, p. 79),

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[2]As used herein, "Badlands" refers to the Badlands of North Dakota especially well developed along the Little Missouri River, but also occurring along the Missouri River and lesser tributaries. The Badlands of North Dakota are formed in the Tongue River formation (of Paleocene age) and older formations; the "Little Badlands" just southwest of Dickinson are developed in the White River formation of Oligocene age as are the Badlands of South Dakota.

". . . . the superstratum, forming the tops of these mounds (where they remain high enough to support anything of the original surface) is composed, for the depth of fifteen feet, of red pumice; terminating at its bottom, in a layer of several feet of sedimentary deposit, which is formed into endless conglomerates of basaltic crystals.

"This strange feature in the country arrests the eye of a traveller suddenly, and as instantly brings him to the conclusion, that he stands in the midst of the ruins of an extinguished volcano."

Erosion in the Badlands impressed Catlin greatly and he paused to paint and write (p. 89) less than a day's journey north of the Mandan villages,

"These stupendous works are produced by the continual washing down of the sides of these clay-formed hills; and although, in many instances, their sides, by exposure, have become so hardened, that their change is very slow; yet they are mostly subjected to continual phases, more or less, until ultimately their decomposition ceases, and their sides becoming seeded and covered with a green turf. . . ."

Thus, in spite of his "conclusion" regarding volcanoes in North Dakota, Catlin's ideas of badland erosion were relatively modern; this is remarkable since they came so hard on the heels of the catastrophic theories expounded elsewhere in the world.

One of the finest scientists and observers to reach the Upper Missouri country was the German nobleman, Alexander Philip Maximilian, Prince of Wied-Neuwied who reached Fort Clark, founded in 1831 near the present town of Stanton, on June 18, 1833. A careful observer, he too, commented (Thwaites, 1905, p. 338) on the "cannonballs" near the mouth of the Cannonball River, and he observed, in this area, the dip of the strata into what is now known as as the Williston Basin.

In the vicinity of Fort Union he wrote (p. 383),

"The strata of sand-stone occurring in the above-mentioned hills are filled, at least in part, with impressions of the leaves of phanerogammic plants, resembling the species still growing in the country."

He apparently made the first extensive fossil collection in North Dakota for in a short but touching footnote (p. 383) he says of his fossil leaves, "Unfortunately, all these interesting specimens were destroyed in the fire on board the steam-boat." This refers (**fide** Thwaites, 1905, p. 240) to the burning of the "Assiniboine" near present-day Bismarck on June 1, 1835. Maximilan's was returning separately, but the "Assiniboine" went down on her return voyage

carrying a large cargo of furs as well as all of Maximilian's biological and geological collections. A sad loss for paleontology as well as all biological science!

During the summer of 1843, John James Audubon undertook a voyage up the Missouri River to study the quadrupeds of North America. Traveling with him on this journey was geologically-inclined Edward Harris. The entourage passed the mouths of the Cannonball River and Beaver Creek (in Emmons County) on June 5; therefore, it is probable that they entered North Dakota for the first time on Sunday, June 4, 1843. Upon leaving, they passed the same landmarks on Sunday, September 1, 1843. The majority of the time spent in North Dakota was spent in the area around Fort Union, near the present site of Williston (Audubon and Coues, 1898).

As Audubon's chief interests were biological, he made only a few geological observations. After one excursion to the north of Fort Union to search for petrified wood, he (Audubon and Coues, 1898, p. 37) wrote, "though we found many specimens, they were of such indifferent quality that we brought home but one."

After another trip into the Badlands in which he observed "clinker" capping the hills, he said (p. 149), "This whole is evidently the effect of volcanic action . . ." He continued,

> ". . . in the sand at the tops of some of the highest hills I have found marine shells [they are not, for there are no marine fossils near Williston], but so soft and crumbling as to fall apart the instant they were exposed to the air. I spent some time over various lumps of sand, hoping to find some perfect ones that would be hard enough to carry back to St. Louis; but t'was 'love's labor lost', and I regretted exceedingly that only a few fragments could be gathered."

He further recorded on this trip,

> ". . . numbers of petrified stumps from one to three feet in diameter; the *Mauvais Terres* abound with them; they are to be found in all parts from the valleys to the tops of the hills, and appear to be principally of cedar."

Edward Harris (McDermott, 1951) spent much more time observing geological phenomena. He, also, observed the dipping strata in southern North Dakota. He discussed the concretions of the Cannonball River area and during his stay at Fort Union, he made trips into the surrounding country side to search for petrified wood and other fossils. On August 24, 1843, on the trip downstream he found (p. 177) ". . . Red Stones with impressions of leaves &c &c petrified wood."

Another member of the Audubon group, John G. Bell, took an extensive trip through the Badlands and, upon returning, gave an account (McDermott, 1951, p. 173) of burning lignite beds which

convinced Harris (even though it apparently did not similarily affect Audubon) that ". . . neither in the recently or more anciently burnt portions is there the least appearance of *Pumice Stone* as stated so confidently by Catlin . . . ."

During the summer of 1850, Thaddeus A. Culbertson visited North Dakota with the purpose of studying the fauna of the area. As with most of the early naturalists, he was also interested in the geological aspects of the area. He recorded (Culbertson, 1851) that he found petrified wood in the White Earth River area, but lists of his collection do not record fossils.

The 1850's witnessed the greatest expansion of scientific traffic and observation in the Upper Missouri country with the advent of vast surveys of western lands conducted by the Federal Government.

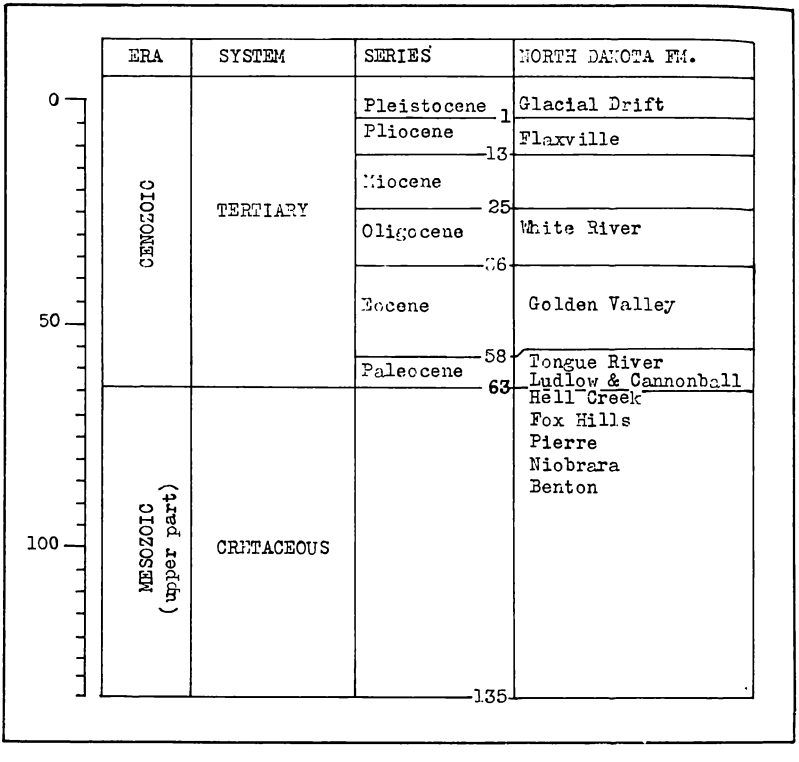


FIGURE 1. Surface formations of North Dakota and the geologic time scale. Numbers indicate millions of years ago. None of the formations of the Triassic and Jurassic Systems of the Mesozoic Era nor those of the Paleozoic or Precambrian Eras are exposed in North Dakota. They lie buried in the subsurface of the Williston Basin. (Adapted from Kulp, 1961.)

In 1853, John Evans, geologist with the Northern Pacific Railroad Survey wrote (Evans, 1854, p. 21) in his scientific instructions to Isaac I. Stevens, Governor, Washington Territory, and leader of the survey,

> "From the Sioux river to the falls of the Missouri, on both sides of the Missouri, you pass through the cretaceous and tertiary formations, perhaps as rich in fossil remains as any other region in the country, or it may be in the world."

His evaluation of the fossiliferous nature of the formations mentioned may be a little overly enthusiastic but locally would certainly be true. Thus, it seems he knew much more than the above sparse references to paleontology in North Dakota might otherwise indicate.

Much of this information came from exploration of areas that are now parts of adjacent states. Jean N. Nicolett and John C. Fremont ascended the Missouri in 1839, but apparently collected no fossils in the North Dakota portion of their trip. However, they had collected a large number of Cretaceous mollusks, south of Fort Pierre, which were described in the East by S. G. Morton in 1842 and Timothy A. Conrad in 1843.

Evans himself, had collected extensively in the Badlands of South Dakota while on a side trip from the famous trip of David Dale Owens down the Red River to Fort Gary (Winnipeg) in 1849. The vertebrate remains collected by Evans caused a sensation when studied and reported on in a series of papers by Dr. Joseph Leidy of Philadelphia. It has been said (Merrill, 1924) that, "this was the first systematic account published of the Bad Lands fossils and it might not unjustly be considered as marking the beginning in America of studies in vertebrate paleontology."

It was about this time that the two men, Dr. Frederick V. Hayden and Dr. Fielding Bradford Meek, who had the most to do with paleontology in North Dakota (and indeed with geologic and paleontologic exploration in the west) first entered these lands. Both were veritable giants in the early days of the Federal surveys; they went on to play a large part in subsequent explorations of the northern Great Plains and Rocky Mountain states and in the organization of the present U. S. Geological Survey in 1879. Hayden was the leader and administrator, a man of great physical stamina; Meek was the more scholarly, a man shy, unassuming and oftimes in ill health.

The exploits of Evans and the reports of his fossils by Leidy had whetted the interest of that most avid collector and outstanding paleontologist of his day, James Hall, State Geologist of New York. Hall dispatched Meek with Hayden as his assistant (although their positions were reversed on subsequent expeditions) to the Badlands (now in South Dakota) in 1853 by way of steamer up the Missouri

River as far as Fort Pierre. In spite of hostile Indians they collected enormous quantities of fossils. The mammalian remains were described by Leidy and the Cretaceous fossils by Hall and Meek in 1856 in a paper which gave the first geological section for the region.

The following spring (1854) Hayden severed his connections with Hall and ascended the Missouri River partly under the auspices of the American Fur Company. He remained in the Upper Missouri Country for two years supporting himself "in various ways as he went along". In 1856 he returned to explore and collect with Lt. G. F. Warren of the U. S. Topographic Engineers, from Fort Pierre to a point 60 miles north of the mouth of the Yellowstone. In 1857 Hayden was reappointed geologist by Warren on an expedition to the Black Hills. During 1858 Hayden explored Kansas with Meek, and with Capt. W. F. Raynolds of the Topographic Engineers he explored in Montana in 1859. After Civil War services as a surgeon, Hayden made some seventeen extensive expeditions in Colorado, Utah, Idaho, Montana, South Dakota and North Dakota. It was largely through the efforts of Hayden that the Yellowstone region was set aside as our first National Park.

The Sioux Indians gave to Hayden the name "The-man-who-picks-up-rocks-running"—such were his exploits in the field. It is related (Merrill, 1924, p. 527) that once while collecting alone in the Upper Missouri country, he was surprised by a band of hostile Indians. "Finding him armed only with a hammer and carrying a bag of rocks and fossils, which they emptied out and examined with much surprise and curiosity, they concluded he was insane and let him alone." A reaction experienced by most paleontologists sooner or later yet today!

Meek, when not in the field with Hayden, was busy describing the the invertebrate fossils in a series of papers jointly authored with Hayden. Although ill much of the time he worked and drove himself at a prodigious rate, writing once (in 1869) to John Strong Newberry (Merrill, 1924, footnote p. 528) "Is there any little nook or corner about your museum rooms where I could have a little cot to sleep on while I am with you? I can bring my blankets and sheets with me . . . I also prefer to spend my evenings with the books and specimens." In spite of his ill health and humbleness, he, with the exception of James Hall, is called (Merrill, 1924, p. 528), "perhaps the most widely known of American paleontologists."

Such was the nature of the two men, Meek and Hayden, who collaborated in a series of papers describing Cretaceous and Tertiary fossils from the western United States beginning with their first work in 1856 and terminating with a monumental quarto volume by Meek which was published in 1876, the year of Meek's death. In his letter of transmittal of this tome to the Secretary of the Interior, Hayden acclaims Meek's work "as one of the most important contributions ever made to the science of palaeontology in any por-

tion of the world." This is still the standard reference for invertebrate paleontology in North Dakota!

Until the activity of recent years at the University of North Dakota, the only significant additions to invertebrate paleontology in North Dakota were the publication of a great many new localities (but no taxonomic work) by Arthur Gray Leonard, State Geologist from 1902-1932; small but excellent descriptive papers by T. W. Stanton and T. W. Vaughan on mollusks and corals (respectively) from the Cannonball formation in 1920; a list of Foraminiferida from the Cannonball by Steven K. Fox, Jr., and Reuben J. Ross, Jr., in 1942; and the report of a small marine fauna in the otherwise non-marine Hell Creek formation by Wilson M. Laird and R. H. Mitchell in the same year.

The first extensive collections of North Dakota *vertebrate* fossils following the expeditions of Hayden were made in 1883 by Edwin Drinker Cope. In a letter written from his camp near Sully Springs (8.2 miles east of Medora) he described (Cope, 1884) his visit to White Butte in present Slope County and listed, with a field identification, the vertebrate fossils found. In 1883 Cope described in more detail two new species of excellently preserved fossil fish from the Percidae or perch family found in the siliceous limestones (White River formation) atop Sentinel Butte. In the same year C. A. White assigned these to a new genus. This locality has become so famous that the exposure has been absolutely minded out and no fish remains can be found there today.

The Carnegie Museum sent Earl Douglass in 1905 to collect vertebrate fossils in western North Dakota, and he reported on these from the White River formation in a charmingly descriptive, reconnaissance manner (Douglass, 1909). The material collected in North Dakota and states farther west was the subject of numerous papers by Douglass.

There are few other systematic reports of North Dakota vertebrate fossils. The vertebrate record is mostly compiled from reports of isolated finds of fragments — a mosasaur from the Pembina Escarpment (Berkey, 1905), a dinosaur from Marmarth (Leonard, 1908), a titanothere from near Buford (Gidley, 1917), a mammoth from near Watford City (Haraldson, 1952), and a few other reports by Leonard in the course of other investigations with the North Dakota Geological Survey. The American Museum of Natural History in New York and Princeton University have had collecting parties in the field in North Dakota in more recent years, but published reports of their work are unknown to me.

J. S. Newberry and F. H. Knowlton loomed large in the history of paleobotany of the western states. Early paleobotanists, however, created a large number of form genera and form species based on fragmentary remains. Therefore details of the history of the collection of fossil plants are even more difficult to obtain. The literature is

old, rare, dispersed and modern paleobotanical taxonomic revisions make such a historical study difficult in this field.

However, it is known that the now nearly treeless plains of North Dakota were once covered with splendid forests of hardwoods such as oak, elm, hickory, and walnut interspersed with conifers, gingkoes, fig trees, cypress, *Sequoia,* etc. Certainly the strata of western North Dakota (especially the Paleocene) abound with fine specimens; even the "clinker" carries delicate impressions of beautiful leaves. As early as 1922 a press release of the U. S. Geological Survey recorded that from the Fort Union group alone some 300 species had been identified.

Also interesting are the common finds of petrified wood (usually reported as *Sequoia* and recently reinterpreted by Chaney, 1951), of specimens of logs bored by shipworms, of cones of *Sequoia dakotensis* Brown, 1935) from the Cretaceous Hell Creek formation, and even of fossil amber from North Dakota (Langenheim, Smiley and Gray, 1960, p. 1356). Even more interesting is a fossil shelf fungus described and named (Brown, 1936) from the Upper Cretaceous of the Cannonball River area. Two years later the author (Brown, 1938) had the commendable scientific (or should I say intestinal?) fortitude to admit he was wrong in an article entitled "Two Fossils Misidentified as Shelf-Fungi" and to admit their more correct placement as otherwise unidentifiable fossil corals.

## A View Around Us

Since I came to North Dakota, I have been working toward the preparation of a systematic catalogue of all of the fossils and fossil collecting localities reported from North Dakota. To that end I have prepared a card file with species each recorded on a key punch card containing a bibliographic citation to each locality from which the fossil has been reported. I make no claims for the completeness of this record; in fact, I consider it incomplete. I believe it to be tolerably complete as far as invertebrates go but inadequate regarding the vertebrates and especially the fossil plants. Nevertheless, some idea of the paleontological record from North Dakota can be gained from the following.

There are 703 cards in the file; eliminating the obvious synonyms, these record a total of 488 species and subspecies distributed among 294 genera and subgenera. Of this 488, 54 species occur in the subsurface only (discounting occasional finds in glacial drift). Ninety of the total are vertebrates of which 44 are conodonts (tiny tooth-like fossils of uncertain origin, perhaps an extinct order of fish) from the subsurface and but 46 are plants. One fossil bird has been reported from North Dakota, eight reptiles, no amphibians, but 10 species of fish and 27 species of mammals.

Excluding plants, 85 species have been based on specimens first described from North Dakota. These holotypes include 59 gastropods,

21 pelecypods, five corals, and two each of crustaceans (crabs), fish, and mammals.

A sidelight that is perhaps interesting is that 14 species of fossil animals and at least one plant have names utilizing North Dakota place names (five gastropods, three pelecypods, three corals and one each crustacean, cephalopod, and mammal). They are:

Cyclichnella dakotensis
Epitonium dakotense
Eriphyla? mandanensis
Eucrotaphus dickinsonensis
Fasciolaria? mandanensis
Fasciolaria dakotensis
Fusus (Serrifusus) dakotensis
Modiolus schallerensis
Paracyathus kayserensis
Ranina (?) burleighensis
Scaphites mandanensis
Sequoia dakotensis
Sterophonotrochus leithensis
Trochocyathus dakotaensis
Turricula janesburgensis

Thus even the abandoned post office of Schaller in southern Morton County is immortalized for all posterity by having a fossil clam named after it!!

**A Glance into the Future**

First, I think it is unfortunate that the state has so few trained paleontologists working in it. A number of oil companies have geologists who are studying fossil algae in connection with subsurface reefs and fossil spores and other microfossils in connection with subsurface correlation problems. Unfortunately, their reports are reports with a direct and immediate commercial aspect and have a habit of finding their way into company files and so do not reach the scientific public. These men are applying the knowledge gained in finding oil for their respective companies, and therefore have not (nor cannot be expected to have) a sole and abiding interest in furthering paleontological knowledge.

The greatest need, perhaps, lies in the lack of library reference material. I have compiled a bibliography of over 300 articles, books, and monographs dealing directly or not so indirectly with paleontology in North Dakota. Over half are not locally available! Most of the great monographs of the early Federal surveys and such publications as Nautilus, the Carnegie Museum Annals, and the early volumes of the Academy of Natural Science of Philadelphia, the Boston Academy of Arts and Science, and the American Journal of Science are not in our library. These cannot be bought on microfilm since it is impossible to make comparative identifications from

microfilmed plates especially when these are housed in the library and are thus not available for constant comparison in the laboratory.

Another great need is comparative collections and collections from within our own state. As implied above, the great collections are in the United States National Museum, the Carnegie Museum, the Philadelphia Natural History Museum, the American Museum of Natural History, etc. These specimens will never return to North Dakota! But it is possible, in many instances, where the specimens are not absolutely unique, to make extensive collections of many of our abundantly fossiliferous strata. We need constantly to be out searching the outcrops and building our collections.

Now, the University of North Dakota and the North Dakota Geological Survey have been cooperative, and in the Department of Geology we are rapidly expanding our facilities for storing and labelling our expanding collections. We have over 25 cases of fossils where less than a decade ago we had three. This is still a small number and we obviously need yet to grow!

But who wants to work a farm where the substance is drained from the soil and opportunity is gone? Challenges lie where there are frontiers! What direction shall we take?

My personal interest has long been in the Cannonball formation —named from a North Dakota river and cropping out almost wholly within the boundaries of the state, this deposit from the last marine invasion of the interior of the continent in a time of waning seas in front of a newly rising cordillera 60 million years ago, is yet virtually unstudied. Its surface expression and subsurface extent are not accurately known, and its fauna is largely undescribed and unfigured. Yet I have collected two large trays of tiny gastropods from one outcrop in one afternoon. Most of these are new to science or have never been reported from North Dakota. Over 70 species of foraminiferids have been listed from a few outcrops but none described or figured. The fauna of the Cannonball formation, commonly said to have Gulf Coast affinities, I believe has boreal rather than austral connections.

Another problem is the recent finds by students and members of the University staff, reported by Lee S. Clayton and S. J. Tuthill (see elsewhere in this volume of the Proceedings), of aquatic molluscan faunas in ice-contact lakes of the Pleistocene or Great Ice Age. The Pleistocene terrestrial and aquatic invertebrate faunas have not been studied in North Dakota nor in detail elsewhere in the United States. Before we can well interpret Pleistocene aquatic environments, and perhaps climate, it will be necessary to study the distribution of present day mollusks in North Dakota—an untrammeled field. Study of Pleistocene mollusks, now underway at the University of North Dakota, will come at an opportune time to help unravel the complicated glacial history of the state which is now

being undertaken in an accelerated program by the Geological Survey and the Department of Geology. This glacial geology is of prime importance in ground water studies so essential to an agricultural state like North Dakota.

Within the last month geology students have discovered abundant ostracods in the sediments of Glacial Lake Agassiz—the first invertebrates collected from these ancient lake deposits in North Dakota to my knowledge. The extent of their occurence on their usefulness in deciphering the history of this famous lake, about which so much has been written but about which we know so little, remains to be seen.

The invertebrates of the Tongue River formation (underlying all of the Little Missouri Badlands in North Dakota) have not been studied since the days of Meek and Hayden. We have not even collected topotypes of the 30 molluscan species first described from this formation in North Dakota (nor has anyone else).

The exact age and correlation of the various Pierre shale outcrops has not been determined nor has the fauna been completely described in the past 85 years. A good start has been made in this direction by the staff and graduate students of the University of North Dakota, but eastern universities are looking for new problems and have students in South Dakota who are systematically working their way north. We may be "scooped"! The fauna of the Fox Hills formation even more urgently needs work. Micropaleontology of the Niobrara formation is now in progress.

In 1959 at the Geological Society of America meetings in Pittsburgh, a paper was read on spores and pollen from the basal Paleocene lignites in South Dakota. Yet, in spite of the proven usefulness to industry of polospore analysis, this is an untouched field in North Dakota except for the work done by employees of oil companies. We have no accomplished paleobotanist at the University of North Dakota, and this has hampered studies of fossil plants; but I feel there must, and will, soon be a beginning in this direction.

The subsurface of the vast Williston Basin offers immense opportunities, especially for micropaleontology. Clarence Carlson (1960) and I (Holland and Waldren, 1955) have well advanced a study of the conodonts of the Winnipeg formation, but we have not touched its abundant bryozoan fauna. The Devonian bears spores and chitinozoans and I am confident that microformaniniferids will be found in insoluble residues of the limestones. The Mississippian carries abundant endothyroid foraminiferids and the Pennsylvanian and Permian strata will yield fusulinids. A former student of mine and I began, in a desultory way, a study of radiolarians in the Pierre formation and he has reported to me (Everett E. Wilson, oral communication) that he has since carried this "zone" of radiolarians into the subsurface and found it a useful marker for tracing on electric logs even beyond the point where he could find these tiny microfos-

sils. Serendipity? We can't tell the value of many of these things until they are tried!

The necessity for paleobotanical studies in determining paleogeography and stratigraphy of the lignite deposits will make the need for these studies even more apparent than the above paucity of file information would indicate. The fossil floras of the western part of the state are scarcely touched in a modern manner.

When the descriptive and taxonomic work on the fossils of North Dakota is completed the true paleoecological work can fairly begin. While the modern ecologist and biologist has only the Recent to deal with, the paleontologist has the accumulated record of ½ a billion years to interpret. We shan't want for things to do. The future of paleontology in North Dakota looks bright indeed!

## Acknowledgments

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# ALTERNATING CURRENT HALL VOLTAGE AND MAGNETORESISTANCE OF THIN IRON NICKEL FILMS

(A Progress Report)

*E. N. Mitchell and J. V. Cross*

*University of North Dakota, Grand Forks, North Dakota*

## INTRODUCTION

In an effort to study the anisotropy in the resistance of thin permalloy films it was found desirable to first investigate the galvanomagnetic effects in the film. It is the purpose of this paper to report continuing progress on the study of the galvano-magnetic effects in thin permalloy films. Mitchell and Henizel (1) reported previously studies of the resistance of such films in the plane of the films as a function of the magnitude and orientation of an applied magetizing field when a fixed current was passed along the plane of the film through the film. Pugh *et al* (2) have reported the study of the anisotropy in resistance of thin iron nickel films as a function of composition. The anistropy of these films was induced by introducing a texture axis in the film whereas the work of Mitchell and Heinzel has been done on films whose anisotropy was induced by evaporation in the presence of an orienting field.

## APPARATUS

Earlier work done here was carried out with a D.C. current. A comprehensive study of this problem shows that in general one cannot

eliminate thermomagnetic effects using such a method. If the current is made alternating, however, these last effects can be in general eliminated (3). The use of alternating current simplifies the problem of amplifying the error current in the brideg circuit used to measure the voltage developed across the film. In addition, all of the galvanomagnetic effects except the Hall effect and the magnetoresistance should be negligible in the type of material studied here. If two appropriate voltages ($V_{rw}$ and $V_{wb}$ see Figure 1) are measured at specified field values then it is possible to separate these two effects. This, in effect, makes the network for examining the film a six terminal network instead of a four terminal network as is used more commonly in precision resistance measurements.

The measurement circuit here used represents a modification of one reported by Donoghue and Eatherly (4). (Fig. 1). The essential feature of this potentiometer is that the current passed through the film is always proportional to that passed through the potentiometer making the individual measurements independent of fluctuations in the current through the film.

A phase problem arises when an effort is made to balance the voltage across the film against that of the potentiometer. A fixed phase shift network is used in the feedback network to correct this difficulty. To get the proper phase shift the frequency of the driving signal is altered for balance. In order to make an absolute measurement one still must make a calibration of the current through the potentiometer at one value. Relative measurements can be made precisely with this system and hence small difference in the potential drop across the film can be detected.

The voltage drop across the resistance network in a Rubicon potentiometer is used to provide the necessary potentiometer voltage. A transistorized A.C. amplifier with an overall gain at the null of the order of fifty is used to amplify the unbalance signal which is then detected on a vacuum tube voltmeter. This amplifier being inherently low in noise is able to detect an unbalance voltage of the order of .25 microvolt. The overall voltage drop across the film is the order of 2500 microvolts; hence, an overall precision between readings of .01% can be obtained.

In order to study the potential differences in the plane of the film when the film was magnetized perpendicular to the plane of the film it was necessary to supply a field of the order of 10,000 gauss in this direction; a four-inch electromagnet with two-inch tapered pole caps was incorporated for this purpose.

## MEASUREMENT AND RESULTS

The films to be studied were prepared by vacuum deposition of an alloy of 82% Ni. and 18% Fe. onto a heated glass substrate in the presence of a magnetic field oriented parallel to the plane of the glass. The substrate temperature before and during deposition was

300° C., the pressure of the order of $5 \times 10^{-5}$ mm-Hg., the time of deposition of the order of one minute, and the field during and after deposition 24 oersteds. Films so deposited exhibit uniaxial magnetic anisotropy in the plane of the film along a preferred axis. In such a film it is not possible to achieve a truly demagnetized state because while the net magnetization can be reduced to zero, the domains into which the film degenerates will be oriented parallel to this anisotropy axis. This is not sufficient to allow measurement of the resistance of the film in the demagnetized state because the magnetoresistance is an even order effect with respect to the direction of the magnetization of the film. This quantity is needed in the study of magnetoresistance as is done in the conventional manner.

For an initial study of this material using the present apparatus it was decided to study the change in the resistance of the film in the plane of the film at an angle of 45° with the easy axis when a strong field was applied perpendicular to the plane of the film. The Hall voltage in the plane of the film was studied under the same circumstances. Because of the shape and induced anisotropy in the film, it is nearly certain that any Hall voltage which is detected will be the result of the application of the external field and not any residual internal fields in the film. The change in the resistance, however, will represent a change from a magnetized state in one direction to one in a new direction depending on the magnitude and direction of the applied field. This change in resistance divided by the initial resistance is called the magnetoresistance of the film in this article. In order to simultaneously obtain the Hall voltage and magnetoresistance for a given applied field it was necessary to measure the voltage $V_{rw}$ and $V_{wb}$ both in the presence and absence of the applied field. Such measurements can be related as follows to yield the Hall voltage and magnetoresistance of the film.

$$V_{rw} - V^{\circ}_{rw} = V_h + V^{\circ}_{rw} \qquad (\Delta r/r)$$
$$V_{wb} - V^{\circ}_{wb} = {}_h + V^{\circ}_{wb} \qquad (\Delta r/r)$$

In the above paragraph $V^{\circ}_{rw}$ and $V^{\circ}_{wb}$ refer to the potential differences in the absence of an applied field while $V_{rw}$ and $V_{wb}$ to the potential differences in the presence of a magnetic field. $V_h$ is the Hall voltage due to the applied field and $\Delta r/r$ is the fraction change in resistance due to magnetoresistance effects upon the application of the field. The results of such measurements are shown in Figure 2 where the bottom curve represents the magnetoresistance effects as a function of field. In this case, the two different sets of data represent two independent sets of data taken on the same film. The precision of the measurements is indicated by the error bars on the data.

In an effort to get repeatable results in such circumstances, it was found necessary to keep the film at a constant temperature and to orient the film in the magnetic field so that the applied field was very accurately perpendicular to the plane of the film. Proof of

this was established by measuring the magnetoresistance of the film as a function of the angular orientation of the film when a field of 4000 oersteds was applied. Whereas the value at normal incidence was the order of .3%, the value when measured as a function of angle varied from zero to the order of 3% when the angle was changed from normal incidence to plus or minus ten degrees from normal in a continuous manner. This, in all probability, is due to the complications which arise from magnetoresistance effects in the plane of the film.

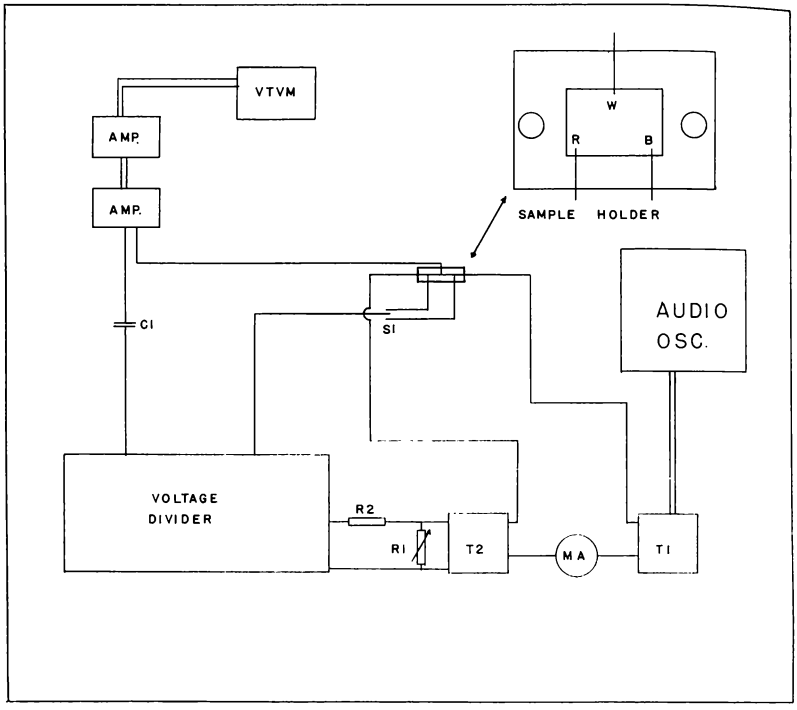


FIGURE 1. Block diagram of the A. C. Potentiometer for measurement of the potential differences across the film. The film holder configuration is shown at the upper right.

## CONCLUSIONS

The interpretation of these results is quite complicated inasmuch as little data on bulk permalloy is available for comparison. In addition to this, the presence of strong demagnetizing fields due to free poles on the surfaces of the film make determination of the magnetic state of the system difficult. Furthermore, the magnetoresistance measured here is unlike that usually measured as has previously been stated. No numbers are quoted for the ordinary and extra-

ordinary Hall coefficients because of the difficulty in interpreting the slope of the given curves. However, the current through the film was 3.6 ma., and the film thickness of the order of 2000 A.U. Using these values one gets results which are the same order of magnitude as those obtained for nickel films by Colombani and Goureaux (5).

One would expect to observe a decrease in the slope of the magnetoresistance curve when the material becomes saturated. How-

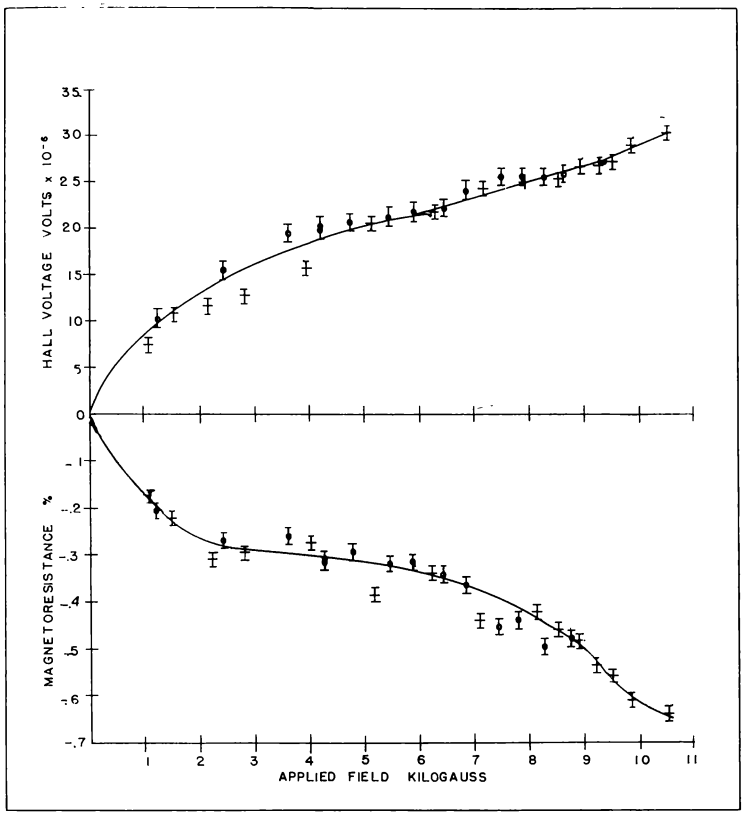


FIGURE 2. At the top is plotted the Hall voltage developed across the film as a function of the applied field; at the bottom the magnetoresistance of the film is plotted as a function of the applied field.

ever, this would occur for some value of applied field in excess of 10,000 gauss. Such a field is not available in our laboratory at present.

It is planned to extend this work to higher fields and to also study these effects in the plane of the film when the needed field becomes available.

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# LOW TEMPERATURE ANNEALING OF THIN IRON NICKEL FILMS AS A FUNCTION OF COMPOSITION

*E. N. Mitchell and C. O. Heinzel*

*Department of Physics, University of North Dakota*
*Grand Forks, North Dakota*

## INTRODUCTION

Considerable interest has been aroused concerning the annealing characteristics of thin permalloy films. Williams and Sherwood (1), Mitchell (2), Segmuller (3), and Weiss and Smith (4) have reported work on the high temperature (of the order of 300° C.) anneal of iron nickel films of near zero magnetostriction and Mitchell and Segmuller have reported on the intermediate temperature (below 200° C.) annealing characteristics of similar films. Weiss and Smith (4) have reported the difference in the high temperature annealing characteristics of angle of incidence films made of differing compositions of nickel and iron in particular with regard to the change in the sign of the magnetostriction of the films.

It is the purpose of this paper to report preliminary results of the low temperature annealing characteristics of normally vacuum deposited iron nickel films using the amount and sign of the magnetostriction as a parameter.

## APPARATUS AND MEASUREMENTS

The films to be annealed were prepared by vacuum deposition of an appropriate alloy of iron and nickel onto a heated glass substrate in the presence of a magnetic field oriented parallel to the plane of the glass. The substrate temperature before and during deposition was 300° C., the pressure was of the order of $5 \times 10^{-5}$

mm-Hg., the time of deposition of the order of one minute and the field during and after deposition 24 oersteds. The melt compositions from which the films were deposited were 70% Ni.—30% Fe; 78% Ni.—22% Fe; and 88% Ni.—12% Fe. The films so deposited exhibited respectively quite positive, near zero though slightly positive and quite negative magnetostrictions. A melt of 82% Ni. and 18% Fe. using this evaporation technique yields a film of a very near zero magnetostriction. All of the films were circular in cross section, eight-tenths centimeter in diameter and of the order of 2000 A. U. thick.

Though some earlier annealing work has been done in silicone oil (2), this work has been done in a vacuum which was always lower than $5 \times 10^{-6}$ mm-Hg. This vacuum was achieved in a system which contained virtually no organic material and in which the vacuum was attained and maintained by means of an evaporion pump. The annealing temperature was attained by containing the slides to be annealed in a large substrate heater made of copper which was heated by passing current through a molybdenum filament heater non-inductively wound and imbedded in the substrate heater.

Temperature was monitored by means of a thermocouple. In order to maintain the temperature in the substrate heater at a specified value during an annealing run a servomechanism which could control the current through the heater was necessary. Because the thermal capacity of the temperature sensor had to be maintained at a low value and be very sensitive, it was not possible to use the thermocouple for the feedback device. Instead, a bead thermistor was used as the sensing element on the substrate. This thermistor was placed in one arm of a Wheatstone Bridge type circuit whose unbalance current when the temperature was not the desired temperature was fed into a transistor amplifier which in turn energized a plate relay whose contacts controlled the current through the heater. By changing the variable resistance in the opposing arm of the bridge, the balance temperature could be altered. With this device the temperature could be maintained at the film surface to within plus or minus one degree centigrade. Because of the hysteresis in the resistance of the thermistor upon heating and cooling the thermistor through a wide temperature range it was necessary to rebalance the bridge each time the system first reached the desired operating temperature. Thereafter, the control circuit would maintain the temperature as specified.

The annealing work was performed in the presence of a 24 oersted steady field which was oriented in the plane of the film. Measurements were made of the magnetic properties of the films before and after the individual annealing cycles. Most of these measurements were made by switching the magnetic state of the film at sixty cycles per second while observing the change of its magnetic state with a hysteresis loop display apparatus though some

additional observations were made using a Kerr magnetooptic display apparatus with which the domains of the films could be observed.

Two parameters were in particular controlled during each annealing operation. These were the temperature of the substrate and the direction in the plane of the film along which the annealing field was applied. The annealing time for all of the individual anneals was of the order of ten hours. In general one hour was required to raise the film to and be stabilized at the selected temperature and about an equal time to cool again to the ambient temperature of the vacuum system (40. C.).

## RESULTS

Measurements of magnetic characteristics were made on these films before and after each annealing cycle along the easy and difficult direction of the film. The easy direction is defined here as the direction in the plane of the film of the predominant walls in the film when in a demagnetized state; the difficult direction is perpendicular to the easy axis and parallel to the plane of the film. The parameters of particular interest here are the direction of the easy and difficult axis with respect to the direction of the orienting field during the deposition of the film, the magnitude of coercive force of the film along the easy direction and the magnitude of the anisotropy field along the difficult direction. This last parameter is defined as $H_k = H_o \frac{M_s}{M_o}$ where $H_o$ is the field necessary to cause an initial magnetic moment/unit volume ($M_o$) along the difficult diection and $M_s$ is the saturation magnetic moment/unit volume. The hysteresis loops of the positive magnetostriction films are in general rectangular along the easy axis and much like that of a normal ferromagnetic material along the difficult direction (Figure 1). The hysteresis loops of the nickel rich films were quite open in both directions and determinations of the easy axis could be made only by examination of the domains with the Kerr apparatus or by examination of the initial permeability with the hysteresis loop dsplay apparatus.

Annealing of the films was performed at 42°, 50°, 60°, 70°, 80°, 90°, and 95° centigrade. The annealing character of the two kinds of positive magnetostriction films differed only in degree. Annealing was performed with the field along the difficult direction (perpendicular to the direction of the applied field during film deposition), and the value of $H_k$ decreased with increasing temperature (see Figure 2) with a sharp drop in the value of $H_k$ when the films were annealed at 80° C. and a change in direction of the easy axis by 90° when the film was annealed at 90° C. Within limits of precision of the experiment it would appear that the annealing threshold for the 70% Ni. film was lower than that of the 78% Ni. film.

In the case of the nickel rich film the easy axis originally was oriented at 45° with respect to the direction of the applied field during the deposition of the film. On the basis of the behavior of two films of this type, it was found that the easy axis of the film lined up along this 45° axis independent of whether the applied annealing field was oriented along the easy axis or perpendicular to it after the initial annealing operations. As can be seen from Figure 2, $H_k$ fluctuated widely as the temperature rose. The annealing field was maintained along the easy axis as the temperature was raised. After being annealed at 80° C., the new easy axis was found to be 90° to the direction of the applied field during the deposition of the film and therefore at 45° to the direction of the annealing field during that annealing cycle. During subsequent annealing cycles at 90° C. and 95° C. in which the annealing field was applied either parallel or perpendicular to the deposition field the easy axis after anneal was always parallel to the applied annealing field during that cycle.

## CONCLUSIONS

Though these results are preliminary and annealing work is continuing one can conclude tentatively at least the following: The results of intermediate temperature annealing are a function of the sign of the magnetostriction and materials exhibiting positive magnetostriction anneal in a manner similar to zero magnetostriction materials while strongly negative magnetostriction materials do not. This difference is probably related to the fact that the effect of the negative magnetostriction on the film characteristics is to endeavor to align the spins in the film in a direction perpendicular to the surface of the film, whereas the effect of positive magnetostriction is

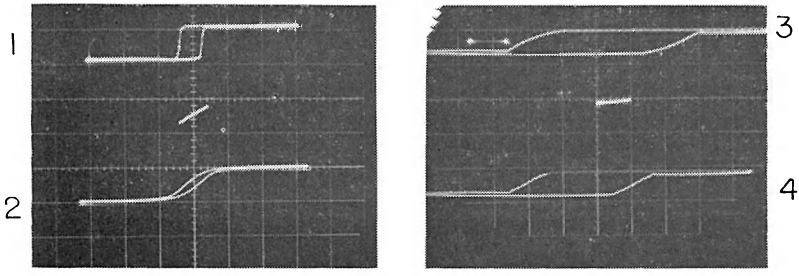


FIGURE 1. Typical hysteresis loops for the films of this study: (1) positive magnetostriction material along easy axis, (2) positive magnetostriction material along difficult axs, (3) negative magnetostriction material along easy axis, (4) negative magnetostriction material along difficult axis.

to align the spins in the plane of the film in the case under consideration.

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of North Dakota, and the National Science Foundation, without whose support this work would not have been possible.

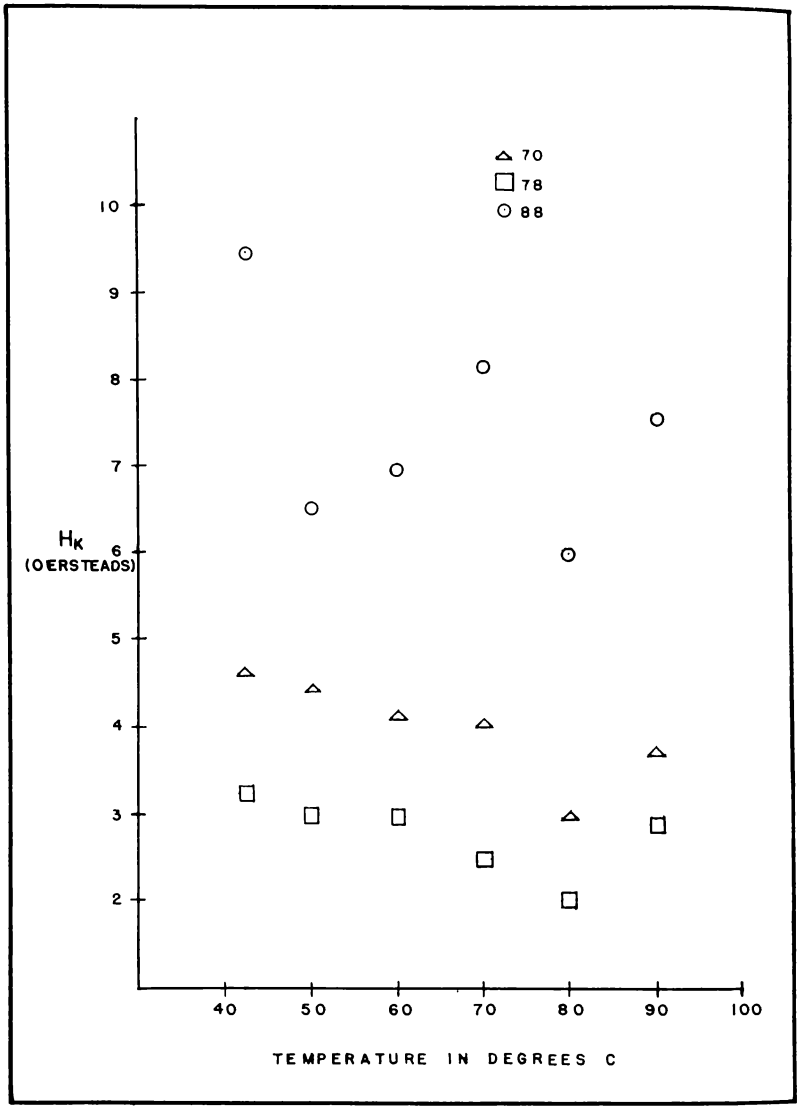


FIGURE 2. Anisotropy fields for films studied in this report as a function of annealing temperature just prior to measurement of $H_k$. The numbers in the legend refer to the per cent nickel in the melt from which the film was deposited.

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# SLOW DOMAIN WALL MOTION IN THIN FERROMAGNETIC FILMS

*Darold J. Frantsvog*
*Department of Physics*
*University of North Dakota, Grand Forks, North Dakota*[1]

## Introduction

On the basis of models developed to explain the energy of the Bloch wall and changes in the direction of magnetization by domain wall motion, the motion of the Bloch wall was described by investigators (1) as

$$m_w \frac{d^2x}{dt^2} + B\frac{dx}{dt} + ax = 2I_sH,$$

with $m_w$ being the effective mass of the wall per unit area, B a viscous damping coefficient, and a is a stiffness coefficient. $m_w$ and B are characteristics of the material and a arises from interaction of the wall with imperfections. It is, therefore, a structure sensitive parameter. $2I_sH$ is the pressure exerted by an external field on the wall. Usually the velocity is nearly constant and the first term disappears. For fields greater than the coercive force the x term also disappears and the equation takes the form

$$B\frac{dx}{dt} = 2I_s\,(H - H_o).$$

A number of investigators (2, 4) report results of measurements of domain wall velocities in different materials using instruments and direct visual observations. A study of domain wall velocity, as a function of the switching field and temperature, in thin iron-nickel films was made by Olmen and Mitchell (5). Visual and photographic measurements of the progress of a point of a spike shaped domain were made using longitudinal Kerr techniques. It is the purpose of the present investigation to extend the experiment by introducing better temperature control, checking for reproducibility and comparing results.

The film used in this investigation was a circular specimen about 1500 Angstrom units thick and one centimeter in diameter. It was

[1]Now at Concordia College, Moorhead, Minn.

prepared by vacuum evaporation from an alloy of 17.25% iron and 82.75% nickel onto a heated glass substrate (300°C) in the presence of a magnetic field. The direction parallel to the orienting magnetic field is defined as the easy direction of the film and the direction in the surface of the film perpendicular to the orienting magnetic field is the difficult direction of the film. It has a composition of about 78% nickel and 22% iron. Films of the group exhibited negative magnetostriction. When placed in a 60 cycle alternating field, with the direction of magnetization the easy direction, the characteristic rectangular hysteresis loop was observed with the coercive force about 9.0 oersteds.

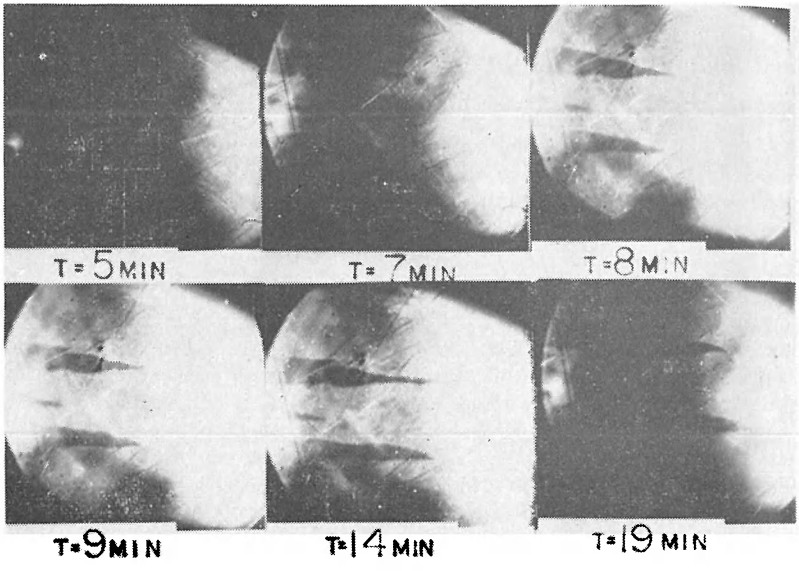


FIGURE 1. Photographic record of the progress of the point of a spike shaped domain on the surface of the film. H = 4.4 oersteds, T = 26° C. At t = 0, the film appeared to be a single domain.

**The Experiment**

Domain wall velocity was measured visually and photographically using the longitudinal Kerr effect, with apparatus described by Mitchell and Boknecht (6). The film was mounted with its surface perpendicular to the horizontal component of the earth's magnetic field. Paired Helmholtz coils were mounted perpendicular to each other with the film at the center. One bucked out the vertical component of the earth's magnetic field and the other furnished the controlled switching field parallel to the easy direction of the film. A hole in a disc, illuminated by a 100 watt incandescent projection lamp, served as a source. Light from the source was collimated by a lens,

passed through a Glan Thomson Prism which acted as a polarizer, and on to the film at an incident angle of about 25 degrees. A reticle of spider silk strung in a lucite frame at 1 mm intervals at the surface of the film provided a means of measuring displacement of the point of a spike shaped domain across the surface of the film in the easy direction of the film. Reflected light was passed through a lens system which could be changed to allow either visual or photographic observation, analyzed by a Nicol prism and on to the observer or the photographic film. The apparatus was housed in an oven with temperature control of the order of $\pm$ 0.1°C. A time interval of several hours elapsed after a temperature was reached before any measurements were made.

Measurements were made of the spike domain traversing the space from .2 cm to .6 cm from the edge of the film at switching fields ranging from H = 3.67 oersteds to H = 5.24 oersteds in a temperature range from T = 13.4°C to T = 56.2°C. Normal wall velocity is the product of the velocity of the point of a spike shaped domain and the sine of one-half the vertex angle of the spike. The mean value of the angle was 19.5°.

## RESULTS

The velocity curves peculiar to each temperature at which at least 16 readings were made are plotted in Figure 2. In general, point velocity may be expressed as $V = V_o (T) \exp 6.50 (H - H_o)$ where V is measured in cm-sec$^{-1}$ and H in oersteds. The exponential coefficient varies within plus 22% and minus 17% with temperature in the interval studied.

Reports available from an earlier investigation made on the same film are included in Plate II. The point velocity may be expressed as $V = V_o(T) \exp 8.8(H - H_o)$. It is noted that in addition to the change in the exponential coefficient, the velocities observed previously were larger than those presently experienced.

The velocity may also be expressed as a function of temperature with the driving field as a parameter. Where V is measured in cm-sec$^{-1}$, H in oersteds and T in degrees Centigrade $V = V_o (H) \exp .17(T - T_o)$.

## CONCLUSIONS

Movement of the point of a spike shaped domain across the surface of a thin ferromagnetic film by slow domain wall motion is not perfectly uniform in all areas of the film. However, it appears that the change in velocity is uniform with change in temperature and applied magnetic field. The irregularities in the velocity are apparently due to potential barriers at various points in the film. Such barriers would exist at inhomogeneities in the film, e.g. inclusions, pinholes and areas of internal stress.

The movement of a spike shaped domain is highly sensitive to changes both in temperature and switching field. In the sample

studied the velocity was found to be an exponential function of the switching field. It also appears that the velocity is an exponential function of the temperature in the interval of temperature and switching field of the experiment, and the exponent is independent of the switching field within the limits of accuracy of the experiment.

Differences between results presently obtained and those previously obtained might be explained as a low temperature, slow anneal.

No attempt has been made to relate the results to models of the thermal sensitive mechanisms within the wall though this should be done. It is, however, apparent that the theory cited earlier does not explain the phenomenon observed here.

Further experiments extending the temperature range and including other films might prove interesting.

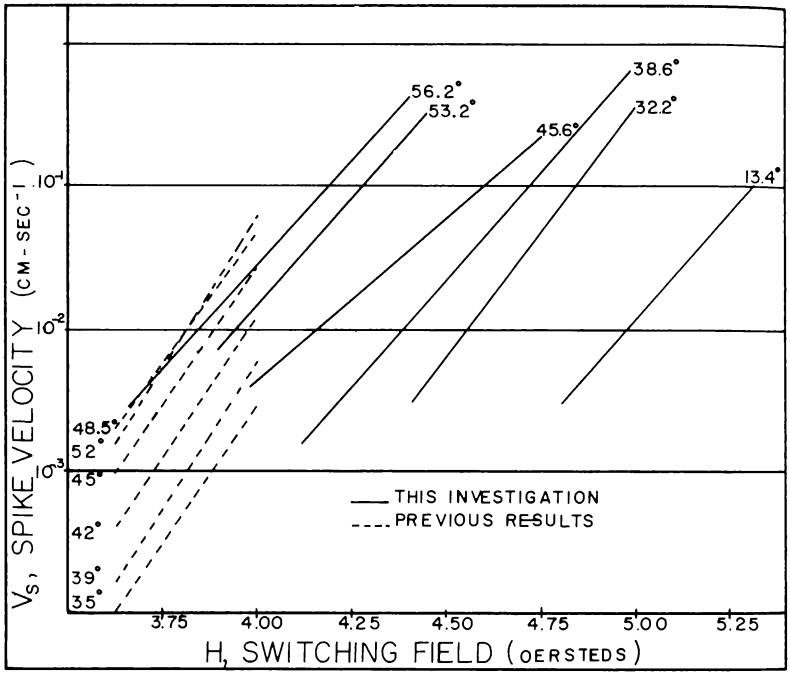


FIGURE 2. Velocity of the point of a spike shaped domain $V_s$ (cm-sec$^{-1}$) as a function of H (oersteds), the drive field. The temperature, T (°C), is the parameter. Normal wall velocity, $V_w = .1693\ V_s$.

The author wishes to thank Dr. E. N. Mitchell for his direction and encouragement and the Physics Department of the University of North Dakota for its cooperation and for providing facilities.

Gratitude is extended to the Physics Department of Remington Rand Univac, St. Paul, Minnesota, for the loan of the film and to the National Science Foundation under whose sponsorship thin film research is carried on at the University of North Dakota.

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# BRAIN SULFATIDE METABOLISM

*Eric A. Glende[1], Cecil H. Chally[2] and W. E. Cornatzer*

*Guy and Bertha Ireland Research Laboratory*

*Department of Biochemistry*

*University of North Dakota, Grand Forks, North Dakota*

## ABSTRACT

A time course of the incorporation of $SO_4$-$S^{35}$ into rat brain tissue following administration of intraperitoneal or intracranial injection of 45 $\mu$c of the isotope. Male albino rats of Sprague-Dawley strain (72-133 gms body weight) were injected with the $SO_4$-$S^{35}$ and sacrificed 1, 3, 4, 5, 6, 10, 30 and 120 hours later. The brain was removed, weighed and sulfalipids extracted. The radioactive uptake of the $SO_4$-$S^{35}$ into brain sulfatides was 20 times greater following an intracranial administration of the isotope than an intraperitoneal injection. Preliminary experiments in which brain tranquilizers, chloropromazine (2 mg/100 gm of body weight for 4 days), and reserpine (0.05 mg/100 gm of body weight for 7 days) were administered showed an increase in concentration of brain sulfatide S/gm of wet tissue. The role of these agents on uptake of $SO_4$-$S^{35}$ and metabolism of brain sulfatides is being investigated. (Supported in part by U. S. Atomic Energy Grant No. AT(11-1)-479).

[1]National Defense Fellow
[2]Honor Student.

# INFLUENCE OF AGE ON HEART, LIVER, SPLEEN AND KIDNEY PHOSPHORUS METABOLISM OF MICE

*Michael Poston and W. E. Cornatzer*

*Guy and Bertha Ireland Research Laboratory*

*Department of Biochemistry*

*University of North Dakota, Grand Forks, North Dakota*

**ABSTRACT**

Alteration of inorganic P, phospholipid P, nucleic acid P and phosphoprotein P metabolism and distribution in heart, liver, spleen and kidney with increasing age (9 to 227 days old) was studied in an inbred strain of female mice BALB/C without the mammary tumor agent. Two hours before sacrifice, 40 $\mu$c of $NaH_2P^{32}O_4$ was administered intraperitoneally. This time interval corresponds to the ascending part of the specific and relative specific activity time curve, where synthesis of phosphorus compounds occurs to a degree greater than breakdown. The tissues were removed, the acid-soluble P, phospholipid P, nucleic acid P and phosphoprotein P were fractionated, and radioactivity and P were determined on each fraction. There is a marked change in liver and kidney phospholipid and phosphoprotein relative specific activity at weaning time. Nucleoprotein relative specific activity in all tissues gradually increases with age. There is a similar increase in phospholipid relative specific activity of heart and spleen. This is a preliminary study of a problem concerning the effect of the mammary tumor agent on phosphorus metabolism of mice. (Supported in part by American Cancer Society Grant No. E-107C).

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# ACTION OF CHOLINE ON LIPID PHOSPHORYLATION IN THE KIDNEY, HEART AND AORTA

*George Sarosi[1], James R. Newland[2], Donald Hegge[3] and W. E. Cornatzer*

*Guy and Bertha Ireland Research Laboratory*

*Department of Biochemistry*

*University of North Dakota, Grand Forks, North Dakota*

**ABSTRACT**

Male albino rats of Sprague-Dawley strain (100-150 gms) were divided into two series. The animals in series I were maintained on 5% casein-32% fat diet for 5 weeks. In series II the rats were

[1]Post-Sophomore Research Fellow, N.I.H.

[2]National Science Foundation Undergraduate Research participant.

[3]Medical Student Summer Research Fellow, N.I.H.

maintained on a similar diet supplemented with 1% guanidoacetic acid for 2 weeks. At the end of the dietary regime the rats were stomach-tubed with a single dose of choline (100 mg in 1 ml of water), and the controls received water. One minute later, the animals were injected with 100 $\mu$c of $NaH_2P^{32}O_4$. Six hours later the animals were sacrificed and the heart, kidney and aorta removed. Acid-soluble P, and lipid P were fractionated and phosphorus and radioactivity were determined on each fraction. A control group of rats were injected with $P^{32}$ and sacrificed at 3, 6 and 10 hours to determine the time uptake of the isotope in the liver, heart, kidney and aorta. The acid-soluble P and lipid P were extracted, and the radioactivity and P determined. The six-hour interval after administration of $NaH_2P^{32}O_4$ corresponds to the ascending point of the specific activity time curve where synthesis of phospholipid in liver, kidney, heart and aorta occurs to a degree greater than their breakdown. The administration of a single dose of choline stimulated lipid phosphorylation in the kidney, heart and aorta. A statistically significant increase occurred in lipid phosphorylation when a choline deficiency was produced by administration in diet of a methyl acceptor, guanidoacetic acid. (Supported in part by U. S. Atomic Energy Research Grant No. AT (11-1)-479).

## REACTION OF TITANIUM TETRACHLORIDE WITH SOME ORGANIC ACIDS

*C. A. Kiefer[1], H. H. Weyland[2], and D. Schwartz*

*College of Chemical Technology*

*North Dakota State University, Fargo, North Dakota*

### ABSTRACT

During the last ten years a considerable amount of work has been carried out utilizing organo-titanium compounds as catalysts. These catalysts are used for polymerization reactions (3) and also for esterification of organic acids (1). A lesser amount of work has been done on incorporating titanium into polymers (2). The present paper discloses preliminary studies on attempts to prepare titanium containing organic polymers.

Reacting titanium IV chloride with organic reagents may lead to a variety of products since all or some of the chlorine atoms may be replaced. The disubstituted dichloro titanium appears to be the most desirable product if a condensing agent is sought which can produce a high molecular weight linear type polymer. The mono-

[1]National Science Foundation Undergraduate Research Participant.
[2]Present address, 35455 Yucaipa Blvd., Yucaipa, California.

substituated trichloro titanium would form cross-linked resinous material, while the trisubstituted monochloro titanium would not be capable of propagating a chain-like reaction.

Titanium tetrachloride has been reacted with some low molecular weight organic acids, such as acetic, propionic, and the like yielding products which appear to act as good condensing agents. Some of these compounds, namely diacetyl dichloro titanium, reacted with dihydroxy compounds such as Bisphenol A [2, 2-bis-(4-hydroxyphenyl) propane], yielded polymeric materials which appear to have valuable applications in the coatings field as shown in preliminary evaluation.

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# THE INFLUENCE OF CONCENTRATION ON THE INTESTINAL ABSORPTION OF D-GLUCOSE[1]

*F. A. Jacobs, D. Person, and R. C. Flaa*

*Guy and Bertha Ireland Research Laboratory*

*Department of Biochemistry*

*University of North Dakota School of Medicine,*

*Grand Forks, North Dakota*

## ABSTRACT

To extend the investigations on intestinal absorption, the concentration of D-glucose perfused through an isolated segment of the intestine of the rat was varied.

All animals used in these experiments were male Sprague-Dawley rats maintained on a stock diet and fasted 18 to 20 hours before perfusion. The concentrations of glucose perfused were 25, 50, 100, 200, and 400 mg.% carried in 0.85% NaCl. This brought the level perfused into a range in which active absorption against a concentration gradient was reached and surpassed. Glucose was measured by a modification of the micro-Somogyi-Nelson procedure.

[1]This work was supported in part by a research grant (A-2023) from the National Institutes of Health U.S.P.H. Service and by the National Science Foundation.

The results of these experiments demonstrate that D-glucose is actively transported against a concentration gradient in the living animal, in view of the definition of active transport (i.e. absorption against a concentration gradient). The resulting pattern for active transport differed significantly from the diffusion pattern exhibited by urea.

## THE INFLUENCE OF CONCENTRATION ON THE INTESTINAL ABSORPTION OF L-TYROSINE[1]

*F. A. Jacobs, T. J. Pacholl[2], D. Person, and R. C. Flaa*

*Guy and Bertha Ireland Research Laboratory*

*Department of Biochemistry*

*University of North Dakota School of Medicine*

*Grand Forks, North Dakota*

**ABSTRACT**

In a previous study on the intestinal absorption of glycine in the rat (Jacobs and Luper, Proc. N. Dak. Acad. of Sci., 10:43-44, 1956) there seemed to be little difference in the percentage absorbed over a concentration range of 20 to 80 mMolar glycine in saline, perfused through a loop of the upper small intestine, *in situ*.

In these investigations the range of amino acid concentration was lowered from a solute level of 2.0 mMolar to 0.02 mMolar L-Tyrosine-C-14 in 0.9% NaCl solution; this brought the level into a range in which active absorption against a concentration gradient was reached and surpassed. Measurements of absorption from the perfused intestinal segment were made by counting residual radioactivity in the perfusate by liquid scintillation.

These experiments demonstrated a more rapid transport against a concentration gradient (when expressed as percentage of that amount perfused), and the resulting data yielded an absorption pattern similar to that for glucose. This absorption pattern differed markedly from the typical diffusion pattern for urea.

[1]This work was supported in part by a research grant (A-2023) from the National Institutes of Health, U. S. Public Health Service.

[2]T. J. Pacholl, Research Participant, National Science Foundation, R.P.T.T. program (N.S.F.-G10995).

# THE INFLUENCE OF 2,4-DINITROPHENOL ON THE INTESTINAL ABSORPTION OF L-TYROSINE[1]

*F. A. Jacobs, R. C. Flaa, D. Person, and T. J. Pacholl*[2]

*Guy and Bertha Ireland Research Laboratory*
*Department of Biochemistry*
*University of North Dakota School of Medicine*
*Grand Forks, North Dakota*

**ABSTRACT**

In previous studies a mediated intestinal absorption process which has an apparent demand for pyridoxal-5-phostphate in the rat, *in situ,* (Jacobs, Flaa, and Belk, J. Biol. Chem., 235:3224-3227, 1960) was demonstrated. To extend these studies, the effects of varied concentration levels from 2.0 mMolar to 0.02 mMolar L-Tyrosine were investigated in respect to the influence that the metabolic antagonist, 2,4-dinitrophenol (DNP) would have on this process.

Systemic DNP was found to depress the amino acid absorption (this could be reversed metabolically by pyridoxal-5-phosphate). The experimental data showed two slopes in the absorption pattern for tyrosine over the varied range of perfusate concentration. The response to this antagonist over this concentration range leads us to postulate a possible second mediated absorptive process for the amino acid, tyrosine.

[1]This work was supported in part by a research grant (A-2023) from the National Institutes of Health, U.S.P.H. Service.
[2]T. J. Pacholl, Research Participant, National Science Foundation, RPTT program (NSF-G10995).

# FURTHER STUDIES ON THE INTESTINAL ABSORPTION OF METHIONINE[1]

*F. A. Jacobs, J. M. Poston, and W. Tarnasky*

*Guy and Bertha Ireland Research Laboratory*
*Department of Biochemistry*
*University of North Dakota, School of Medicine*
*Grand Forks, North Dakota*

**ABSTRACT**

Previous studies using perfusion of a 0.020 Molar L-methionine solution through an upper intestinal segment (Jacobs, Coen, and

[1]This work was supported in part by a research grant (A-2023) from the National Institutes of Health, U. S. Public Health Service.

Hillman, J. Biol. Chem. 235:1372-1375, 1960) have been extended to include the effects of pyridoxine, pyridoxal, pyridoxamine, pyridoxal phosphate, and pyridoxamine phosphate upon the absorption of methionine in rats fed an otherwise normal diet. There was an increase in the ability of the intact rat to absorb methionine under the influence of extra pyridoxine (either as the hydrochloride or as the phosphate) but not for the other $B_6$-vitamin factors.

Various concentration levels (down to 0.001 Molar) were perfused and the data obtained agree very closely to the pattern of absorption found with D-glucose and L-tyrosine (reported in this issue Proc. N. Dak. Acad. Sci.).

The pyridoxine antagonist, isonicotinyl hydrazide (isoniazid) failed to influence the absorptive process.

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# THE USE OF CHEMICAL MICROSCOPY IN THE CORRELATION OF CRYSTAL STRUCTURE AND THIXOTROPIC BEHAVIOR OF ALIPHATIC URETHANES

*Raphael C. Hendrickson*[1] *and Sol Shulman*
*College of Chemical Technology*
*North Dakota State University, Fargo, North Dakota*

## ABSTRACT

Chemicals which impart thixotropic character are important in the manufacture of greases, paints, polyester resins, adhesives and other classes of products.

Certain aliphatic esters of N-substituted carbamic acid exhibit thixotropic behavior in ethanol, hexane, soybean oil, solvent thinned resins and other similar materials at concentrations as low as 0.5%[2]. Better defined crystal structure and poorer thixotropic properties were observed with an increase in symmetry of the molecule.

The use of photomicroscopy as an aid in the characterization of organic compounds has been investigated by Dunbar *et al*[3].

This interesting technique has been used to correlate thixotropic behavior with the crystal structure of a series of hexadecyl N-*n*-alkylcarbamate and *n*-alkyl eters of N-*n*-hexadecylcarbamic acid. The *n*-alkyl group of the urethanes contained from 8 to 32 carbon atoms in even numbers.

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[1]Dow Chemical Co. Undergraduate Scholarship Winner, 1960-1961.
[2]S. Shulman, M. W. Formo and A. E. Rheineck. J. Amer. Oil Chemists' Soc. 38:205 (1961).
[3]R. E. Dunbar, Proceedings of the North Dakota Academy of Science 14, 53 (1960).

All urethanes showing thixotropic properties used in this study had a fine needle—or cluster of needles type structure. The more pronounced the cluster of needles structure, the better thixotropic properties were observed. Compounds showing no such behavior had rod-like structures.

No correlation could be found between the extinction angle and thixotropic behavior of the compounds used in this study.

## EFFECTS OF GLUCAGON ON BLOOD ALCOHOL LEVELS AND BLOOD SUGAR CONCENTRATION IN THE DOG[1]

*B. DeBoer, R. Brown, and Donna Schut*

*University of North Dakota, Grand Forks, North Dakota*

### ABSTRACT

Mongrel dogs of 15 to 20 kg were fasted approximately 16 hours. After control samples of blood were taken for alcohol content and blood sugars, the animals were infused intravenously with 10 ml/kg of a 20% ethyl alcohol. After allowing approximately 1½ hours for the alcohol to distribute to the tissues, blood samples were taken at hourly intervals for the next seven hours. The alcohol content of these samples and the blood sugar content were determined. In experimental animals glucagon was given in various doses after the third hourly sample and again after the fourth, fifth, and sixth samples were obtained. It was shown that glucagon increased the rate of alcohol disappearance from the blood stream as compared to the preglucagon controlled rate. Blood sugar samples after glucagon were markedly increased especially after the initial dose of glucagon.

[1]Research supported in part by A. M. A. Grant No. 564.

## ALCOHOL DISAPPEARANCE DURING INDUCED DIURESIS IN THE DOG

*Delbert R. Nelson*

*Department of Physiology and Pharmacology*

*University of North Dakota, Grand Forks, North Dakota*

### INTRODUCTION

Alcohol taken into the body is eliminated by three major routes, namely metabolism, expired air and urinary excretion. The metabolism accounts for by far the largest portion, well over 90% and perhaps as much as 98% under most experimental conditions (6). Expired air and urine account for the remainder which is relatively

insignificant. The alcohol dehydrogenase system in the liver oxidizes the alcohol to acetaldehyde which is subsequently oxidized in much the same manner as are carbohydrates to carbon dioxide and water (6). This oxidation in the liver accounts for all or nearly all of the alcohol metabolized.

The rate at which alcohol is metabolized as indicated by the rate at which it disappears from the blood is relatively constant except at very low blood alcohol concentrations according to Marshall and Fritz (7). They also pointed out the fact that the alcohol lost in expired air and urine is relatively insiginificant and has little effect on the total alcohol loss from the animal except at very high blood alcohol concentrations.

Many experiments have been designed to increase the rate at which the alcohol disappears from the blood. Most have been attempts to increase the rate at which the alcohol is metabolized in the liver since this accounts for the greatest part of the alcohol lost. Alanine, pyruvate, monosaccharides and thiamine have all been reported to increase alcohol metabolism (6). Insulin has been shown by some to increase alcohol metabolism while others report no effect. The drug dinitrophenol elevates the body temperature and has been shown to increase alcohol metabolism (4). The results of such experimentation, however, have been quite variable and often show only a slight effect.

Eggleton (1) found that there is a free diffusion of alcohol between tubal fluid, renal cells and tissue fluid in the kidney, and that urine alcohol concentration equals that in blood. Harger *et al.* (3) reported that alcohol given orally or intravenously penetrates rapidly into all tissues and fluids of the body, and reaches equilibrium readily.

The literature indicates that alcohol is freely and rapidly diffusible into all body fluids including urine. It was postulated that an increase in the amount of alcohol lost in the urine would increase the rate at which the alcohol disappears from the blood. The increased urinary alcohol loss could be obtained by experimentally increasing the urine flow with diuretic agents or water.

## METHODS AND MATERIALS

Female mongrel dogs ranging in weight from 10 to 21 kg were used. Food and water were withheld for 16 hours. Then 2 gm of alcohol (10 ml of 20% w/v alcohol in physiological saline) were given intravenously. After the alcohol was allowed to equilibrate into the body fluids, hourly blood and urine samples were taken to determine the rate at which the alcohol was disappearing from the blood, the volume of urine produced, and the amount of alcohol lost in the urine for each hour. Alcohol determinations were made using the method of Harger (2) in which the alcohol is oxidized by potassium dichromate and the excess dichromate is reduced to a methyl orange end point with a standard ferrous sulfate solution.

Control values were obtained with the animal in a relatively dehydrated state, hence the urine volumes were very low and constant. The urine flow was experimentally increased in each of the animals used by the administration of 30 ml per kg of water orally, 2 mg of mercury per kg as mercuhydrin sodium intramuscularly, 20 mg of chlorothiazide per kg intravenously, or combinations of these agents. The blood alcohol disappearance rate and the urinary alcohol loss were then compared at various diuretic levels to determine if increased urinary elimination has any effect on blood alcohol disappearance.

## RESULTS

It was found that the amount of alcohol lost in the urine accounts for a relatively constant but small part of the total alcohol lost per hour. At control diuretic levels the urinary loss averages 1.5% of the total alcohol loss. At higher diuretic levels urinary loss accounts for much larger portions of the total loss, averaging about 20% when the urine flow is greater than ten times the control levels.

It was found, however, that the increase in urinary alcohol loss did not consistently bring about an increase in the total alcohol loss as measured by the blood alcohol disappearance rate. Table 1 summarizes the comparison of the actual blood alcohol disappearance rate with that predicted on the basis of the control rate plus the increase that would be brought about by the increased urinary loss. The comparisons are made for each animal at each of four diuretic levels. It can be seen that only one animal—number 3—shows an increase in blood alcohol disappearance similar to the predicted increase based on increased urinary output. The other animals show no relationship between blood alcohol disappearance and the amount of alcohol lost in the urine.

## DISCUSSION

The rate at which alcohol disappears from the blood has been used by most investigators in the field of alcohol metabolism and elimination as an index of alcohol metabolism. The literature clearly shows that the rate of blood alcohol disappearance is relatively constant although Marshall and Fritz (7) report considerable variation from hour to hour in an individual animal. There is also some variation between individuals in a given species. A procedure that could markedly increase blood alcohol disappearance would be of practical value in the treatment of acute alcohol toxicity, but would have to bring about a rather marked effect to be of value.

Previous work indicates that alcohol metabolism is quite constant. It could be assumed that increasing one of the other routes of alcohol elimination such as urinary loss would increase the blood alcohol disappearance rate. Assuming that metabolism is constant, one could predict the increase in blood alcohol disappearance that

would be brought about by such an increased urinary loss. The blood alcohol loss at control diuretic levels is accounted for chiefly by metabolism as evidenced by the rather insignificant 1.5% of total loss accounted for by urinary loss. The amount of alcohol eliminated in the urine per unit of time at high diuretic levels can be determined and the rate of blood alcohol loss due to urinary elimination alone can be calculated. This value, that is the rate of blood alcohol disappearance accounted for by urinary loss added to the control value, is the predicted blood alcohol disappearance rate at the higher diuretic level.

The results of this study show that only one dog out of five shows an increase in blood alcohol disappearance rate that is similar to that predicted on the basis of increased loss of alcohol in the urine. This suggests that alcohol metabolism decreases when urinary alcohol loss is increased in the other dogs. The fact that the one dog shows an increase in blood alcohol disappearance with increased urinary alcohol elimination, however, suggests that the compensatory decrease in metabolic rate does not occur in all animals.

A decrease in the metabolic rate can be considered the factor responsible for the failure of the alcohol disappearance rate to increase when urinary loss is increased. The only other route of alcohol elimination—expired air—accounts for only an insignificant part of total alcohol loss (7) and would probably not be altered in this type of experiment as alcohol has little effect on respiration rate in the dog (5).

**TABLE 1**

**Comparison of Blood Alcohol Disappearance Rate and Rate Predicted on Basis of Increased Urinary Loss**

| Diuresis level | < 2 X control | 2-5 X control | 5-10 X control | > 10 X control |
|---|---|---|---|---|
| Dog #1 | | | | |
| actual rate | 22.2* | 21.1 | 21.7 | 16.0 |
| predicted rate | | 22.5 | 23.8 | 25.6 |
| Dog #2 | | | | |
| actual rate | 17.6 | 22.8 | 13.3 | 24.0 |
| predicted rate | | 18.2 | 19.1 | 23.6 |
| Dog #3 | | | | |
| actual rate | 20.3 | 21.5 | 22.0 | 23.4 |
| predicted rate | | 21.0 | 22.0 | 24.6 |
| Dog #4 | | | | |
| actual rate | 17.6 | 23.0 | 17.0 | 23.4 |
| predicted rate | | 18.2 | 19.1 | 21.2 |
| Dog #5 | | | | |
| actual rate | 20.6 | 21.8 | 20.2 | 20.3 |
| predicted | | 20.2 | 22.9 | 23.4 |

*Blood alcohol disappearance rate is given in mg%/hr.

**SUMMARY**

1. Urinary alcohol elimination accounts for a small but relatively constant part of total alcohol loss at low diuretic levels.
2. Diuresis induced by hydration, chlorothiazide, mercuhydrin, or combinations of these agents markedly increases the rate of urinary loss of alcohol.
3. Increased urinary alcohol loss is not consistently accompanied by an increase in the rate of blood alcohol disappearance although this effect is suggested in some animals.
4. Since increased alcohol loss via urine does not cause an increase in blood alcohol disappearance, it would appear that the rate of alcohol metabolism may decrease when the urinary loss is increased.

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# DEVELOPMENTAL ANATOMY OF THE AIRSAC OF THE HOUSE SPARROW, *Passer domesticus* (*Linnaeus*)

*John M. Delphia*[1]

*Department of Zoology*

*North Dakota State University, Fargo, North Dakota*

The pupose of this study is to establish the origin and development of the airsacs in the house sparrow and the development of the airsacs of this species with other birds described in the literature.

[1]Now at Ohio State University, Columbus, Ohio.

Embryos of the house sparrow were studied by means of serial sections. The respiratory systems of hatching sparrows were injected with liquid latex: these specimens were studied either by gross dissection or by study of the rubber casts obtained by digestion of the tissues.

The origins, locations, lobations and further subdivisions, connections to the lungs, communications between airsacs or airsacs and subdivisions are described.

Cervical airsacs compare by origin, location and subdivisions with those of other birds described in the literature.

Interclavicular airsacs are composed of mesial and lateral moieties as in numerous other birds. The mesial and lateral moieties by origin are homologous with the respective moieties in the chicken.

Numerous subdivisions of the mesial moieties indicate that some of the lobations or ramifications common to the lateral moieties of certain birds are performed by the mesial moieties. Numerous communications between the mesial moieties and the intermediate airsacs explain the conception of a common single anterior thoracic airsac encompassing all the area occupied by the mesial and lateral moieties and the intermediate airsacs.

Separation of the mesial and lateral moieties by the thoracic lobes of the intermediate airsacs and the lack of subdivisions or lobes of the lateral moieties is coincident with the development of the posterior scapular lobes which occupy the area held by lobes or diverticula of the lateral moieties in certain other birds. The dorsal canals of the posterior scapular lobes are comparable to the connections between the subscapular lobes and diverticula of the cervical airsacs in other birds.

Anterior abdominal airsacs, their primary and secondary ostia, the auxiliary connections and the location of these airsacs are homologous with those of the white pekin duck.

Origins and locations of the posterior abdominal airsacs are typical for all birds possessing these posterior projections from the lungs. Migration of the mouths of certain secondary bronchi from the lungs to the airsacs is as described for the white pekin duck. The lobes of these airsacs are comparable to those of the pigeon.

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# THE EFFECT OF MORPHINE ON THE METABOLISM AND GROWTH OF TETRAHYMENA PYRIFORMIS

*Gail L. Schuster, William B. Henry and John W. Vennes*

*Department of Bacteriology*
*University of North Dakota, Grand Forks, North Dakota*

## ABSTRACT

*Tetrahymena pyriformis,* a ciliated protozoan, was grown in a simple basal medium of peptone and sodium chloride. In the experi-

ments designed to determine the effect of morphine sulfate on growth, the optical density of the growing cultures was taken daily. Flasks were prepared with the basal medium as controls and the experimental flasks contained basal medium and morphine sulfate 0.0001M. The morphine-containing flasks showed about 27 per cent increase in optical density over the control flasks.

In the experiments designed to determine the effect of morphine sulfate on cellular metabolism, cells grown in the basal medium were harvested after two to eight days of growth. Manometric determinations were made with a standard Warburg apparatus with the following reactants: cells in buffer, cells in buffer plus morphine, and cells in buffer plus glucose and morphine or no morphine. Certain experiments incorporated the use of iodoacetic acid, an agent which blocks the triose split in the Embden-Meyerhof breakdown of glucose. Results from these experiments suggest that morphine sulfate releases glucose from glycogen in resting cell metabolism.

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## FLUORIDE CONTENT OF MUNICIPAL WATER SUPPLIES IN NORTH DAKOTA

*David D. Swenson, Jerome E. Kwako, and John K. Peterson*

*University of North Dakota Medical School and Division of Dental Health, North Dakota State Department of Health*

*Grand Forks and Bismarck, North Dakota*

### ABSTRACT

Many municipal waters in North Dakota have had no fluoride determinations and others have had determinations only prior to 1950.

Although there are no known communities in North Dakota which have a fluoride content in their water supply high enough to cause detrimental effects to the health of its populace, certain areas have sufficient fluorides to cause mottling of the teeth.

In this project 193 water samples from 100 North Dakota municipalities were assayed for their fluoride, iron, manganese and sulfate content. An attempt was made to correlate regions of fluoride excess with mottling of teeth and to assess the relationship of fluoride content and depth of wells.

The method used in fluoride determinations is usually the Scott-Sanchis. A more recent method, the Eriochrome cyanine R, has not been previously used in this State; therefore, both methods were used in this study in an attempt to determine the more accurate and suitable assay.

# THE MODE OF ESTERASE ACTION

*J. A. Stewart*
*Department of Chemistry*
*University of North Dakota, Grand Forks, North Dakota*

**ABSTRACT**

No scheme has been reported that satisfactorily explains the behavior of the esterase enzymes. The purpose of this report is to discuss a new mechanism that is based on an internal ester linkage within the enzyme. This internal linkage is believed to catalyze the hydrolysis of an ester by simple interchange. Although direct proof of mechanism has not been obtained, the scheme does explain the experimental findings so far reported.

One of the major pieces of experimental evidence readily accounted for is nature's common sequence at the active site. Degradation studies have revealed that the active site of many esterases is comprised of a serine residue neighbored by a dibasic acid, glutamic or aspartic. The role of this common sequence is brought to light by the proposed mechanism, and furthermore the specificity requirements of enzymes such as trypsin, chyomtrypsin, and certain cholinesterases can be accounted for.

Finally, in order to encompass all the factors exposed by experiment, it is necessary to include a nucleophilic group as part of the site. This nucleophilic group functions in partnership with the internal ester linkage and aids in the release of products; its failure to do so results in inhibition.

# FAILURE OF BOVINE HEMOGLOBIN TO "BIND" WATER IN ELECTROLYTE SOLUTIONS[1]

*Edwin G. Olmstead and Richard Stone*[2]
*University of North Dakota, School of Medicine,*
*University of North Dakota, Grand Forks, North Dakota*

It has been necessary to introduce the concept of intracellular "bound" water to bring total osmolar concentrations of the human erythrocyte into agreement with the osmolar concentrations of the plasma—a necessary condition because the red cell is isotonic with the plasma.

A method was developed to study the "bound" water (i.e. water not available to exert solvent action) in solutions of crystalline bovine hemoglobin. It can be shown that

[1]This study was supported by a grant from the United Fund of Grand Forks.
[2]National Institutes of Health Summer Fellow.

$$W = \frac{C_2 - C_1}{R_2 - R_1} (100)$$

where,

W = water available to dissolve Na and K salts

$C_1$ = $\Delta^t$ (molal freezing point depression) of 2 ml of distilled water added to a dried residue of 2 ml of a standard Na and K solution.

$C_2$ = $\Delta^t$ of 2 ml of distilled water added to dried residue of 4 ml of same standard Na and K solution.

$R_1$ = $\Delta^t$ of Na and K solution of bovine hemoglobin.

$R_2$ = $\Delta^t$ of 2 ml and Na and K solution of bovine hemoglobin added to dried residue of 2 ml of Na and K solution.

Water in hemoglobin solutions measured by the above method and measured gravimetrically by dessication in the same solutions showed no significant differences. It was concluded that crystalline bovine hemoglobin does not "bind" water in electrolyte solutions.

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# STUDIES ON THE MECHANISM OF REACTIVE HYPEREMIA

*R. J. Bache and H. E. Ederstrom*

*Department of Physiology and Pharmacology*
*School of Medicine, University of North Dakota, Grand Forks, North Dakota*

## ABSTRACT

Temporary interruption of the arterial blood supply to the limb of an animal is followed by a transient augmentation of the inflow of blood to the ischemic tissue. Reactive hyperemia was measured following clamping of the femoral artery for ten minutes using bubble flow meters in the femoral veins of anethetized normal dogs, and dogs with chronic unilateral lumbar sympathectomy. To study effects of temperature on reactive hyperemia, animals were cooled to 30° C. rectally and blood flows were recorded at intervals as the animals were warmed with radiant heat or 2,4-Dinitrophenol (DNP). In normal dogs repayment of the blood-flow debt acquired during occlusion was least at 32-34°C. and rose linearly as the temperature was increased. Chronic sympathectomy did not greatly increase the absolute rate of flow during reactive hyperemia, but since basal flows were lower in these limbs, the percent debt repayment was greater than normal. The administration of DNP at 30°C. caused a significant increases in the basal blood flow rate, in the repayment and duration of the reactive hyperemia, and the oxygen consumption of the animals.

# THE PREPARATION AND PROPERTIES OF ZIRCONIUM SEBACATE AND ANALOGOUS ZIRCONIUM DICARBOXYLATES

*Gustav P. Dinga and John E. Maurer*[1]

*Department of Chemistry*
*Concordia College, Moorhead, Minnesota*

The reactions between zirconyl chloride octahydrate and the dicarboxylic acids from $C_3$ through $C_{10}$ have been studied in various solvents. The white hydrous products obtained in all reactions were dried and analyzed for percentages of zirconium, carbon, and hydrogen. The compounds were further analyzed by x-ray diffraction, infrared spectrophotometry, and emission spectroscopy. Further studies regarding solubilities, melting points, and molecular weights indicate that the zirconium carboxylates are new compounds and the evidence generally supports the theoretical estimates that these compounds may be polymeric. Homogeneous percipitations involving the diethyl esters of the acids and zirconyl chloride octahydrate are presently being completed.

## INTRODUCTION

A review of the literature on the reactions of dicarboxylic acids from $C_3$ through $C_{10}$ with zirconyl chloride octahydrate (ZCO) indicates that no systematic study of these reactions and the resultant products have been carried out (1). The initial studies regarding this work have been previously summarized (2).

The reaction of sebacic acid with (ZCO) formed a white product, due to the success of this initial experiment, the work was extended to the other dicarboxylic acids from $C_3$ through $C_9$. The only aliphatic dicarboxylate of zirconium that has been extensively studied is zirconium oxalate (3, 4, 5, 6), consequently, further work on this compound was not included in this study. Carbonated hydrous zirconia is reported to react with succinic acid to form a solid product that is insoluble in water and ethanol and very soluble in acetone (1). The present study generally supports the contention of Dr. John C. Bailar that the compounds should be polymeric (7).

## EXPERIMENTAL

The (ZCO) and succinic acid were Fisher Scientific Company purified products. The sebacic acid azelaic acid, pimelic acid, adipic acid, and glutaric acid were Eastman Organic Chemicals products. The malonic acid and suberic acid (recrystallized prior to use) were Matheson Company, Inc. products. The diethyl ester of sebacic acid was an Eastman Organic Chemicals product. Zirconium sebacate (ZIO) — (ZCO), 8.00g., 0.0248 moles, was dissolved in 60 ml. of 1M HCl and while stirred, sebacic acid, 5.00 g, 0.0247 moles, dissolved

[1]Professor of Chemistry, University of Wyoming, Laramie, Wyo.

in 50 ml. of 10% $Na_2C0_3$ solution, was slowly added to the (ZCO) solution. A white ppt. formed in the solution which had a pH of 1.5 after adding 40 ml. of distilled water, used to wash the beaker that had contained the sebacic acid solution. After 2 hours the solid was collected by filtration through a Buchner funnel, washed with 100 ml. of distilled water and air dried. The product was dried in a vacuum desiccator over $CaCl_2$ at reduced pressure, followed by drying in a vacuum desiccator over $P_20_5$ at 2-3 mm. pressure and 55°C. (labelled vac. dried Z10). A small portion of the initial hydrous product was also dried separately in an oven at 100-110 C°. (labelled oven dried X10). A similar procedure was used to prepare zirconium azelate (Z9), zirconium suberate (Z8), zirconium pimelate (Z7), zirconium adipate (Z6), zirconium glutarate (Z5), zirconium succinate (Z4), and zirconium malonate (Z3). Analysis.—Samples of the dried products were carefully charred in a porcelain crucible prior to ignition at 900-1000 C. for 3-4 hours. The ignition product, zirconium (IV) oxide, was a white solid with a green tint. Carbon and hydrogen analysis was performed by the usual semimicro combustion techniques.

All the zirconium dicarboxylates gave an x-ray diffraction pattern that had the "halo effect". The x-ray was a copper K alpha transmitted through a nickel filter with a wavelength of 1.5405 Angstroms. The results were recorded by a recorder attached to a Geiger tube detector. The zirconium dicarboxylates were further examined for hafnium content. The (ZCO) contained less than 0.5% hafnium according to x-ray fluorescence and the zirconium dicarboxylates contained about 0.2% hafnium when anlyzed with a 1.5 meter emission spectrograph, Bausch and Lomb. The emission spectrograph was used with a 220 volt, d. c., 6 amp arc light source.

The (Z10) was further examined, in the infrared range, with a Beckman spectrophotometer, model IR-4, using KBr as the solvent and reference. The characteristic infrared absorption spectrum of (Z10) is different from that of the two reactants, sebacic acid and (ZCO) in the infrared regions studied, 1-16 micron and 10-25 micron regions. A mixture containing 95% (Z10) and 5% sebacic acid gives a pattern similar to the pure (Z10) but the absorption peaks are shifted and the intensities are generally decreased.

The solubilities of the zirconium dicarboxylates were determined by placing 0.002 gram samples in 5 ml. of 32 different solvents and treated as follows: (a) occasionally stirring the material for 3 days at rm. temperature; and (b) heating the material in another test tube for 2 hours at or near the b. p. of the solvent. In each case, after the above treatment, a portion of the solvent was removed and evaporated to determine if any zirconium dicarboxylate had dissolved.

The melting points of all the zirconium dicarboxylates were determined by utilizing an aluminum melting point block and a

calibrated thermometer. In all cases, except one (Z7), the compounds would contract (also termed softening temp.) prior to decomposition at 200-300° C.

The molecular wt. of (Z10) was determined by utilizing the Cottrel apparatus, Beckmann thermometer and glacial acetic acid as the solvent. The molecular weight decreased with time indicating that the compound was probably being decomposed by the solvent. This method of determining molecular wt. will be carried out with the other zirconium dicarboxylates.

## RESULTS AND DISCUSSION

### TABLE 1

**Composition and Properties of the Zirconium Dicarboxylates**

| | | | | x-ray diffraction halo peaks Zr-Zr distance, A ↓ | | | |
|---|---|---|---|---|---|---|---|
| | | | | | | M.P. °C | |
| Product | %Zr | %H | %C | calc'd. | obs. | contracts | dec. pt. |
| Z3 over dried | 37.71 | 1.246 | 10.19 | | | | |
| vac dried | 32.38 | 1.650 | 10.42 | 9.4 | 8.7 | 222.0 | 283.5 |
| Z4 oven dried | 37.88 | 1.797 | 14.93 | | | | |
| vac dried | 38.01 | 2.126 | 13.96 | 10.6 | 9.7 | 200.2 | 301.5 |
| vac dried* | 37.80 | | | | | | |
| Z5 oven dried | 39.09 | 2.390 | 17.36 | | | | |
| vac dried | 37.85 | 4.643 | 17.05 | 11.9 | 10.0 | 204.5 | 283.5 |
| Z6 oven dried | 38.76 | 2.766 | 21.23 | | | | |
| vac dried | 39.01 | 3.107 | 19.72 | 13.2 | 10.7 | 191.0 | 286.5 |
| vac dried* | 38.22 | | | | | | |
| Z7 oven dried | 36.24 | 2.678 | 20.78 | | | | |
| vac dried | 34.24 | 1.742 | 15.81 | 14.4 | 11.4 | not contract | 270.3 |
| vac dried* | 35.38 | | | | | | |
| Z8 oven dried | 27.41 | 5.084 | 36.54 | | | | |
| vac dried | 27.69 | 5.365 | 35.59 | 15.6 | 12.3 | 154.6 | 187.1 |
| vac dried* | 33.80 | | | | | | |
| Z9 oven dried | 32.72 | 4.651 | 34.30 | | | | |
| vac dried | 32.07 | 4.767 | 32.62 | 16.9 | 13.4 | 239.6 | 256.6 |
| vac dried* | 31.59 | | | | | | |
| vac dried* | 30.81 | | | | | | |
| vac dried# | 30.84 | | | | | | |
| Z10 oven dried | 29.73 | 5.304 | 37.42 | | | | |
| vac dried | 29.91 | 5.365 | 36.19 | 18.2 | 14.8 | 197.6 | 274.1 |
| vac dried* | 27.03 | | | | | | |
| vac dried## | 27.56 | | | | | | |
| vac dried** | 27.73 | | | 18.2 | 15.5 | | |
| vac dried*** | 28.83 | | | 18.2 | 14.5 | | |

* another preparation using the same or nearly the same method.
\# ethyl alcohol solvent used for azelaic acid, no sodium carbonate used.
\## homogeneous pptn. using diethyl sebacate plus (ZCO) dissolved in 1M HCl.
** $ZrCl_4$ plus (ZCO) both dissolved in diethyl ether, mixed, and washing the precipitate collected by filtration with distilled water.
*** $ZrCl_4$ dissolved in distilled water and 1M HCl and adding sebacic acid dissolved in 10% sodium carbonate solution.

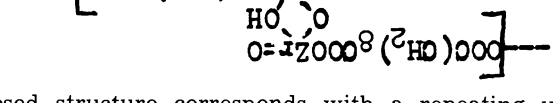
All of the zirconium dicarboxylates were insoluble in acetone, 15M $NH_4OH$, isoamyl alc., benzene, $CS_2$, $CCl_4$ $CHCl_3$, cyclohexane, diethyl ether, dimethyl formamide, dioxane, ethyl acetate, 95% ethanol, symethylene dichloride, ethylene glycol, 40% HCHO, methanol, nitrobenzene, petroleum ether, pyridine, 5M NaOH, and water.

**Table II**

| | Z3 | | Z4 | | Z5 | | Z6 | | Z7 | | Z8 | | Z9 | | Z10 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| solvent | a | b | a | b | a | b | a | b | a | b | a | b | a | b | a | b |
| glacial HAc | i | i | i | ss | i | i | i | s | i | ss | i | s | ss | s | i | s |
| 6M HCl | i | ss | i | s | i | s | i | s | i* | ss | i | s | i | s | ' | ss |
| 12M HCl | i | s | i | s | ss | s | ss | s | ss | s | ss | s | ss | s | ss | s |
| 6M $HNO_3$ | i | s | i | s | i | s | ss | s | s | s | ss | ss | ss | ss | i | ss |
| 16M $HNO_3$ | ss | d | i* | d | ss | d | s | d | s | | ss | d | s | d | : | s |
| 70% $HClO_4$ | i | i | i | d | i | i | i | i | i | i | i | i | i | s | i | d |
| 85% $H_3PO_4$ | i | s | i | s | i | s | i | s | i | s | i | s | i | s | i | . |
| 3M $H_2SO_4$ | s | s | s | s | s | s | s | s | s | s | i | ss | i | s | i | i |
| 18M $H_2SO_4$ | s | s | s | s | s | s | s | s | s | s | s | s | s | s | s | s |

a—occasionally stirring the material for three days at room temperature.
b—heating for two hours at or near the boiling point of the solvent.
*—solid swells in the solvent.
i—insoluble, s—soluble, ss—slight soluble, d—decomposes.

The percentages of zirconium, carbon, and hydrogen in the zirconium sebacate correpsonds to the following proposed structure:



The proposed structure corresponds with a repeating unit having the empirical formula, $Zr_2C_{20}H_{33}O_{11}$, and provides a C.N. of 6 for each zirconium atom.

| %Zr | | %C | | %H | | %O | |
|---|---|---|---|---|---|---|---|
| Calc'd. | obs. | Calc'd. | obs. | Calc'd. | obs. | Calc'd. | obs. |
| 28.82 | 28.83 | 38.20 | 37.42 | 5.252 | 5.304 | 27.80 | 28.45 |

The above percentage values correlate very well when the hydrous nature of the product, which lost 79.13% of its weight as water during drying, is considered. The proposed "ol" and "oxo" bridge between the two zirconium atoms is an established unit in zirconium oxide hydrosols.[9,9] The formation of such bridging groups in hydrated zirconyl chloride is catalyzed by the presence of carbonate ion[10] which was present during the synthesis of the (Z10).

The x-ray diffraction patterns all contain the halo effect which is indicative of polymer formation, but all that this actually proves is that the compounds are not crystalline. The halo effect is produced by a polymer but it must be admitted that occasionally one finds a non-polymeric substance which gives the same effect. It is observed from the data in Table I that the observed distances between zirconium atoms were smaller than the calculated distances. Just how this comes about is explained by Clark.[11] In the crystals, if the zirconium atoms are parallel to the crystal axis, the experimental values should equal the calculated values. However, if the rows of zirconium atoms lie at an angle to the crystal axes, as is frequently the case, then the distances found will be shorter than those calculated. In this work x-ray diffraction patterns were obtained for all reactants, (ZCO) and the dicarboxylic acids, and none of the characteristic peaks of the reactants were observed in the products. This would indicate that the products or zirconium dicarboxylates probably contain less than 1% impurity.

The melting points as tabulated in table I are indicative of polymeric materials. The softening temperature or as indicated on the table, the temperature at which contraction occurs, indicates that the network is collapsing. The swelling that occurs with (Z4) and (Z7), in nitric acid and hydrochloric acid, also supports the presence of a polymer network in the compound. The fact that the melting points exceed the decompostion point is also used as evidence that the compound will be insoluble in most solvents, this supports the solubility data of the compounds as shown by table II and the paragraph proceeding the table. The melting point and solubility data generally support the presence of the proposed polymeric network structure in the zirconium dicarboxylates.

The results obtained while determining the molecular weight of (Z10) by boiling point elevation with acetic acid are tabulated as follows:

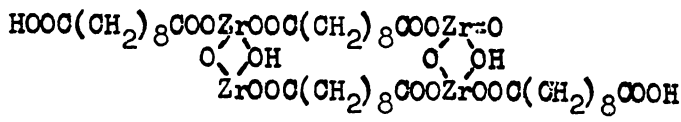
**TABLE III**

Molecular weight by boiling point elevation

| | | |
|---|---|---|
| 0.910 | 10 | 1326 |
| 0.922 | 15 | 1038 |
| 0.929 | 20 | 920 |
| 0.930 (const. after 25 minutes) | 25 | 906 |

The molecular weight decreasing with increasing time indicates that the (Z10) is decomposing in the acetic acid solution. This is confirmed by the fact that the (Z10) recovered from the cold acetic acid after the experiment contained 38.63% zirconium instead of the 29.91% zirconium as inthe original (Z10).

An empirical formula for a repeating unit in (Z10) as given previously, $Zr_2C_{20}H_{32}O_{11}$, has a wt. of 631.9 g/unit. The molecular weight of (Z10) as shown in table III is 1326 g/m, consequently, assuming the boiling point elevation is correct, one mole of compound should contain two repeating units and weigh 1236.8 g/m. The molecular weight when determined by boiling point elevation has an experimental error of ± 5%, the values as determined for the molecular weight above fall within the experimental error. A structure that is proposed for this dimeric product is the ring or spiral shown below.



Space does not permit a discussion of the structures proposed for (Z9), (Z8), (Z7), (Z6), (Z5), (Z4), (Z3). Some of the structures are difficult to predict because the end group in any given case may be either a carboxyl group or a zirconium atom. It is also possible that the C. N. of 8 is attained by coordinating water or hydroxo groups which will give rise to high percentages of H and O and resultant low values for C and Zr. Some of the zirconium atoms are bound together by the long chain dicarboxylates anions; others are bound together by short chain dicarboxylic anions and hydroxo groups. The dibasic anions and the OH anions do not necessarily occur at regular spaced intervals in the polymer, consequently, relative numbers of these kinds of groups will vary from one preparation to another. This type of non-uniformity of polymeric structures is simply inherent in the nature of these materials, consequently, carbon and hydrogen analysis will not necessarily give a simple calculated formula.

The data thus far indicates that the zirconium dicarboxylates may have a network of polymeric structure. This study is being continued in order to develop some consistent result for the structures of the zirconium dicarboxylates from $C_3$ through $C_9$. The (Zr10), as indicated, in this paper is a large molecule which corresponds to a proposed structure, $Zr_2C_{20}H_{32}O_{11}$, as a repeating polymeric unit. The molecular weight determination supports a dimeric structure for the molecule, $Zr_4C_{10}H_{68}O_{22}$, which contains two carboxyl end groups.

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